γ-Al₂O₃ Supported Bimetallic Catalysts: Synthesis and Applications for Hydrazine Decomposition

A dissertation submitted to the Department of Chemistry, Quaid-i-Azam University, Islamabad, in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

in

Physical Chemistry

by

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Islamabad
2017
IN THE NAME OF ALLAH
THE COMPASSIONATE
THE MERCIFUL
DEDICATED

TO

My Loving Parents
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Naveeda Firdous
Abstract

The main objective of the present research work was to explore the potentially unique properties and possible synergistic effect in supported bimetallic catalysts which were synthesized in two stages by adopting simple route. γ-Al₂O₃ granules were selected as a support material and prepared by sol gel process followed by oil drop method for granulation purpose. Co was chosen as low cost, basic metal and four noble metals (M): Ir, Ru, Pt, and Pd were selected as promoters. Four series of γ-Al₂O₃ supported bimetallic catalysts, (CoMₓ/γ-Al₂O₃) were synthesized via wet impregnation by loading ~ 20 wt% of Co metal and 0-5 wt% of promoter metals onto γ-Al₂O₃ in each series. On the basis of mole fraction (x) of promoter metals, the catalyst series were named as CoIrₓ/γ-Al₂O₃, CoRuₓ/γ-Al₂O₃, CoPtₓ/γ-Al₂O₃, and CoPdₓ/γ-Al₂O₃.

The prepared catalysts were characterized by various techniques i.e., Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM) along with EDX analysis, transmission electron microscopy (TEM), surface area analysis, and temperature programmed reduction/oxidation (TPR/TPO) processes. In order to explore the diverse role, the synthesized catalysts were applied for hydrogen generation from two model reactions i.e., catalytic decomposition of hydrazine in a self-designed reactor and electro-oxidation of hydrazine by cyclic voltammetry (CV) technique.

The catalytic decomposition of hydrazine (0.5 M) was performed at 25 °C and volume of gaseous products (H₂+N₂) was measured by a gravimetric water displacement method. The catalytic efficiency was evaluated in terms of turn over frequency (TOF) and selectivity (X) towards hydrogen generation. The optimal composition from each series was selected on the basis of activity and selectivity. Hydrazine decomposition reaction was further tested at various temperatures and activation energy (E_a) values were calculated from the kinetic profiles using Arrhenius equation. In particular, the kinetic studies depicted an increase in rate of hydrogen generation with an increase in temperature up to 65 °C. The effect of support was also studied by loading the selected optimal composition on various supports including MgO, ZnO, SiO₂, and zeolite; (γ-Al₂O₃ proved to be the best
support candidate). For electrochemical studies, glassy carbon electrode was modified with each catalyst powder by drop-casting and used for investigating electro-oxidation of hydrazine analyte in 0.1 M phosphate buffer solution (pH 7.2). Cyclic voltammetry was performed to elucidate the redox behavior of synthesized electroactive materials. A linear current-voltage response was observed on the modified electrodes in each catalyst series. The stability and reproducibility of all the catalytic materials was substantiated by the catalytic activity as measured in many successive cycles.

All bimetallic catalysts showed potentiality for hydrogen generation and electrochemical applications. The combination of high TOF and selectivity for hydrogen generation as well as prominent current response in CV studies rendered CoIr\textsubscript{0.081}/\gamma-Al\textsubscript{2}O\textsubscript{3}, CoRu\textsubscript{0.11}/\gamma-Al\textsubscript{2}O\textsubscript{3}, CoPt\textsubscript{0.034}/\gamma-Al\textsubscript{2}O\textsubscript{3}, and CoPd\textsubscript{0.093}/\gamma-Al\textsubscript{2}O\textsubscript{3} catalysts as optimal compositions in respective series.

Out of these optimal compositions, CoPt\textsubscript{0.034}/\gamma-Al\textsubscript{2}O\textsubscript{3} bimetallic catalyst exhibited maximum performance for hydrogen generation from hydrazine decomposition as well as for electro-oxidation of hydrazine. CoPt\textsubscript{0.034}/\gamma-Al\textsubscript{2}O\textsubscript{3} catalyst presented 100% H\textsubscript{2} selectivity with TOF of 190 h\textsuperscript{-1}, and activation energy of 29 kJ mol\textsuperscript{-1}. All bimetallic catalysts also showed robust electrocatalysis and presented good peak current response for electro-oxidation of hydrazine. These results reflected better alloying effect between Co and Pt metals in addition to presence of more active sites and better metal dispersion. The electroanalytical activity was in the order of: CoPt\textsubscript{0.034}/\gamma-Al\textsubscript{2}O\textsubscript{3} > CoPd\textsubscript{0.093}/\gamma-Al\textsubscript{2}O\textsubscript{3} > CoIr\textsubscript{0.081}/\gamma-Al\textsubscript{2}O\textsubscript{3} > CoRu\textsubscript{0.11}/\gamma-Al\textsubscript{2}O\textsubscript{3}, with peak current values of 183.2 µA, 59.4 µA, 50.3 µA, and 46.1 µA, respectively.

The maximum performance of the optimal catalysts can be attributed to tuning of catalyst’s properties by synergistic effect of two metals, better metal dispersion, metal-support interactions besides the excellent features of \gamma-Al\textsubscript{2}O\textsubscript{3} granular support as confirmed by XRD, H\textsubscript{2} chemisorption, BET, SEM, TEM, TPR and TPO analyses. In addition, noble metals in low contents promoted the activity and selectivity tremendously, and were quite suitable for making the process cost effective for selective decomposition of hydrazine, a toxic material into clean future energy fuel (H\textsubscript{2} + N\textsubscript{2}).
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<td>Atomic force microscope</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Alpha</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>Alumina</td>
</tr>
<tr>
<td>AAS</td>
<td>Atomic absorption spectroscopy</td>
</tr>
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<td>E</td>
<td>Applied potential</td>
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<tr>
<td>$E_a$</td>
<td>Activation energy</td>
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<tr>
<td>Å</td>
<td>Angstrom</td>
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<tr>
<td>$N_A$</td>
<td>Avogadro’s number</td>
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<tr>
<td>BET</td>
<td>Brunauer, Emmett and Teller</td>
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<td>B.C</td>
<td>Before Christ</td>
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<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
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<tr>
<td>s</td>
<td>Second</td>
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<tr>
<td>CO</td>
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<td>CVD</td>
<td>Chemical vapor deposition</td>
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<tr>
<td>DP</td>
<td>Deposition-precipitation</td>
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<tr>
<td>D</td>
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<td>Degree Celsius</td>
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<td>δ</td>
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<tr>
<td>D</td>
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<td>fcc</td>
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<td>GC</td>
<td>Glassy carbon</td>
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IR  Infrared spectroscopy
IUPAC  International union of pure and applied chemistry
K  Kelvin
kJ  Kilojoule
MSI  Metal-support interactions
MS  Mass spectrometry
µm  Micrometer
x  Molar fraction
M  Molar
min  Minute
µL  Microliter
µm  Micrometer
mm  Millimeter
mL  Milliliter
µA  Microampere
mM  Millimolar
mV  Millivolt
PDF  Pair distribution function
i_p  Peak current
PBS  Phosphate buffer solution
%  Percentage
P/P_o  Relative pressure
R  Reference
<table>
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<tr>
<td>( v )</td>
<td>Scan rate</td>
</tr>
<tr>
<td>( v^{1/2} )</td>
<td>Square root of scan rate</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
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<tr>
<td>STM</td>
<td>Scanning tunneling microscope</td>
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<td>SMSI</td>
<td>Strong support-metal interactions</td>
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<td>Surface area analysis</td>
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<td>Selectivity for hydrogen</td>
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<td>Temperature programmed reduction</td>
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<td>TPO</td>
<td>Temperature programmed oxidation</td>
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<td>TOF</td>
<td>Turn over frequency</td>
</tr>
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<td>( \theta )</td>
<td>Theta</td>
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<tr>
<td>TCD</td>
<td>Thermal conductivity detector</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultra violet-visible</td>
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<tr>
<td>R</td>
<td>Universal gas constant</td>
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<td>V</td>
<td>Volt</td>
</tr>
<tr>
<td>WI</td>
<td>Wet impregnation</td>
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<tr>
<td>( \lambda )</td>
<td>Wavelength</td>
</tr>
<tr>
<td>wt</td>
<td>Weight</td>
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<td>XRD</td>
<td>X-ray diffraction</td>
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<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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Chapter 1

Introduction

Nanoscience and nanotechnology are broad and interdisciplinary fields that have been growing explosively worldwide in the area of research and development since last few years. The emphasis has been made on the development of number of structural and functional materials. A great focus has been given on the manipulation of mechanical, catalytic, electric, magnetic, optical, and electronic functions. Keeping in mind the importance of nanomaterials in the field of catalysis, the current chapter addresses their role and applications in several dimensions. The objectives for present research work and thesis outlines are also presented at the end of the chapter.

1.1 Nanotechnology

The term “nanotechnology” was used for the first time by Norio Taniguchi in 1974 at the International Conference on Precision Engineering (ICPE) held in Tokyo [1]. Rapid progress in nanotechnology was made in 1980s after the development of instruments including the scanning tunneling microscope (STM) and atomic force microscope (AFM). These instruments allowed scientists to "see" atoms around the surface [2]. Nanotechnology describes the creation, analysis, and applications of the materials with at least one dimension less than 100 nm. The fabrication schemes in nanotechnology are dual (Fig. 1.1): the bottom up approach involves assembling of atoms into supramolecular assembly and the top down approach leads to disassembling of bulk solid into fine particles [3]. Both approaches can be followed in either gas, liquid, solid states or in vacuum. The important parameters in nanosynthesis to be controlled are: i) particle size, ii) particle shape, iii) size distribution, iv) particle composition, and v) degree of agglomeration. The materials at nanoscale have shown significantly different properties from their bulk counterparts. Suitable control of the properties of nanostructures has led to the improvement of existing products and the development of new products, devices, and technologies. These new technologies have numerous applications in the field of nano devices, energy, optical engineering, nano fabrics, nano coatings, medicines, health care, gene delivery, and space industry [4].
1.2 Nanomaterials

Nanomaterials are cornerstones of nanoscience and nanotechnology. Nanomaterials are defined as a set of substances which possess the morphological features with at least one dimension of 100 nm or less [6]. Nanomaterials possess a large surface area to volume ratio in this size regime due to which they become chemically more reactive. Quantum effects also become dominant at the nanoscale resulting to a change in optical and electrical properties. Nanomaterials dispose of drastically modified properties including optical, magnetic, electrical, mechanical, and other properties without any change in chemical composition. These progressive properties have the potential for great applications in electronics, biomedicine, aerospace industry, automobiles, and other related fields [7].

1.2.1 Properties of nanomaterials

The properties of nanomaterials are considerably different from those of atoms and bulk materials due to their nanometric size of the particles which render them: i) large fraction of surface atoms, ii) high surface energy, iii) spatial confinement, and iv) reduction in imperfections. An improvement in the mechanical properties of nanomaterials can lead to modification of the properties like hardness, elastic...
modulus, fracture toughness, fatigue strength, and scratch resistance which are generally achieved from the structural perfection of the materials. The enhanced mechanical properties of the nanomaterials could have many nanoscale and macroscale applications. Due to nanometeric size, materials also have spatial confinement effects which ultimately bring the quantum effects. The energy band structure and charge carrier density in the materials can be altered, which results in the modification of the electronic and optical properties of the nanomaterials [8]. For nanomaterials, impurities and intrinsic defects will move to the surface upon thermal annealing and allow them free of internal structural imperfections such as dislocations, micro twins, and impurity precipitates. This improved perfection influences the properties of nanomaterials to a greater extent [9].

1.2.2 Classification of nanomaterials

There are two primary types of nanomaterials i.e., zero dimensional and one dimensional. The self-assembling of these nano sized building blocks can result in 2D and 3D structures which may produce exclusively new devices. Nanomaterials can be synthesized with various structures i.e., zero dimensional (nanoparticles, nanoclusters, nanocrystals, and cluster assemblies), one dimensional (nanotubes, nanowires, and nanofibers), two dimensional (nanofilms, nanosheets, and nanowalls), and three dimensional (bulk materials composed of nanometer sized individual blocks) as illustrated in Fig. 1.2. Most common types of nanomaterials include colloids, nanotubes, quantum dots, thin films, metal nanopowders, and dendrimers.

Fig. 1.2: Classification of nanomaterials a) 0D spheres and clusters, b) 1D nanofibers, wires and rods, c) 2D films and plates, and d) 3D nanomaterials. Adopted from [10].
1.3 Metal nanoparticles

Metals nanoparticles (NPs) have been considered of prime importance in chemistry, physics, and materials science. Scaling down the materials to nanometric size usually results in a significant change in their physical properties. It can be correlated to large specific surface of the nanoparticles, which makes them chemically more reactive than the bulk components. Moreover, the transition from macroscopic to nanometric scale leads to the appearance of totally new properties such as a change in color of solutions of semi conductors nanoparticles, and their luminescence properties as well. Modern science concentrates on the synthesis and characterization of metal nanoparticles. A variety of wet chemical methods are already being applied for fabrication of nanoparticles in polar as well as in non-polar solvents. In this way, metal particles can be prepared with different sizes, shapes, crystal phases, and composition [11, 12]. Nanometric scale features control the activity, selectivity, intrinsic properties, and lifetime of catalysts.

Since few decades, many areas of chemical industry have witnessed the importance of nanoparticles. Transition and noble metal particles have great potential in the field of catalysis and fuel cell applications, owing to lower the activation energy and large specific surface area for certain reactions [13, 14]. The transition metals such as Fe, Co, and Ni are ferromagnetic in nature, which have been heavily utilized in different magnetic and spintronic devices [15]. Surface plasmon is shown in the visible light region by metal nanoparticles (Cu, Ag, and Au) depending upon the size and shape of particles as shown in Fig. 1.3. The excitation of these localized surface plasmons occurs with an improved absorption at the respective wavelength of the exciting light. These particles display the color opposite to absorbed one and find versatile applications in in sensorics [16], photonics [17] and medical diagnostics [18]. Metal nanoparticles offer additional applications in fluorescence enhancement and surface enhanced Raman spectroscopy [19]. Fluorescent metal nanoclusters of Au, Ag, and Pt are composed of a large number of atoms with sizes comparable to the Fermi wavelength of electrons. They provide stable emission than organic dyes and good compatibility in comparison to quantum dots. Metal nanoparticles are of universal importance and found applications in various fields including catalysis [20-22], fuel cells [23], energy conversion devices [24], chemical and biological sensing.
[25], optical imaging [26], development of electrochemical sensors [27, 28], drug delivery [29], and laser deposition [30].

**Fig. 1.3:** Noble metal NPs display different colors at various particle sizes.
Adopted from [31].

### 1.4 Catalysis

The term catalysis was coined for the first time by Baron J.J. Berzelius in 1835 to describe the property of substances that speeds up the chemical reactions. Since few decades, catalysis brought a drastic progress to different aspects of our life especially in the environment and energy regimes. Catalysis is a multidimensional scientific field, constantly being brought forward by academic and industrial circles.

With the help of catalysis, the development has been made to synthesize new drugs, effective fuels, and modified polymer materials. Without catalysis, the petroleum and chemical industries would not improve and grow in further. The term catalyst can be defined as:

“A substance that alters the reaction pathways of a chemical reaction without itself undergoing any permanent chemical change” [32].

In fact, catalytic reaction is a cyclic event as illustrated in Fig. 1.4 where, a catalyst can accelerate a chemical reaction by forming bonds with the reacting
molecules. After the formation of intermediate complex, the reactants are transformed to product which detaches from the catalyst so that it is available for the next reaction. However, catalysts do not have infinite life span. The presence of poisonous by products or changes in the catalyst structure can lead to the catalyst deactivation. For practical applications and cost effectiveness, spent catalysts must be reactivated or replaced [32].

Fig. 1.4: The schematic representation of a catalytic reaction involving a sequence of elementary steps of: bonding of reactants (A and B) with catalyst, formation of intermediate complex, and separation of product (P) from the catalyst.

Adopted from [33].

1.4.1 Types of catalysts

Depending upon different phases present during a reaction, catalysts can be classified into two broad categories i.e., homogeneous and heterogeneous catalysts:

1.4.1.1 Homogeneous catalysts

For homogeneous catalysis, both the catalyst and reactants exist in the same phase, usually liquid or gas phase. Homogeneous catalysts have many advantages such as greater exposure to the reactants, easy process of diffusion, better heat transfer and well defined active sites [34]. However, there are some major disadvantages of the homogeneous catalysts such as difficult separation of the catalyst from reaction mixture and their recycling. These catalysts can be easily decomposed, so reaction temperature must be well controlled. They can also be deactivated (poisoned) in the
presence of by products. Metal salts of organic acids, organometallic compounds, and
carbonyls of Co, Fe, and Rh are typical homogeneous catalysts [35]. Mixed metal
complexes are especially important in the pharmaceutical industry for the synthesis of
drugs when only one of the two enantiomers is bio-active. Homogeneous catalysis is
important to the petrochemical industry on a large scale production of important
hydrocarbons such as aldehydes and ketones.

1.4.1.2 Heterogeneous catalysts

The development of heterogeneous catalysts has been initiated for the
production of chemicals on a technical scale, since many decades. In heterogeneous
catalysis, the catalysts are present usually in solid form and catalyze the reaction
either in liquid or gaseous phase. The catalytic reactions occur at the surface by the
adsorption of reactants from a fluid phase on a solid surface, surface reaction of
adsorbed species, and desorption of products into the fluid phase [36, 37]. The use of
heterogeneous catalysts is more advantageous due to their facile separation from
reaction solution which further helps in the continuion of chemical processes. In
addition, heterogeneous catalysts can tolerate more extreme operating conditions than
their homogeneous analogues [38]. Heterogeneous catalysts are workhorses of the
chemical and petroleum industry. Typical examples of heterogeneously catalyzed
reactions include ammonia synthesis from the elements over promoted iron catalysts
in the gas phase, and hydrogenation of edible oils on Ni-kieselguhr catalysts in the
liquid phase. Most common heterogeneous catalysts are inorganic solids (metals,
metal oxides, sulfides salts etc.) as well as organic materials such as organic
hydroperoxides and enzymes.

Heterogeneous catalysts are further classified into two main catagories

i. **Bulk catalysts:** In this case, entire catalyst is comprised of catalytic active
component with nanoscale or partly nanoscale microstructures. Most common
examples include silica-alumina catalysts for catalytic cracking, iron-
molybdate for oxidation of methanol to formaldehyde, iron doped with
alumina and potassium oxide for the synthesis of ammonia.

ii. **Supported catalysts:** For supported catalysts, an active phase (metal/metal
oxide) is dispersed on a support material. The catalytic reaction occurs inside
the pores of the catalyst. The use of support provides relatively high metal
dispersion along with a high thermal stability of the active component.
Moreover, the support might enable the formation of tiny crystals of active phase which are easily separated by the support component. Pre-shaped supports are more advantageous because of their textural properties.

1.5 **Significance of supported catalysts**

Generally, unsupported catalysts face the problems of agglomeration, random metal dispersion, lower active sites, ease in deactivation, and difficult separation from reaction mixture. In contrast, supported metal catalysts have more advantages in many ways than unsupported counterparts [39, 40]. In heterogeneous catalysis, supported catalysts consist of active phase (metal or metal oxide nanoparticles) dispersed on some support (Fig. 1.5). The main purpose for depositing the metal particles on a support material is to achieve a maximum dispersion of the metal particles which eventually results an improvement in the catalytic activity [41, 42]. In addition, the support is used to improve the catalyst's stability which is dependent upon the nature of the support and the interaction between the metallic phase and the support [43]. Generally, supports are porous materials having high mechanical and thermal stability. The support materials provide high surface area and stabilize the dispersion of active phase. Usually, supports are considered to be inert but in some cases supports might interfere the catalytic reaction. Moreover, the support assists in metal recovery and provides a greater resistance to poison the catalyst. The major prerequisite for preparation of supported catalyst includes surface area, porosity and shape of the substrate. High surface area can be achieved for the porous support material but high porosity might results in a decrease of mechanical stability, formation of fins, and loss of active material.

The catalytic functionality might arise from the combined effect of active phase (metal nanoparticles) and support. Although, support serves to anchor the active species but interaction between them might also exist to some extent. The properties of supported catalysts can be tuned by altering each component independently. Metal-support interactions (MSI) may greatly influence the electronic properties of the metal nanoparticles compared to bulk phase [44-46].
The catalytic performance can be improved by controlling the particle size distribution for a typical reaction. Therefore, a comprehensive understanding is required for the underlying principles and different variables during the synthesis of these materials. Novel techniques have been developed to disperse metal nanoparticles on some support having narrow particle size distribution. The properties of solid catalysts are strongly affected by the preparation method, reaction conditions, and quality of precursors. Thereby, it is essential to control each preparation step and the properties of all intermediates. In order to achieve a better reproducibility, the production processes are followed by continuous operations, such as precipitation, filtration, drying, calcination, and forming. The most common technique used to produce supported metal catalysts is impregnation method which involves absorbing the metal salt onto the support surface and then reduce the salt to metal at high temperatures under inert atmosphere \([48]\). Another approach is to produce the metal NPs and subsequently deposit them onto the support material \([49-51]\).

Supported metal catalysts are highly important for preparation of chemicals due to minimum loss of catalyst and their easy separation from reaction mixture. Supported catalysts have wide applications in many chemical processes. For industrial applications, these catalysts are generally used in the shape of spheres or cylindrical extrudates. The desired metal concentration within the pellet can be achieved in a controlled way via impregnation procedures. The choice of the appropriate concentration of precursors may be crucial for the selectivity of a process because of the interplay between transport and reaction in the porous mass of pellet.
1.6 Classification of heterogeneous supported catalysts

On the basis of types of metals used, supported catalysts can be distinguished into following sub disciplines:

1.6.1 Supported monometallic catalysts

The catalytic performance of a supported metal catalyst is affected by both electronic and geometric effects. Usually, monometallic catalysts are comprised of noble (Pt, Pd, Rh etc.) or non-noble (Ru, Ni, Fe, Co etc.) metals deposited on some support like Al₂O₃, SiO₂, or active carbon and are applied for hydrogenation/dehydrogenation reactions. Al₂O₃ supported Ag catalyst is used for ethene selective epoxidation [52]. Supported Au catalysts are found active for CO oxidation at low-temperature [53]. Supported metal catalysts have also been used for various industrial applications such as carbon-carbon coupling reactions [54], water gas shift (WGS) reactions [55], hydrogen peroxide production [56], and removal of CO from effluents [57].

1.6.2 Supported bimetallic catalysts

Bimetallic supported catalysts contain two different metals having a certain mixing pattern and various architectures and perform some specific functions [58, 59]. Bimetallic catalysts present the better performance due to “synergy” between two metals in order to enhance activity and selectivity in many ways not seen in monometallic catalysts. They have many interesting new properties with a combination of multiple functions which are derived from the synergistic effects of metal nanoparticles and their interaction with the support [60, 61]. For bimetallic catalysts, both metals may either be miscible or immiscible and the combination of an active and an inactive metal can dilute the active metal on the particle surface. Therefore, the catalytic performance of reactions is influenced by assembling of several active metals rather than monometallic element [62, 63]. In this way, the catalytic processes can be made selective. Usually, the surface composition of binary alloys differs from that of the bulk phase and it is the major contributing factor to tailor the catalytic properties.

Moreover, preparation methods also affect the properties of bimetallic catalysts and consequently their catalytic performances. Various methods have been reported for the synthesis of bimetallic catalysts, namely chemical vapor deposition (CVD), wet impregnation (WI), co-precipitation (CP), deposition-precipitation (DP),
liquid phase synthesis, and aerosol-derived approach [64]. In general, metal nanoparticles are characterized by many probing tools such as UV-visible (UV-Vis) spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), extended X-ray absorption spectroscopy (EXAFS), infrared spectroscopy (IR), and atomic force microscopy (AFM) [65].

Bimetallic catalysts show different structures according to metal’s properties, metal-support interactions, atmosphere (oxidant, reductive, presence of water, etc.), and temperature. They evolve with various architectures including crown-jewel structure, hollow structure, heterostructure, core-shell structure, alloyed structure, and porous structure as shown in Fig. 1.6. Commonly, bimetallic catalysts found applications in CO hydrogenation [66], selective hydrogenations [67], Fischer-Tropsch synthesis [68], oxidative reactions [69], CO selective oxidation [70], and hydrogen generation reactions [71, 72].

![Diagram of various structures of bimetallic nanoparticles](image)

**Fig. 1.6:** Examples of various structures of bimetallic nanoparticles
Adopted from [73].

### 1.7 Factors effecting the properties of bimetallic catalysts

The properties of bimetallic catalysts could be controlled by monitoring various factors like geometry, composition, particle size, morphology, and structure-property relationship. These factors are briefly discussed as follows:
1.7.1 Structural effect

Bimetallic nanomaterials present greater potential in their catalytic performance than the monometallic nanocatalysts due to superior properties [74, 75]. Moreover, bimetallic catalytic systems present more flexible design according to the activity and selectivity requirements for a particular reaction. For instance, Pt is the most active electrocatalyst for oxygen reduction reaction (ORR) in proton-exchange membrane fuel cells (PEMFC). In order to improve the activity of Pt, bimetallic nanostructure is constructed consisting of Pt and some other metals. The addition of second metal to Pt can modify electronic properties of Pt by changing Pt-Pt bond distance and coordination number of Pt. Friebel and co-workers investigated the anodic oxidation of Pt/Rh(111) and Pt/Au(111). For ORR these bimetallic catalysts, the strain and vertical ligand effects can be minimized with better control of structure and metal distribution. It was predicted that Pt/Rh(111) would show good long-term stability under ORR conditions [76].

Yang et al. demonstrated high activity of nanostructured Pt monolayer electrocatalyst for hydrogen evolution reaction [77]. The catalyst was fabricated by depositing monolayer of Pt onto the faceted C/Re (1121) surface. Strasser et al. prepared Pt-Cu core-shell electrocatalyst with a pure Pt shell that surrounded a Pt-Cu alloy core [78]. This structure can modify the electronic band gap structure of Pt and weaken the adsorption energy of oxygenated species, leading to an increase in the catalytic activity for the oxygen reduction reaction. Zhong and co-workers designed alloy electrocatalysts through alloying Pt with some transition metals [79]. The correlation between atomic coordination structure and the electrocatalytic performance was studied by treating the catalysts at different temperatures. The heteroatomic coordination number was noticed to increase with an increase in treatment temperature, resulting in enhanced Pt-alloying surface sites and higher specific electrocatalytic activity. The atomic reorganization in reactive environments indicates the structural flexibility of bimetallic nanocrystals and a potential way to design bimetallic nanostructures based on the interplay of structure and surface active components.
1.7.2 Composition effect

The molar ratio of two metals plays an important role in determining the catalytic performance of bimetallic nanomaterials [80, 81]. Lim and co-workers established the composition-dependent properties of Pt-Y alloy catalysts for electrocatalytic oxygen reduction [82]. Sun et al. verified the composition-dependent activity of monodispersed CoPd nanoparticles for formic acid oxidation and showed that alloying of Pd with Co is beneficial for the enhanced oxidation of HCOOH [83]. Thus, the activities of CoPd nanoparticles decreased in the following sequence: Co50Pd50 > Co60Pd40 > Co10Pd90 > Pd. The composition effect is also shown by core-shell bimetallic nanoparticles.

The composition-dependent catalytic activity of Cu@M (M = Co, Fe, Ni) nanoparticles was studied for hydrogen generation from ammonia borane decomposition [84]. In Cu@M core-shell architectures, the interaction of Cu and M can change the width of surface d band which is advantageous for the improvement of catalytic performance. For bimetallic nanocatalysts, changing the molar ratio of two metals can lead to the modification of their structures, especially the atomic distribution of two species on the surface.

1.7.3 Particle size effect

The catalytic properties of bimetallic nanoparticles are greatly influenced by the particle sizes and their distribution. With the decrease of particle size, the distribution of two metals usually varies spontaneously to reduce the surface energy and produce the most thermodynamically stable mixing pattern. For nanomaterials, quantum-size effects become prominent upon particle size reduction due to which surface-to-volume ratio increases and much more atoms are exposed on the surface. Subsequently, novel physical and chemical properties may evolve that differ significantly from their bulk counterparts [85, 86]. For instance, the effect of metal particle size of supported metal catalysts (Au, Pd, Au–Pd)/C was studied for liquid phase oxidation of glycerol. A progressive decrease of activity and simultaneously an increase in the selectivity to sodium glycerate was observed upon tuning the metal particle size from 2 to 16 nm [87]. Recently, Somorjai’s group have investigated the size effect of bimetallic Rh0.5Pt0.5 nanoparticle arrays on their activity for CO oxidation [88]. Rh0.5Pt0.5 nanoparticles with smaller size were found
to retain higher catalytic activity for CO oxidation compared to the bigger ones. XPS measurements depicted that the surface segregation of Rh with a decrease in particle size can lead to its higher activity.

### 1.7.4 Shape effect

Generally, the catalytic reactions take place on the surface of catalysts. Therefore, the exposed crystal faces of catalysts have significant effect on their catalytic activity. For bimetallic nanocatalysts, the shape of particle is highly important for optimizing the structure of active sites. The catalytic performance of supported Au-Pd alloy nanoparticles has been extensively studied for the oxidation of primary carbon-hydrogen bonds in toluene [89]. The catalytic activity of AuPd/C was found quite different from AuPd/TiO$_2$, although both of them had a similar size of Au-Pd nanoparticles. This difference in activity can be correlated to the morphology and exposed crystal faces of the Au-Pd nanoparticles. For AuPd/C catalyst, most particles have decahedral geometry with (111) planes. The decrease of catalytic activity was examined for AuPd/TiO$_2$ catalyst with cuboctahedral or single/double-twinned geometry corresponding to (100)/(111) planes in proportion with (100) planes.

Yan et al. synthesized monodispersed single-phase Pt-Pd nanocubes with (100) planes and Pt-Pd nanotetrahedrons corresponding (111) faces, respectively. The catalytic activity of synthesized materials was tested for methanol electrooxidation [90]. Pt-Pd nanocubes presented a better activity while Pt-Pd nanotetrahedrons showed a good durability. Such behavior could be explained by occurrence of different reaction pathways on the (100) or (111) surfaces.

### 1.7.5 Structure-property relationship

Due to small sized particles, nanomaterials exhibits fantastic properties. In the case of bimetallic catalysts, the incorporation of second component may result in complexity of the system. The interaction between two metals greatly tuned the properties and in turn performances of the catalysts. The alloyed section containing two different metals has a strong chemical bonding, which will change localized electron structure thus leading to interesting chemical and physical properties. For instance, the formation of the FePd alloyed NPs in a Pd/CeO$_2$ presented improved activity for water gas shift (WGS) [91]. Alloying of Pd with Fe (magnetic metal)
diminish the cost economics and issues associated with monometallic Pd/CeO$_2$ for fuel cell applications. The addition of metal(s) to another metal effects the structural properties which results in an improvement of thermal stability of the active components. The sintering of metal NPs reduces by increasing their dispersion and/or interaction with substrate. In the case of Au-Ag core-shell bimetallic NPs [92] the excellent thermal resistance was presented due to the formation of a surface Ag oxide layer that boosts the interaction with silica support. The unique catalytic, optical, and magnetic properties of bimetallic NMs are exploited for a variety of applications including improved activity and selectivity, fine tuning of optical properties, magnetism, drug delivery, and electronic materials [93].

1.8 Research objectives

The main objectives of the present research work were:

- To synthesize $\gamma$-Al$_2$O$_3$ support using sol gel method followed by its fabrication into granules via oil drop method.
- To prepare bimetallic catalysts supported on $\gamma$-Al$_2$O$_3$ via wet impregnation method.
- To evaluate structural properties of synthesized nanomaterials using different techniques like XRD, FTIR, atomic absorption spectroscopy, BET surface area analysis, H$_2$ chemisorption, SEM, EDX, TEM, TPR, and TPO.
- To focus on the synergistic effect of both metal nanoparticles for their better catalytic activity.
- To apply prepared catalysts:
  - For hydrogen generation from catalytic decomposition of hydrazine.
  - As potential electrocatalysts for oxidation of hydrazine using cyclic voltammetry.

1.9 Thesis layout

The present thesis deals with the synthesis, characterization, and applications of CoM$_x$$\gamma$-Al$_2$O$_3$ (M= Ir, Ru, Pt, and Pd) supported bimetallic catalysts for hydrazine decomposition. The thesis is divided into 9 chapters including chapter 1 that provides the introduction of nanomaterials, catalysis, types of catalysts, importance of supported bimetallic catalysts, and factors affecting their properties. Chapter 2
includes a brief review of support materials, significance of $\gamma$-Al$_2$O$_3$ support, properties, preparation, and applications of supported metal catalysts. Chapter 3 gives an account of characterization techniques employed in the present work. Chapter 4 focuses on the adapted method for synthesis and granulation of $\gamma$-Al$_2$O$_3$ support, preparation of supported bimetallic catalysts, designing of reactor for catalytic testing, and fabrication of modified electrode for electrochemical studies. Chapter 5, 6, 7, and 8 include the experimental results and discussion for CoIr$_x$/γ-Al$_2$O$_3$, CoRu$_x$/γ-Al$_2$O$_3$, CoPt$_x$/γ-Al$_2$O$_3$, and CoPd$_x$/γ-Al$_2$O$_3$ catalytic series, respectively. Conclusions and future prospects of present research work are presented in chapter 9.
References


Chapter 2

Supported Metal Catalysts

Supported metals nanoparticles play a significant role in environmental science, catalysis, biological, and industrial fields. They have novel properties with a combination of multiple functions. Broadened applications are derived from the alloying effects of metal nanoparticles and their interaction with the support. This chapter gives a brief view of supported bimetallic catalysts used in the present work and their various applications.

2.1 Support materials for metal catalysts

The applications of an appropriate support have attained great consideration in the field of catalysis, since many years. The reason is that supported metal catalysts show better stability and activity compared to bulk catalysts. The main advantages of supported metal catalysts are: uniform metal distribution, less agglomeration, optimal performance, deposition of low content of noble metal, facile recovery of precious noble metal, and recycling of the catalyst [1, 2].

Generally, support materials offer following advantages: (a) act as an inert substrate for metal deposition, (b) stabilize the metal nanoparticles, (c) prevent sintering, and (d) improve the mechanical strength of a catalyst. Furthermore, a support offers the benefits of mass transport and electron transfer in addition to porous features; all of these contribute towards a superior catalytic efficiency [3]. The properties of a catalyst may suffer by the structural features of support and metal-support interactions (MSI) [4]. The physical properties and morphology of smaller particles can be affected to a greater extent by these interactions. The features of the support material also have great impact on the catalytic properties of the metal particles. Therefore, the selection of support material for heterogeneous catalyst is highly significant in order to retain its specific properties i.e., porosity, pore size distribution, and surface area. The morphology and pore size distribution of the selected support may also contribute to the stability and performance of the catalyst [5].
Although, different carbon materials have been applied as a catalytic support due to their large surface area, high electrical conductivity, fine pore structures, and relatively good stability [6]. Typical examples include carbon nanofibers, carbon nanotubes, charcoal, and active carbon. However, the diffusion limitations and high temperature requirement for activation of carbon supports have been pointed as major obstacles for their practical applications. In addition, silica, MCM-41, and polymers can be functionalized as a support for the preparation of immobilized or hybrid catalysts [7, 8]. Metal oxides play a very important role in the field of catalysis. These are of paramount importance in heterogeneous catalysis as support materials having high surface area, good mechanical strength, and high thermal/hydrothermal stabilities. Most common examples of these supports are binary oxides such as Al₂O₃ [9], TiO₂ [10], La₂O₃ [11], CeO₂ [12], MnO₂ [13], ZrO₂ [14], and ternary oxides (SiO₂-Al₂O₃, zeolites etc.) [15]. Theses metal oxides can play a key role in heterogeneous catalysis.

### 2.2 Alumina as a support material

Among different support materials, alumina has been widely used as a catalyst support because of its high surface area, porous structure, thermal stability, and cost economics which make it suitable for many applications [16]. Alumina is an amphoteric oxide which exists in different phases depending upon the nature of hydroxide precursors and the conditions of their thermal decomposition. Various mineral forms of aluminum hydroxide such as bayerite, nordstrandite, boehmite, and gibbsite can be used as precursors which upon thermal dehydration transform into a variety of crystalline transitional phases of Al₂O₃ as shown in Fig. 2.1.

![Figure 2.1: Crystallographic phases of alumina at different temperatures.](image)

Adopted from [17].
Alumina is structurally a complex oxide with several transition phases (χ, η, κ, γ, δ, α, and θ) according to their calcination temperatures that have vast technological and industrial significance [18]. The gamma (γ), theta (θ), delta (δ), and eta (η) phases of alumina have face centered cubic (fcc) structures while kappa (κ), alpha (α), and chi (χ) phases have hexagonal close packed (hcp) structures. The properties of alumina are significantly changed with calcination temperature. The gamma phase of alumina is reported to appear at 350-1000 °C by using either crystalline or amorphous precursors [19]. These metastable phases of alumina can be produced by variety of methods which ultimately convert to α-Al₂O₃ at ~ 1200 °C and these transformations to α phase are irreversible. α-Al₂O₃ can be used as a refractory material, abrasive material, and color pigment. Other phases of Al₂O₃ (i.e.; χ, η, κ, γ, δ, and θ) are porous in nature which are commonly used as adsorbents, desiccants, and catalyst supports.

2.2.1 Gamma alumina

2.2.1.1 General aspect

Gamma alumina (γ-Al₂O₃) is most commonly used as a support material for the preparation of catalysts because of its good adsorptive nature. γ-Al₂O₃ is obtained by dehydration of aluminum hydroxide below 800 °C with controlled and reproducible properties like particle size, morphology, and pore size distribution. Hence, control of these properties is highly important to improve the potentialities of γ-Al₂O₃ in catalysis, composite reinforcement applications, coating, and alumina derived ceramics.

According to the IUPAC notation, porous materials (e.g., alumina, silica, and other metal oxides) can be classified into three main categories depending on the sizes of their pore diameters:

i. Microporous materials (Pore diameter: < 2 nm)
ii. Mesoporous materials (Pore diameter: 2-50 nm)
iii. Macroporous materials (Pore diameter: > 50 nm)

Among these, mesoporous materials are highly valuable due to the advantages of minimizing the pore collapsing as it often occurs in microporous materials. In this context, the preparation of porous alumina with well-defined and controllable porous structure is highly beneficial for catalyst support applications. The main advantages of mesoporous γ-alumina are as follows:
- High surface area of γ-Al₂O₃ can result in an increase in surface density which leads to higher loadings of active components (i.e., metals, metal oxides, and metal sulfides).
- Maximum dispersion of the active phase can be achieved.
- High density of basic sites is present in mesoporous γ-Al₂O₃ in comparison to conventional non-porous alumina that increases the interaction between metal oxides, and alumina supports, thereby improve the catalytic performance of oxide catalysts.

Although, α-Al₂O₃ is highly thermally stable phase but it has non porous structure, low surface area, and large crystallite sizes that make it less effective as a support material for catalytic applications. In contrast, γ-Al₂O₃ is synthesized using boehmite (AlO(OH)) as primary precursor at ~ 500 °C with controlled surface properties including surface area, particle size, pore sizes, and their distribution. γ-Al₂O₃ is widely used as a catalyst supports in many industrial processes. Clearly the preparation method effect the activity of the catalysts as activity varies with both precursor type and preparation procedures. For instance, γ-Al₂O₃ can be prepared using different precursors as aluminum nitrate [21], aluminum chloride [22] or from aluminum isopropoxide [23]. Many wet chemical procedures based on liquid phase reaction, gas phase synthesis or hydrothermal reaction at high pressures have been used to control the particle size and the morphology of boehmite precursor as well as that of γ-Al₂O₃. That is why γ-Al₂O₃ finds huge applications for catalysis, electrocatalysis, chromatography, super conductors, and water treatment [24].

2.2.1.2 Microstructure

The microstructure and thermal/hydrothermal stability of γ-Al₂O₃ intensely depend on the preparation methods and reaction conditions. The structure of γ-Al₂O₃ is usually considered as a cubic defect spinel type with the aluminum ions more or less randomly distributed between octa- and tetrahedral sites (Fig. 2.2).
Fig. 2.2: The cubic structure of aluminum oxide. Adopted from [25].

Fig. 2.3 presents the arrangement of ions in first two layers of $\gamma$-$\text{Al}_2\text{O}_3$. The arrangement is considered as close-packed layers of oxo anions with $\text{Al}^{3+}$ cations distributed between tetrahedral and octahedral vacancy positions [26]. The $\text{Al}^{3+}$ positions are not fully occupied and vacancies may distribute over both the tetrahedral and octahedral sites. However, Zhou and coworkers pointed that $\text{Al}^{3+}$ can also be located in non-spinal positions [27]. The precise distribution of cations is controversial and may depend on the reaction conditions for $\gamma$-$\text{Al}_2\text{O}_3$ synthesis. Paglia et al. established a tetragonal structure for $\gamma$-$\text{Al}_2\text{O}_3$ derived from highly crystalline boehmite and it has been further confirmed thoroughly by pair distribution function (PDF) analysis [28]. In another studies, NMR and PDF analyses have been shown that $\gamma$-$\text{Al}_2\text{O}_3$ has boehmite-like stacking-fault defects that gradually disappear during calcination [29].

Fig. 2.3: Schematic drawing of the first two layers of $\gamma$-$\text{Al}_2\text{O}_3$ structure having $\text{Al}$ cations at octahedral and tetrahedral sites as shown by black and grey circles, respectively. Adopted from [26].
2.2.1.3 Preparation method

The synthetic scheme and reaction kinetics for preparation of \( \gamma \)-\( \text{Al}_2\text{O}_3 \) depend on the properties of the precursors and the reaction conditions [30]. Hence, the choice of synthesis method for controlling the particle size and high specific surface area would be favorable. To this end, a number of investigations have been made on the synthesis of alumina particles by various methods including chemical vapor deposition [31], sol-gel technique [32, 33], supramolecular templating methods [34, 35], precipitation method [36, 37], thermal plasma jet process [38], spark plasma sintering [39, 40], freeze drying process [41], polyol synthesis [42], and microwaves [43]. Sol-gel is the preferred method for the synthesis of \( \gamma \)-\( \text{Al}_2\text{O}_3 \). In sol gel process a colloidal suspension “sol” is prepared by the hydrolysis of precursor’s solutions followed by polycondensation in which sol eventually, converts to a gel consisting of an inorganic continuous network in a liquid phase. The drying process serves to remove the liquid phase from the gel and forming a porous material. The porous solid is calcined at high temperature (350-800 °C) in order to obtain \( \gamma \)-phase. The sol-gel method is preferred over other available methods due to the following advantages:

2.2.1.3.1 Advantages of sol gel method

- Multicomponent compounds can be synthesized by controlling the stoichiometry of mixing sols. In addition, there is possibility of incorporating nanoparticles and organic materials into sol-gel-derived oxides.
- Particle size, pore size distribution of the final product can be tuned by appropriate modification of the precursors and monitoring the rate of reaction.
- The desired pore size can be obtained by controlling the aging and drying conditions.
- The reaction conditions are mild with no need of extreme pH and temperature.
- The materials are easily fabricated into desired shape in a gel state.
- The precursors are mixed homogeneously at molecular level and a high purity product is obtained.
- Templates/additives are used in sol-gel process to create pores with controlled size and shape. They can be eliminated from the product by acid treatment or calcination at high temperature.
• The fabrication of any oxide composition is possible as well as the production of new hybrid organic-inorganic materials, which do not exist naturally.
• The method is simple and cost effective with no need of special precursors and equipments.

2.2.1.4 Morphological forms

\( \gamma{-}\text{Al}_2\text{O}_3 \) in powder form is problematic for large scale applications due to facing the issues of agglomeration and separation from reaction mixture. In order to solve this problem, \( \gamma{-}\text{Al}_2\text{O}_3 \) can be designed in various morphological forms such as spheres/pills, pellets, and extrudates etc. It can be activated prior to use either by drying, calcination or steaming.

2.2.1.4.1 Methods for granulation

The bulk properties of alumina can be improved by granulation process. Many attempts have been made to develop alumina support in spherical shape in order to: facilitate the transport of reactants and products, reduce dust loss, improve reaction kinetics, pore structure, and product appearance [44, 45]. The methods used for the granulation of \( \gamma{-}\text{Al}_2\text{O}_3 \) support include:

1. Spray-drying

In spray drying, microdroplets of the product are suspended in a hot air stream. This method is suitable for preparing granules with small diameter (7-700 µm). The reason is that superheating of solids in the hot gas results in mechanical degradation of large size beads.

2. Drop coagulation (Oil drop method)

This method involves the suspension of sol droplets in a different liquid phase (e.g., paraffin oil), whose temperature is increased to 100 °C. The surface tension allows the formation of spheres during the flow of droplets through the solvent. It is followed by ripening and drying of granules [46]. This method is used to prepare either microbeads or granules of a few millimeters. The main aims of thermal treatment are to eliminate volatile impurities, develop the porous structure, and improve the mechanical strength.
3. **Pelletizing**

Pelletizing results from compressing the dry powder in die between punchers. The quality of intergranular contact is dependent on the adhesive properties of the powder. For this purpose, an appropriate amount of lubricant (water, mineral oil etc.) and solid (talc, graphite, and stearic acid) can be added which help in sliding and positioning of the granules. Binders are also mixed to increase post-compression adhesion. The operating variables in this method are characteristics of pelletizer, type of powder, and concentration of binder/lubricant. This method is applied to form pellets, spheres, hollow cylinders, and toroids.

4. **Extrusion**

In extrusion technique, the paste is forced through a die and another device cuts off the extruded material of the desired length. The properties of paste affecting the quality of product include viscosity, homogeneity, and stability. The granules can obtained with diameter of 0.5-10 mm using this method.

5. **Pan granulation**

Pan granulation involves the agglomeration of powder into granules by wetting it in a rotating pan. The granulation is followed by a ripening period. For good granulation, the powder should be fine. The operating variables in this method are: quality and quantity of binder, flow rate of water, inclination of pan, and rotating speed.
2.2.1.5 Applications

$\gamma$-Al$_2$O$_3$ is an effective catalyst support for both transition and noble metals in different applications. High surface area, uniform pore size distribution, controlled particle size, mesoporous structure, electrical properties, mechanical and thermal stability, and cost economics make it as an attractive material for catalyst support, fabrication of superconductors, abrasives, grinding media, glass manufacturing, electronic substrate, chromatography media, and bioceramics. In the field of catalysis, typical examples of $\gamma$-Al$_2$O$_3$ supported catalysts include Pt, Pd catalytic converters [47, 48], Fe-based catalyst for phenol hydroxylation [49], active phase Ni, Co or Cu for hydrogen production via steam reforming [50], Ni catalyst in hydrogenation [51], Ni$_2$P catalyst for hydrotreating of petroleum feedstocks [52], and Co catalyst for Fischer-Tropsch synthesis (FTS) [53]. The optimization of pore size and pore volume of $\gamma$-Al$_2$O$_3$ support are highly desired for the preparation of these supported catalysts. Moreover, $\gamma$-Al$_2$O$_3$ can also be used as an active catalytic phase in applications that require Bronsted and Lewis acid sites e.g., alkylation, isomerization, polymerization, hydrogenation, and Claus reaction. $\gamma$-Al$_2$O$_3$ also presents itself as an active catalyst for many important reactions such as dehydration of methanol to dimethyl ether [54] and degradation of volatile organic compounds [55].

2.3 Solid catalysts: properties and preparation

Generally, supported catalysts can be prepared by immersing a pre-shaped support to a solution of suitable metal precursor which is converted to active phase by following further preparation steps. The schematic presentation of various possible morphologies and dispersions of supported metals is shown Fig. 2.5. The dispersion of metal precursor typically occurred well after impregnation of the support. Low-temperature calcination may result in well-dispersed oxide over layers while, reduction at low-temperature leads to high dispersion of metal particles.
The formation of surface compound may also arise due to a reaction between the metal precursor and the support at high calcination temperatures. The cohesive forces become dominant at high reduction temperatures which may lead to particle agglomeration. When adhesive forces are dominant then, pillbox morphologies appear. In both cases, the metal phase must be mobile. On the hand, when the support is mobile, sintering of the support can take place. The small metal particles are stabilized over the reduced surface area (cohesive forces). In contrast, if adhesive forces are dominant then encapsulation (SMSI effect) may arise.

A sufficient interaction exists between the support and metal precursor at the time of catalyst preparation which ultimately results in the desired metal distribution, and high dispersion. The interactions of active phase with the substrate can be classified in following two categories.

**i. Physical adsorption (Physisorption)**

In physical adsorption, molecular interactions might exist between active phase and support either in the form of permanent/induced dipole or a quadrupole. These van der Waals forces are weak in nature. The rate of physical adsorption increases with an increase in gas pressure and usually reduces with an increase in temperature. Overall, physisorption takes place at a low reaction temperature.

**ii. Chemical adsorption (Chemisorption)**

The chemisorption involves the formation of covalent bonds due to rearrangement of electrons of the interacting gas molecules and the solid surface. The attractive forces are much stronger in chemisorption process compared to
physisorption and monolayer is formed. During chemisorption usually, higher temperatures are required to modify the surface composition with a release of a large amount of heat [57].

2.3.1 Methods of catalyst preparation

The supported catalysts have broad applications on industrial scale and therefore, the development of different preparation methods is highly desired. Some of these methods will be discussed here very briefly.

1. Impregnation

Impregnation is the most common method used for introducing the active phase into the porous support during which solid support is contacted with a certain volume of precursor solution containing the active phase. The impregnation can be further classified into two main types depending on the volume of solution. In wet impregnation (WI), solid support is immersed in an excess of precursor solution. After a certain time period the solid is separated and the excess solvent is removed by drying. The heat of adsorption is released in a short time. In incipient wetness method the volume of the precursor solution of appropriate concentration is added equivalent or slightly less than the pore volume of the support. Control of the operation must be rather precise and repeated impregnations may be necessary. The maximum loading is limited by the solubility of the precursor in the solution. For both methods the operating variable is the temperature which influences both the solubility of precursor in solvent and viscosity of solution. The concentration of precursor solution depends on the mass transfer conditions within the pores during impregnation and drying. The choice of precursor is also considered of prime importance for the quality of active phase, its structure, grain size, and distribution as a function of granule’s diameter. The metal dispersion increases with a decrease in metal crystallite size because a larger fraction of the active metal atoms would be accessible at the surface of the catalyst. The impregnation process is followed by drying which involves in crystallizing the active phase from the precursor solution in the pores of support by evaporation. Then calcination is performed whose aim is to adjust the surface and texture of deposit prior to further activation (reduction and sulfurization) [58].
2. Ion exchange

This method involves the exchange of ions except protons. Ions with low valance state such as Na\(^+\) or NH\(_4^+\) can be exchanged with higher valence ions (Ni\(^{2+}\) or Pt\(^{4+}\)). This method is used mainly in the preparation of metal-containing zeolites, e.g., Ni- or Pd-containing Y zeolites or mordenites zeolite used in petroleum-refining processes.

3. Deposition-precipitation

In this case, supports usually in powder forms are slurried in the salt solution followed by the addition of alkali. Rapid mixing is required to avoid precipitation in the bulk. Generally, a uniform precipitation can be achieved by using urea instead of conventional alkalis. For this purpose, metal precursor-support slurry is mixed with an appropriate amount of urea and mixture is heated along with stirring. Urea decomposes slowly to NH\(_3\) and CO\(_2\) upon reaching the temperature to 360 K. Consequently, precipitation occurs homogeneously over the surface and inside the pores of the support [59]. This method is used especially in the production of highly active Ni/SiO\(_2\) or Ni/Al\(_2\)O\(_3\) catalysts.

4. Reductive-deposition

During this preparation method, precious metals are deposited on the carrier surface by reduction of aqueous metal salts (mainly chlorides or nitrates) with reducing agents like H\(_2\), Na formate, formaldehyde, and hydrazine. Common examples of commercial catalysts produced by this method are precious metals on active carbon, SiO\(_2\) or \(\alpha\)-Al\(_2\)O\(_3\). Reductive deposition is desired especially for bimetallic supported catalysts such as Pt-Re or Pd-Rh.

5. Adsorption

This method is highly appreciated to achieve a uniform deposition active component on a support. Powders or particles exposed to metal salt solutions adsorb equilibrium quantities of salt ions as per adsorption isotherms. Adsorption may be either cationic or anionic depending on the properties of the substrate and adsorption conditions mainly pH of the solution. For instance, alumina adsorbs both cations and anions. Silica weakly adsorbs cations but magnesia strongly adsorbs anions [60].
2.4 Choice of supported bimetallic materials

Initial studies on bimetallic catalysts by Sinfelt [56] date back to the early 1960s, which have since stimulated intensive research interests worldwide. The development of nanotechnology for energy generation has provided some insight into the catalytic behavior in terms of the catalyst structure-property relationship. Supported metal catalysts are comprised of active phase (metal or metal oxide NPs) dispersed on some high surface area support as shown in Fig. 2.6 [61]. Bimetallic catalysts often emerge as materials of a new category with catalytic properties quite different from monometallic components depending on the composition, size, and morphology [62]. Supported bimetallic nanoparticles presented high performance in terms of improved activity and selectivity to desired products, extended lifetime, and high resistance to sintering. The improvement in the performance of these catalysts may arise due to surface, structure and alloying effects. Bimetallic catalysts offer superior performance due to “synergy” between two metals. Both metals cooperate with each other in order to increase the activity and selectivity that are not seen in individual metals. The particle size and degree of dispersion are the crucial factors for an enhancement of the catalytic activity. The small particle size and better metal dispersion allow adequate contact of the reactants with the catalysts thus leading to fast rate of reaction and lower catalyst loading.

![Fig. 2.6: The schematic presentation for preparation of bimetallic catalyst. Adopted from [61].](image)

The performance of bimetallic catalysts can be evaluated using many well established techniques. Theoretical modeling enables us to analyze and rationalize the experimental observations at any stage. This approach has many advantages. At first, synthesis, deposition, and activation steps help us in characterization of bimetallic
nanaostructures. Secondly, this approach makes possible control over different variables during the synthesis of bimetallic catalysts which are not attainable via conventional means. Thirdly, this approach enables to relate structure and performance relationship of these catalysts. In this way, supported bimetallic catalysts can be designed with optimum activity and selectivity for a target reaction. In general, bimetallic catalysts are composed of two metals, out of these one is base metal and second is promoter metal. The addition of second metal to monometallic system is highly desired for tailoring the electronic and geometrical structure of the metal nanoparticles to improve their activity and selectivity. As bimetallic catalysts are comprised of two metals, out of which one is primary/base metal and second is promoter metal. The primary/base metal is present in great proportion in the catalyst composition. In order to increase the activity and selectivity of the catalyst promoter metal is added in small content.

2.4.1 Transition metals based catalysts

The use of transition metal nanoparticles (NPs) is essential as they simulate metal surface activation and catalysis at the nanoscale; thereby bring selectivity and efficiency to heterogeneous catalysis [63]. Transition metal NPs can be stabilized by ligands, surfactants, polymers, and dendrimers protecting their surfaces. Transition metal NPs can also be heterogenized by fixation on some support such as silica, alumina, other oxides, and different carbon materials [64].

Transition metals and their compounds act as catalysts for many reactions due to their electronic configurations which permit them to temporarily exchange electrons with reacting species. Transition metals are good conductors and have another great tendency to easily mix with one another and other metals to form alloys. Typical examples of transition metals are iron, cobalt, nickel, chromium, manganese. These metals and their compound are commonly used as catalysts in different industrial processes now days. On commercial scale, transition metal based catalysts find applications in various processes such as: hydrogenation of oils over finally divided nickel catalyst, ammonia synthesis by Haber’s process using finally divided iron catalyst, sulphuric acid preparation by contact process over V$_2$O$_5$, and high density polyethylene synthesis using TiCl$_4$. Transition metals are technically an important class of materials having many applications. For instance, on industrial
scale transition metal based catalysts are used in a large number of processes for the conversion of hydrocarbons to other chemicals. Transition metal NPs are commonly used as catalysts due to their high surface-to-volume ratio and high surface energy. However, these nanoparticles may become unstable during the catalytic reaction owing to the presence of very active surface atoms.

2.4.1.1  Cobalt as a base metal

In recent years, cobalt (Co) NPs have emerged as one of the most active catalysts among other transition metals due to their high activities under mild conditions in various catalytic reactions [65]. Alumina supported Co catalysts are employed for various chemical reactions due to their high thermal stability and the strong resistance to attrition. Al₂O₃ support may stabilize the small metal clusters and suppress the aggregation of Co metal particles during the catalytic reaction. However, the strong interaction between Co particles and Al₂O₃ support often makes the difficult reduction of Co oxides. Resultantly, it reduces the number of active Co metal species thus leading to the suppression of catalytic activity. The cobalt catalysts may deactivate mainly due to: cobalt oxidation, cobalt-support interactions, metal migration into the porous support, and agglomeration of cobalt particles over the surface of catalyst [66]. Since noble metal additives can promote the reduction of Co oxide species and increase the number of active Co metal sites, apparently by hydrogen dissociation and spillover from the promoter surface. Therefore, small amount of any noble metal (e.g., Pt, Pd, Ru, and Re) is often added to Co/Al₂O₃ catalysts. The alloy composition compromised of the transition metal and noble metal has higher catalytic activity and selectivity than individual metal indicating the synergistic effect between two metals [67].

2.4.2  Selection of noble metals as promoters

The application of noble metals at the micro or nano scale is not exclusively restricted to the modern societies. Perhaps, ancient people have controlled the properties of materials at micro scale. For instance, soluble gold (or colloidal gold) was applied in the Middle Ages for treatment of various diseases for example heart problems, dysentery, and epilepsy. These fields are now further extended into cancer diagnostics and therapeutics [68]. Although silver has proven to be effective for treating bacteria-caused infections since 1000 B.C. [69]. Recently, the novel
properties (electrical, optical, magnetic, and chemical) of noble metals in the nanoscale regime have not only motivated many scientific researches but also found immense applications in a wide range of fields including photonics, electronics, catalysis, imaging, sensing, biomedicine, and therapeutics [70].

Commonly, non-noble metal catalysts were found inactive at room temperature which limits their practical applications. To this end, development of catalysts with low noble metal content is highly desired to achieve high selectivity and efficiency for various applications. The introduction of a noble metal (i.e., Ir, Ru, Rh, Pt, Pd etc.) to a monometallic system results in: formation a bimetallic alloy particles, textural effect, improvement in dispersion of metal particles, low fraction of reducible species, inhibition of catalyst deactivation, appearance of additional active sites and increase in the intrinsic reactivity of surface sites [71]. The promoting effect of noble metals can modify either the support or the metallic phase in order to stabilize the metallic particles. Since few decades, different synthetic routes have been developed for preparing noble metal nanoparticles with various sizes, shapes, compositions, and geometries which would in turn affect their fundamental properties and related applications.

2.4.2.1 Promoting effect of Ir metal

Crabtree presented a historical perception of the development of iridium in catalysis and focused on the wide spread use of iridium catalyst for various reactions [72]. Currently, Co-Ir nanoalloys supported on Zr-doped mesoporous silica have been tested for the selective reduction of NO in an excess of oxygen. The catalytic performance was observed to increase upon the incorporation of iridium metal with an ease in the reducibility and the dispersion of cobalt oxides thus minimizing the formation of the cobalt spinel during the calcination process [73]. Ir modified Ni/Al₂O₃ catalyst has been applied for the selective decomposition of hydrous hydrazine to generate H₂. XRD and XAFS studies predicted the formation of Ni-Ir alloy which may tune the interactions between N₂H₄ molecule and the catalyst. As a result, the N-H bond made easier to break and also facilitate the desorption of reaction intermediates [74]. Ir incorporated Ru/ZnO supported catalyst was applied for vapor-phase selective hydrogenation reaction. Fig. 2.7 shows that the addition of Ir enhanced the catalytic performance and stability which can be attributed to the modified electronic property of Ru by the formation of Ru-Ir alloy and weakened
surface acidity [75]. Nickel-iridium bimetallic catalysts with different iridium contents were explored for ammonia decomposition. The efficiency of nickel catalyst in the temperature range of 300-450 °C was significantly improved with the addition of iridium to the catalyst that resulted in a better dispersion of active nickel species as confirmed by XRD studies. Furthermore, temperature programmed reduction (H2-TPR) profiles presented a synergetic effect between two metals and also weakening of interaction between the active species and support [76]. In this context, carbon supported Pd-Ir nanowires (with a Pd/Ir atomic ratio of 2:1) have been inspected for oxygen reduction reaction (ORR) in acidic medium. The prepared bimetallic catalyst displayed comparable catalytic activity but much higher durability which might be attributed to the high accessible area, rough surface, and iridium incorporation [77].

![Graph](image)

**Fig. 2.7:** The promoting effect of Ir on the catalytic property of Ru/ZnO catalysts for selective hydrogenation of crotonaldehyde. Adopted from [75].

### 2.4.2.2 Promoting effect of Ru metal

Numerous heterogeneous catalysts have been applied for oxidation reactions. Among these catalysts, the activity of PtRu, and Pt3Sn bimetallic catalysts supported on Vulcan (commercial carbon) was evaluated for ethanol oxidation reaction (EOR) by electrochemical measurements. Addition of Ru or Sn in binary Pt catalysts decreases the onset potential for ethanol electro-oxidation and results in an increase in the efficiency of Pt3Sn/Vulcan catalyst. However, the selective oxidation of ethanol to CO₂ is about 1% for all the prepared catalysts thus demonstrating that the
potentialities of the catalysts is limited by their ability for C-C bond breaking rather than by their activity for the oxidation of poisonous adsorbed intermediates like CO\textsubscript{ad} or CH\textsubscript{x,ad} species [78]. In another study, PtRu/Cu NWs with 1D morphology (Fig. 2.8) investigated as a promising anode catalyst for DMFCs due to their good mass activity and their potential benefit in improving the mass transport [79]. The effect of ruthenium as a promoter on Co/SBA-15 catalysts has been studied for the Fischer-Tropsch synthesis (FTS), where the addition Ru in a small amount to Co/SBA-15 catalysts provokes a significant enhancement of the reducibility, by a decrease of reduction temperatures for various Co species [80]. Haghtalab et al. have successfully synthesized Co@Ru supported on γ-Al\textsubscript{2}O\textsubscript{3} with core-shell structures and applied for FTS [81]. A strong electronic interaction of core atoms with shell surface ones in special Co@Ru/γ-Al\textsubscript{2}O\textsubscript{3} catalyst could lead to great increment in FTS performance. Hosseini et al. demonstrated the promoting effect of Ru over Co/γ-Al\textsubscript{2}O\textsubscript{3} catalyst for CO hydrogenation. The addition of Ru loadings up to 1 wt% could lead to an increase in reducibility, dispersion of cobalt particles on the support, reduction of particle size of the metal, and higher CO conversions [82].

![Fig. 2.8: SEM and TEM images of (a,c) PtRu(6-1)NTs and (b,d) PtRu(4-1)/CuNWs; HAADF-STEM image and corresponding elemental spectrum images of (e) PtRu(6-1)NT, and (f) PtRu(4-1)/CuNW. Adopted from [79].]
2.4.2.3 Promoting effect of Pt metal

Nanosized platinum (Pt) catalysts display greatly improved activity and selectivity compared to bulk catalysts due to their large surface to volume ratios. In addition, the shape or morphology of Pt nanocrystals also results in the tuning of catalytic and electrocatalytic properties of the particles. Recently, Pt-Ru/C alloys were successfully synthesized by keeping Pt:Ru atomic ratio of 1:1 via polyl process. Due to alloying effect, the electro-catalytic performance of synthesized hybrid catalyst was examined better for oxidation reactions [83]. Various bimetallic supported catalysts have been prepared with low content of Pt for hydrogen generation purpose. Typical examples include Co-Pt/graphene [84], NiPtₓ/Al₂O₃ [85], Ni-Pt@graphene [86], Ni-Pt@ MIL-101 [87] and Ni₀.₅Pt₀.₁/Ce₂O₃ [88]. The improved catalytic activity and stability of these catalysts can be attributed to strong interaction between metals involved and excellent features of support. Fig. 2.9 presents the dependence of the turn over frequency (TOF) for CO oxidation over the particle size of bimetallic Rh₀.₅Pt₀.₅ NPs [89]. Small sized bimetallic nanoparticles depicted higher catalytic activity compared to the bigger ones. XPS analysis explored that Rh was prone to segregate on the particle surface with the particle size reduction which in turn led to the higher catalytic activity. The role of Pt as a promoter has been examined on supported Co catalysts for Fischer-Tropsch synthesis. Upon Pt addition, a significant shift in the reduction temperature of cobalt oxide has been observed towards lower values [90]. The addition of Pt significantly increases the CO hydrogenation rate of supported Co catalysts which can be attributed to: (i) an increased reducibility, (ii) high dispersion of reduced Co nanoparticles, and (iii) maximum coverage of reaction intermediates. The promoting effect of Pt in bimetallic catalysts results in modified electronic properties and improvement in active surface area. For that reason these catalysts have been widely in many reactions like oxygen reduction reaction (ORR) [91], selective oxidation of CO [92], electro-oxidation [93], and preferential oxidation of carbon monoxide (PROX) [94].
Fig. 2.9: The relationship between the turnover frequency on bimetallic Rh$_{0.5}$Pt$_{0.5}$ nanoparticle arrays and their particle size. Adopted from [89].

2.4.3.4 Promoting effect of Pd metal

Palladium nanoparticles (NPs) have attracted considerable attention for their high activity and selectivity in several catalytic reactions such as hydrogen generation from chemical hydrogen storage materials [95], fuel cell electrocatalysis [96, 97], steam reforming [98], and oxidation-reduction organic reactions [99]. Pd NPs have a wide application in the industrial field and also in basic chemical research. Xu and coworkers synthesized Ni-Pd bimetallic nanocatalyst (Ni$_{1-x}$Pd$_x$) by alloying Ni and Pd with different Pd contents and applied for hydrogen generation from hydrazine decomposition at mild conditions [100]. Bimetallic Ni$_{0.6}$Pd$_{0.4}$ nanocatalyst was found to exhibit appreciably high H$_2$ selectivity (> 80%) compared to corresponding monometallic counterparts (Fig. 2.10). These observations present a uniform alloy composition with inter-metallic bonding which is a crucial factor for high catalytic performance of the Ni-Pd nanocatalysts.
Fig. 2.10: Hydrogen selectivity for decomposition of hydrous hydrazine catalyzed by Ni$_{1-x}$Pd$_x$ at 323 K. Adopted from [100].

2.5 Applications of supported bimetallic catalysts

Bimetallic nanoparticles have found various applications in technologies and industries due to their immense features and additional degree of freedom than monometallic counterparts. Main applications of bimetallic catalysts in various fields include plasmonic, electrocatalytic activities, fuel cell, petroleum industry, pharmaceutical, pollution control, and catalysis. However, in spite of intensive research in size and shape manipulation of bimetallic NPs, it is still a major challenge to control their internal structures and particle size.

The main objective of this work is to apply the synthesized supported bimetallic catalysts for the decomposition of hydrazine. The brief description of hydrazine, mechanism of decomposition, and its electrochemical studies are as follows:

2.5.1 Hydrazine (N$_2$H$_4$)

The term "hydrazine" was coined for the first time by Emil Fischer in 1875 when he was preparing organic compounds that consisted of mono-substituted hydrazine. Later on, hydrazine sulfate was prepared by Theodor Curtius in 1887 by treating organic diazides with dilute sulfuric acid but he was unable to obtain pure
hydrazine, instead of repeated efforts. Pure anhydrous hydrazine was first prepared by the Dutch chemist Lobry de Bruyn in 1895.

Hydrazine (N\textsubscript{2}H\textsubscript{4}) is an inorganic compound. It is a colorless flammable liquid with an ammonia-like odor. Hydrazine is highly toxic and dangerously unstable. Acute exposure can damage the liver, kidneys, and central nervous system in humans. The liquid is corrosive and may also cause irritation of the eyes, nose, and throat, dizziness, headache, and nausea. Therefore, most commonly it is handled in solution form. Hydrazine is used as raw material in the preparation of polymers, plant growth regulators, antioxidants, emulsifiers, insecticides, pesticides, and photographic developers. In addition, hydrazine is used as a propellant in various rocket engines. The catalytic decomposition of hydrazine results in the release of heat and energy. Hydrazine can be decomposed to generate gases for driving turbines and operation of altitude control jets for rockets. Hydrazine is used in boilers as an oxygen scavenger in order to reduce the corrosion. Keeping in mind the strategy of present research work, hydrazine can be applied by following two ways:

2.5.1.1 Catalytic decomposition of hydrazine for hydrogen generation

2.5.1.1.1 Literature review

The energy utilization is increasing day by day to fulfill the demand of continuously growing worldwide population and meeting this energy demand will become a great challenge in future [101]. In this regard, hydrogen is recognized as an efficient and clean energy carrier because it generates water vapors as an exhaust upon combustion with oxygen. [102, 103]. Furthermore, it will become a key future fuel to control the greenhouse effect and global warming due to its volatile and non-toxic nature. However, low density of hydrogen is a main hindrance for its safe storage in compressed form [104]. The application of hydrogen as an energy source for fuel cells and electronic appliances demands novel materials which can provide hydrogen along with the advantages of high energy content, easy handling and transportation, recycling of byproducts, and cost economics [105]. For this purpose, different chemical hydrogen storage materials become an attractive and safe approach to generate hydrogen [106]. A number of solid materials have been investigated as hydrogen carrier including metal hydrides and imides, metal-organic frameworks (MOFs), carbon materials, complex hydrides, sorbent materials [107, 108], and
inorganic nanomaterials [109-111]. Among these, no single material can execute all requirements such as safe storage, temperature and pressure handling, recycling of by-products, and price. Consequently, a hydrogen storage material in liquid-phase is highly desired to produce hydrogen under mild conditions. The development of liquid-phase hydrogen storage materials such as formic acid [112], liquid organic hydrides [113], ammonia [114], and hydrous hydrazine [115, 116] have been considered more valuable over solid materials to deliver hydrogen.

Recently, hydrazine monohydrate (N₂H₄·H₂O) is considered as most probable energy carrier for hydrogen generation by a complete decomposition reaction. The major advantages of hydrazine as a source of hydrogen are its high hydrogen content (8.0 wt%), selective decomposition to hydrogen (along with nitrogen), wide range of working temperature (213-392 K), easy recharging as a liquid, COₓ-free hydrogen production, and usage of the existing infrastructure of other liquid fuels [117]. In addition, nitrogen gas (by-product) can be easily recycled to ammonia via Haber-Bosch process, and finally to hydrazine via catalytic or electrolytic on a large scale [118]. The decomposition of hydrazine does not follow the fixed stoichiometry. Hydrazine can be catalytically decomposed by two ways (Eqs. 2.1 and 2.2) depending upon the nature of catalyst and reaction conditions (temperature and pressure) [119].

The incomplete/undesired decomposition:

\[
3\text{N}_2\text{H}_4 \rightarrow 4\text{NH}_3 + \text{N}_2 \quad (\Delta H = -157 \text{ kJ mol}^{-1}) \quad (2.1)
\]

The complete/desired decomposition:

\[
\text{N}_2\text{H}_4 \rightarrow \text{N}_2 + 2\text{H}_2 \quad (\Delta H = -95.4 \text{ kJ mol}^{-1}) \quad (2.2)
\]

The proposed mechanism for hydrazine decomposition is given as follows:
The adsorbed hydrazine transfers two hydrogens to another hydrazine molecule. Resultantly, N–N bond breaks up to form two molecules of ammonia and an adsorbed cis diazine (HN₅NH). The diazine then disproportionates to give N₂ and hydrazine or decomposes to N₂ and H₂.

Nano catalysts comprising of noble and non-noble metals or their alloys [120, 121] have been widely applied for selective decomposition of hydrazine due to their large surface to volume ratio and presence of more active sites in comparison to the bulk phase catalysts. However, high noble metal content in these nanocatalysts discouraged their practical applications due to cost economics and limited resources. Furthermore, nanocatalysts presented poor activity towards hydrogen generation upon a decrease or removal of the noble metal content. On the other hand, supported metal catalysts are cost-efficient substituent for hydrazine decomposition. Till now, different mono and bimetallic supported catalysts have been investigated for hydrazine decomposition to generate hydrogen [122, 123]. The main advantages of supported metal catalysts are better metal dispersion, less agglomeration, use of noble metal in low content, synergistic effect, easy separation from reaction mixture, recovery of precious noble metal, and recycling of the catalysts [124]. Bimetallic supported catalysts based on nickel and noble metal alloys have been extensively applied for hydrazine decomposition, offering better efficiency due to synergistic effect of metal alloy particles. Zhang’s group prepared Al₂O₃ supported bimetallic (NiPtₓ and NiIrₓ) catalysts which displayed 98% H₂ selectivity for hydrazine decomposition [125-128]. Recently, researchers have applied cobalt (Co) in many important reactions owing to its relatively low price and better catalytic efficiency. Tong et al. studied different types of Co-B NPs for hydrazine decomposition to produce hydrogen [129, 130] but these catalysts depicted poor performance due to occupation of active sites of catalysts by surfactant molecules. Currently, amorphous CoPt/CeOₓ bimetallic catalyst showed remarkably high performance for hydrazine decomposition but it was found only 72% selective for H₂ at 298 K [131]. Regardless of the optimistic results of Co metal, limited studies have been made to use these catalysts for hydrous hydrazine decomposition. Therefore, the development of advanced catalysts is highly required for exploring hydrous hydrazine as a valuable hydrogen storage material.
2.5.1.2 Electro-oxidation of hydrazine

2.5.1.2.1 Literature review

Hydrazine fuel cell technology is considered more valuable for electronic devices and fuel cell applications [132]. The electrochemical studies are found to be more promising due to their quick response time, greater sensitivity, simple operation, ease of miniaturization and cost-effectiveness [133]. In this context, the design and development of novel electrocatalysts have been made for hydrazine oxidation reaction (HOR). The morphology and composition of the electrocatalysts are key factors to effect their performance [134]. However, the electro-oxidation of hydrazine at typical carbon electrodes are facing the problems of slow kinetics and large over potentials. The over potential for hydrazine electro-oxidation is dependent on the nature of electrode material [135]. Much effort has been made to increase the rate of electron transfer and minimize over potential of hydrazine.

The mechanism and kinetics of hydrazine oxidation has been studied under a wide range of solution conditions and at different electrodes like silver, gold and mercury [136], nickel [137], and platinum [138]. The mechanism of hydrazine electro-oxidation mainly involves with four-electron transfer with releases of N$_2$ gas as a final product. The oxidation mechanism of hydrazine can be described by following equations [139, 140]: It appeared that the rate determining step is a one-electron transfer followed by a three-electron transfer to give N$_2$ as a final product.

\[
\begin{align*}
N_2H_4 + H_2O & \rightarrow N_2H_3 + H_3O^+ + e^- \quad \text{(slow)} \\
N_2H_3 + 3H_2O & \rightarrow N_2 + 3H_3O^+ + 3e^- \quad \text{(fast)}
\end{align*}
\]

The electrochemically pretreated glassy carbon electrodes [141], carbon paste containing cobalt phthalocyanine [142], ultrafine platinum and ruthenium particles dispersed in porous carbon films [143] or on carbon fiber [144], poly(4-vinyl) pyridine-palladium film [145], ruthenium cyanide film coated electrodes [146], and cobalt hexacyanoferrate modified glassy carbon electrodes [147] have depicted remarkable catalytic properties towards the electro-oxidation of hydrazine compounds. The modification of electrode surfaces has contributed a great part towards electron transfer kinetics and electrocatalytic studies [148]. In this way, the desirable properties of active material can be assigned directly to the electrode.
surface. The modified electrodes have a wide range of potential practices to electrochemical technology, energy conversion, chemical analysis, as well as possible applications to information storage, electrochromism devices, and displays [149]. The use of nanomaterials in electrocatalysis have attracted much interest in recent years owing to the unique size-dependent properties [150] which make them applicable in the field of catalysis, electrocatalysis, microelectronics, and photonic devices [151]. Metal nanoparticles based electrocatalytic systems have some advantages including high surface area, durability, good dispersion, controlled particle size, and morphology of the attached nanoparticles [152] chemical inertness, good electrical, and mechanical properties [153-155]. In recent years, various noble metals (Ag, Au, Pt, and Pd), transition metals, and multi-wall carbon nanotubes (MWCNTs) supported nanocatalysts have been widely explored for HOR [156].
References


Chapter 3

Characterization Techniques

Various modern techniques are employed nowadays to characterize the prepared samples for their morphology, chemical composition, crystal structure, phase identification, and surface details. The present chapter provides description of the these techniques including X-ray diffraction, Fourier transform infra-red spectroscopy, scanning electron microscopy, transmission electron microscopy energy dispersive analysis, BET surface area analysis, temperature programmed reduction/oxidation, mass spectrometry, and cyclic voltammetry.

3.1 Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) is considered as workhorse technique for the analysis of organic compounds, although some inorganic materials can also be characterized. An infrared spectrum represents a fingerprint of a sample with absorption bands corresponding to the molecular vibrations of stretching and bending types. IR spectrum consists of a number of absorption bands which are obtained as a function of frequency number over a range of 4000-400 cm$^{-1}$. FTIR is a sensitive technique for identifying the chemical bonds in a molecule, presence of impurities, and pure structure of the sample as each functional group represents a characteristic absorption peak in IR region [1].

In IR technique, a beam of electromagnetic radiation is passed through a sample. IR radiations are either absorbed or transmitted depending upon their frequency and molecular structure. The transition takes place between two energy levels, when the frequency of incident electromagnetic wave matches with particular molecular vibration. The frequency (ν) of the absorbed radiations is related to the energy difference (ΔE) between two energy levels as described by Planck’s law [2]:

$$\Delta E = h\nu = hc/\lambda.$$  \hspace{1cm} (3.1)

The intensity of absorption peaks depends upon the energy of transition (ΔE) and is also directly correlated to the number of bonds present in the molecule.
3.1.1 FTIR instrumentation

The essential features of IR spectrophotometer are as follows:

- **Source**

  The source of radiant energy is a glowing ceramic rod which is heated electrically up to 1700 °C. Three most common sources are Nernst glower, Globarand, and Nichrome coil. A beam of continuous radiations is generated from the specific source. It is passed through an aperture which controls the amount of energy offered to the sample and eventually, to the detector.

- **Interferometer**

  The beam enters the interferometer where the “spectral encoding” takes place. The resulting interferogram signal then goes out of the interferometer.

- **Sample**

  The beam enters the sample compartment where it is transmitted through the surface of the sample. The electromagnetic radiations of the specific frequencies are absorbed according to the characteristics of the sample.

- **Detector**

  The beam finally passes to the detector for final measurement. The detector is a device to measure the special interferogram signal.

- **Computer**

  The measured signal is digitized and sent to the computer where the Fourier transformation takes place.

  The background spectrum must be analyzed to develop a relative scale for the absorption intensity. For this purpose a blank measurement (without sample) is taken and results are then compared in term of “percent transmittance.” with the measurement of the sample. This technique results in a spectrum with the removal of all instrumental errors so that; all spectral features are very closely related to the sample. Modern FTIR spectrophotometers are usually equipped with a powerful, computerized data system. It can perform a wide variety of data processing tasks such
as Fourier transformation, interactive spectral subtraction, baseline correction, smoothing, integration, and library searching [4].

![Schematic representation for instrumentation and data processing for FTIR spectroscopy. Adopted from [3].](image)

All FTIR spectra in this work were recorded on Pro 660 Cary Aligent Fourier transform spectrometer with a spectral resolution of 4 cm\(^{-1}\) in the region of 400-4000 cm\(^{-1}\).

### 3.2 X-ray diffraction technique (XRD)

X-ray diffraction (XRD) is considered as a suitable technique for both qualitative and quantitative phase analysis of solids on the basis of structure and morphology. It is a non-destructive analytical technique which reveals the informations about the crystallographic structure such as texture, crystallinity, phases, grain size, and crystal defects of materials.

#### 3.2.1 Fundamental principle

XRD technique involves the plotting of scattered intensity of an X-ray beam (hitting a sample) as a function of incident and scattered angle, polarization, and wavelength. The crystalline phase is obtained from the acquired data and is identified by matching with the standard patterns such as ICDD cards and Cambridge files. These patterns are built in software used with X-ray powder diffractometer. X-ray diffraction peaks are generated as a result of constructive interference of monochromatic beam that is scattered from each set of lattice plans at specific angles.
The peak intensities are determined by the atomic decoration within the lattice plans. Consequently, XRD pattern is the fingerprint of periodic atomic arrangements in a given material and enables quick phase identification for a large variety of crystalline samples. The condition for constructive interference is given by Bragg’s law which relates wavelength of X-rays to diffraction angle and lattice spacing as follows [5]:

\[ n \lambda = 2d \sin \theta \]  

where;

- \( d \) = distance between atomic layers in a crystal
- \( \lambda \) = wavelength of the incident X-ray beam
- \( n \) = an integer
- \( \theta \) = incident angle (angle between incident ray and scattered plane)

![Bragg's Law](image)

**Fig 3.2:** Bragg’s diffraction. Adopted from [6].

### 3.2.2 X-ray generation process

X-rays are the basic source of XRD technique which are generated in the form of high-energy electron beam by a cathode ray tube and are filtered to produce monochromatic radiation. The electrons are directed towards the sample where they interact with the target atoms thus knocking out the electrons from their orbital creating a high-energy excitation site. Electron falls to lower energy state on de-
excitation and emits an X-ray in the process. With several electrons bombarding the target electrons, X-rays of different wavelengths are produced [7].

**Fig. 3.3:** Schematic of a X-ray diffractometer. Adopted from [7].

Commonly, monochromatic incident beams are used in which there is only one wavelength of X-rays can be filtered by directing them through a foil. Different foils filter different wavelengths so it is important to choose the correct foil for the wavelength desired. One can also monochromize the beam using single crystal as a diffractor. The crystal can be set to diffract a certain wavelength by choosing different incident angles for the X-rays. When a sample is irradiated with a parallel beam of monochromatic X-rays, the atomic lattice of the sample acts as a three dimensional diffraction grating causing the X-ray beam to be diffracted to specific angles [8].

The diffraction patterns that include position (angles) and intensities (I) of the diffracted beam provide several informations about the sample and are discussed below:

- Angles are used to calculate the interplanar atomic spacings (d-spacings). The position (d) and intensity (I) information are used to identify the type of material by comparing them with patterns in the International Powder Diffraction File (PDF) database.
- The position (d) of diffracted peaks also provides information about the arrangement of atoms within the crystalline compound, unit cell volume, and other lattice parameters.
- Width of the diffracted peaks is used to calculate crystallite size and microstrain in the sample.
• The position and intensity from a phase can also be used to quantitatively estimate the amount of that phase in a multi-component mixture.

• **Calculations for crystallite size**

Crystallite size is calculated by using Debye Scherrer’s formula [9]:

\[
D = \frac{57.3K\lambda}{\beta \cos \theta} \text{ (nm)}
\]  

(3.3)

where:

D is the crystallite size, \(\beta\) is the full width at half maxima of peak (FWHM), \(K\) is the shape factor with value close to unity for cubic crystal system, and \(\lambda\) is the X–ray wavelength.

The crystallite size is inversely related to the peak broadening i.e., more narrow the peak larger will be the crystallite size and vice versa. If the crystals are defect free and periodically arranged then X-ray beam would be diffracted to the same angle. On the other end, crystals with random arrangement results in peak broadening.

### 3.2.3 Advantages

• Measure the average spacing between layers or rows of atoms.
• Determine the orientation of a single crystal or grain.
• Find the crystal structure of an unknown material.
• Identify crystalline phases and orientation.
• Measure thickness of thin films and multi-layers.
• Determine atomic arrangement and internal stress of small crystalline regions.

All XRD measurements for this work were carried out on PANalytical X'Pert High Score’s diffractometer with a Cu K\(\alpha\) radiation, operating in the range of 20° – 80°.
3.3 Atomic absorption spectroscopy (AAS)

Atomic absorption spectrometry (AAS) is a useful analytical technique that measures the concentrations of elements. This technique is used to analyze the metallic composition of alloys, catalysts, water, soil, and other inorganic materials. Atomic absorption spectroscopy is so sensitive that it can measure up to ppb scale in a sample. In this technique, the wavelengths of light are specifically absorbed by an element. The absorption of photons by an atom makes the basis of AAS. They correspond to the energies needed to promote electrons from one energy level to higher energy level. During analysis, the solution of metallic compound is aspirated into air/acetylene flame. The light of resonance wavelength is passed through the flame and extent of light absorption will be proportional to the number of ground state atoms present in the flame [10]. When metal solution is aspirated into a flame, following steps are involved:

- **Evaporation**: The solvent is evaporated, leaving a solid residue.
- **Vaporisation**: The solid is dissociated into the constituent atoms which are initially in ground state.
- **Excitation**: Atoms get excited to high energy level by the thermal energy of flame.

3.3.1 Atomic absorption spectroscopy instrumentation

- **Light source**

The light source is usually a hollow-cathode lamp of the element that is being measured. Lasers are also used in research instruments. Since lasers are intense enough to excite atoms to higher energy levels, they allow atomic absorption (AA) and atomic fluorescence measurements in a single instrument. The disadvantage of these narrow-band light sources is that only one element is measurable at a time.

- **Atomizer**

AA spectroscopy requires the analyte atoms in the gas phase. Ions or atoms in a sample must undergo desolvation and vaporization in a high-temperature source such as a flame or graphite furnace. Flame AA can only analyze solutions while graphite furnace AA can accept solutions, slurries, or solid
samples. Flame AA uses a slot type burner to increase the path length which results an increase in total absorbance.

- **Light separation and detection**

Atomic absorption spectrophotometers use monochromators and detectors for UV-visible light. The main purpose of the monochromator is to isolate the absorption line from background light. Simple dedicated AA instruments often replace the monochromator with a bandpass interference filter. Photomultiplier tubes are the most common detectors for AA spectroscopy.

![Schematic diagram of an atomic absorption analyzer. Adopted from [10].](image)

In this work, atomic absorption analysis was carried out on Perkin Elmer AA 400 atomic absorption spectrophotometer using an acetylene/air flame after fusion of samples with sodium peroxide and potassium hydroxide mixture (1:1 ratio) at 600 °C followed by dissolution in aqua regia.

### 3.4 Surface area analysis (SAA)

Surface area analysis is useful technique which is based on BET isotherm providing the surface area evaluation of porous materials. Surface area can affect dissolution rates of pharmaceuticals, activity of an industrial catalyst, adsorption capacity of air and water purifiers, and processing of different porous materials. Surface area analysis is performed by the physical adsorption of an inert gas (usually, nitrogen) as function of relative pressure (P/P₀) using fully automated analyzer. The amount of adsorbed gas is a function of not only of the total amount of exposed
surface, but also (i) temperature, (ii) gas pressure, and (iii) strength of interaction between gas and solid surface.

Gas adsorption measurements are widely used for the characterization of a variety of porous solids e.g., different forms of carbon, metal oxides, zeolites, and organic polymers. Physical adsorption is of peculiar importance for the determination of the surface area and pore size distribution of catalysts, industrial adsorbents, pigments, fillers, and other materials. Gas adsorption will measure pore size by recording isotherms from low pressures to saturation pressure. The pressure range is determined by the size range of the pores to be measured. Isotherms of microporous materials are measured over a pressure range of approximately 0.00001 to 0.1 mmHg. Isotherms of mesoporous materials are typically measured over a pressure range of 1-760 mmHg. A number of different theories or models can be applied to determine the pore size distribution. Available mesopore methods include: Barrett, Joyner and Halenda method (BJH), and Density Functional Theory (DFT). The t-plot analysis is also available for total micropore area measurement [11]

3.4.1 Overview of BET theory

The BET theory was developed by Stephen Brunauer, Paul Emmett Edward Teller in 1938. BET theory is a rule involving the physical adsorption of gas molecules on a solid surface and makes basis of an important analytical technique for specific surface area measurement of a material. The amount of gas adsorbed depends on many factors like temperature, gas pressure, strength of interaction between the gas and solid and exposed surface area. In BET surface area analysis, nitrogen (N\textsubscript{2}) gas is adsorbed at liquid N\textsubscript{2} temperature (-196 °C). A low temperature must be maintained to develop the strong interaction between the gas molecules and the surface of the sample so that measurable amounts of adsorption can occur. At the end of experiment, the sample is removed from the nitrogen atmosphere and heated to release the adsorbed nitrogen from the material and quantified. The collected data is obtained in the form of a BET isotherm, which plots the amount of gas adsorbed as a function of the relative pressure (P/P\textsubscript{0}).
3.4.2 Types of isotherms

There are six types of adsorption isotherms whose shapes are presented in Fig. 3.6.

**Type I isotherm:** Type I isotherm depicts the formation of monolayer adsorption when partial pressure (P/Po) < 1. Microporous materials with pore diameters less than 2 nm can be characterized by this type of isotherm.

**Type II isotherm:** The flatter region in the middle of type II isotherm represents the formation of a monolayer. At very low pressures, nitrogen gas is filled in micropores while, capillary condensation occurs at high pressures.

**Type III isotherm:** Type III isotherm shows the formation of multilayer. It is recognized principally by heats of adsorption which are less than the adsorbate heat of liquefaction. The adsorbate interaction with an adsorbed layer is greater than the interaction with the adsorbent surface.

**Type IV and V isotherms:** These isotherms appear when capillary condensation takes place. Gases condense in the tiny capillary pores of the solid at pressures below the saturation pressure of the gas. At the lower pressures, it depicts the formation of a monolayer followed by a formation of multilayers. Mesoporous materials with pore diameters between 2-50 nm shows this type of isotherm.

**Type VI isotherms:** It is a new type of isotherm exhibits a series of steps.
3.4.3 BET calculations

The informations obtained from the isotherm are used to calculate the surface area of the sample on the basis of BET equation as follows:

\[
\frac{1}{X\left(\frac{P}{P_0}\right)^{-1}} = \frac{1}{X_mC} + \frac{C-1}{X_mC} \frac{P}{P_0}
\]  

(3.4)

where;

- \(X\) is the weight of nitrogen adsorbed at a given relative pressure (P/Po), \(X_m\) is monolayer capacity, which is the volume of gas adsorbed at standard temperature and pressure (STP), and \(C\) is constant.

In this study, the measurement of specific surface area, pore volume and pore size distribution of the synthesized samples were performed on Sorptometer Kelvin 1042 using nitrogen adsorption-desorption isotherms at liquid nitrogen temperature (-196 °C). The total surface area was obtained by the Brunauer, Emmett and Teller (BET) method from the linear part of the nitrogen adsorption isotherm. The pore size distribution was achieved from Barrett, Joyner and Halenda (BJH) method using the desorption branch of the isotherm.
3.5 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is an extremely versatile technique capable of providing structural informations over a wide range of magnification. SEM technique delivers the informations about sample including nanostructure, surface topography, composition, and crystal orientation. SEM is also useful to study phase information and approximate size calculation of the system under consideration [13].

In most measurements, electron beam is focused on the selected area of the sample and these accelerated electrons have significant amounts of kinetic energy that is dissipated as a variety of signals generated by electron-sample interactions. These signals include secondary electrons, primary backscattered electrons, auger electrons X-rays, visible light, and heat. Secondary electrons are responsible for showing morphology and topography of the samples while primary backscattered electrons are highly valuable for demonstrating the composition in multiphase samples [14]. SEM technique finds applications in material sciences, soft matter analysis, life sciences, and nanotechnology.

3.5.1 Fundamental principle of SEM

In SEM technique the emission of secondary electrons is a major phenomenon that takes place due to bombardment of incident electrons over the surface of sample. A resulting electron vacancy is filled by another electron from a higher shell and X-ray is emitted to balance the energy difference between the two electrons. The emitted electron current is collected and amplified. The interaction of the primary beam with the sample results in the emission of electrons and electromagnetic radiations. The sample emitted electrons are focused onto a detector to produce two dimensional images in detail, which have a high tri-dimensional quality due to high depth of focus [15]. SEM analysis is considered to be "non-destructive"; that is, X-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyze the same materials repeatedly.
Fig. 3.7: Schematic representation of SEM. Adopted from [15].

Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm. The SEM is also capable of performing analysis of selected point locations on the sample; this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions (using EDX), crystalline structure, and crystal orientations.

3.6 Energy dispersive X-ray spectroscopy (EDX)

The elemental analysis of a sample can be carried out using EDX technique performed in conjunction with a scanning electron microscope (SEM). This technique relies on the investigation of a sample through interactions between electromagnetic radiation and matter, and analyzing X-rays emitted by the matter in response to being hit with charged particles. X-rays are emitted from the sample by the bombardment of the incident electron beam and are used to characterize the elemental composition of the sample under consideration. Qualitative analysis of the elements involves the identification of the lines in the spectrum. Quantitative analysis entails the measuring
line intensities for each element in the sample and for the same elements in calibration standards of known composition

3.6.1 **Fundamental principle**

To stimulate a measurable response from a specimen, a beam of charged particles (electrons or photons) is directed towards the sample. An electron presents in the inner energy shell of the atom within a sample get excited and is ejected from the shell thus creating a vacant space. Consequently, X-ray is emitted to balance the energy difference between low and high energy shells. The energies of X-rays generate a spectral line which is corresponding to the atomic structure of elements present in the sample. The energy versus relative counts of the detected X-rays produces a spectrum which is evaluated for quantitative and qualitative elemental composition of the specimen [16].

3.6.2 **Instrumentation**

There are four primary components of EDX setup; X-ray detector, pulse processor, and analyzer usually installed with TEM or SEM. X-ray energy is converted into voltage signals by detector. This information is sent to a pulse processor, which must measure the signals. The signals are passed to the analyzer for data analysis and display. The variations in X-ray intensity indicate the relative elemental concentrations across the surface. EDX mapping is recorded using image brightness as a direct function of the local concentration of the elements present.

In this research work, the surface morphology and elemental composition, and their distribution was examined by MIRA3 (Tescan) scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDX) analysis unit.

3.7 **Transmission electron microscopy (TEM)**

Transmission electron microscopy (TEM) technique deals with transmission a beam of electrons through an ultra-thin specimen and interaction with the specimen as they pass through it. Consequently, an image is formed which is magnified. Then it is focused by an objective lens onto an imaging device i.e., fluorescent screen and
finally detected by a sensor such as a CCD camera. TEM operates on the same basic principles as the light microscope but uses electrons instead of light. TEM uses electrons as “light source” and their much lower wavelength make it possible to get a resolution a thousand times better than with a light microscope. The possibility for high magnifications has made the TEM a valuable tool in medical, biological, and materials research. Electrons are usually generated in an electron microscope via thermionic emission from a tungsten filament, in the same manner as a light bulb, or alternatively by field emission. After acceleration by an electric potential, electrons are focused by electrostatic and electromagnetic lenses onto the sample. The transmitted beam contains information about electron density, phase, and periodicity; this beam is used to form an image. TEM is used heavily in material science, metallurgy and biological sciences. For TEM analysis, the specimens must be very thin and able to withstand the high vacuum present inside the instrument. TEM technique finds application in cancer investigation, materials science, pollution studies, nanotechnology, and semiconductors research.

In the present work, microstructure of the samples was evaluated using Philips TEM CM12.

3.8 Temperature programmed reduction and oxidation measurements

Temperature programmed methods are used to investigate the temperature-dependence of specific adsorption or desorption processes of samples in a well-defined gas atmosphere. Two most common temperature programmed techniques include:

- Temperature programmed reduction (TPR)
- Temperature programmed oxidation (TPO)

TPR and TPO are complimentary techniques for evaluation of reduction-oxidation properties of a catalyst. Temperature programmed reduction (TPR) is an important technique in the field of heterogeneous catalysis that involves the exposure of oxidized catalyst to a programmed temperature rise under a flow of dilute reducing gas mixture (e.g., H₂/Ar). TPO is similar to TPR except the sample in the reduced
form is exposed to a dilute oxidant (e.g., O$_2$/He) under a programmed temperature increase. The reduction/oxidation rates are monitored by analysis of the change in composition of the reactor effluents. The use of low partial pressures of the reactant makes it possible to observe the intermediate reactions depending on conditions including ramp rate, flow rates, and concentration of reactive gas. Moreover, the temperatures at which the reduction/oxidation occur are indicative of the strength of surface bonds [17].

3.8.1 Fundamental principle

TPR/TPO measurements are performed on fully automated chemisorption analyzer. For this purpose, the catalyst sample is loaded in U shape quartz tube and is positioned in a furnace with automatic temperature control. A thermocouple is inserted in U tube for temperature measurement. Pretreatment of the sample is the first step during which sample is activated in order to clean the surface of the catalyst and remove all adsorbed species. For this purpose, the sample is heated at high temperature in the flow of inert gas to ensure the elimination of moisture and other physisorbed impurities. Subsequently, the sample can be saturated with some reactive gas mixture at a given temperature. The excess gas is removed by flowing an inert gas at the same saturation temperature and then sample is cooled to room temperature. For TPR measurement, the sample is activated in 10% O$_2$/He gas mixture at a specific temperature ramp. After that, the sample is flushed with inert gas to remove moisture and physical adsorbed impurities. After cooling to room temperature, a reactive gas (10% H$_2$/He mixture) is passed over the sample until the base line was stable.

For TPO measurement, a catalyst in reduced form is subjected to reactive gas (10% O$_2$/He mixture). The composition of the gaseous mixture is measured at the exit of the sample tube with thermal conductivity detector (TCD). Now, the sample tube is heated inside the furnace from ambient up to predefined values (900-1000 °C) at a specific ramp rate (1-20 °C/min). The temperature is raised and a change in TCD signal is recorded upon the reduction of sample at a certain temperature. Finally, a plot of temperature versus TCD signal was obtained [18].

3.8.2 Advantages

- Identify the supported precursor phases and their interaction with support.
- Study the reaction intermediates depending on various conditions e.g., ramp rate, flow rates, and concentration of reactive gas.
• Measure the strength of surface bonds by correlating with the temperatures of reduction /oxidation.
• Provide qualitative and quantitative analysis, and the ‘spectra’ produced are characteristic for a given solid.
• Allow calculation of the metal phase percentage in the catalyst by knowing the stoichiometry of the reactive gas with metal.
• Examine the interactions between the components in multi-metallic systems
• Observe the role of promoters in alloy composition.
• Measure the reduction degree of active sites from TPR data.
• Calculate the activation energy related to reduction and oxidation.

In the present study, TPR/TPO measurements were performed on Chemisorb Analyzer 2750 (Micromeritics) to evaluate the phases of Co and Al oxides in Co based catalysts supported on γ-Al₂O₃ as well as promoting effect of noble metals on the reduction of cobalt oxide.

3.9 Hydrogen chemisorption

The chemisorption technique is used to evaluate the active metal surface area and metal dispersion. Chemisorption is an analytical technique to characterize a catalyst material, to determine a catalyst’s relative efficiency in promoting a particular reaction, to study catalyst poisoning, and in monitoring the degradation of catalytic activity over time of use. It is based on a chemical reaction between a suitable reactive gas and surface active sites. Catalytic activity depends on rate of chemisorption and strength of the chemisorption bond. If the bond is too weak then molecule may desorb prior to reacting. While, strong bonding may retard the release of the product and regeneration of the site.

Prior to measurement, the pretreatment is performed in order to clean the catalyst surface from water and other physisorbed species. The degassing can be done in vacuum or inert atmosphere. There are two methods to perform chemisorption: a) static volumetric chemisorption, and b) dynamic (flowing gas) chemisorption. In static method, known doses of reactive gas are introduced to sample which is already kept under high vacuum. After that equilibrium pressure (establishing between sample and gas) is measured. In dynamic technique known quantities of reactive gas are injected in the form of pulses till to saturation of sample. A calibrated thermal conductivity detector (TCD) monitors the quantity of adsorptive that is not taken up
by active metals. The amount of gas adsorbed is determined by integrating the peaks generated by TCD signal as a function of time [19].

The choice of reactive gas for chemisorption process is highly critical according to the active phase of the catalyst. The stoichiometric ratio between metal and gas should be known. Hydrogen is most commonly used reactive gas for chemisorption measurements of noble metals of group VIII. Usually, hydrogen is adsorbed in dissociative form but it may also adsorb in residual form or spilled over. Oxygen is also used with metals to show their oxidation properties. Carbon monoxide gas is highly reactive gas to evaluate many metals. It forms reactive carbonyls especially with iron and nickel. Nitrogen oxide can be conveniently used with cobalt and silver catalyst but the main issue is its toxicity.

Metal dispersion is an important parameter that can be related to the activity of a catalyst. Metal dispersion represents the fraction of active sites over the total sites of the catalyst and can be calculated as follows:

\[
\text{Metal dispersion} (\%) = \frac{\text{Gas adsorbed (moles g}^{-1}\text{)} \times \text{metal atomic weight} \times 10^{4}}{\text{Metal content} (\%) \times \text{H/M factor}}
\]

Where, H/M is a stoichiometric factor showing molecules of gas per surface of metal atom.

Metal particle diameter (in nm) is calculated as: 100/metal dispersion (\%)

In the present research work, hydrogen chemisorption measurements were performed on Chemisorb 2750 (Micromeritics).

3.9.1 Advantages
This chemisorption technique is used to evaluate active surface area, metal dispersion, active sites, metal particle size, acid/base surface properties, gas-solid interactions, and heat of adsorption.

Hydrogen chemisorption measurements were performed on Micromeritics ChemiSorb 2750 using 100% H₂ (N5 grade) as a reactive gas and Ar (N5 grade) as a carrier gas.

3.10 Mass spectrometry

Mass spectrometry is highly required characterization technique to record the mass spectra of organic compounds. The most common use of mass spectrometry is

i. Accurate determination of molecular weight
ii. Provide information about the structure of a compound by an examination of the fragmentation patterns

In a typical mass spectrometer; an organic compound under vacuum is bombarded with electrons. Accordingly, an electron is lost from the molecule followed by various fission steps which give rise to ions and neutral fragments. The positive ions are ejected from the ionization chamber and resolved by magnetic or electric field. The mass spectrum is obtained in the form of record of current generated by these ions as they arrive at detector. The intensity of peak is related to the presence of relative number of ions. More number of ions will produce intense peak and vice versa. The most intense peak in the spectrum is known as the base peak. Ions in the spectrum are separated according to their mass charge ratio (m/z). Instruments differ by their limit to which they can separate ions according to their m/z values [20]. In this work, the generated gaseous products were analyzed on mass spectrometer (MS) QMG-420 (Balzers). For MS analysis, the gas samples were collected in a separate flask by connecting it directly to the outlet of the reaction flask without using acid trapper assembly.

### 3.11 Cyclic voltammetry (CV)

Cyclic voltammetry (CV) is an important electrochemical technique in which working electrode potential is ramped linearly versus time. After the set potential is reached, the working electrode's potential is ramped in the opposite direction to return to the initial potential. These cycles of ramps in potential may be repeated as many times as needed. The current at the working electrode is plotted versus the applied voltage to give the cyclic voltammogram. Cyclic voltammetry is usually used to study the electrochemical properties of an analyte in solution. The power of cyclic voltammetry results from its ability to provide considerable information on the thermodynamics and kinetics of heterogeneous electron transfer reactions, and coupled chemical reactions. It also provides mathematical analysis of an electron transfer process at an electrode [21, 22].

**3.11.1 Basic principle**

In cyclic voltammetry, the potential is applied between the working electrode and the reference electrode while the current is measured between the working
electrode and the counter electrode. This data is plotted as current (i) versus applied potential (E). Fig. 3.8 shows that during the initial forward scan, an increasingly reducing potential is applied. As a result the cathodic current will rise thus showing the presence of reducible analytes in the system. During the reverse scan, reduced analyte will be re-oxidized, giving rise to anodic peak current. CV data can provide informations about redox potentials and electrochemical reaction rates.

![Cyclic voltammogram](image)

**Fig. 3.8:** A typical cyclic voltammogram. Adopted from [23].

### 3.11.2 Instrumentation

CV system consists of an electrochemical cell, a potentiostat, a current-to-voltage converter and a data acquisition system. The electrochemical cell consists of a working electrode, counter or auxiliary electrode, reference electrode, and electrolytic solution (Fig. 3.9). The working electrode’s potential is varied linearly with time, while the reference electrode maintains a constant potential. The counter electrode conducts electricity from the signal source to the working electrode. The purpose of the electrolytic solution is to provide ions to the electrodes during oxidation and reduction.
Fig. 3.9: A typical electrochemical cell. Adopted from [24].

A potentiostat is an electronic device which uses a dc power source to produce a potential which can be maintained and accurately determined, while allowing small currents to be drawn into the system without changing the voltage. The current-to-voltage converter measures the resulting current and the data acquisition system produces the resulting voltammogram. Common materials for the working electrode include glassy carbon, platinum, and gold. These electrodes are generally encased in a rod of inert insulator with a disk exposed at one end.

Fig. 3.10: Potentiostat interface 1000, Gamry. Adopted from [24].
3.11.3 Applications

CV is most useful technique in order to:

- Understand the preliminary electrochemical reaction.
- Show better sensitivity and fast reaction.
- Perform quantitative and qualitative analysis in conjunction with other techniques.
- Study qualitative information about electrochemical processes under various conditions e.g., the presence of intermediates in oxidation-reduction reactions, and the reversibility of a reaction.
- Determine the electron stoichiometry of a system, the diffusion coefficient of an analyte and the formal reduction potential, which can be used as an identification tool.
- Analyze the concentration of an unknown solution by generating a calibration curve of current vs. concentration.

In the present work, the electrochemical measurements were performed at room temperature on potentiostat interface 1000 by Gamry. A standard three electrode cell system was used for collecting cyclic voltammetric data which was equipped with modified glassy carbon as working electrode, a platinum wire as an auxiliary/counter electrode, and Ag/AgCl (3 M KCl) as reference electrode. All solutions were prepared in freshly deionized water and 10 mL of supporting electrolyte (0.1 M phosphate buffer, pH 7.2) was utilized for each electrochemical measurement. All cyclic voltammetry measurement were performed in the potential window of 0.5 to 1.0 V.
References

Chapter 4

Synthesis of $\gamma$-Al$_2$O$_3$ Supported Bimetallic Catalysts

The novel properties of supported bimetallic catalysts are derived from the synergistic effects of both the metals and their interaction with the support. The tuning of catalytic and electrocatalytic properties of supported bimetallic catalysts render them highly active and selective for multiple functions, and wide applications. This chapter presents the synthesis of supported bimetallic catalysts as envisioned in the present study. It involved two-step sequence: sol gel method was employed to synthesize catalyst support ($\gamma$-Al$_2$O$_3$) and then active phase (Co-M, M=Ir, Ru, Pt, and Pd) was loaded onto $\gamma$-Al$_2$O$_3$ support via wet impregnation method. The performance of prepared catalysts was evaluated by two different ways i.e., catalytic decomposition of hydrazine to generate hydrogen and electrocatalytic oxidation of hydrazine using cyclic voltammetry. The catalytic decomposition of hydrazine was performed in a self-designed assembly. For electrocatalytic measurements, glassy carbon electrode was modified with the prepared materials by simple drop casting method.

4.1 Synthesis of $\gamma$-Al$_2$O$_3$ granular support

Synthesis of $\gamma$-Al$_2$O$_3$ was carried out in two steps. In the first step, Al$_2$O$_3$ gel was synthesized by sol gel method, followed by the conversion of alumina gel into granules in the second step.

4.1.1 Basics of sol gel method

The sol gel processing seems to be the most convenient for the synthesis of nanoparticles because of its simplicity, better control over crystallite size, and other properties of the product [1]. The sol-gel process may be described as “formation of an oxide network through polycondensation reactions of a molecular precursor in a liquid.” A sol is a stable dispersion of colloidal particles in a solvent. Generally, the sol particles may interact by van der Waals forces or hydrogen bonds. The particles may be amorphous or crystalline. When all metal hydroxide species are linked in one network like structure, a dense gel is obtained. A gel consists of a three dimensional continuous network, which encloses a liquid phase. In the most gel systems used for materials synthesis, the interactions are of a covalent nature and the gelation process is irreversible. Removal of solvents and appropriate drying of the gel results in a
powder of the metal hydroxide. If the gel is dried by evaporation, then the capillary forces will result in shrinkage, the gel network will collapse. Resultantly, dense porous xerogel is formed which retain high porosity (15-50%), enormous surface area (150-900 m²/g), and very small pore size (1-10 nm). Porosity is defined as fraction of pore volume to total bulk volume. Porosity cannot be quantified easily because it can be modified or changed by a variety of processes such as deformation, hydrothermal alteration and, formation of fracture porosity. Pore size is not direct measure of porosity [1]. However, porosity can be increased by increasing size and density of pores. Moreover, calcination of the hydroxide leads to the corresponding ultrafine powder of the metal oxide. Since, the process undergoes a reaction on nanometer scale; the resultant material is of nanometer-sized [1].

**4.1.2 Adapted procedure for synthesis of γ-Al₂O₃ support**

Aluminum oxide (Al₂O₃) was synthesized by sol gel method for the purpose of its application as catalyst support. The experimental detail for synthesis of Al₂O₃ substrate is given as under:

**4.1.2.1 Preparation of alumina gel**

Aqueous solution (0.40 M) of ammonium hydroxide (NH₄OH, Fisher, 33%) was prepared and its initial pH was recorded as 12. Similarly, aqueous solution (0.40 M) of aluminum chloride hexahydrate (AlCl₃. 6H₂O, Sigma-Aldrich, ≥ 98%) was prepared with initial pH of 2.2. At first, ammonium hydroxide solution was saturated with carbon dioxide gas to produce a solution of ammonium bicarbonate with pH of 9.5. The presence of ammonium bicarbonate in sufficient quantity acted as a buffer to maintain pH in the range of 7 to 9 and carbon dioxide freely evolved during the reaction. The flow of CO₂(g) was stopped at pH 9.5. After that, aluminum chloride solution was added in a slow stream to buffered NH₄OH solution along with constant stirring [2, 3]. The solution temperature was maintained at 25 °C throughout the reaction. The reaction mixture was stirred initially at a speed of 200 rpm. Alumina sol thus formed became viscous with the passage of time. Hence, stirring rate was raised to 300 rpm for homogenous mixing of precursor solutions. The reaction was completed at pH 8.0. The aging of sol was done at 85 °C for 24 h for complete gelation. After that, sol was transformed to transparent gel which was washed with plenty of deionized water under vacuum filtration to remove chloride and other water soluble impurities.
The precipitation reaction proceeded according to the following scheme:

\[
\begin{align*}
\text{AlCl}_3 + 3\text{NH}_2\text{OH} & \rightarrow \text{Al(OH)}_3 \downarrow + 3\text{NH}_4\text{Cl} \quad \text{(4.1)} \\
\text{Al(OH)}_3 & \rightarrow \text{AlOOH} \downarrow + \text{H}_2\text{O} \quad \text{(4.2)} \\
2\text{AlOOH} & \rightarrow \text{Al}_2\text{O}_3 \downarrow + \text{H}_2\text{O} \quad \text{(4.3)}
\end{align*}
\]

### 4.1.2.2 Granulation of alumina gel

Alumina gel was fabricated in the shape of granules by adopting well established oil drop granulation method [4]. Briefly, the gel was added dropwise using peristaltic pump into a long column filled with paraffin oil in upper layer and ammonia solution in the bottom layer. The gel was converted to droplets under the surface tension effect during passage through the oil layer and collected in ammonia solution where, conditioning of gel droplets occurred for 1 h. After that, granules became rigid. The granules were washed with deionized water and then filtered. The granules were dried at room temperature for 12 h and further in oven at 200 °C for 3 h. The granules were subjected to calcination up to 750 °C in order to achieve gamma phase. The heat treatment at high temperature in single step can induce cracks in alumina granules thus lowering their mechanical strength. Therefore, calcination was carried out in multiple steps in order to avoid the cracks in the granules by performing heat treatment at 120, 450, 550, and 750 °C with stay time of 10 h at each step using programmable muffle furnace. Finally, sieving was done to obtain the granules of required mesh size: 0.60-1.70 mm. Physical characterization of γ-Al₂O₃ granular support was carried out via FTIR, XRD, SEM, EDX, TEM, and BET surface area analyses (discussion is provided in chapter 5).
4.2 Preparation of bimetallic catalysts/γ-Al$_2$O$_3$

Various methods have been developed to prepare supported catalysts for industrial applications including impregnation, ion-exchange, adsorption, and deposition-precipitation etc. Impregnation is a simplest and common procedure for dispersing the catalytic species on carrier. The brief description of impregnation process is given as follows:

4.2.1 Basics of impregnation method

Impregnation is the simplest and common procedure for dispersing a catalytic species on a carrier. For this purpose, the pre-dried support is immersed in an aqueous or non-aqueous solution containing salt precursor(s) of the catalytic components. This solution is added slowly to the support in which capillary forces draw the liquid into the pores followed by evaporation and drying. Impregnation process depends on many factors such as nature of solvent, pH, temperature, concentration of precursor solution, and aging time. The impregnation conditions should be adjusted in such a manner to obtain deep penetration of salt solution into the pores of support at the beginning of the coating. In this way, a heavy exterior metal coating will not be formed in the early stages which otherwise spoils the main goal. Multiple impregnation method is more advantageous for achieving better metal dispersion [5]. The most common solvents such as water, methanol, ethanol, isopropyl alcohol, tertiary butyl alcohol are more beneficial for multiple impregnations. Prior to impregnation, the aging of aqueous or alcoholic solution of metal precursor is of
prime importance to obtain: i) homogenous metal solution, ii) gradual penetration of metal ions inside the granule, and iii) uniform distribution of metal throughout the carrier. pH of the impregnating solution also has influence on the loading of metal on the surface of support. The acidic solutions of metal precursors are more suitable with pH ranging from 0.5 to 4. However, alkaline solutions (e.g., ammonical solution) having a pH 8 to 10 are also suitable. After impregnation, drying is done preferably at 120-200 °C and further at 250-450 °C. Then, catalyst is cooled and impregnation is repeated until the required metal loading has been achieved. Impregnation is followed by calcination step which involves heating of the catalyst in oxidizing atmosphere at a higher temperature. The purpose is to decompose the metal precursor with formation of metal oxide and removal of gaseous products. Finally, metal precursor is converted into the active phase (metal particles) which can be obtained by heating the catalyst in hydrogen (or diluted hydrogen) flow at high temperature. Next to metals, common active phases include metal oxides or sulfides. The activation treatment results in the formation of supported nanoparticles [6]. Different variables such as temperature, heating rate, heating time, and nature of atmosphere can affect the process and have to be selected according to the different system requirements [7].

4.2.2 Scheme for impregnating supported bimetallic catalysts

Four series of bimetallic catalysts supported on γ-Al₂O₃ granules were prepared via wet impregnation method using Co as base metal and noble metals (i.e., Ir, Ru, Pt, and Pd) as promoters in each catalytic series. All catalytic series were prepared in a similar manner by adopting wt/wt% method as shown by schematic presentation in Fig. 4.2. The nominal content of Co base metal was fixed at 20 wt% while loadings of noble metals were varied from 0 to 5 wt%, respectively in each series. These catalytic series were notated as CoIrₓ/γ-Al₂O₃, CoRuₓ/γ-Al₂O₃, CoPtₓ/γ-Al₂O₃, and CoPdx/γ-Al₂O₃ where, x is the mole fraction of Ir, Ru, Pt, and Pd metals in their respective series. The metal precursors used for impregnating the active component include cobalt acetate tetrahydrate (Co (C₂H₃O₂)₂.4H₂O, Merck, 99.9%), hexachloroiridic acid (H₂IrCl₆, Heraeus, ~35% Ir basis), ruthenium chloride trihydrate (RuCl₃.3H₂O, Aldrich, ~38% Ru basis), chloroplatinic acid hydrate (H₂PtCl₆.xH₂O, Aldrich, ~38% Pt basis), and palladium chloride (PdCl₂, Aldrich, 99%). The schematic diagram for theoretical composition of catalysts is shown in Fig. 4.3.
Prior to each metal loading, γ-Al₂O₃ granules were oven dried at 120 °C for 2 h. In a typical catalyst synthesis, γ-Al₂O₃ granules were wetted with aqueous solution of cobalt acetate for 1 h and subsequently, with hexachloroiridic acid at room temperature for 1 h. The volumes of metal solutions are added equivalent to the pore volume of the γ-Al₂O₃ support. The concentration of both metal solutions and multiple steps of impregnation were adjusted in such a manner to obtain the desired metal loadings. The use of multiple impregnations with dilute metal salt solution is beneficial to obtain the small size metal particles and good metal dispersion which ultimately results in superior catalytic activity [8]. After each metal coating, the catalysts were dried at room temperature for 2 h and calcined at 550 °C for 4 h. Finally, catalysts were subjected to H₂ reduction at 550 °C for 4 h in order to obtain CoIrₓ/γ-Al₂O₃ bimetallic catalyst series. In a similar way, remaining catalysts (CoRuₓ/γ-Al₂O₃, CoPtₓ/γ-Al₂O₃, and CoPdₓ/γ-Al₂O₃) were prepared by using their respective precursors in designed molar ratios. For comparison purpose, monometallic catalysts i.e., Co/γ-Al₂O₃, Ir/γ-Al₂O₃, Ru/γ-Al₂O₃, Pt/γ-Al₂O₃, and Pd/γ-Al₂O₃ were also synthesized by following the same scheme as used for bimetallic series.

The prepared catalysts were physically characterized by FTIR, XRD, SEM, EDX, TEM, BET analysis, H₂ chemisorption, TPR, and TPO measurements (discussion is provided in chapters 5, 6, 7 and 8).

![Flow chart for impregnation method.](image)
Fig. 4.3: Theoretical composition of prepared bimetallic catalysts.

4.3 Reactor for catalytic decomposition of hydrazine

The catalytic decomposition of hydrazine hydrate was carried out in a self-designed assembly as shown in Fig. 4.4. Hydrazine monohydrate \((\text{N}_2\text{H}_4\text{H}_2\text{O}, \text{Panreac, 80\%})\) was used as precursor to prepare 0.5 M solution of hydrazine in deionized water. Prior to each experiment, the catalyst was dried at 120 °C for 2 h to remove moisture and assembly was purged with Ar gas flow for 15 min to replace air. Generally, 10 mL of hydrazine hydrate solution (0.5 M) was added to a reaction flask. The reaction was initiated by introducing 10 mg of the catalyst to the reaction flask along with continuous stirring at 25 °C. The gaseous products were passed through a trapper containing 0.5 M HCl to ensure the absorption of ammonia. The volume of hydrogen gas along with nitrogen was measured by a gravimetric water displacement method using a calibrated electric balance [9, 10]. In order to determine the activation energy \((E_a)\), hydrazine decomposition was also carried out at different temperatures (35, 45, 55, and 65 °C).
The decomposition of hydrazine occurs in two steps: $3\text{N}_2\text{H}_4 \rightarrow 4\text{NH}_3 + \text{N}_2$ and/or $\text{N}_2\text{H}_4 \rightarrow \text{N}_2 + 2\text{H}_2$. The overall reaction for hydrazine decomposition is described as follows:

$$3\text{N}_2\text{H}_4 \rightarrow 4(1-X)\text{NH}_3 + (1 + 2X) \text{N}_2 + 6X\text{H}_2 \quad (4.2)$$

Where; $X$ is the selectivity towards hydrogen generation and can be evaluated on the basis of following relationship [11]:

$$X = (3\lambda - 1)/8 \quad (4.3)$$

where; $\lambda = n(\text{H}_2 + \text{N}_2)/(n\text{N}_2\text{H}_4)$

The gas volume was used to derive the number of moles of gases ($\text{H}_2 + \text{N}_2$). For $\lambda = 3X$ becomes unity (equivalent to 100% $\text{H}_2$ selectivity) thus showing complete decomposition of $\text{N}_2\text{H}_4$ to $\text{H}_2$.

Turn over frequency (TOF) is the number of product molecules formed per metal active site per unit time. TOF was calculated for all the catalysts at 50% hydrazine conversion as follows [12]:
$\text{TOF} = \frac{(PV/RT)}{(3n_{\text{metal}} t)}$  \hspace{1cm} (4.5)

where; $P$ is the atmospheric pressure, $V$ is the volume of generated gases ($H_2 + N_2$), $R$ is universal gas constant, $T$ is the reaction temperature, $n_{\text{metal}}$ is the mole number of metal in catalyst, and $t$ is the reaction time for the 50% conversion of hydrazine hydrate.

4.4 **Electrode modification for electrochemical studies**

The modification of electrode surfaces has been extensively studied research area in electrochemistry since few last decades [13]. The electrodes are modified by depositing a thin film on the electrode surface which results in special properties including physical, chemical, electrochemical, optical, electrical, transport etc. Generally, the performance of modified electrodes heavily depends on the electron transfer reaction. At a modified electrode, a substance undergoes redox reaction which accomplished by transferring electrons from the electrode to a reactant or a reaction substrate.

The electrodes can be modified by various techniques and are commonly termed as derivatized, polymer-coated, functionalized, and electrostatically-bound electrodes. The coating on the electrode surface should be electroactive, i.e., it can exchange electrons between electrode surface and solution. Generally, the electrode surface can be modified by following the chemisorption process. In this case, some species from the bulk solution find great attraction for electrode surface and get attached spontaneously to the surface. For instance, organic species containing double bonds are hydrophobic in nature and strongly adsorb from aqueous solution on carbon or platinum surfaces. Chemical reaction between the substrate and a molecule of interest results in the formation of bonds. The oxidation of a metal or carbon surface leads to the formation of hydroxyl groups which can be "silanized" by reaction with an organosilane and then reacted with another molecule of interest. This technique is expected to form a monolayer on the electrode. A polymer film of 0.1 to 10 $\mu$m thickness can also be deposited on the electrode surface by dipping the electrode into a polymer solution followed by solvent evaporation. The electrode surface can also be tuned by electrodeposition of polymer layers or by inducing the polymerization of monomers by electrochemical ways. Moreover, some types of polymers contain ionic...
groups which can extract charged ions from the solution and held them by electrostatic binding (e.g., Nafion) [14].

4.4.1 Adapted procedure for electrode modification

Glassy carbon (GC) was selected as a working electrode owing to its wide-range potential window (-1.5 to 1.5 V), low background current, excellent surface chemistry, cost economics, and broad applications of sensing and detection [15].

Fig. 4.5: A typical electrochemical cell. Adopted from [15].

Fig. 4.6 shows step wise procedure for electrode modification. Prior to modification, GC was polished to a mirror finish on a felt pad using alumina powder (0.3 μm) and then rinsed thoroughly with deionized water. The electrode was ultrasonicated in deionized water for 2 min in order to remove any loose alumina particles from grinding medium. The catalyst sample was grounded into fine powder. After that, 0.1 mg of catalyst powder was dispersed in 5 μL ethanol via ultrasonication for 5 min. The modification was done by introducing 2 μL of catalyst/ethanol dispersion on a clean surface of working electrode followed by drop casting of 2 μL Nafion (0.5%) solution [16]. The electrode was allowed to dry at room temperature for 15 min and further in oven for 30 min. The prepared (GC/(bimetallic catalyst/γ-Al₂O₃)/Nafion) electrode was used for acquiring the electrochemical data. The pre-conditioning steps (10 cycles) were performed before each electrochemical measurement in respective potential windows in order to reduce background current and to obtain a steady voltammogram, resultantly.
**Fig. 4.6:** Stepwise procedure for electrode modification and data acquisition including
1) dispersion of 0.1 mg of catalyst in ethanol, 2) insertion of 2 µL of ethanol solution onto working electrode, 3) drying of modified electrode, 5) electrochemical cell containing hydrazine analyte, working (W), reference (R) and counter (C) electrodes 6) stirrer, and 7) cyclic voltammetry profile. Adopted from [16].

### 4.5 Conclusions

A modest synthesis route was adapted for supported bimetallic catalysts. Simple sol gel method was adapted to prepare γ-Al₂O₃ substrate which was further converted to granules by oil drop method. γ-Al₂O₃ was subjected to FTIR, XRD, SEM, EDX, TEM, and BET analyses to explicate the purity and other structural characteristics. Cobalt as base metal with 20 wt% and promoter metals (Ir, Ru, Pt, and Pd) with 0-5 wt% were loaded onto γ-Al₂O₃ via successive wet impregnation technique to prepare four catalysts series namely, CoIrₓ/γ-Al₂O₃, CoRuₓ/γ-Al₂O₃, CoPtₓ/γ-Al₂O₃, and CoPdₓ/γ-Al₂O₃, respectively. The prepared catalysts were physically characterized by FTIR, XRD, BET, SEM, EDX, TEM, H₂ chemisorption, TPR, and TPO techniques in order to gain insight into their morphological and structural features. The activity of prepared catalysts was tested by two ways i.e; catalytic hydrazine decomposition for hydrogen generation and hydrazine electro-oxidation using cyclic voltammetry.
References


Chapter 5

CoIr$_x$/γ-Al$_2$O$_3$ Bimetallic Catalysts

A series of CoIr$_x$/γ-Al$_2$O$_3$ bimetallic catalysts with Ir mole fraction (x) of 0, 0.03, 0.046, 0.062, 0.081, and 0.094 was prepared by wet impregnation method followed by calcination and hydrogen reduction. The catalysts were characterized by various techniques to ensure the formation of Co-Ir nanoalloy particles well dispersed on γ-Al$_2$O$_3$ support. The catalytic performance was evaluated for hydrazine decomposition to generate hydrogen at room temperature and gaseous products were analyzed on mass spectrometer. The redox properties of the synthesized materials were comprehended using cyclic voltammetry. All bimetallic catalysts (CoIr$_x$/γ-Al$_2$O$_3$) showed potentiality for hydrogen generation and electrochemical applications. CoIr$_{0.081}$/γ-Al$_2$O$_3$ catalyst was found to exhibit highest performance owing to alloying effect between Co and Ir species, better metal dispersion, and metal-support interactions. Additionally, low Ir contents promoted the reactivity and selectivity tremendously thus making the process cost effective.

5.1 Physical characterization of γ-Al$_2$O$_3$ support

5.1.1 Results and discussion

5.1.1.1 FTIR analysis

FTIR spectrum of Al$_2$O$_3$ calcined at 750 °C is presented in Fig. 5.1. Thermal annealing of Al$_2$O$_3$ at 750 °C results in the conversion of amorphous phase of Al$_2$O$_3$ into γ-phase. The broad absorption bands in the range of 400-1000 cm$^{-1}$ are related to the stretching modes of AlO$_4$ and AlO$_6$ [1, 2]. It indicates the presence of tetrahedral and octahedral coordination in γ-Al$_2$O$_3$. The intense peak at 1632 cm$^{-1}$ is due to bending vibration of weakly bound molecular water. The absorption peak at around 2073 cm$^{-1}$ is attributed to adsorbed atmospheric CO$_2$ [3]. The vibrational band around 3452 cm$^{-1}$ also corresponds to OH group of adsorbed H$_2$O. These moisture impurities may come from KBr used in pellet making.
5.1.1.2 XRD analysis

XRD pattern of calcined $\gamma$-$\text{Al}_2\text{O}_3$ at 750 °C is shown in Fig 5.2. The XRD diffractogram presents the significant peaks at $2\theta \sim 37.3^\circ$, $45.7^\circ$, and $67.1^\circ$ having (311), (400), and (440) hkl values, respectively. These values match with standard ICDD Card No. 00-001-1303 thus indicating the formation of pure cubic phase $\gamma$-$\text{Al}_2\text{O}_3$ nanoparticles [4].

- **Calculations from XRD data**
  - Crystallite size ($D_{\text{XRD}}$) of $\gamma$-$\text{Al}_2\text{O}_3$ was derived from Debye Scherrer’s formula using the peak of high intensity. Its calculated value was: 5.8 nm.
- Lattice constant “a” for cubic unit cell was calculated as 0.80 nm by using the expression:

\[
a = \left[ d^2 (h^2 + k^2 + l^2) \right]^{1/2}
\]  

(5.1)

where; \( d \) is the value of d-spacing of line in XRD pattern and \( hkl \) are corresponding indices to each line in XRD pattern.

- Cell volume was found to be 512 Å\(^3\) from the expression: \( V_{cell} = a^3 \)

- X-ray density was also derived as 3.31 g cm\(^{-3}\) using the formula:

\[
d_{x-ray} (g/cm^3) = \frac{ZM}{N_V V_{cell}}
\]  

(5.2)

where; \( Z \) is the number of atoms per formula unit (\( Z = 10 \) for cubic system), \( M \) is the molecular mass of \( \text{Al}_2\text{O}_3 \), \( V \) (cm\(^3\)) is the unit cell volume, and \( N_v \) is the Avogadro’s number.

5.1.1.3 Electron microscopy and EDX analyses

After calcination at 750 °C, the structural features of prepared \( \gamma \)-\( \text{Al}_2\text{O}_3 \) granules were checked using SEM technique. Fig 5.3a presents the spherical shape of \( \gamma \)-\( \text{Al}_2\text{O}_3 \) granular support. SEM images of the sample at high magnification (25 kx) showed a smooth surface of \( \gamma \)-\( \text{Al}_2\text{O}_3 \) support (Fig. 5.3b). TEM image displayed the spherical shaped alumina particles as shown by arrow heads in Fig. 5.3c. Moreover, EDX analysis (Fig. 5.3d) confirmed the phase purity of \( \gamma \)-\( \text{Al}_2\text{O}_3 \) where peaks corresponding to Al and O elements are observed only.
Fig. 5.3: SEM images at magnifications of (a) 75x and (b) 25kx, (c) TEM image, and (d) EDX spectrum of prepared γ-Al₂O₃ support.

5.1.1.4 Surface area analysis

Fig. 5.4a presents the nitrogen adsorption-desorption isotherm of the calcined γ-Al₂O₃ granules with type IV shape which is the characteristic of mesoporous materials according to the IUPAC classification [5]. The major adsorption was noticed at relative pressure (P/P₀) range of 0.4-0.8 which can be related to filling of N₂ gas in mesopores. In addition, the appearance of desorption isotherm in the same range of relative pressure confirmed the formation of mesopores in γ-Al₂O₃ [6]. Fig. 5.4b shows the pore size distribution plot as measured from the adsorption isotherm using BJH method. The curve exhibited unimodal distribution with maxima centered at 7.68 nm. The pore volume valued was determined as 0.47 cm³ g⁻¹. Moreover, the surface area of alumina support was found to be 195 m² g⁻¹. Such a high surface area value may be attributed to the formation of the γ-phase upon calcination up to 750 °C [7, 8]. These results are complimented by XRD results.
Fig. 5.4: (a) N$_2$ adsorption-desorption isotherm and (b) pore size distribution curve of γ-Al$_2$O$_3$ support.

5.2 Physical characterization of CoIr$_x$/γ-Al$_2$O$_3$ catalysts

5.2.1 Results and discussion

5.2.1.1 AAS and XRD results

The metal components of the synthesized catalysts were estimated by atomic absorption spectroscopy (AAS) and results were found close to the initial metal loadings (Table 5.1).
Table 5.1: Chemical composition, surface and structural properties of CoIr\textsubscript{X}/\gamma-Al\textsubscript{2}O\textsubscript{3} catalysts.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Chemical Composition</th>
<th>Surface properties</th>
<th>Structural properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co\textsubscript{exp}\textsuperscript{a}</td>
<td>Ir\textsubscript{exp}\textsuperscript{b}</td>
<td>Ir/Co\textsuperscript{c}</td>
</tr>
<tr>
<td>\gamma-Al\textsubscript{2}O\textsubscript{3}</td>
<td>0</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>Co</td>
<td>17.96</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CoIr\textsubscript{0.03}</td>
<td>18.72</td>
<td>1.8</td>
<td>0.03</td>
</tr>
<tr>
<td>CoIr\textsubscript{0.046}</td>
<td>18.57</td>
<td>2.78</td>
<td>0.046</td>
</tr>
<tr>
<td>CoIr\textsubscript{0.062}</td>
<td>17.97</td>
<td>3.66</td>
<td>0.062</td>
</tr>
<tr>
<td>CoIr\textsubscript{0.081}</td>
<td>18.22</td>
<td>4.81</td>
<td>0.081</td>
</tr>
<tr>
<td>CoIr\textsubscript{0.094}</td>
<td>18.82</td>
<td>5.79</td>
<td>0.094</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Metal content of Co determined by AAS, \textsuperscript{b} Metal content of Ir determined by AAS, \textsuperscript{c} Ir/Co molar ratio calculated using experimental values, \textsuperscript{d} Total experimental metal content, \textsuperscript{e} Total theoretical metal content, \textsuperscript{f} % error in theoretical and experimental metal content, \textsuperscript{g} BET specific surface area, \textsuperscript{h} Pore volume determined by SAA, \textsuperscript{i} Crystallite size measured by XRD.

In addition to the characteristic peaks of \gamma-Al\textsubscript{2}O\textsubscript{3} (Fig. 5.5a), monometallic Co/\gamma-Al\textsubscript{2}O\textsubscript{3} catalyst (Fig. 5.5b) presented two peaks of Co in XRD profile that appeared at 2\theta values \sim 30.1° and 59.6° corresponding to (202) and (411) hkl values (ICDD Card No 01-070-2633). XRD profile of monometallic Ir/\gamma-Al\textsubscript{2}O\textsubscript{3} catalyst (Appendix, Fig. 1) showed a prominent peak of Ir metal at 2\theta \sim 40.6° corresponding to (111) plane, as well [9].
Fig. 5.5: XRD patterns of (a) χ-Al₂O₃, (b) Co/χ-Al₂O₃, (c) CoIr₀.03/χ-Al₂O₃, (d) CoIr₀.046/χ-Al₂O₃, (e) CoIr₀.062/χ-Al₂O₃, (f) CoIr₀.081/χ-Al₂O₃, and (g) CoIr₀.094/χ-Al₂O₃.

For CoIrₓ/χ-Al₂O₃ bimetallic catalyst series, the diffraction peak of Co are shifted to 2θ ~ 29.9° and 59.55°, respectively (Fig. 5.5(c-g)). No XRD peak was noticed for iridium metal, may be due to low contents of Ir metal. This shift of Co° peaks toward lower angles can be considered due to substitution of larger Ir atoms for the smaller Co atoms and all these observations clearly indicate the formation of Co-Ir alloy nanoparticles [10-12]. The crystallite sizes were calculted by the Scherrer equation and results are listed in Table 5.1. The crystallite size for Co NPs was found 5.30 nm. It was observed that an increase in the Ir mole fraction in bimetallic catalysts from 0 to 0.094 led to a decrease in average crystallite size from 5.30 to 4.82 nm, repectively. Notably, the formation of Co-Ir alloys perturbs the crystal growth of Co nanocrystallites which would affect the corresponding catalytic activity.

5.2.1.2 Surface area analysis

Fig. 5.6a presents the nitrogen adsorption-desorption isotherms for CoIr₀.081/γ-Al₂O₃ catalyst of type IV shape thus indicating the presence of mesopores with uniform pore size distribution [13, 14]. BET specific surface area, and pore volume of the catalysts (Table 1) were observed to decrease with respect to χ-Al₂O₃ support which can be explained by considering the blockage of χ-Al₂O₃ pores with metal particles during impregnation and/or sintering of pores at high temperature or may be
due to both factors [15]. The pore size distribution plot (Fig. 5.6b) of CoIr$_{0.081}$/γ-Al$_2$O$_3$ catalyst exhibited unimodal distribution with maxima centered at ~6 nm in mesoporous region (2-50 nm).

![N2 adsorption-desorption isotherm and pore size distribution curve of CoIr$_{0.081}$/γ-Al$_2$O$_3$ catalyst.](image)

**Fig. 5.6:** (a) N$_2$ adsorption-desorption isotherm and (b) pore size distribution curve of CoIr$_{0.081}$/γ-Al$_2$O$_3$ catalyst.

### 5.2.1.3 SEM and TEM analyses

The morphological characterization of the prepared catalysts was performed at different magnifications using SEM. Co/γ-Al$_2$O$_3$ catalyst presented the dispersion of metallic Co particles with different shapes and sizes (Fig. 5.7a). For CoIr$_{0.094}$/γ-Al$_2$O$_3$ sample (Fig. 5.7b), the particles were not well dispersed, which might be due to high metal loading. In contrast, CoIr$_{0.081}$/γ-Al$_2$O$_3$ catalyst (Fig. 5.7c) showed the
homogenous dispersion of Co-Ir alloy aggregates over the surface of $\gamma$-$\text{Al}_2\text{O}_3$ support. TEM image (Fig. 5.7d) further ensured the uniform distribution of spherical shaped alloy NPs. The average particle size of metal particle was calculated as $\sim$ 5 nm and these results were in good accordance with particle size evaluated from XRD. The high metal dispersion of this optimal catalyst composition later on was manifested by hydrazine. Here, high metal dispersion of nanoparticles corresponded to better catalytic activity for the hydrazine decomposition over this particular bimetallic catalyst.

Fig. 5.7: SEM images of: (a) Co/$\gamma$-$\text{Al}_2\text{O}_3$, (b) CoIr$_{0.094}$/$\gamma$-$\text{Al}_2\text{O}_3$ and (c) CoIr$_{0.081}$/$\gamma$-$\text{Al}_2\text{O}_3$ catalyst, and (d) TEM image of CoIr$_{0.081}$/$\gamma$-$\text{Al}_2\text{O}_3$ catalyst.
5.2.1.4 EDX analysis

EDX profiles of the prepared catalysts are shown in Fig. 5.8. EDX analysis of Co/γ-Al₂O₃ nanoparticles presented the presence of Co particles on the surface of alumina support. In contrast, EDX profiles of CoIrₓ/γ-Al₂O₃ bimetallic catalysts pointed to the co-existence of Co-Ir particles. The presence of Ir, Co, Al, and O in EDX pattern depicted the synergistic effect of Co and Ir metals to form alloy particles over the surface of alumina.
Fig. 5.8: EDX profiles of (a) Co/γ-Al₂O₃, (b) CoIr₀.₀₃/γ-Al₂O₃, (c) CoIr₀.₀₄₆/γ-Al₂O₃, (d) CoIr₀.₀₆₂/γ-Al₂O₃, (e) CoIr₀.₀₈₁/γ-Al₂O₃, and (f) CoIr₀.₀₉₄/γ-Al₂O₃. Moreover, EDX mapping confirms the uniform distribution of elements for CoIr₀.₀₈₁/γ-Al₂O₃ catalyst (Fig. 5.9). A uniform distribution of Co and Ir metals along with the constitution elements of support (Al and O) depicted the formation of Co-Ir alloy NPs.
Fig. 5.9: EDX mapping for elemental distribution in CoIr\textsubscript{0.081}/\gamma-Al\textsubscript{2}O\textsubscript{3} catalyst.

The results of EDX analysis for the prepared catalysts are listed in Table 5.2. EDX results were found in good agreement with AAS results. These results also ensured that the adapted synthesis route worked well for the metal loadings.

Table 5.2: EDX analysis of the prepared catalysts in CoIr\textsubscript{γ}/\gamma-Al\textsubscript{2}O\textsubscript{3} series.

<table>
<thead>
<tr>
<th>Catalyst/\gamma-Al\textsubscript{2}O\textsubscript{3}</th>
<th>Wt% O</th>
<th>Wt% Al</th>
<th>Wt% Co</th>
<th>Wt% Ir</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>56.53</td>
<td>28.18</td>
<td>15.19</td>
<td>0</td>
</tr>
<tr>
<td>CoIr\textsubscript{0.03}</td>
<td>57.17</td>
<td>30.03</td>
<td>11.67</td>
<td>1.13</td>
</tr>
<tr>
<td>CoIr\textsubscript{0.046}</td>
<td>51.61</td>
<td>29.65</td>
<td>16.18</td>
<td>2.56</td>
</tr>
<tr>
<td>CoIr\textsubscript{0.062}</td>
<td>47.94</td>
<td>31.24</td>
<td>17.52</td>
<td>3.30</td>
</tr>
<tr>
<td>CoIr\textsubscript{0.081}</td>
<td>48.52</td>
<td>30.21</td>
<td>16.37</td>
<td>4.90</td>
</tr>
<tr>
<td>CoIr\textsubscript{0.094}</td>
<td>46.43</td>
<td>33.68</td>
<td>13.75</td>
<td>6.14</td>
</tr>
</tbody>
</table>

5.2.1.5 TPR and TPO measurements

Generally, temperature programmed reduction studies have shown the reduction of Co\textsubscript{3}O\textsubscript{4} occurred in following two steps:[16]:

\[ \text{Co}_3\text{O}_4 + \text{H}_2 \rightarrow 3\text{CoO} + \text{H}_2\text{O} \]  \hspace{1cm} (5.3)

\[ 3\text{CoO} + 3\text{H}_2 \rightarrow 3\text{Co}^0 + 3\text{H}_2\text{O} \]  \hspace{1cm} (5.4)
TPR profiles of the prepared catalysts are presented in Fig. 5.10. The TPR profile of Co/γ-Al₂O₃ catalyst showed the reduction peaks in three main regions i.e., a low temperature peak in the region of 160-250 °C with a shoulder at 145 °C, followed by a broad band in the range of 250-450 °C and a high temperature peak at 450-800 °C. The appearance of first peak may attributed to the reduction of Co₃O₄ to CoO, whereas the broad band at 250-450 °C can be ascribed to complete reduction of CoO to metallic Co⁰ [17, 18]. The high temperature band (450-800 °C) appears due to difficult reduction of cobalt aluminates (CoAl₂O₄) which are formed as result of intense cobalt-support interaction. Al³⁺ ions may polarize Co-O bond in CoAl₂O₄ spinel which results in an increase in the effective charge of Co²⁺ ions. As a consequence, the lattice energy also rises which is responsible for reduction of cobalt aluminates at high temperatures [19]. CoIrₓ/γ-Al₂O₃ bimetallic catalysts presented an ease in reduction behavior in comparison to monometallic Co/γ-Al₂O₃ catalyst (Fig. 5.10(b-f)), where the incorporation of Ir metal in a small content led to a decrease in the reduction temperature of cobalt oxide [20]. With an increase of Ir/Co molar ratio up to 0.094, the reduction band in the region of 250-450 °C was observed to shift towards a lower temperature region (240-345 °C). The alloying effect of Ir was considered for the reduction of CoO to form Co⁰ which may be possibly due to weak interactions between cobalt oxide and support [21]. The promoting effect of some other noble metals over the reducibility of cobalt oxides has been reported earlier in detail [22, 23]. In this aspect, present study suggested that the alloying effect of the different catalytic materials may promote the in-situ reduction and catalytic performance. The overall synergistic effect seems to be responsible for the progress in the field of catalysis.
Fig. 5.10: H$_2$ TPR profiles for $\gamma$-Al$_2$O$_3$ supported: (a) Co, (b) CoIr$_{0.03}$, (c) CoIr$_{0.046}$, (d) CoIr$_{0.062}$, (e) CoIr$_{0.081}$, and (f) CoIr$_{0.094}$ catalysts.

Fig. 5.11 shows TPO profiles of the prepared catalysts which were also recorded following the TPR studies. For monometallic Co/$\gamma$-Al$_2$O$_3$ catalyst, the oxidation peak appeared in the region of 200–450 °C with a maxima at 325 °C which can be attributed to the oxidation of Co$^0$ to CoO and finally, to Co$_3$O$_4$ [24]. During TPR measurements, Co/$\gamma$-Al$_2$O$_3$ catalyst was reduced to Co$^0$ and cobalt aluminate (CoAl$_2$O$_4$). While, in the subsequent TPO studies only Co$^0$ was only oxidized to Co$_3$O$_4$ and no oxidation peak was noticed for CoAl$_2$O$_4$ [25]. Therefore, the absence of TPO peak for CoAl$_2$O$_4$ and a shift in the peak position upon incorporation of Ir metal manifested a strong interaction between Co$^{2+}$ and Ir$^{4+}$ ions to form Co-Ir bimetallic nanoalloys.
Fig. 5.1: TPO profiles for $\gamma$-Al$_2$O$_3$ supported: (a) Co, (b) CoIr$_{0.03}$, (c) CoIr$_{0.046}$, (d) CoIr$_{0.062}$, (e) CoIr$_{0.081}$, and (f) CoIr$_{0.094}$ catalysts.

5.3 Applications of CoIr$_x$/γ-Al$_2$O$_3$ catalysts

The catalytic activity of CoIr$_x$/γ-Al$_2$O$_3$ bimetallic catalysts was tested by adopting following two model reactions: (i) catalytic decomposition of hydrazine for hydrogen generation and (ii) electro-oxidation of hydrazine using cyclic voltammetry. The promoting role of Ir metal in CoIr$_x$/γ-Al$_2$O$_3$ and optimum composition within CoIr$_x$/γ-Al$_2$O$_3$ catalytic series was also evaluated. The results are discussed below:

5.3.1 Results and discussion

5.3.1.1 Hydrogen generation from decomposition of hydrazine over CoIr$_x$/γ-Al$_2$O$_3$ catalysts

The catalytic decomposition of hydrazine was performed using Co/γ-Al$_2$O$_3$ and CoIr$_x$/γ-Al$_2$O$_3$ catalysts in order to generate hydrogen at 25 °C. The metal/N$_2$H$_4$ molar ratio was kept constant at the value of 1:10 in all reactions. Fig. 5.12 presents the kinetic profiles for H$_2$ release from N$_2$H$_4$ decomposition over CoIr$_x$/γ-Al$_2$O$_3$ nanoparticles. All the prepared bimetallic catalysts performed well, showing their
catalytic potentiality for hydrogen generation from hydrazine decomposition. The catalytic activity and H\textsubscript{2} selectivity was found to depend on the Ir/Co ratio. The catalytic performance was noticed to increase significantly upon the incorporation of Ir in different proportions to Co/γ-Al\textsubscript{2}O\textsubscript{3} catalysts. The formation of Co-Ir alloy nanoparticles was considered responsible for the selective transformation of N\textsubscript{2}H\textsubscript{4} to H\textsubscript{2} by following the reaction path according to Eq. 2.2.

![Fig. 5.12: Kinetic profiles for H\textsubscript{2} release from the decomposition of hydrous hydrazine (0.5 M) over Co/γ-Al\textsubscript{2}O\textsubscript{3} and CoIr\textsubscript{x}/γ-Al\textsubscript{2}O\textsubscript{3} catalysts (x= 0, 0.03, 0.046, 0.062, 0.081, and 0.094) at 25 °C (Metal:N\textsubscript{2}H\textsubscript{4} molar ratio = 1:10).](image)

The detailed analysis of Fig. 5.12 depicted that the catalytic efficiency of CoIr\textsubscript{x}/γ-Al\textsubscript{2}O\textsubscript{3} catalysts enhanced with an increase in Ir content and became maximum at x = 0.081. Further increase in Ir content resulted to a slight decrease in the rate of reaction that can be correlated with an optimal loading and enrichment of the active sites of the catalyst. CoIr\textsubscript{0.081}/γ-Al\textsubscript{2}O\textsubscript{3} executed optimum performance by completing the reaction within 28 min with 100% H\textsubscript{2} selectivity and TOF value of 27.76 h\textsuperscript{-1}. Such high performance can be correlated to the high metal dispersion, small particle size, and more number of active sites over the surface of catalyst as confirmed by SAA,
SEM, TEM, and XRD analyses. On the other hand, synthesized monometallic catalysts (Co/γ-Al₂O₃ and Ir/γ-Al₂O₃) were also analyzed for the hydrogen generation but presented poor activity and selectivity for hydrazine decomposition while pure γ-Al₂O₃ support showed no activity at all. It may be inferred from these observations that the synergistic effect of metal alloying played a role to the hydrazine catalysis for the hydrogen generation in the presently fabricated materials. The rate of reaction was derived from the linear portion of kinetic profiles shown in Fig. 5.13. The rate of reaction was plotted against Ir contents (both in the logarithmic scale). A straight line with the slope value of 1.1 indicated first order reaction for H₂ generation with respect to Ir contents (Fig. 5.14).

![Graph showing reaction rate vs. Ir contents](image)

**Fig. 5.13:** A plot of reaction rate versus Ir contents (both in logarithmic scale).

Mass spectral (MS) analysis further confirmed the formation of hydrogen along with nitrogen having H₂:N₂ ratio of 2:1 (Fig. 5.14). The gas volumetric and MS results are in accordance with 100% selectivity for hydrogen generation.
5.3.1.1.1 Turn over frequency and \( \text{H}_2 \) selectivity

Turns over frequency (TOF) values were estimated using Eq. 4.5. The results in Table 5.3 present better selectivity and TOF for hydrogen generation using \( \text{CoIr}_{0.081}/\gamma-\text{Al}_2\text{O}_3 \) and a comparison of activities of all analogues in the series.

**Table 5.3:** Reaction time, TOF values, and \( \text{H}_2 \) selectivity of the catalysts.

<table>
<thead>
<tr>
<th>Catalyst/ ( \gamma-\text{Al}_2\text{O}_3 )</th>
<th>Reaction time (h)</th>
<th>TOF (h(^{-1}))</th>
<th>( \text{H}_2 ) Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>1.1</td>
<td>2.03</td>
<td>8.6</td>
</tr>
<tr>
<td>( \text{CoIr}_{0.03} )</td>
<td>1.32</td>
<td>6.55</td>
<td>71.08</td>
</tr>
<tr>
<td>( \text{CoIr}_{0.046} )</td>
<td>0.97</td>
<td>9.94</td>
<td>81.97</td>
</tr>
<tr>
<td>( \text{CoIr}_{0.062} )</td>
<td>0.84</td>
<td>12.10</td>
<td>85.95</td>
</tr>
<tr>
<td>( \text{CoIr}_{0.081} )</td>
<td>0.43</td>
<td>27.76</td>
<td>100</td>
</tr>
<tr>
<td>( \text{CoIr}_{0.094} )</td>
<td>0.66</td>
<td>15.84</td>
<td>98.09</td>
</tr>
</tbody>
</table>

Recently, it has been reported that the catalytic activity and selectivity of bimetallic catalysts depend on the type of active metals and their molar ratio [24]. The
dependency of H₂ selectivity and TOF over Ir content is shown in Fig. 5.15. CoIr₀.₀₈₁/γ-Al₂O₃ catalyst depicted better performance in comparison to monometallic counterparts owing to the strong interaction between Co and Ir over the surface of γ-Al₂O₃ support. Such behaviour is also well correlated with the high metal dispersion over the surface of catalyst as also confirmed by SEM and EDX analyses. The selectivity towards H₂ evolution might have resulted from the formation of heterometallic bonds in bimetallic catalysts which tuned the bonding patterns of the catalyst surface with the reactant molecules (N₂H₄). This strong metal-metal interactions may stabilize the possible reaction intermediates resulting to effective selectivity for H₂ generation [26].

![Fig. 5.15: Plot of H₂ selectivity versus Ir molar ratio over CoIrₓ/γ-Al₂O₃ catalysts (x= 0, 0.03, 0.046, 0.062, 0.081, and 0.094).](image)

### 5.3.1.1.2 Effect of temperature

In order to study the effect of temperature on the rate of reaction hydrous hydrazine (0.5M) was decomposed at different temperatures (i.e., 35, 45, 55, and 65 °C) using Co/γ-Al₂O₃ and CoIr₀.₀₈₁/γ-Al₂O₃ catalysts (Fig. 5.16). The hydrogen generation rate was found to rise with an increase in reaction temperature for both catalysts. However, CoIr₀.₀₈₁/γ-Al₂O₃ catalyst showed the maximum H₂ selectivity over the entire temperature range in comparison to Co/γ-Al₂O₃ catalyst.
Fig. 5.16: Kinetic profiles for H$_2$ release from decomposition of hydrous hydrazine (0.5 M) at different temperatures using 10 mg of (a) Co/γ-Al$_2$O$_3$ catalyst and (b) CoIr$_{0.081}$/γ-Al$_2$O$_3$ catalyst.

The apparent activation energy (E$_a$) was calculated at 50% conversion of hydrazine for Co/γ-Al$_2$O$_3$ and CoIr$_{0.081}$/γ-Al$_2$O$_3$ catalysts at different temperatures on the basis kinetic profiles shown in Fig. 5.16. Arrhenius plots (Fig. 5.17) were used to calculate the activation energy (E$_a$) values of 40.8 kJ mol$^{-1}$ for CoIr$_{0.081}$/γ-Al$_2$O$_3$ and
51.9 kJ mol\(^{-1}\) for Co/\(\gamma\)-Al\(_2\)O\(_3\) catalyst, respectively. These results infer an ease of \(\text{N}_2\text{H}_4\) decomposition over CoIr\(_{0.081}/\gamma\)-Al\(_2\)O\(_3\) catalyst thus chosen as an optimal composition for catalytic applications.

**Fig. 5.17:** A comparison of Arrhenius plots for \(\text{N}_2\text{H}_4\) decomposition on Co/\(\gamma\)-Al\(_2\)O\(_3\) and CoIr\(_{0.081}/\gamma\)-Al\(_2\)O\(_3\) catalysts.

**5.3.1.1.3 Recycling test**

To study the stability and reusability of prepared materials, CoIr\(_{0.081}/\gamma\)-Al\(_2\)O\(_3\) catalyst was removed from the reaction flask and filtered out. It was washed with excess of distilled water and dried at 120 °C for 2 h. This dried catalyst was employed for repeated decomposition of hydrous hydrazine (0.5 M) at 25 °C in three cycles. Fig. 5.18 shows that the reaction rate decreased slightly after each cycle but the catalytic activity was retained for the decomposition reaction and the 100% hydrogen selectivity was still achievable. There is the possibility that the presence of residual hydrazine or its fragments might block certain active sites of the catalyst resulting a decrease in the reaction rate in the subsequent reaction cycles.
5.3.1.1 Effect of support

The optimal composition CoIr\textsubscript{0.081} was further tested for its catalytic role in hydrazine decomposition but with different supports. CoIr\textsubscript{0.081} catalyst was deposited on two different supports, MgO, and ZnO besides γ-Al\textsubscript{2}O\textsubscript{3} via wet impregnation method. The activities of CoIr\textsubscript{0.081}/γ-Al\textsubscript{2}O\textsubscript{3}, CoIr\textsubscript{0.081}/MgO, and CoIr\textsubscript{0.081}/ZnO catalysts were evaluated for H\textsubscript{2} generation from the hydrous hydrazine decomposition (0.5 M) at 25 °C. γ-Al\textsubscript{2}O\textsubscript{3} supported CoIr\textsubscript{0.081} catalyst was found to be the most functional for hydrogen generation in comparison to CoIr\textsubscript{0.081}/MgO, and CoIr\textsubscript{0.081}/ZnO catalysts. The robust activity of γ-Al\textsubscript{2}O\textsubscript{3} supported CoIr\textsubscript{0.081} catalyst could be inferred from the value of molar ratio, n(H\textsubscript{2}+N\textsubscript{2})/n(N\textsubscript{2}H\textsubscript{4}) as 3 which corresponds to the complete decomposition of hydrous hydrazine and its evolution to H\textsubscript{2}. The kinetic profiles (in Fig. 5.19) manifest a steep conversion and fast rate of H\textsubscript{2} formation for this composition supported on γ-Al\textsubscript{2}O\textsubscript{3} as compared to MgO and ZnO supported CoIr\textsubscript{0.081} catalysts. One can conclude that γ-Al\textsubscript{2}O\textsubscript{3} supported catalysts present robust and fast H\textsubscript{2} generation.
5.3.1.1.5 **FTIR studies of spent catalysts**

In order to ensure the role of catalyst and $\gamma$-Al$_2$O$_3$ support in hydrazine decomposition reaction, FTIR analysis was performed. Fig. 5.20 shows the FTIR spectra of hydrazine hydrate, fresh $\gamma$-Al$_2$O$_3$, spent $\gamma$-Al$_2$O$_3$, fresh CoIr$_{0.081}$/γ-Al$_2$O$_3$ catalyst, and spent CoIr$_{0.081}$/γ-Al$_2$O$_3$ catalyst, respectively. It can be noticed that hydrazine hydrate has three major IR characteristics bands at 3190-3333 cm$^{-1}$, 1609 cm$^{-1}$, and 1282 cm$^{-1}$ (Fig. 5.20a). The absorption band at 3190-3333 cm$^{-1}$ can be assigned to the vibrations of N-H stretching while the band at 1609 and 1282 cm$^{-1}$ can be attributed to N-H bending vibrations. The absorption peak at 3333 cm$^{-1}$ corresponded to the stretching mode of OH group. For $\gamma$-Al$_2$O$_3$ and CoIr$_{0.081}$/γ-Al$_2$O$_3$ samples, the absorption bands in the region of 600-660 cm$^{-1}$ raised from the stretching mode of AlO$_4$ and AlO$_6$ while absorption bands below 600 cm$^{-1}$ could be attributed to the bending vibrational mode of AlO$_6$ groups. The absorption band around 3400 cm$^{-1}$ was assigned to OH stretching mode. Fig. 5.20c presents the FTIR spectrum of spent $\gamma$-Al$_2$O$_3$ sample after the reaction with hydrous hydrazine (0.5 M) at 25 ºC and no change in IR spectrum was observed on comparison with the FTIR spectrum of fresh $\gamma$-Al$_2$O$_3$ sample thus indicating no contribution of $\gamma$-Al$_2$O$_3$ support in the decomposition of hydrazine. On the other hand, FTIR spectrum (Fig. 5.20e) was
recorded for spent CoIr$_{0.081}$/$\gamma$-Al$_2$O$_3$ catalyst after its application in hydrous hydrazine decomposition (0.5 M) at 25 °C. Upon comparison with FTIR spectrum of fresh CoIr$_{0.081}$/$\gamma$-Al$_2$O$_3$ catalyst, two new absorption peaks at 1629 cm$^{-1}$ and 1381 cm$^{-1}$ in minor intensity appeared thus confirming that hydrous hydrazine was decomposed over CoIr$_{0.081}$/$\gamma$-Al$_2$O$_3$ catalyst to produce H$_2$ due to the contribution of metal nanoalloys. The nominal change in the FTIR spectrum (in the spent catalyst) may also have resulted from the presence of residual hydrazine or its fragments which may have affected the reaction rate in the following reaction cycles.

**Fig. 5.20:** FTIR spectra of (a) hydrazine hydrate, (b) fresh $\gamma$-Al$_2$O$_3$, (c) spent $\gamma$-Al$_2$O$_3$, (d) fresh CoIr$_{0.081}$/$\gamma$-Al$_2$O$_3$ catalyst, and (e) spent CoIr$_{0.081}$/$\gamma$-Al$_2$O$_3$ catalyst.
5.3.1.2 Electro-oxidation of hydrazine over CoIr₀.₀₈₁/γ-Al₂O₃ modified electrodes

The electrocatalytic activities of the CoIrₓ/γ-Al₂O₃ modified electrodes were evaluated for hydrazine oxidation by cyclic voltammetry (CV) using 2 mM hydrazine solution in 0.1 M phosphate buffer solution (PBS) of pH: 7.2. Fig. 5.21 shows the comparative CV profiles of CoIr₀.₀₈₁/γ-Al₂O₃ modified working electrode in the presence and absence of hydrazine using 0.1 M PBS at the scan rate of 25 mV s⁻¹. No anodic peak current was detected in the absence of hydrazine. However, in the presence of hydrazine an obvious anodic peak was obtained with a peak current value of 47.2 µA at ~0.89 V peak potential which clearly indicated that bimetallic alloy NPs could accelerate the electron transfer process.

![Fig. 5.21: Electrochemical response of CoIr₀.₀₈₁/γ-Al₂O₃ modified electrode in the absence and presence of hydrazine.](image)

In a similar manner, the cyclic voltammetric studies were performed on bare and modified GC electrodes with other compositions as shown in Fig. 5.22. No anodic peak current was observed for bare working electrode while, poor current response was found for (Co/γ-Al₂O₃) modified GC electrode without any oxidation peak for hydrazine. In contrast, CoIr₀.₀₈₁/γ-Al₂O₃ modified electrode presented a well defined oxidation peak at potential value of ~0.87 V with peak current value of 48.7 µA. Hence, it is appropriated that the synergistic effect of bimetallic alloy plays its role in promoting the catalytic activity [27].
Fig. 5.22: Cyclic voltammograms of CoIr$_{0.081}$/\(\gamma\)-Al$_2$O$_3$ modified electrodes for 2 mM hydrazine electro-oxidation in 0.1 M PBS (pH 7.2) @ 25 mV s$^{-1}$.

All the prepared CoIr$_x$/\(\gamma\)-Al$_2$O$_3$ catalysts (x = 0, 0.03, 0.046, 0.062, 0.081, and 0.094) were used to modify GC electrode in order to check their catalytic activity in electrocatalysis of hydrous hydrazine. Fig. 5.23 presents the CV profiles for the oxidation of 2 mM hydrazine analyte on the modified electrodes, separately. The data extracted from CV profiles is tabulated in Table 5.4. There are two aspects in these comparative profiles: the peak current values and peak potential position. In the case of CoIr$_{0.081}$/\(\gamma\)-Al$_2$O$_3$, both of these parameters pointed towards the improved and promotional activity for hydrazine analyte. The oxidation of hydrazine occurred at 0.88 V with peak current of 50.3 \(\mu\)A for CoIr$_{0.081}$/\(\gamma\)-Al$_2$O$_3$ composition thus showing better response as compared to rest of the samples. This behavior was also depicted for the catalytic hydrazine decomposition thus rendering it an optimal composition. Thus, one can readily assign a robust catalytic potentiality to this optimal composition.
Fig. 5.23: Cyclic voltammograms of CoIr\textsubscript{x}/γ-Al\textsubscript{2}O\textsubscript{3} modified electrodes for 2 mM hydrazine electro-oxidation in 0.1 M PBS (pH 7.2) @ 25 mV s\textsuperscript{-1}, inset showing CV profile of CoIr\textsubscript{0.081}/γ-Al\textsubscript{2}O\textsubscript{3} modified electrode @ 25 mV s\textsuperscript{-1}.

Table 5.4: Data extracted from CV plots for CoIr\textsubscript{x}/γ-Al\textsubscript{2}O\textsubscript{3} modified electrodes @ 25 mV s\textsuperscript{-1}.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Peak potential (V)</th>
<th>Peak current (µA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoIr\textsubscript{0.03}/γ-Al\textsubscript{2}O\textsubscript{3}</td>
<td>0.85</td>
<td>7.33</td>
</tr>
<tr>
<td>CoIr\textsubscript{0.046}/γ-Al\textsubscript{2}O\textsubscript{3}</td>
<td>0.89</td>
<td>19.1</td>
</tr>
<tr>
<td>CoIr\textsubscript{0.062}/γ-Al\textsubscript{2}O\textsubscript{3}</td>
<td>0.90</td>
<td>31.17</td>
</tr>
<tr>
<td>CoIr\textsubscript{0.081}/γ-Al\textsubscript{2}O\textsubscript{3}</td>
<td>0.88</td>
<td>50.3</td>
</tr>
<tr>
<td>CoIr\textsubscript{0.094}/γ-Al\textsubscript{2}O\textsubscript{3}</td>
<td>0.90</td>
<td>34.5</td>
</tr>
</tbody>
</table>

5.3.1.2.1 Effect of scan rate

Normally, the electrochemical (EC) response of any electrode/active material is analyzed on the basis of ease in electron transfer process. Accordingly, the peak current may rise linearly with an increase in scan rate (ν). The effect of scan rate on
oxidation peak current was also examined in the range of 10-100 mV s\(^{-1}\) as shown in Fig. 5.24a. With increasing scan rate, the anodic peak potential was noticed to shift slightly towards more positive region suggesting a kinetic limitation in the reaction between the modified electrode and hydrazine [28]. However, the anodic peak current was found to increase linearly with the square root of scan rate as shown in Fig. 5.24b thus presenting a diffusion limitation. These trends suggest that the overall electro-oxidation process is governed by diffusion of hydrazine to the redox sites of the modified electrode.

![Cyclic voltammograms of 2 mM hydrazine over CoIr\(_{0.081/\gamma}\)-Al\(_2\)O\(_3\) modified electrode in 0.1 M PBS (pH 7.2) at scan range of 10-100 mV s\(^{-1}\) and (b) dependence of \(i_p\) on \(\nu^{1/2}\).](image)

**Fig. 5.24:** (a) Cyclic voltammograms of 2 mM hydrazine over CoIr\(_{0.081/\gamma}\)-Al\(_2\)O\(_3\) modified electrode in 0.1 M PBS (pH 7.2) at scan range of 10-100 mV s\(^{-1}\) and (b) dependence of \(i_p\) on \(\nu^{1/2}\).
The dependence of \( i_p \) on \( \nu^{1/2} \) for anodic peak is described by the following relation:

\[
i_p (\mu A) = 623.2 (\nu)^{1/2} + 29.99, \quad (R^2 = 0.98) \tag{5.5}
\]

The diffusion character of hydrazine electro-oxidation was also confirmed by linear dependence of \( \ln i_p \) on \( \ln \nu \) (Fig. 5.25) and described as follows:

\[
\ln i_p (\mu A) = 0.54 \ln \nu + 6.10, \quad (R^2 = 0.99) \tag{5.6}
\]

A linear relationship existed in such plots corresponds to diffusion controlled process \([29, 30]\). This linear relationship indicates that electro-oxidation of hydrazine is a diffusion controlled process at CoIr\(_{0.08}/\gamma\)-Al\(_2\)O\(_3\) modified electrode under given sets of conditions.

5.3.1.2.2 Effect of concentration

To study the effect of hydrazine concentration, the electro-oxidation measurements were performed on CoIr\(_{0.08}/\gamma\)-Al\(_2\)O\(_3\) modified electrode by varying hydrazine concentration from 2 to 10 mM in 0.1 M PBS (pH 7.2) as shown in Fig. 5.26a. The anodic peak current at the modified electrode was found proportional to the concentration of hydrazine (Fig. 5.26b). Such behavior can be correlated to well dispersed Co-Ir bimetallic alloy nanoparticles as electroactive centers in this optimal material; thus corresponding to the very even and fine distribution of metal particles as shown by EDX mapping \([31]\).
Fig. 5.26: (a) Hydrazine concentration effect in the range of 2-10 mM for CoIr\(_{0.08}/\gamma\)-Al\(_2\)O\(_3\) modified electrode in 0.1 M PBS (pH 7.2) @ 25 mV s\(^{-1}\) and (b) linear dependence of anodic peak current (\(i_p\)) on hydrazine concentration.

5.3.1.2.3 Reproducibility and stability studies

The repeatability and stability of the CoIr\(_{0.08}/\gamma\)-Al\(_2\)O\(_3\)/GCE were investigated by CV method in 10 successive cycles using 2 mM hydrazine as shown in Fig. 5.27.
The CV profiles of the modified electrode was maintained in all cycles with a relative standard deviation (RSD) of 2.78%, indicating its good repeatability and stability.

![CV profiles of CoIr0.081/γ-Al2O3 modified GCE in 10 successive cycles for hydrazine electro-oxidation in 0.1 M PBS (pH 7.2) @ 25mV s⁻¹.](image)

**Fig. 5.27:** CV profiles of CoIr0.081/γ-Al2O3 modified GCE in 10 successive cycles for hydrazine electro-oxidation in 0.1 M PBS (pH 7.2) @ 25mV s⁻¹.

### 5.4 Conclusions

We have established a facile synthesis of CoIrₓ/γ-Al₂O₃ bimetallic nanomaterials by wet impregnation method. These synthesized catalysts exhibited the superior catalytic performances towards the dehydrogenation of hydrous hydrazine at room temperature. The prepared CoIrₓ/γ-Al₂O₃ catalysts proved to be highly promising and were quite suitable for making the process cost effective and efficient for H₂ generation from hydrazine decomposition. Among the analogues in the series, CoIr₀.₀₈₁/γ-Al₂O₃ catalyst presented 100% H₂ selectivity with TOF of 27.76 h⁻¹. The superior performance of CoIr₀.₀₈₁/γ-Al₂O₃ made it as optimal catalyst for hydrogen generation from decomposition of N₂H₄·H₂O. The robust activity might be due to synergistic effect of Co-Ir alloy along with excellent features of granular γ-Al₂O₃ support.
To investigate the electrochemical behavior of the synthesized CoIr\textsubscript{x}/\textgamma-Al\textsubscript{2}O\textsubscript{3} catalysts, cyclic voltammetry studies were employed for hydrazine oxidation using GC electrode modified with these catalysts. All catalysts presented better mechanical and chemical stability. The modified electrodes displayed a linear relationship of scan rate and anodic peak current for hydrazine electro-oxidation. CoIr\textsubscript{0.08}/\textgamma-Al\textsubscript{2}O\textsubscript{3} catalyst exhibited prominent current response compared to its analogues. On the basis of electrochemical results, this catalyst is also proposed as a promising candidate for extensive electroanalytical applications prospects. In conclusion, the optimal loading of Co and Ir onto \textgamma-Al\textsubscript{2}O\textsubscript{3} support has proven as an effective composition.
References

Chapter 6

CoRu\textsubscript{x}/γ-Al\textsubscript{2}O\textsubscript{3} Bimetallic Catalysts

Advanced materials were prepared to obtain highly dispersed CoRu\textsubscript{x}/γ-Al\textsubscript{2}O\textsubscript{3} bimetallic catalysts with Ru molar fraction (x) = 0, 0.04, 0.07, 0.11, 0.14 and 0.16 using wet impregnation method followed by calcination and reduction. The catalytic activity was assessed by two ways i.e., catalytic decomposition and electrocatalytic oxidation of hydrazine, respectively. All catalysts presented their potentialities for both model reactions. In order to confirm the structure and properties of Co-based catalysts the samples were characterized by XRD, AAS, BET, H\textsubscript{2} chemisorption, SEM, TEM, EDX, TPR, and TPO techniques. Especially, CoRu\textsubscript{0.11}/γ-Al\textsubscript{2}O\textsubscript{3} exhibited superior activity and satisfactory stability due to synergistic effect of metals involved, small particle size and metal-support interactions.

6.1 Physical characterization of CoRu\textsubscript{x}/γ-Al\textsubscript{2}O\textsubscript{3} catalysts

6.1.1 Results and discussion

6.1.1.1 AAS and XRD results

Table 6.1 presents the metal composition of the prepared catalysts as determined by AAS and results were found close to the initial metal loadings.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Co\textsubscript{exp}\textsuperscript{a} (wt%)</th>
<th>Ru\textsubscript{exp}\textsuperscript{b} (wt%)</th>
<th>Ru/Co\textsuperscript{c}</th>
<th>M\textsubscript{exp}\textsuperscript{d} (wt%)</th>
<th>M\textsubscript{th}\textsuperscript{e} (wt%)</th>
<th>%\textsuperscript{f} Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co/γ-Al\textsubscript{2}O\textsubscript{3}</td>
<td>18.22</td>
<td>0</td>
<td>0</td>
<td>18.22</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>CoRu\textsubscript{0.04}/γ-Al\textsubscript{2}O\textsubscript{3}</td>
<td>18.59</td>
<td>1.28</td>
<td>0.04</td>
<td>19.87</td>
<td>21</td>
<td>5.38</td>
</tr>
<tr>
<td>CoRu\textsubscript{0.07}/γ-Al\textsubscript{2}O\textsubscript{3}</td>
<td>18.92</td>
<td>2.27</td>
<td>0.07</td>
<td>21.19</td>
<td>22</td>
<td>3.68</td>
</tr>
<tr>
<td>CoRu\textsubscript{0.11}/γ-Al\textsubscript{2}O\textsubscript{3}</td>
<td>18.10</td>
<td>3.41</td>
<td>0.11</td>
<td>21.51</td>
<td>23</td>
<td>6.48</td>
</tr>
<tr>
<td>CoRu\textsubscript{0.14}/γ-Al\textsubscript{2}O\textsubscript{3}</td>
<td>17.99</td>
<td>4.32</td>
<td>0.14</td>
<td>22.31</td>
<td>24</td>
<td>7.04</td>
</tr>
<tr>
<td>CoRu\textsubscript{0.16}/γ-Al\textsubscript{2}O\textsubscript{3}</td>
<td>18.63</td>
<td>5.11</td>
<td>0.16</td>
<td>23.74</td>
<td>25</td>
<td>5.04</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Co metal content determined by AAS, \textsuperscript{b} Ru metal content determined by AAS, \textsuperscript{c} Ru/Co molar ratio calculated using experimental values, \textsuperscript{d} Total experimental metal content, \textsuperscript{e} Total theoretical metal content, \textsuperscript{f} % error in theoretical and experimental metal content.
Fig. 6.1 shows XRD patterns of the prepared samples. In the case of CoRu/γ-Al$_2$O$_3$ catalysts, no additional diffraction peak was noticed due to either low metal content or small sized Ru NPs which cannot be detected by XRD [1]. Furthermore, the crystallite sizes were determined from XRD patterns of the catalysts using Scherrer equation at 44.64°. It was found that an increase of the Ru content resulted to a decrease of the average crystallite size up to 4.82 nm (Table 6.2) which would affect the corresponding catalytic activity.

![XRD patterns of various samples](image)

**Fig. 6.1:** XRD patterns of: (a) γ-Al$_2$O$_3$, (b) Co/γ-Al$_2$O$_3$, (c) CoRu$_{0.04}$/γ-Al$_2$O$_3$, (d) CoRu$_{0.07}$/γ-Al$_2$O$_3$, (e) CoRu$_{0.11}$/γ-Al$_2$O$_3$, (f) CoRu$_{0.11}$/γ-Al$_2$O$_3$, and (g) CoRu$_{0.16}$/γ-Al$_2$O$_3$. 
Table 6.2: Adsorption parameters, structural properties, and hydrogen chemisorption measurements of CoRu$_x$/$\gamma$-Al$_2$O$_3$ catalysts.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Adsorption parameters</th>
<th>Structural properties</th>
<th>H$_2$ chemisorption measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$S_A^a$</td>
<td>$V_p^b$</td>
<td>$d_P^c$</td>
</tr>
<tr>
<td></td>
<td>(m$^2$ g$^{-1}$)</td>
<td>(cm$^3$ g$^{-1}$)</td>
<td>(nm)</td>
</tr>
<tr>
<td>$\gamma$-Al$_2$O$_3$</td>
<td>195</td>
<td>0.47</td>
<td>8.6</td>
</tr>
<tr>
<td>CoRu$_0.04$/$\gamma$-Al$_2$O$_3$</td>
<td>107.6</td>
<td>0.41</td>
<td>8.5</td>
</tr>
<tr>
<td>CoRu$_0.07$/$\gamma$-Al$_2$O$_3$</td>
<td>102.8</td>
<td>0.40</td>
<td>7.3</td>
</tr>
<tr>
<td>CoRu$_0.11$/$\gamma$-Al$_2$O$_3$</td>
<td>100.3</td>
<td>0.38</td>
<td>6.5</td>
</tr>
<tr>
<td>CoRu$_0.14$/$\gamma$-Al$_2$O$_3$</td>
<td>98.6</td>
<td>0.31</td>
<td>6.2</td>
</tr>
<tr>
<td>CoRu$_0.16$/$\gamma$-Al$_2$O$_3$</td>
<td>98.1</td>
<td>0.30</td>
<td>5.8</td>
</tr>
</tbody>
</table>

*a* BET specific surface area, *b* Pore volume obtained at P/$P_0$ = 0.99, *c* Average pore diameter calculated by BJH method using desorption isotherm., *d* Crystallite size of Co NPs measured by XRD, *e* Metal dispersion, and *f* metal particle size from hydrogen chemisorption measurement.

6.1.1.2 FTIR analysis

Fig. 6.2 shows FTIR spectra of $\gamma$-Al$_2$O$_3$ support, Co/$\gamma$-Al$_2$O$_3$ and CoRu$_{0.11}$/\$\gamma$-Al$_2$O$_3$ catalysts. The absorption bands in the region of 400-1000 cm$^{-1}$ raised from Al-O vibration modes in AlO$_4$ and AlO$_6$ groups. The absorption band around 3400 cm$^{-1}$ was assigned to OH stretching mode. No additional peak was observed in FTIR spectra of the catalysts, probably as a result of low metal content.
Fig. 6.2: FTIR spectra of (a) $\gamma$-Al$_2$O$_3$ support, (b) Co/$\gamma$-Al$_2$O$_3$ catalyst, and (c) CoRu$_{0.11}$/γ-Al$_2$O$_3$ catalyst.

6.1.1.3 Surface area analysis

Fig. 6.3a presents the N$_2$ adsorption-desorption isotherms of CoRu$_{0.11}$/γ-Al$_2$O$_3$ catalyst. The sample exhibited type IV shape isotherms with a sharp inflection at relative pressure ($P/P_o$) of 0.8 thus indicating the presence of mesopores with uniform and narrow size distribution [2]. Table 6.2 listed the textural parameters of the samples measured by surface area analysis. BET surface area, pore volume, and pore diameter values were observed to decrease for all the catalysts with respect to bare $\gamma$-Al$_2$O$_3$ support which might be due to partial blockage of $\gamma$-Al$_2$O$_3$ pores with metal particles or sintering of pores at high temperature treatment. With an increase of Ru content, pore volume and pore diameter were observed to decrease along with a decrease in surface area from 107.6 to 98.1 m$^2$ g$^{-1}$. Fig. 6.3b shows the unimodal pore size distribution plot of CoRu$_{0.11}$/γ-Al$_2$O$_3$ catalyst with maxima centered at 6.6 nm in mesoporous region (2-50 nm).
Fig. 6.3 (a): N\textsubscript{2} adsorption-desorption isotherm and (b) pore size distribution curve of CoRu\textsubscript{0.11}/\textgamma-Al\textsubscript{2}O\textsubscript{3} catalyst using BJH method.

6.1.1.4 Hydrogen chemisorption

Table 6.2 presents the results of metal dispersion and metal crystallite size measured by hydrogen chemisorption technique. Metal dispersion was observed to increase at first with an increase of Ru content up to 0.11. Further increase in Ru
content resulted to a lowering of metal dispersion which might be correlated to optimal loading and richness of the active sites of the catalysts. CoRu$_{0.11}$/γ-Al$_2$O$_3$ catalyst gave maximum metal dispersion (22.1%) compared to analogues in the series, owing to small metal particle size, better surface area, and optimized metal loading. All these factors later on contributed towards the superior catalytic activity of CoRu$_{0.11}$/γ-Al$_2$O$_3$ catalyst for hydrous hydrazine decomposition.

6.1.1.5 Electron microscopy and EDX analyses

SEM images of CoRu$_{0.11}$/γ-Al$_2$O$_3$ catalysts at two different magnifications are shown in Fig. 6.4(a-b). Metal alloy NPs were distributed evenly on the surface of alumina support. The particles appeared spherical in shape with the average diameter of about 85 nm. TEM image of CoRu$_{0.11}$/γ-Al$_2$O$_3$ catalyst (Fig. 6.4c) shows uniform dispersion of Co-Ru alloy NPs with average diameter of ~ 10 nm. Furthermore, EDX mapping further confirms the distribution of elements for CoRu$_{0.11}$/γ-Al$_2$O$_3$ catalyst (Fig. 6.4d). A uniform distribution of Co and Ru metals along with the constitution elements of support (Al and O) indicated the formation of Co-Ru alloy NPs. The EDX spectra of whole series are shown in Fig. 6.5. The co-existence of Co and Ru metals in EDX patterns depicted the synergistic effect of both metals to form Co-Ru alloy NPs over the surface of Al$_2$O$_3$ support. The results of EDX analysis for the prepared catalysts are listed in Table 6.3. EDX results were found in good agreement nominal metal loadings as determined by AAS technique.
Fig. 6.4: SEM micrographs at magnifications of (a) 25 kx and (b) 50 kx, (c) TEM image, and (d) EDX mapping for elemental distribution of CoRu₀.₁₁/γ-Al₂O₃ catalyst.
Fig. 6.5: EDX spectra of the catalysts: (a) CoRu$_{0.04}$/γ-Al$_2$O$_3$, (b) CoRu$_{0.07}$/γ-Al$_2$O$_3$, (c) CoRu$_{0.11}$/γ-Al$_2$O$_3$, (d) CoRu$_{0.14}$/γ-Al$_2$O$_3$ (e) CoRu$_{0.16}$/γ-Al$_2$O$_3$, and (f) Co/γ-Al$_2$O$_3$. 
TPR and TPO measurements

The reduction activities of the samples were conducted by TPR analysis. Fig. 6.6a represents TPR profile of Co/γ-Al₂O₃ catalyst which has already been discussed in section 5.2.1.5 (chapter 5). The profile of Ru/γ-Al₂O₃ catalyst (Appendix, Fig. 3) had an intense peak at 169 °C corresponding to reduction of RuO₂ to Ru⁰ [3]. In the case of CoRuₓ/γ-Al₂O₃ catalysts, with an addition of Ru a facile reduction behavior was observed [4]. With an increase in Ru loading, the reduction peaks were shifted towards the lower temperature region. Such behaviour can be correlated to alloying effect of Co and Ru metals, as reported earlier [5-7]. The coexistence of Ru and Co, and their synergistic effect were of vital importance to improve the activity of CoRuₓ/γ-Al₂O₃ catalysts.

Fig. 6.6b shows the oxidation profiles of monometallic and bimetallic catalysts. Co/γ-Al₂O₃ catalyst showed an oxidation band at 200-450 °C, attributing to the oxidation of Co to Co₃O₄ [8]. No oxidation peak was observed for cobalt aluminates indicating their difficult oxidation, once they have formed. For CoRuₓ/γ-Al₂O₃ catalysts, the oxidation peak was shifted to a lower temperature upon the addition of Ru loadings. This shift in peak position can be ascribed to the synergistic effect of Co and Ru metals to form Co-Ru nanooalloys.

Table 6.3: EDX analysis of synthesized CoRuₓ/γ-Al₂O₃ bimetallic catalysts.

<table>
<thead>
<tr>
<th>Catalyst/γ-Al₂O₃</th>
<th>Wt% Al</th>
<th>Wt% O</th>
<th>Wt% Co</th>
<th>Wt% Ru</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>56.53</td>
<td>25.53</td>
<td>17.94</td>
<td>0</td>
</tr>
<tr>
<td>CoRu₀.04</td>
<td>47.94</td>
<td>32.34</td>
<td>18.67</td>
<td>1.05</td>
</tr>
<tr>
<td>CoRu₀.07</td>
<td>51.61</td>
<td>28.05</td>
<td>18.18</td>
<td>2.13</td>
</tr>
<tr>
<td>CoRu₀.11</td>
<td>49.52</td>
<td>29.81</td>
<td>17.52</td>
<td>3.15</td>
</tr>
<tr>
<td>CoRu₀.14</td>
<td>52.32</td>
<td>23.56</td>
<td>19.37</td>
<td>4.75</td>
</tr>
<tr>
<td>CoRu₀.16</td>
<td>48.43</td>
<td>28.41</td>
<td>17.76</td>
<td>5.40</td>
</tr>
</tbody>
</table>
Fig. 6.6: (a) TPR and (b) TPO profiles of $\gamma$-Al$_2$O$_3$ supported Co-Ru bimetallic catalysts.
6.2 Applications of CoRu\textsubscript{x}/γ-Al\textsubscript{2}O\textsubscript{3} catalysts

The prepared CoRu\textsubscript{x}/γ-Al\textsubscript{2}O\textsubscript{3} bimetallic catalysts were applied for two designed reactions: (i) catalytic decomposition of hydrazine for hydrogen generation and (ii) electro-oxidation of hydrazine using cyclic voltammetry. The promoting role of Ru metal on Co/γ-Al\textsubscript{2}O\textsubscript{3} was studied and optimal composition within catalytic series was also optimized. The influence of various parameters on the catalytic performance and reaction kinetics were also investigated. The results are discussed below.

6.2.1 Results and discussion

6.2.1.1 Hydrogen generation from decomposition of hydrazine over CoRu\textsubscript{x}/γ-Al\textsubscript{2}O\textsubscript{3} catalysts

The prepared CoRu\textsubscript{x}/γ-Al\textsubscript{2}O\textsubscript{3} catalysts with different composition were tested for hydrogen generation from the decomposition of hydrous hydrazine at 25 °C with a metal/N\textsubscript{2}H\textsubscript{4} molar ratio of 1:10. For comparison, monometallic catalysts (Co/γ-Al\textsubscript{2}O\textsubscript{3} and Ru/γ-Al\textsubscript{2}O\textsubscript{3}) were also tested for the hydrous hydrazine decomposition. Fig. 6.7a shows the comparative studies for hydrogen evolution from the decomposition of hydrous hydrazine. Pure γ-Al\textsubscript{2}O\textsubscript{3} support exhibited no activity at all. Without Ru addition, Co/γ-Al\textsubscript{2}O\textsubscript{3} catalyst reflected poor activity and selectivity for hydrazine decomposition. Although Ru/γ-Al\textsubscript{2}O\textsubscript{3} showed better catalytic activity but it was only 81% selective towards H\textsubscript{2} generation. For CoRu\textsubscript{x}/γ-Al\textsubscript{2}O\textsubscript{3} catalysts, by increasing the Ru molar ratio (x) a different behavior of catalytic activity and selectivity was observed showing their dependence on Ru to Co molar ratio in bimetallic catalysts.

The initial rate of hydrogen generation was determined from the linear portion and was plotted against Ru contents (both in the logarithmic scale). A straight line with the slope of 0.95 was obtained thus indicating first order kinetics of hydrous hydrazine decomposition with respect to Ru content (Fig. 6.7a inset). MS analysis of the generated gaseous products (Fig. 6.7b) corresponded well with H\textsubscript{2} to N\textsubscript{2} molar ratio of 2.0. MS results are in good agreement with the volumetric results, indicating the complete decomposition of hydrous hydrazine into hydrogen and nitrogen at room temperature.
Fig. 6.7: Kinetic profiles for H\textsubscript{2} release from hydrous hydrazine decomposition (0.5 M) over the prepared catalysts at 25 °C (Metal: N\textsubscript{2}H\textsubscript{4} molar ratio = 1:10), (inset) a plot of rate of H\textsubscript{2} generation versus Ru contents (both in logarithmic scale), and (b) MS profiles for generated gases.

6.2.1.1.1 **TOF and H\textsubscript{2} Selectivity**

Fig. 6.8 presents the dependency of H\textsubscript{2} selectivity and TOF over Ru molar ratio. TOF was noticed to increase gradually by increasing the molar ratio of Ru from...
Further increasing the Ru molar ratio resulted to a slight decrease in the activity which could be correlated with an optimal loading and fullness of the active sites of the catalyst. As a result, CoRu$_{0.11}$/\(\gamma\)-Al$_2$O$_3$ was selected as optimal composition in CoRu$_x$/\(\gamma\)-Al$_2$O$_3$ series with 100% H$_2$ selectivity within 44 minutes corresponding to TOF value of 21.93 h$^{-1}$. Such a high performance can be attributed to the formation of Co-Ru alloy NPs with high metal dispersion and more active sites over the surface of alumina support. It could be deduced that the synergistic effect of metal alloying is vital to the hydrazine catalysis for the hydrogen generation in the presently fabricated materials. The alloying effect develops due to the strong interaction between both metals (Co and Ru) over the surface of high surface area \(\gamma\)-Al$_2$O$_3$. It is also well correlated with the high metal dispersion over the surface of catalyst which has been confirmed by SEM and EDX analyses. The selectivity towards H$_2$ evolution might result from the formation of heterometallic bonds in bimetallic catalysts that might tune the bonding patterns of the catalyst surface with the reactant molecules (N$_2$H$_4$). This strong metal-metal interaction might stabilize the possible reaction intermediates leading to effective selectivity for H$_2$ generation [9].

![Fig. 6.8](chart.png)

**Fig. 6.8:** Plot of H$_2$ selectivity and TOF of CoRu$_x$/\(\gamma\)-Al$_2$O$_3$ bimetallic catalysts versus Ru molar ratio (x= 0, 0.04, 0.07, 0.11, 0.14, and 0.16).
6.2.1.1.2 Effect of temperature

The kinetic studies were done by performing hydrazine decomposition over CoRu$_{0.11}$/γ-Al$_2$O$_3$ and Co/γ-Al$_2$O$_3$ catalysts in the temperature range of 35-65 °C. Ru$_{0.11}$/γ-Al$_2$O$_3$ catalyst showed the maximum H$_2$ selectivity (100%) over the entire temperature range. Rate constant (k) values were calculated from the slope of plot for each temperature. The Arrhenius plots of ln k vs 1/T were plotted for both catalysts (Fig. 6.9). The apparent activation energy ($E_a$) value of 37.4 kJ mol$^{-1}$ was derived from the Arrhenius plot for CoRu$_{0.11}$/γ-Al$_2$O$_3$ catalyst.

![Arrhenius plot of CoRu$_{0.11}$/γ-Al$_2$O$_3$ catalysts.](image)

6.2.1.1.3 Effect of support

In order to study the effect of different supported materials, the optimal composition CoRu$_{0.11}$ was deposited on different supports i.e., γ-Al$_2$O$_3$, SiO$_2$, and zeolite. The prepared catalysts; CoRu$_{0.11}$/γ-Al$_2$O$_3$, CoRu$_{0.11}$/SiO$_2$, and CoRu$_{0.11}$/zeolite were tested for the hydrous hydrazine decomposition for H$_2$ generation at 25 °C. The catalytic activity of CoRu$_{0.11}$/γ-Al$_2$O$_3$ catalyst was found superior compared to other two samples (Fig. 6.10). This highlighted the peculiarity features of γ-Al$_2$O$_3$ support.
due to its high porosity, uniform pore size distribution besides good thermal, mechanical, and chemical stability.

![Graph showing performance comparison](image)

**Fig. 6.10:** Comparison of the performance for CoRu$_{0.11}$ bimetallic catalyst supported on various substrates for the decomposition of hydrous hydrazine (0.5 M) at 25 ºC.

### 6.2.1.1.4 Recycling test

The reusability of the catalysts is vital for their practical applications. For that purpose, CoRu$_{0.11}/\gamma$-Al$_2$O$_3$ catalyst was removed from the reaction solution. It was washed with excess of distilled water and dried at 120 ºC for 2 h. The dried catalyst was employed for decomposition of hydrous hydrazine (0.5 M) at 25 ºC. The reusability test was performed in three cycles. The reaction rate was found to decrease slightly after each cycle for the decomposition reaction but 100% hydrogen selectivity was still achievable (Fig. 6.11). The presence of residual hydrazine or its fragment might block certain active sites of the catalyst which resulted to a decrease in the reaction rate in the following reaction cycles. For CoRu$_{0.11}/\gamma$-Al$_2$O$_3$ catalyst no agglomeration of metal NPs over $\gamma$-Al$_2$O$_3$ was observed after third cycle as shown by SEM image (Fig. 6.1 inset), indicating that Al$_2$O$_3$ support can stabilize the CoRu$_{0.11}$NPs even after third cycle. Furthermore, the synthesized CoRu$_{0.11}/\gamma$-Al$_2$O$_3$
catalyst is magnetic in nature and can be easily separated from reaction mixture by attracting with a magnet (Appendix, Fig. 4) making its practical recycling applications more convenient.

![Graph](image)

**Fig. 6.11:** Kinetic profiles for the decomposition of hydrous hydrazine (0.5 M) at 25 °C over CoRu$_{0.11}$/$\gamma$-Al$_2$O$_3$ catalyst in three runs and (inset) SEM image of spent CoRu$_{0.11}$/$\gamma$-Al$_2$O$_3$ catalyst after 3$^{rd}$ run.

6.2.1.2 Electro-oxidation of hydrazine over CoRu$_x$/$\gamma$-Al$_2$O$_3$ modified electrodes

Electrochemical studies were performed on GC electrode modified with CoRu$_x$/$\gamma$-Al$_2$O$_3$ bimetallic catalysts. For comparison purpose, the cyclic voltammetry profiles were taken on bare and modified GC electrode with Co/$\gamma$-Al$_2$O$_3$ and CoRu$_{0.11}$/$\gamma$-Al$_2$O$_3$ catalysts (Fig. 6.12a). The electroanalytical data was summarized in Table 6.4. No peak current response was given by bare GC electrode while, monometallic cobalt catalyst presented poor current response. On the other hand, a significant response was achieved for CoRu$_{0.11}$/$\gamma$-Al$_2$O$_3$ modified electrode with peak current value of 46.1 µA.
Fig. 6.12: (a) CV profiles of bare and modified GC electrodes, and (b) comparison of the performance of CoRu$_x$/$\gamma$-Al$_2$O$_3$ modified electrodes for 2 mM hydrazine electro-oxidation in 0.1 M PBS (pH 7.2) @ 25 mV s$^{-1}$.

Fig. 6.12b presents the comparison for the oxidation of 2 mM hydrazine on the modified electrodes. All the modified electrodes had the ability to oxidize hydrazine;
however CoRu$_{0.11}$/$\gamma$-Al$_2$O$_3$ depicted the best performance in terms of peak current. An increase in the oxidation peak current ($i_p$) shows the better electrochemical efficiency of this electrode towards hydrazine oxidation, which may be attributed to the higher surface area and facile electron transfer ability [10].

Table 6.4: Data extracted from CV plots for CoRu$_x$/$\gamma$-Al$_2$O$_3$ modified electrodes @ 25 mV s$^{-1}$.

<table>
<thead>
<tr>
<th>Catalyst/$\gamma$-Al$_2$O$_3$</th>
<th>Peak potential (V)</th>
<th>Peak current (µA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>0.89</td>
<td>1.6</td>
</tr>
<tr>
<td>CoRu$_{0.04}$</td>
<td>0.88</td>
<td>5.7</td>
</tr>
<tr>
<td>CoRu$_{0.07}$</td>
<td>0.88</td>
<td>18.3</td>
</tr>
<tr>
<td>CoRu$_{0.11}$</td>
<td>0.87</td>
<td>46.1</td>
</tr>
<tr>
<td>CoRu$_{0.14}$</td>
<td>0.87</td>
<td>40.5</td>
</tr>
<tr>
<td>CoRu$_{0.16}$</td>
<td>0.88</td>
<td>37.9</td>
</tr>
</tbody>
</table>

6.2.1.2.1 Effect of scan rate

The nature of hydrazine oxidation process was further explored for CoRu$_{0.11}$/$\gamma$-Al$_2$O$_3$ modified electrode by varying scan rate ($v$) in the range of 10 to 100 mV s$^{-1}$ (Fig. 6.13). The generated oxidation current was observed via cyclic voltammetry in 0.1 M PBS (pH 7.2) solution containing 2 mM hydrazine. The anodic peak potential was shifted slightly towards more positive region upon increasing scan rate, suggesting a kinetic limitation in the reaction between the modified electrode and hydrazine.
A linear relationship was achieved by plotting oxidation peak current (corresponding to a potential of +0.88 V) versus the square root of scan rate (Fig.6.14a). The relationship between square root of scan rate \( (\upsilon)^{1/2} \) and anodic peak current \( (i_p) \) showed a linear regression as follows:

\[
i_p (\mu A) = 266.6 \ (\upsilon)^{1/2} - 18.88 \quad (R^2=0.99)
\]  

This linear trend is an indicative of diffusion controlled reaction and suggests that the overall oxidation of hydrazine at CoRu\(_{0.11}/\gamma-\text{Al}_2\text{O}_3\) modified electrode is monitored by diffusion of hydrazine [11, 12], explained by Randle-Sevcik equation as follows [13]:

\[
i_p = (2.99 \times 10^5) \ n(\alpha n)^{1/2} A C D^{1/2} \upsilon^{1/2}
\]  

where; \( n \) is number of transferred electrons, \( A \) is electrode surface area (cm\(^2\)), \( C \) is concentration of electroactive species (mol cm\(^{-3}\)), \( D \) is diffusion coefficient (cm s\(^{-1}\)), \( \upsilon \) is scan rate (V s\(^{-1}\)), and \( \alpha \)= the charge transfer coefficient.

Moreover, the cyclic voltammograms on the modified electrode in hydrazine solution exhibited no characteristic peak during the cathodic scan, thereby showing that electron transfer is completely irreversible. Fig. 6.14b presents the linear dependence of peak current on the scan rate (both in logarithmic scale) which further confirmed the diffusion character of hydrazine electro-oxidation as described by the equation:
\[
\ln i_p (\mu A) = 0.34(\mu A \text{ V s}^{-1}) + 1.24, \quad (R^2 = 0.998) \quad (6.3)
\]

![Graph](image)

**Fig. 6.14:** (a) Linear dependence of peak current on square root of scan rate and (b) linear dependence of peak current on scan rate (both in logarithm scale).

### 6.2.1.2.2 Effect of concentration

The electro-oxidation of hydrazine was performed at CoRu_{0.11}/\gamma-Al_2O_3 modified electrode by selecting hydrazine concentration in the range of 2-10 mM in 0.1 M PBS (pH 7.2). The anodic peak current at the modified electrode was observed proportional to hydrazine concentration (Fig. 6.15a) thus corresponding to the better distribution of metal alloy particles over the surface of this modified electrode. Fig.
6.15b presents the linear dependence of anodic peak current on hydrazine concentration in the range of 2-10 mM.

Fig. 6.15: Effect of hydrazine conc. (range: 2-10 mM) on peak current using CoRu$_{0.11}$/γ-Al$_2$O$_3$ modified electrode in 0.1M PBS (pH 7.2) @ 25 mV s$^{-1}$ and (b) calibration plot for N$_2$H$_4$ conc. versus peak current.
6.3 Conclusions

In summary, a series of CoRu\textsubscript{x} catalysts supported on $\gamma$-Al\textsubscript{2}O\textsubscript{3} granules has been synthesized by wet impregnation method, which exhibited the superior catalytic performances towards the dehydrogenation of hydrous hydrazine at room temperature. The activity of prepared catalysts was evaluated by two model reactions. During the first model reaction, the efficiency of CoRu\textsubscript{0.11}/$\gamma$-Al\textsubscript{2}O\textsubscript{3} catalyst for high activity, selectivity, and durability makes it optimal catalyst for hydrogen generation from decomposition of N\textsubscript{2}H\textsubscript{4}.H\textsubscript{2}O which might be due to synergistic effect of Co-Ru alloy along with excellent features of granular $\gamma$-Al\textsubscript{2}O\textsubscript{3} support. The prepared CoRu\textsubscript{x}/$\gamma$-Al\textsubscript{2}O\textsubscript{3} catalysts with low noble metal content proved to be highly promising and were quite suitable for making the process cost effective and efficient for H\textsubscript{2} generation from hydrazine decomposition.

In the second model reaction, redox behavior of the specimens was studied for hydrazine oxidation via cyclic voltammetry. CoRu\textsubscript{0.11}/$\gamma$-Al\textsubscript{2}O\textsubscript{3} substantiated prominent electro catalysis for hydrazine. All materials proved to be active catalysts. The present data also signifies that this set of materials can contribute towards further applications in the field of electro analysis.
References

Chapter 7

CoPt_{x}/\gamma-Al_{2}O_{3} Bimetallic Catalysts

Another series of stable and highly active bimetallic catalysts (CoPt_{x}/\gamma-Al_{2}O_{3}, x = 0, 0.017, 0.034, 0.048, 0.065, and 0.081) was prepared by wet impregnation method followed by calcination and temperature programmed reduction (TPR). The samples were characterized using XRD, FTIR, AAS, BET, SEM, EDX, TPR, and TPO methods. The catalytic activity was tested in two ways i.e., hydrazine decomposition for hydrogen generation and hydrazine electro-oxidation via cyclic voltammetry. The activity and stability of the catalysts were assessed by estimating TOF, H\textsubscript{2} selectivity and electrochemically anodic peak current generated. Notably, CoPt_{0.034}/\gamma-Al_{2}O_{3} exhibited the highest catalytic activity (TOF 117.8 h\textsuperscript{-1}). The apparent activation energy value of 29.14 kJ mol\textsuperscript{-1} was evaluated for hydrazine decomposition using CoPt_{0.034}/\gamma-Al_{2}O_{3}. All these materials also showed robust catalytic potentiality for hydrazine electro-oxidation; CoPt_{0.034}/\gamma-Al_{2}O_{3} was found to exhibit highest electrochemical responses. The robust responses for this composition may have arisen due to accessible surface area, fast electron transfer, and hence better potentiality as electrocatalyst. Based on these outcomes, CoPt_{0.034}/\gamma-Al_{2}O_{3} has been suggested as optimal composition among its analogues.

7.1 Physical characterization of CoPt_{x}/\gamma-Al_{2}O_{3} catalysts

7.1 Results and discussion

7.1.1 AAS and XRD results

The chemical composition of the prepared catalysts was determined by AAS and results are summarized in Table 7.1. The AAS results illustrated that the samples are quite homogeneous and the metal loadings are relatively near the nominal values for Co and Pt stoichiometric loadings. It indicated the effectiveness of adapted procedures for incorporation of these metal phases together.
Table 7.1: The elemental composition of CoPt$_x$/$\gamma$-Al$_2$O$_3$ bimetallic catalysts from AAS.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Co$_{exp}^a$ (wt%)</th>
<th>Pt$_{exp}^b$ (wt%)</th>
<th>Pt/Co$_c^c$</th>
<th>M$_{exp}^d$ (wt%)</th>
<th>M$_{th}^e$ (wt%)</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co/$\gamma$-Al$_2$O$_3$</td>
<td>18.92</td>
<td>0</td>
<td>0</td>
<td>18.92</td>
<td>20</td>
<td>5.4</td>
</tr>
<tr>
<td>CoPt$_{0.017}$/γ-Al$_2$O$_3$</td>
<td>19.10</td>
<td>1.07</td>
<td>0.017</td>
<td>20.17</td>
<td>21</td>
<td>3.95</td>
</tr>
<tr>
<td>CoPt$_{0.034}$/γ-Al$_2$O$_3$</td>
<td>18.99</td>
<td>2.13</td>
<td>0.034</td>
<td>21.12</td>
<td>22</td>
<td>4.0</td>
</tr>
<tr>
<td>CoPt$_{0.048}$/γ-Al$_2$O$_3$</td>
<td>19.22</td>
<td>3.05</td>
<td>0.048</td>
<td>22.27</td>
<td>23</td>
<td>3.17</td>
</tr>
<tr>
<td>CoPt$_{0.065}$/γ-Al$_2$O$_3$</td>
<td>18.95</td>
<td>4.11</td>
<td>0.065</td>
<td>23.06</td>
<td>24</td>
<td>3.92</td>
</tr>
<tr>
<td>CoPt$_{0.081}$/γ-Al$_2$O$_3$</td>
<td>19.15</td>
<td>5.12</td>
<td>0.081</td>
<td>24.27</td>
<td>25</td>
<td>2.92</td>
</tr>
</tbody>
</table>

a Co metal content determined by AAS, b Pt metal content determined by AAS, c Pt/Co molar ratio calculated using experimental values of metal content, d Total experimental metal content, e Total theoretical metal content, f % error in theoretical and experimental metal contents.

Fig. 7.1 presents XRD patterns of $\gamma$-Al$_2$O$_3$ support and CoPt$_x$/$\gamma$-Al$_2$O$_3$ catalysts using the same arbitrary scale. Fig. 7.1a shows XRD pattern of $\gamma$-Al$_2$O$_3$ which is already discussed in section 5.1.1.2 (chapter 5). Fig. 7.1b presents XRD pattern of Co/$\gamma$-Al$_2$O$_3$ catalyst with two peaks of Co at 2$\theta$ values $\sim$ 30.1° and 59.63° corresponding to (202) and (411) hkl values (ICDD Card No 01-070-2633). In the case of CoPt$_x$/$\gamma$-Al$_2$O$_3$ bimetallic catalysts (Fig. 7.1(c-g)), no prominent diffraction peaks of Pt metal were detected in XRD pattern of bimetallic catalysts which might be either due to its low contents or Pt particles are too small that cannot be scattered/detected by this technique [1]. Moreover, the diffraction peak of Co at 20 value $\sim$ 30.1° was noticed to shift towards the lower angle with an increase in Pt molar fraction up to 0.08 which might be due to substitution of larger Pt atoms for the smaller Co atoms. This diffraction shift indicated the formation of Co-Pt alloy NPs [2, 3].
Fig. 7.1: XRD patterns of (a) γ-Al$_2$O$_3$, (b) Co/γ-Al$_2$O$_3$, (c) CoPt$_{0.017}$/γ-Al$_2$O$_3$, (d) CoPt$_{0.034}$/γ-Al$_2$O$_3$, (e) CoPt$_{0.048}$/γ-Al$_2$O$_3$, (f) CoPt$_{0.065}$/γ-Al$_2$O$_3$, and (g) CoPt$_{0.081}$/γ-Al$_2$O$_3$ catalysts.

The crystallite sizes were calculated by selecting the peak of maximum intensity using Debye Scherrer equation and results are presented in Table 7.2. It may be inferred that the crystalline grain sizes got reduced for all the compositions (CoPt$_x$/γ-Al$_2$O$_3$) as compared to γ-Al$_2$O$_3$ alone. Notably, the formation of Co-Pt alloy Nps agitated the crystal growth which would affect the corresponding catalytic performance.
Table 7.2: Adsorption parameters, structural properties, and hydrogen chemisorption measurements of synthesized CoPt/γ-Al₂O₃ samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Adsorption parameters</th>
<th>Structural properties</th>
<th>H₂ chemisorption measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sₐᵃ</td>
<td>Vₚᵇ</td>
<td>dₚᶜ</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>195 (m² g⁻¹)</td>
<td>0.47 (cm³ g⁻¹)</td>
<td>8.6 (nm)</td>
</tr>
<tr>
<td>CoPt₀.017/γ-Al₂O₃</td>
<td>125.1</td>
<td>0.45</td>
<td>6.5 (nm)</td>
</tr>
<tr>
<td>CoPt₀.034/γ-Al₂O₃</td>
<td>123.6</td>
<td>0.43</td>
<td>4.7 (nm)</td>
</tr>
<tr>
<td>CoPt₀.048/γ-Al₂O₃</td>
<td>120.8</td>
<td>0.41</td>
<td>4.1 (nm)</td>
</tr>
<tr>
<td>CoPt₀.065/γ-Al₂O₃</td>
<td>118.4</td>
<td>0.39</td>
<td>3.8 (nm)</td>
</tr>
<tr>
<td>CoPt₀.081/γ-Al₂O₃</td>
<td>113.1</td>
<td>0.35</td>
<td>3.5 (nm)</td>
</tr>
</tbody>
</table>

a BET specific surface area, b Pore volume obtained at P/P⁰ = 0.99, c Average pore diameter calculated by BJH method using desorption isotherm, d Metal crystallite size measured by XRD, e Metal dispersion, and f Active metal particle size from pulse chemisorption measurements.

7.1.1.2 FTIR analysis

Fig. 7.2 shows FTIR spectra of γ-Al₂O₃ support and CoPtₓ/γ-Al₂O₃ catalysts prepared by wet impregnation method. All samples presented similar absorption behavior in IR region indicating structural integrity. A broad absorption band was observed in the region of 400-1000 cm⁻¹ due to Al-O vibration modes in AlO₄ and AlO₆ groups. The bending vibration of weakly bound molecular water also appeared at 1632 cm⁻¹ while, OH stretching was observed at 3400 cm⁻¹. These observations give influence for the successful formation of CoPtₓ/γ-Al₂O₃ compositions.
Fig. 7.2: FTIR spectra of (a) γ-Al₂O₃ support, (b) CoPt₀.017/γ-Al₂O₃, (d) CoPt₀.034/γ-Al₂O₃, (e) CoPt₀.048/γ-Al₂O₃, (f) CoPt₀.065/γ-Al₂O₃, and (g) CoPt₀.081/γ-Al₂O₃ catalysts.

7.1.1.3 Surface area analysis

The adsorption-desorption curves of CoPt₀.034/γ-Al₂O₃ catalyst are shown in Fig. 7.3(a) while, the data of all samples is summarized in Table 7.2. CoPt₀.034/γ-Al₂O₃ catalyst presented Type IV isotherm, which is the characteristic of mesoporous materials [4]. BET surface areas of the CoPtₓ/γ-Al₂O₃ bimetallic catalysts were found in the range of 113-125 m² g⁻¹ (Table 7.2). However, BET surface area and pore volume of catalysts were found lower compared to γ-Al₂O₃ support which might be due to filling of γ-Al₂O₃ pores with metal alloy particles or sintering during high temperature treatment [5]. The pore size distribution of CoPt₀.034/γ-Al₂O₃ catalyst (Fig. 7.3b) was derived from the desorption data using the Barret-Joyner-Halenda (BJH) method. Narrow pore size distribution of the catalyst centered at 4.68 nm was observed which indicated a unimodal distribution of mesopores. All these observations indicated the textural difference in the properties of support after metal loadings [6].
Fig. 7.3 (a): N₂ adsorption-desorption isotherm and (b) pore size distribution curve of CoPt₀.03₄/γ-Al₂O₃ catalyst using BJH method.

7.1.1.4 Hydrogen chemisorption

The results of metal dispersion and metal crystallite size measured via hydrogen chemisorption technique are listed in Table 7.2. The apparent metal dispersion was greatly influenced by the addition of Pt to Co/γ-Al₂O₃ catalyst. For CoPtₓ/γ-Al₂O₃ bimetallic catalyst, H₂ uptake was found three times higher than that of
Co/γ-Al₂O₃. Among all the catalysts in a series, CoPt₀.₀₃₄/γ-Al₂O₃ catalyst showed maximum metal dispersion (22.1%) which can be attributed to better dispersion of metal particles, their small size, high surface area, and optimized metal loading [7].

### 7.1.1.5 SEM and EDX analyses
The surface morphology of prepared catalysts was further characterized by SEM and images are shown in Fig. 7.4. In all samples, metal alloy NPs were well distributed over the surface of alumina support (Fig. 7.4 (a)). However, CoPt₀.₀₃₄/γ-Al₂O₃ catalyst presented the high dispersion of metal particles.

**Fig. 7.4:** SEM images of: (a) CoPt₀.₀₆₅/γ-Al₂O₃ (b) CoPt₀.₀₈₁/γ-Al₂O₃, (c) CoPt₀.₀₄₈/γ-Al₂O₃, and (d) CoPt₀.₀₃₄/γ-Al₂O₃ catalysts.

Energy dispersed X-ray spectral analysis at various points of respective SEMs indicated homogeneous composition of catalysts. The EDX spectra of whole series are shown in Fig. 7.5. The co-existence of Co and Pt metals in EDX patterns
illustrated the synergistic effect of both metals to form Co-Pt alloy NPs over the surface of Al₂O₃ support. Furthermore, EDX mapping confirmed the distribution of elements for CoPt₀.₀₃⁴/γ-Al₂O₃ catalyst (Fig. 7.6), showing a uniform distribution of Co and Pt along with the constitution elements of support (Al and O). EDX results for the prepared catalysts are listed in Table 7.3 and were found in good connection with AAS results thus confirming the initial metal loadings.
Fig. 7.5: EDX patterns of: (a) CoPt$_{0.017}/\gamma$-Al$_2$O$_3$, (b) CoPt$_{0.034}/\gamma$-Al$_2$O$_3$, (c) CoPt$_{0.048}/\gamma$-Al$_2$O$_3$, (d) CoPt$_{0.065}/\gamma$-Al$_2$O$_3$, and (e) CoPt$_{0.081}/\gamma$-Al$_2$O$_3$ catalysts.
Fig. 7.6: EDX mapping for elemental distribution of CoPt$_{0.034}/\gamma$-Al$_2$O$_3$ catalyst having (a) Al, (b) O, (c) Co, and (d) Pt components.

<table>
<thead>
<tr>
<th>Catalyst/$\gamma$-Al$_2$O$_3$</th>
<th>Wt% Al</th>
<th>Wt% O</th>
<th>Wt% Co</th>
<th>Wt% Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>39.74</td>
<td>40.21</td>
<td>20.05</td>
<td>0</td>
</tr>
<tr>
<td>CoPt$_{0.017}$</td>
<td>44.21</td>
<td>33.41</td>
<td>21.33</td>
<td>1.05</td>
</tr>
<tr>
<td>CoPt$_{0.034}$</td>
<td>45.71</td>
<td>32.67</td>
<td>19.49</td>
<td>2.13</td>
</tr>
<tr>
<td>CoPt$_{0.048}$</td>
<td>43.74</td>
<td>34.33</td>
<td>18.78</td>
<td>3.15</td>
</tr>
<tr>
<td>CoPt$_{0.065}$</td>
<td>40.35</td>
<td>35.19</td>
<td>19.71</td>
<td>4.75</td>
</tr>
<tr>
<td>CoPt$_{0.081}$</td>
<td>38.89</td>
<td>36.72</td>
<td>18.99</td>
<td>5.40</td>
</tr>
</tbody>
</table>

7.1.1.6 TPR and TPO measurements

TPR and TPO profiles were recorded for all the materials to comprehend their reducibility and oxidation behavior which ultimately reflect their alloying behavior between Co and Pt metals. In TPR study, the introduction of Pt metal as a promoter even in small amount led to a high increase of Co reducibility in Co-based catalysts supported on alumina. This effect is beneficial because strong interaction between Co metal and support results in sinter ability without Pt, the promoter metal. Batley et al. for the first time showed the influence of Pt atoms on Co reduction [8]. More recently,
Holmen and coworkers [9] illustrated high effect of Pt atoms on Co reducibility especially in the case of alumina supported catalysts [10]. TPR studies reveals that Pt makes the Co reduction easier thus decreasing the temperatures of the Co oxides [11]. Fig. 7.7 presents TPR profiles of all the prepared catalysts. TPR profile of Co/γ-Al₂O₃ catalyst has been discussed in section 5.2.1.5 (chapter 5). Monometallic Pt/γ-Al₂O₃ catalyst presented an intense peak at 458 °C (Appendix, Fig. 2s). In contrast, TPR profiles of CoPtₓ/γ-Al₂O₃ bimetallic catalysts showed lower reduction temperature than Co/γ-Al₂O₃ materials. With an increase of Pt loadings, the reduction peaks of Co₃O₄ were shifted towards the lower temperature region while, the peak position of the cobalt aluminate (450-800 °C) was not shifted in the presence of Pt [12]. The promoting effect of Pt might be due to hydrogen spillover effect from Pt to Co or a direct interaction between Pt and Co in the form of bimetallic CoPt particles. The incorporation of Pt in Co/γ-Al₂O₃ has increased the catalytic activity for hydrazine decomposition which can be correlated to: (i) improved reducibility, (ii) high dispersion of Co particles and (iii) number of active sites for increased coverage of reaction intermediates.
**Fig. 7.7:** TPR profile of: (a) Co/γ-Al₂O₃, (b) CoPt₀.₀₁₇/γ-Al₂O₃, (c) CoPt₀.₀₃₄/γ-Al₂O₃, (d) CoPt₀.₀₄₈/γ-Al₂O₃, (e) CoPt₀.₀₆₃/γ-Al₂O₃, and (f) CoPt₀.₀₈₁/γ-Al₂O₃ catalysts.

Fig. 7.8 shows the oxidation profiles of monometallic and bimetallic catalysts. Co/γ-Al₂O₃ catalyst showed an oxidation band at 200-450 °C, attributing to the oxidation of Co to Co₃O₄ [13]. No oxidation peak was observed for cobalt aluminates indicating their difficult oxidation, once they have formed. For CoPtₓ/γ-Al₂O₃ catalysts, the oxidation peak was shifted to a lower temperature range upon incorporation of Pt loadings. This shift in peak position could be ascribed to the synergetic effect of Co and Pt metals to form Co-Pt nanoalloys.
7.2 Applications of CoPtₓ/γ-Al₂O₃ catalysts

Two model reactions namely, (i) catalytic decomposition of hydrazine for hydrogen generation and (ii) electro-oxidation of hydrazine using cyclic voltammetry were tested for estimating the catalytic activity of CoPtₓ/γ-Al₂O₃ bimetallic catalysts. The role of Pt metal as promoter on Co-based catalysts was investigated and optimum composition within this catalytic series was also finalized. The influence of various parameters on the catalytic performance and reaction kinetics for above mentioned reactions were also investigated. The results are discussed below:

7.2.1 Results and discussion

7.2.1.1 Hydrogen generation from decomposition of hydrazine over CoPtₓ/γ-Al₂O₃ catalysts

The synthesized materials CoPtₓ/γ-Al₂O₃ were evaluated for their catalytic activity to generate hydrogen from the decomposition of hydrous hydrazine at 25 °C. The metal/N₂H₄ molar ratio was kept at 1:10. For comparison purpose, monometallic Co/γ-Al₂O₃ catalyst was also tested for the hydrous hydrazine decomposition. Fig. 7.9
presents a comparative study for the activity of different catalysts for hydrogen evolution from the decomposition of hydrous hydrazine. Pure $\gamma$-Al$_2$O$_3$ support showed no any activity. While, monometallic Co/$\gamma$-Al$_2$O$_3$ catalyst reflected poor activity and selectivity for hydrazine decomposition. In the case of CoPt$_x$/γ-Al$_2$O$_3$ bimetallic catalysts the activity and selectivity was found dependent on Pt/Co molar ratio [14]. Among all the catalysts, CoPt$_{0.034}$/γ-Al$_2$O$_3$ exhibited the highest activity and selectivity. The remarkable enhancement of hydrogen generation and higher catalyst activity of CoPt$_{0.034}$/γ-Al$_2$O$_3$ may be attributed to the formation of smaller size metal nanoparticles, geometric effect, and alloying effect between Co and Pt metals.

![Figure 7.9](image-url)

**Fig. 7.9:** A comparative studies for H$_2$ generation from hydrous hydrazine decomposition (0.5 M) over CoPt$_x$/γ-Al$_2$O$_3$ catalysts at 25 °C.

In addition, the rate of hydrogen generation was calculated from the linear portion of each kinetic profile and was plotted against Pt contents (both parameters in the logarithmic scale). Fig. 7.10a presents a straight line with the slope equivalent to 0.98 thus depicting first order kinetics of hydrous hydrazine decomposition with respect to Pt content. Fig. 7.10b shows MS profile of the generated gases with H$_2$/N$_2$ molar ratio of 2.0. MS results are in good agreement with the volumetric results, indicating the complete decomposition of hydrous hydrazine into hydrogen and nitrogen at room temperature.
Fig. 7.10: (a) A plot of rate of H₂ generation versus Pt contents (both in logarithmic scale) and (b) MS profiles for generated gaseous products.

7.2.1.1.1 TOF and H₂ Selectivity

The selectivity for H₂ and activity in terms of turn over frequency (TOF) was found to depend on Pt/Co molar ratio as shown in Fig. 7.11. CoPt₀.₀₃₄/γ-Al₂O₃ exhibited 100% H₂ selectivity and TOF of 117.8 h⁻¹ which is attributed to the formation of Co-Pt alloy NPs with high metal dispersion and more active sites over the surface of alumina support. It could be deduced that the synergistic effect of metal alloying is crucial to the hydrazine catalysis for the hydrogen generation in the presently fabricated materials. The alloying effect develops due to the strong interaction between both metals over the surface of high surface area γ-Al₂O₃. It is
also well correlated with the high metal dispersion over the surface of catalyst which has been confirmed by SEM and EDX analyses. The selectivity towards H₂ evolution may result from the formation of hetero-metallic bonds in bimetallic catalysts that might tune the bonding patterns of the catalyst surface with the reactant molecules (N₂H₄). This strong metal-metal interaction may stabilize the possible reaction intermediates leading to effective selectivity for H₂ generation [15].

![Graph](image)

**Fig. 7.11:** Plot of H₂ selectivity and TOF of CoPtₓ/γ-Al₂O₃ bimetallic catalysts versus Pt molar ratio.

### 7.2.1.1.2 Effect of temperature

The decomposition of hydrazine was carried out at various temperatures (35-65 °C) for Co/γ-Al₂O₃ and CoPt₀.₀₃₄/γ-Al₂O₃ catalysts. The values of rate constants (k) were calculated from the slope of kinetic profiles for different operating temperatures. The apparent activation energy was determined from the Arrhenius plots (Fig. 7.12) with the value of 29.14 kJ mol⁻¹ for CoPt₀.₀₃₄/γ-Al₂O₃ catalyst which is much lower than 51.9 kJ mol⁻¹ for Co/γ-Al₂O₃ catalyst indicating an ease in decomposition of N₂H₄ over this optimal composition of bimetallic catalyst.
Fig. 7.12: Arrhenius plot for CoPt$_{0.034}$/$\gamma$-Al$_2$O$_3$ catalyst.

7.2.1.1.3 Recycling test

The recycling test of the CoPt$_{0.034}$/$\gamma$-Al$_2$O$_3$ was performed at 25 °C in three cycles as shown in Fig. 7.13. The rate of reaction was observed to decrease slightly after each cycle but 100% H$_2$ selectivity was still attainable. The presence of residual hydrazine or its fragment might block certain active sites of the catalyst which resulted to a decrease in the reaction rate in the following reaction cycles. However the overall performance was retained in three cycles which infers reliable stability under the experimental conditions.
**7.2.1.2 Electro-oxidation of hydrazine over CoPt\textsubscript{x}/γ-Al\textsubscript{2}O\textsubscript{3} modified electrodes**

To compare the efficiency of CoPt\textsubscript{x}/γ-Al\textsubscript{2}O\textsubscript{3} catalysts for electrochemical studies, GC electrode was modified with CoPt\textsubscript{x}/γ-Al\textsubscript{2}O\textsubscript{3} catalysts. Fig. 7.14 presents the comparison for the oxidation of 2 mM hydrazine over the modified electrodes at the scan rate of 25 mV s\textsuperscript{-1}. The data derived from CV plots is summarized in Table 7.4. All the modified electrodes had the ability to oxidize hydrazine. The best current response was noticed for CoPt\textsubscript{0.034}/γ-Al\textsubscript{2}O\textsubscript{3} catalyst having anodic peak current value of 183.2 µA around 0.85 V. An increase in the oxidation peak current shows the better electrochemical efficiency of this electrode towards hydrazine oxidation, which may be attributed to the higher surface area and facile electron transfer ability [16].
Fig. 7.14: Comparison of the performance of CoPt<sub>x</sub>/γ-Al<sub>2</sub>O<sub>3</sub> modified electrodes for 2mM hydrazine electro-oxidation in 0.1 M PBS (pH 7.2) @ 25 mV s<sup>-1</sup>, inset showing CV profile of CoPt<sub>0.034</sub>/γ-Al<sub>2</sub>O<sub>3</sub> modified electrode.

Table 7.4: Data extracted from CV plots for CoPt<sub>x</sub>/γ-Al<sub>2</sub>O<sub>3</sub> modified electrodes @ 25 mV s<sup>-1</sup>.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Peak potential (V)</th>
<th>Peak current (µA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoPt&lt;sub&gt;0.017&lt;/sub&gt;/γ-Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.84</td>
<td>62.7</td>
</tr>
<tr>
<td>CoPt&lt;sub&gt;0.034&lt;/sub&gt;/γ-Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.85</td>
<td>183.2</td>
</tr>
<tr>
<td>CoPt&lt;sub&gt;0.048&lt;/sub&gt;/γ-Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.84</td>
<td>98.8</td>
</tr>
<tr>
<td>CoPt&lt;sub&gt;0.065&lt;/sub&gt;/γ-Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.87</td>
<td>132</td>
</tr>
<tr>
<td>CoPt&lt;sub&gt;0.081&lt;/sub&gt;/γ-Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.84</td>
<td>81.93</td>
</tr>
</tbody>
</table>

7.2.1.2.1 Effect of scan rate

The nature of hydrazine oxidation process was further examined by changing the scan rate in 10-100 mV s<sup>-1</sup> regime (Fig. 7.15a). The resultant oxidation current was observed via cyclic voltammetry in 0.1 M PBS (pH 7.2) solution containing 2 mM hydrazine. A linear relationship was achieved by plotting oxidation peak current...
versus the square root of scan rate (Fig. 7.15b). The relationship between square root of scan rate, \((u)^{1/2}\) and anodic peak current showed a linear regression as follows:

\[
  i_p (\mu A) = 429.3 (u)^{1/2} - 7.4, \ (R^2 = 0.994)
\]  

(7.1)

This linear trend indicates that the hydrazine oxidation is controlled by diffusion process as explained by Randle-Sevcik equation [14].

\[
  i_p = (2.99 \times 10^5) n(\alpha n)^{1/2} ACD^{1/2} v^{1/2}
\]  

(7.2)

where, \(n\) = number of transferred electrons, \(A\) = electrode surface area (cm\(^2\)), \(C\) = concentration of electroactive species (mol cm\(^{-3}\)), \(D\) = diffusion coefficient (cm s\(^{-1}\)), \(v\) = scan rate (V s\(^{-1}\)), and \(\alpha\) = the charge transfer coefficient.

Fig. 7.15c presents the linear dependence of peak current on scan rate (both in logarithmic scale) which further confirms the diffusion character of hydrazine electro-oxidation as described by the equation [17, 18].

\[
  \ln i_p = 0.5403 \ln v (V s^{-1}) + 6.10, \ R^2 = 0.992
\]  

(7.3)
Fig. 7.15: (a) Cyclic voltammetry profiles of CoPt$_{0.034}/\gamma$-Al$_2$O$_3$ modified electrode at scan rate of 10-100 mV s$^{-1}$, (b) dependence of anodic peak current on $\nu^{1/2}$, and (c) linear dependence of peak current on scan rate (both in logarithm scale).

7.2.1.2.2 Effect of concentration

The effect of hydrazine concentration was studied by selecting CoPt$_{0.034}/\gamma$-Al$_2$O$_3$ modified electrode in the range of 2-10 mM in 0.1 M PBS (pH 7.2). The anodic
peak current was found proportional to hydrazine concentration (Fig. 7.16a) which can be correlated to the better distribution of metal alloy particles over the surface of this modified electrode [19, 20]. The current response was found linear to N$_2$H$_4$ concentration with a correlation coefficient of 0.996 as shown in Fig. 7.16b.

Fig. 7.16: (a) Concentration effect of hydrazine in the range of 2-10 mM for CoPt$_{0.034}$/γ-Al$_2$O$_3$ modified electrode in 0.1M PBS (pH 7.2) @ 25 mV s$^{-1}$ and (b) a plot of hydrazine concentration versus anodic peak current.
7.2.1.2.3 Reproducibility and stability studies

The repeatability and stability of the CoPt$_{0.034}$/$\gamma$-Al$_2$O$_3$/GCE were investigated by CV method in 10 successive runs using 2 mM hydrazine. Fig 7.17a shows that CV response of the modified electrode was maintained in all cycles with a relative standard deviation (RSD) of 2.86%, indicating its good repeatability and stability. The stability of projected electrocatalysts was evaluated on the basis of reproducible current response for five identical electrodes using CoPt$_{0.034}$/$\gamma$-Al$_2$O$_3$. Anodic peak current output for 2 mM hydrazine is represented as bar chart in Fig. 7.17b. There was a little variation in the anodic current response of five identical electrodes. The average and relative standard deviation (RSD) of anodic peak current on the modified electrodes are 183.8 $\mu$A and 2.45% suggesting their reproducibility.

![Graph](image-url)
Fig. 7.1: (a) CV profiles of CoPt$_{0.034}$/γ-Al$_2$O$_3$ modified GCE in 10 successive cycles for hydrazine electro-oxidation in 0.1 M PBS (pH 7.2) @ 25mV s$^{-1}$ and (b) anodic peak current response of five identical (CoPt$_{0.034}$/γ-Al$_2$O$_3$)/GCE in 2 mM N$_2$H$_4$.

7.3 Conclusions

In summary, advanced materials CoPt$_x$/γ-Al$_2$O$_3$ bimetallic catalysts ($x= 0, 0.017, 0.034, 0.048, 0.065,$ and 0.081) has been synthesized by wet impregnation method. The catalytic activity was tested by two ways i.e. hydrazine decomposition to generate hydrogen and hydrazine electro-oxidation via cyclic voltammetry technique. For hydrazine decomposition reaction, CoPt$_{0.034}$/γ-Al$_2$O$_3$ catalyst exhibited high activity, H$_2$ selectivity, and durability thus making it optimal composition which might be due to synergistic effect of Co and Pt metals besides the excellent features of granular γ-Al$_2$O$_3$ support. The prepared CoPt$_x$/γ-Al$_2$O$_3$ catalysts with low noble metal content proved to be highly promising and were quite suitable for making the process cost effective and efficient for H$_2$ generation from hydrazine decomposition. The prepared catalysts gave the electrochemical response for hydrazine electro-oxidation. Among these, CoPt$_{0.034}$/γ-Al$_2$O$_3$ catalyst presented a prominent electrocatalytic activity for hydrazine. The present data also indicate that this set of materials can contribute towards further applications in the field of electro analysis.
References


Chapter 8

CoPd$_x$/$\gamma$-Al$_2$O$_3$ Bimetallic Catalysts

A novel bimetallic catalytic series, CoPd$_x$/$\gamma$-Al$_2$O$_3$ was synthesized with Pd molar fraction (x) of 0, 0.034, 0.063, 0.093, 0.114 and 0.554 via wet impregnation method followed by high temperature treatment and H$_2$ reduction. The samples were characterized using XRD, FTIR, AAS, BET, SEM, EDX, TPR, and TPO techniques. The prepared catalysts were applied for two model reactions i.e., hydrogen generation from hydrazine decomposition and hydrazine electro-oxidation via cyclic voltammetry. The catalytic performance was assessed on the basis of TOF, selectivity towards H$_2$ and amount of anodic peak current generated at specific peak potential during electrochemical studies. All the prepared catalysts presented their potntalities for both applications. Specifically, CoPd$_{0.093}$/$\gamma$-Al$_2$O$_3$ catalyst displayed superior activity (TOF 61.5 h$^{-1}$) and H$_2$ selectivity (100%). CoPd$_{0.093}$/$\gamma$-Al$_2$O$_3$ also exhibited better potentiality as electrocatalyst owing to accessible surface area and fast electron transfer. Based on these observations, CoPd$_{0.093}$/$\gamma$-Al$_2$O$_3$ was selected as optimal composition among other members in the series.

8.1 Physical characterization of CoPd$_x$/$\gamma$-Al$_2$O$_3$ catalysts

8.1 Results and discussion

8.1.1 AAS and XRD results

The chemical composition of the prepared catalysts was determined by AAS and results are summarized in Table 8.1. The AAS results illustrated that the samples were quite homogeneous in composition. The experimental metal contents were found relatively near the nominal values for Co and Pd metal loadings thus indicating the effectiveness of adapted procedures for incorporation of these metal phases.
Table 8.1: The elemental composition of CoPd$_x/\gamma$-Al$_2$O$_3$ catalyst series determined by AAS.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Co$_{\text{exp}}$ (wt%)</th>
<th>Pd$_{\text{exp}}$ (wt%)</th>
<th>Pd/Co$^c$</th>
<th>M$_{\text{exp}}$ (wt%)</th>
<th>M$_{\text{th}}$ (wt%)</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co/γ-Al$_2$O$_3$</td>
<td>20.11</td>
<td>0</td>
<td>0</td>
<td>20.11</td>
<td>20</td>
<td>0.55</td>
</tr>
<tr>
<td>CoPd$_{0.034}$/γ-Al$_2$O$_3$</td>
<td>19.32</td>
<td>1.18</td>
<td>0.034</td>
<td>20.50</td>
<td>21</td>
<td>2.38</td>
</tr>
<tr>
<td>CoPd$_{0.063}$/γ-Al$_2$O$_3$</td>
<td>19.19</td>
<td>2.25</td>
<td>0.063</td>
<td>21.44</td>
<td>22</td>
<td>2.55</td>
</tr>
<tr>
<td>CoPd$_{0.093}$/γ-Al$_2$O$_3$</td>
<td>18.74</td>
<td>3.16</td>
<td>0.093</td>
<td>21.90</td>
<td>23</td>
<td>4.78</td>
</tr>
<tr>
<td>CoPd$_{0.114}$/γ-Al$_2$O$_3$</td>
<td>19.20</td>
<td>4.09</td>
<td>0.114</td>
<td>23.29</td>
<td>24</td>
<td>2.96</td>
</tr>
<tr>
<td>CoPd$_{0.554}$/γ-Al$_2$O$_3$</td>
<td>19.11</td>
<td>5.33</td>
<td>0.554</td>
<td>24.44</td>
<td>25</td>
<td>2.24</td>
</tr>
</tbody>
</table>

a Co metal content determined by AAS, b Pd metal content determined by AAS, c Pd/Co molar ratio calculated using experimental values of metal content, d Total experimental metal content, e Total theoretical metal content, f % error in theoretical and experimental metal contents.

The structural features of the samples were analyzed by XRD technique. Fig. 8.1 presents XRD profiles of CoPd$_x/\gamma$-Al$_2$O$_3$ catalysts. XRD pattern of γ-Al$_2$O$_3$ is shown in Fig. 8.1a which has already been summarized in section 5.1.1.2 (chapter 5). XRD pattern of Co/γ-Al$_2$O$_3$ catalyst (Fig. 8.1b) presented two peaks of Co at 2θ values ~ 30.1° and 59.63° corresponding to (202) and (411) hkl values (ICDD Card No 01-070-2633). In the case of CoPd$_x/\gamma$-Al$_2$O$_3$ bimetallic catalysts (Fig. 8.1(c-g)), no additional diffraction peaks were detected in XRD pattern which might be either due to low metal content or metal particles are too small that cannot be detected by XRD [1, 2].
Fig. 8.1: XRD patterns of (a) γ-Al₂O₃, (b) Co/γ-Al₂O₃, (c) CoPd₀.034/γ-Al₂O₃, (d) CoPd₀.063/γ-Al₂O₃, (e) CoPd₀.093/γ-Al₂O₃, (f) CoPd₀.114/γ-Al₂O₃, and (g) CoPd₀.554/γ-Al₂O₃.

The crystallite sizes were derived from the peak of highest intensity using Scherrer equation and results are summarized in Table 8.2. The crystallite size was noticed to decrease from 5.80 nm (for γ-Al₂O₃) to 4.68 nm (for CoPd₀.554/γ-Al₂O₃). It may be inferred that the small sized Co-Pd alloy crystallites were obtained as compared to γ-Al₂O₃.
Table 8.2: Adsorption parameters, structural properties, and hydrogen chemisorption measurements of synthesized CoPd$_x$/$\gamma$-Al$_2$O$_3$ catalysts.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Adsorption parameters</th>
<th>Structural properties</th>
<th>H$_2$ chemisorption measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$S_A^a$ ($m^2 g^{-1}$)</td>
<td>$V_p^b$ ($cm^3 g^{-1}$)</td>
<td>$d_p^c$ (nm)</td>
</tr>
<tr>
<td>$\gamma$-Al$_2$O$_3$</td>
<td>195.0</td>
<td>0.41</td>
<td>8.60</td>
</tr>
<tr>
<td>CoPd$_{0.034}$/$\gamma$-Al$_2$O$_3$</td>
<td>110.2</td>
<td>0.38</td>
<td>7.94</td>
</tr>
<tr>
<td>CoPd$_{0.063}$/$\gamma$-Al$_2$O$_3$</td>
<td>105.6</td>
<td>0.35</td>
<td>6.73</td>
</tr>
<tr>
<td>CoPd$_{0.0093}$/$\gamma$-Al$_2$O$_3$</td>
<td>103.4</td>
<td>0.37</td>
<td>5.95</td>
</tr>
<tr>
<td>CoPd$_{0.0114}$/$\gamma$-Al$_2$O$_3$</td>
<td>98.0</td>
<td>0.33</td>
<td>5.93</td>
</tr>
<tr>
<td>CoPd$_{0.554}$/$\gamma$-Al$_2$O$_3$</td>
<td>95.5</td>
<td>0.35</td>
<td>5.80</td>
</tr>
</tbody>
</table>

a BET specific surface area, b Pore volume, c Average pore diameter calculated by BJH method using desorption isotherm, d Crystallite size of measured by XRD, e Metal dispersion, and f Active metal particle size from hydrogen chemisorption measurement.

8.1.1.2 FTIR analysis

Fig 8.2 shows FTIR spectra of $\gamma$-Al$_2$O$_3$ support and CoPd$_x$/$\gamma$-Al$_2$O$_3$ catalysts. Prepared. All samples presented similar adsorption trend in IR region thus indicating structural integrity. A broad absorption band is observed in the region of 400-1000 cm$^{-1}$ could be attributed to Al-O vibration modes in AlO$_4$ and AlO$_6$ groups. The weakly bound molecular water presented bending vibration peak at 1632 cm$^{-1}$ while, OH stretching was observed at ~ 3400 cm$^{-1}$ [3].
Fig. 8.2: FTIR spectra of: (a) γ-Al₂O₃, (b) CoPd₀.₀₃₄/γ-Al₂O₃, (c) CoPd₀.₀₆₃/γ-Al₂O₃, (d) CoPd₀.₀₉₃/γ-Al₂O₃, and (e) CoPd₀.₅₅₄/γ-Al₂O₃.

8.1.1.3 Surface area analysis

The surface area analysis was performed using the adsorption-desorption isotherms of CoPd₀.₀₉₃/γ-Al₂O₃ composition (Fig. 8.3a) which presented Type IV isotherm. This type of isotherm represents the characteristics of mesoporous materials [4]. The data of surface area analysis is compiled in Table 8.2 for all the samples. BET surface areas of the CoPdₓ/γ-Al₂O₃ bimetallic catalysts were obtained in the range of 95-110 m² g⁻¹. These results were found lower as compared to γ-Al₂O₃ support (195 m² g⁻¹) which might be due to filling of γ-Al₂O₃ pores with metal particles or sintering during calcination [4]. The pore size distribution of CoPd₀.₀₉₃/γ-Al₂O₃ catalyst (Fig. 8.3b) was obtained from the desorption data using BJH method. The narrow pore size distribution of the catalyst was achieved with a maxima centered at 5.95 nm thus indicating a unimodal distribution of mesopores [5].
8.1.1.4 Hydrogen chemisorption

The hydrogen chemisorption results are listed in Table 8.2. The metal dispersion was observed to increase significantly upon the incorporation of Pd metal.
to Co/γ-Al₂O₃ catalyst. Among all samples, CoPd₀.₀⁹³/γ-Al₂O₃ catalyst showed maximum metal dispersion (20.35%) which could be attributed to better dispersion of metal particles, their small size, high surface area, and optimized metal loading [6].

### 8.1.1.5 SEM and EDX analyses

The morphological features of synthesized samples were characterized by SEM. The Co-Pd alloy NPS are distributed uniformly over the surface of alumina support as shown in Fig. 8.4 (a-d). CoPd₀.₀⁹³/γ-Al₂O₃ catalyst depicted the high dispersion of metal particles.

**Fig. 8.4**: SEM images of: (a) CoPd₀.₀₃⁴/γ-Al₂O₃, (b) CoPd₀.₀₆₃/γ-Al₂O₃, and (c) CoPd₀.₀⁹³/γ-Al₂O₃, and (d) CoPd₀.₀₆₃/γ-Al₂O₃ at lower magnification.

Fig. 8.5a presents the EDX spectrum of CoPd₀.₀⁹³/γ-Al₂O₃ catalyst. The synergistic effect between Pd and Co metal was certified by the co-existence of both metals in EDX patterns. Moreover, EDX mapping suggested the elemental distribution of CoPd₀.₀⁹³/γ-Al₂O₃ catalyst (Fig. 8.5b), presenting a uniform distribution
of Co and Pd along with the constitution elements of support (Al and O). For all CoPdx/γ-Al2O3 bimetallic materials, the EDX results are listed in Table 8.3 that were found in good correlation with AAS results ensuring the stoichiometric metal contents.

![EDX pattern and EDX mapping of CoPd0.093/γ-Al2O3 bimetallic catalyst.](image)

**Fig. 8.5:** (a) EDX pattern and (b) EDX mapping of CoPd0.093/γ-Al2O3 bimetallic catalyst.
Table 8.3: EDX analysis of the synthesized CoPdₓ/γ-Al₂O₃ catalysts.

<table>
<thead>
<tr>
<th>Catalyst/γ-Al₂O₃</th>
<th>Wt% Al</th>
<th>Wt% O</th>
<th>Wt% Co</th>
<th>Wt% Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>42.14</td>
<td>37.3</td>
<td>20.56</td>
<td>0</td>
</tr>
<tr>
<td>CoPd₀.₀₃₄</td>
<td>43.35</td>
<td>36.40</td>
<td>19.21</td>
<td>1.04</td>
</tr>
<tr>
<td>CoPd₀.₀₆₃</td>
<td>45.71</td>
<td>33.18</td>
<td>19.09</td>
<td>2.02</td>
</tr>
<tr>
<td>CoPd₀.₀₉₃</td>
<td>40.74</td>
<td>35.88</td>
<td>19.71</td>
<td>3.67</td>
</tr>
<tr>
<td>CoPd₀.₁₁₄</td>
<td>42.35</td>
<td>33.35</td>
<td>19.78</td>
<td>4.52</td>
</tr>
<tr>
<td>CoPd₀.₅₅₄</td>
<td>41.98</td>
<td>33.66</td>
<td>18.58</td>
<td>5.78</td>
</tr>
</tbody>
</table>

8.1.1.6 TPR and TPO measurements

In general, TPR and TPO analyses provide the effect of alloying on the redox behavior in bimetallic catalytic system. The reduction studies of the catalysts were evaluated by TPR technique. The promoting effect of Pd metal led to enhance the reducibility of cobalt in Co/Al₂O₃ which was quite difficult due to development of strong interaction between Co metal and Al₂O₃ support, otherwise. TPR plots of CoPdₓ/γ-Al₂O₃ bimetallic catalysts have shown lower reduction temperature as compared to Co/γ-Al₂O₃. The reduction bands of Co₃O₄ were shifted towards the lower temperature region upon the incorporation of Pd loadings. In contrast, peak position of the cobalt aluminate was not shifted in the presence of Pd. The hydrogen spillover effect or strong interaction between Pd and Co resulted to the formation of bimetallic CoPd particles. The addition of Pd in Co/Al₂O₃ has increased the catalytic performance of bimetallic catalysts owing to facile reducibility, high metal dispersion and, an increase in number of active sites [7-9].
The oxidation profiles of the prepared catalysts (Fig. 8.7) were taken following the TPR studies. In the case of CoPd/γ-Al₂O₃ catalysts, the oxidation peak was shifted to a lower temperature upon the addition of Pd loadings. No oxidation peak was noticed for cobalt aluminates indicating their difficult oxidation, once they have formed. The transfer of peak position towards lower temperature can be ascribed to the synergetic effect of Co and Pd metals to form Co-Pd nanoalloys [10].
Fig. 8.7: TPO profiles of: (a) Co/γ-Al₂O₃, (b) CoPd₀.₀₃₄/γ-Al₂O₃, (c) CoPd₀.₀₆₃/γ-Al₂O₃, (d) CoPd₀.₀₉₃/γ-Al₂O₃, (e) CoPd₀.₁₁₄/γ-Al₂O₃, and (f) CoPd₀.₅₅₄/γ-Al₂O₃ catalyst.

8.2 Applications of CoPdₓ/γ-Al₂O₃ catalysts

Two model reactions were chosen in order to evaluate the catalytic activity of CoPdₓ/γ-Al₂O₃ bimetallic catalysts i.e., (i) hydrogen generation from the catalytic decomposition of hydrazine and (ii) electro-oxidation of hydrazine by cyclic voltammetry. The role of Pd metal as promoter on Co-based catalysts was considered and catalytic composition was optimized. The influence of different kinetic parameters was also explored. The results are discussed below

8.2.1 Results and discussion

8.2.1.1 Hydrogen generation from decomposition of hydrazine over CoPdₓ/γ-Al₂O₃ catalysts

The prepared bimetallic catalysts CoPdₓ/γ-Al₂O₃ (x= 0, 0.034, 0.063, 0.093, 0.114, and 0.554) subjected for hydrogen generation from the decomposition of hydrous hydrazine at 25 °C while, keeping metal to N₂H₄ molar ratio at 1:10. Fig. 8.8
presents a comparative study for all samples for hydrogen evolution from the decomposition of hydrous hydrazine. Monometallic Co/γ-Al₂O₃ catalyst presented poor activity and selectivity for hydrazine decomposition. On the other hand, hydrazine decomposition over CoPdₓ/γ-Al₂O₃ bimetallic catalysts showed remarkable enhancement in the activity and selectivity for hydrogen production [11]. Besides this, CoPd₀.₀₉₃/γ-Al₂O₃ catalyst exhibited the maximum performance among its analogues. All these observations could be proposed to the synergistic effect between Co and Pd metals, and formation of smaller sized alloy nanoparticles.

![Graph](image-url)

**Fig. 8.8:** A comparative studies for H₂ generation from hydrous hydrazine decomposition (0.5 M) over CoPdₓ/γ-Al₂O₃ catalysts at 25 °C.

The rate of hydrogen generation was derived from the linear portion of each kinetic profile (Fig. 8.8). The rate of reaction was then plotted against Pd loadings in wt% (both parameters in the logarithmic scale). A straight line was obtained (Fig. 8.9) with the slope value of 0.15 thus showing order of reaction in fraction with respect to Pd content.
Fig. 8.9: A plot of rate of H₂ generation versus Pd contents (both in logarithmic scale).

8.2.1.1 TOF and H₂ Selectivity

The selectivity for H₂ and TOF values were found to depend on Pd/Co molar ratio as shown in Fig. 8.10. All catalysts presented better behavior as compared to Co/γ-Al₂O₃. CoPd₀.₀₉₃/γ-Al₂O₃ reflected 100% H₂ selectivity with TOF of 61.5 h⁻¹ which was correlated to the formation of Co-Pd alloy NPs due to synergistic effect. Moreover, high metal dispersion and presence of more active sites over the surface of alumina support also contributed to enhance the activity and selectivity. The selectivity towards H₂ evolution might be resulted from the of hetero-metallic bonds formation in bimetallic systems that tuned the bonding patterns of the catalyst surface with the reactant molecules (N₂H₄). This strong metal-metal interaction may stabilize the possible reaction intermediates leading to effective selectivity for H₂ generation [12].
Fig. 8.10: Plot of H₂ selectivity and TOF of CoPdx/γ-Al₂O₃ bimetallic catalysts versus Pd molar ratio (x= 0, 0.034, 0.063, 0.093, 0.114, and 0.554).

8.2.1.1.2 Effect of temperature

In order to study the effect of temperature on rate of reaction, hydrazine decomposition was carried out at different temperatures in the range of 35-65 °C using optimal composition (CoPd₀.₀₉₃/γ-Al₂O₃). The Arrhenius plot (Fig. 8.11) was used to derive the activation energy (E_a) with the value of 44.1 kJ mol⁻¹.
8.2.1.1.3 Recycling test

The stability of CoPd₀.₀₉₃/γ-Al₂O₃ sample was further ensured by performing hydrazine decomposition at 25 °C in three cycles as shown in Fig. 8.12. The rate of reaction was noticed to decrease slightly after each cycle but H₂ selectivity was still achievable 100 percent. The lowering of activity after each run might be due to presence of residual hydrazine or blockage of certain active sites of the catalyst. Instead, the overall performance was retained in three cycles which depicts stability of the catalyst under the experimental conditions.
8.2.1.2  Electro-oxidation of hydrazine over CoPd_{x}/γ-Al_{2}O_{3} modified electrodes

For electrochemical studies, GC electrode was decorated with CoPd_{x}/γ-Al_{2}O_{3} catalysts and these modified electrodes were applied for electro-oxidation of hydrous hydrazine. Fig. 8.13a presents the comparison for the oxidation of 2 mM hydrazine over the modified electrodes at the scan rate of 25 mV s\(^{-1}\). All modified electrodes presented their response for hydrazine electro-oxidation (Table 8.4). The electrochemical behavior was also studied for bare and modified electrodes as shown in Fig. 8.13b. Bare GC electrode presented no current response. On the other hand, Co/γ-Al_{2}O_{3} modified electrode showed very weak current response while, CoPd_{0.093}/γ-Al_{2}O_{3} nanomaterial presented a sharp anodic peak at 0.90 V. The best current response was obtained for CoPd_{0.093}/γ-Al_{2}O_{3} catalyst with anodic peak current value of 61.3 µA around 0.90 V. The enhanced electrochemical efficiency of this electrode towards hydrazine oxidation could be linked to high surface area and facile electron transfer ability.
Fig. 8.13: (a) Comparison of the performance of CoPd$_x$/$\gamma$-Al$_2$O$_3$ modified electrodes for electro-oxidation of 2mM hydrous hydrazine in 0.1 M PBS (pH 7.2) @ 25 mV s$^{-1}$ and (b) a comparative study for bare and modified GC electrodes for electro-oxidation of hydrous hydrazine.
Table 8.4: Data extracted from CV plots for CoPd$_x$/$\gamma$-Al$_2$O$_3$ modified electrodes @ 25 mV s$^{-1}$.

<table>
<thead>
<tr>
<th>Catalyst/(\gamma)-Al$_2$O$_3$</th>
<th>Peak potential (V)</th>
<th>Peak current (µA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoPd$_{0.034}$</td>
<td>0.92</td>
<td>21.23</td>
</tr>
<tr>
<td>CoPd$_{0.063}$</td>
<td>0.91</td>
<td>30.14</td>
</tr>
<tr>
<td>CoPd$_{0.093}$</td>
<td>0.90</td>
<td>61.06</td>
</tr>
<tr>
<td>CoPd$_{0.114}$</td>
<td>0.90</td>
<td>39.84</td>
</tr>
<tr>
<td>CoPd$_{0.554}$</td>
<td>0.91</td>
<td>54.82</td>
</tr>
</tbody>
</table>

8.2.1.2.1 Effect of scan rate

The nature of hydrazine oxidation process was further explored by changing the scan rate from 10 to 100 mV s$^{-1}$ via cyclic voltammetry using 0.1 M PBS (pH 7.2) solution containing 2 mM hydrazine (Fig. 8.14a). An increase in oxidation peak current was observed with an increase in scan rate. Fig. 8.14b shows a linear relationship between oxidation peak current \(i_p\) and square root of scan rate \((v^{1/2})\). This linear regression between \(i_p\) and \((v^{1/2})\) was explained as follows:

\[
i_p (\mu A) = 1543.4 (v)^{1/2} - 1368, \quad (R^2=0.976) \quad (8.1)
\]

This linear trend shows that the hydrazine oxidation is controlled by diffusion process as explained by Randle-Sevcik equation:

\[
i_p = (2.99 \times 10^5) n^2 n (a n)^{1/2} A C D^{1/2} v^{1/2} \quad (8.2)
\]

where, \(n\) = number of transferred electrons, \(A\) = electrode surface area (cm$^2$), \(C\) = concentration of electroactive species (mol cm$^{-3}$), \(D\) = diffusion coefficient (cm s$^{-1}$), \(v\) = scan rate (V s$^{-1}$), and \(\alpha\) = the charge transfer coefficient.

Fig. 8.14c presents the linear dependence of peak current on scan rate (both in logarithmic scale) which further confirms the diffusion character of hydrazine electro-oxidation as explained by the following equation [13, 14].

\[
\ln i_p = 9.32 \ln v \quad (V s^{-1}) + 5.527, \quad (R^2 = 0.94) \quad (8.3)
\]
Fig. 8.14: (a) Cyclic voltammetry profiles of modified electrode at scan rate of 10-100 mV s\(^{-1}\), (b) dependence of anodic peak current on \(\nu^{1/2}\), and (c) linear dependence of peak current on scan rate (both in logarithm scale).

7.2.1.2.2 Effect of concentration

The effect of hydrazine concentration was studied by selecting CoPd\(_{0.093/\gamma}\)-Al\(_2\)O\(_3\) modified electrode by changing N\(_2\)H\(_4\) concentration from 2 to 10 mM in 0.1 M PBS (pH 7.2). The anodic peak current was found proportional to hydrazine concentration (Fig. 8.15) which can be attributed to a better distribution of metal alloy particles over the surface of this modified electrode [15, 16].
Fig. 8.15: a) Concentration effect of hydrazine in the range of 2-10 mM for CoPd$_{0.093}$/$\gamma$-Al$_2$O$_3$ modified electrode in 0.1M PBS (pH 7.2) @ 25 mV s$^{-1}$.

7.3 Conclusions

A set of advanced bimetallic materials with the composition of CoPd$_x$/γ-Al$_2$O$_3$ ($x= 0, 0.034, 0.063, 0.093, 0.114, and 0.554$) was synthesized by wet impregnation method. The catalytic activity was tested for hydrazine decomposition to generate hydrogen and hydrazine electro-oxidation by cyclic voltammetry. During hydrazine decomposition reaction, CoPd$_{0.093}$/γ-Al$_2$O$_3$ catalyst presented high activity, H$_2$ selectivity and durability thus selected as it optimal composition. The high performance could be attributed to synergistic effect of Co and Pd metals in addition to excellent features of granular γ-Al$_2$O$_3$ support. The prepared CoPd$_x$/γ-Al$_2$O$_3$ catalysts with low noble metal content proved to be highly promising and were quite suitable for making the process cost effective and efficient for H$_2$ generation from hydrazine decomposition. The prepared catalysts also depicted the electrochemical response for hydrazine electro-oxidation. Among these, CoPd$_{0.093}$/γ-Al$_2$O$_3$ catalyst showed a prominent electrocatalytic activity for hydrazine. The present data also indicate that this set of materials can contribute towards further applications in the field of electro analysis.
References

Chapter 9

Conclusions and Recommendations

The present chapter summarizes the conclusions drawn from the discussions provided in previous chapters and presents recommendations to future work.

9.1 Conclusions

The primary goal of current research work was to explore the properties, development and applicability of $\gamma$-Al$_2$O$_3$ supported bimetallic catalysts for hydrogen generation from hydrazine decomposition, and potential electrocatalysts for hydrazine oxidation.

A modest preparation scheme was adapted for the preparation of $\gamma$-Al$_2$O$_3$ granules as support followed by loading of bimetallic catalysts; which proved to be an advantageous strategy in emerging materials with high phase purity, better properties, and good mechanical/thermal stability. In this regard, $\gamma$-Al$_2$O$_3$ support in granular shape was synthesized at first by sol gel method and after that, four catalyst series of supported bimetallic materials were prepared by loading four promoter metals (Ir, Ru, Pt, and Pd) in combination with Co base metal on $\gamma$-Al$_2$O$_3$ granules via wet impregnation method. The structural and surface properties of the synthesized samples were characterized using AAS, FTIR, XRD, N$_2$ physisorption, H$_2$ chemisorption, SEM equipped with EDX, TEM, TPR, and TPO techniques.

The activity of prepared sets of catalysts was evaluated via catalytic decomposition of hydrazine to generate hydrogen in self designed reactor at room temperature ($25^\circ$C) and volume of gaseous products (H$_2$+N$_2$) was measured gravimetrically by water displacement method. The catalytic performance was assessed on the basis of selectivity towards hydrogen (X) and turn over frequency (TOF). The catalytic activity (TOF) and H$_2$ selectivity were found to depend strongly on M/Co (M= Ir, Ru, Pt, and Pd) molar ratio in each series. In each catalyst series, the incorporation of promoter metals (Ir, Ru, Pt, and Pd) to Co/$\gamma$-Al$_2$O$_3$ catalyst in different proportions increased the activity to a greater extent. Such a high performance can be correlated to the strong interaction between Co and noble metals over the surface of high surface area $\gamma$-Al$_2$O$_3$ support as confirmed by SEM, TEM, and EDX analyses. All supported bimetallic catalysts showed their better potentiality for hydrogen generation compared to monometallic Co/$\gamma$-Al$_2$O$_3$ catalyst. The
comparison of this work with reported catalysts for hydrazine decomposition is summarized in Table 9.1.

**Table 9.1:** Comparison of catalytic parameters of our synthesized supported bimetallic catalysts with reported ones for hydrogen generation from decomposition of hydrous hydrazine.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction Temp. (°C)</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>TOF (h$^{-1}$)</th>
<th>$H_2$ selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co$<em>{0.20}$Rh$</em>{0.80}$ [1]</td>
<td>25</td>
<td>-</td>
<td>-</td>
<td>21.1</td>
</tr>
<tr>
<td>Co$<em>{0.60}$Pt$</em>{0.07}$ [2]</td>
<td>25</td>
<td>-</td>
<td>-</td>
<td>20</td>
</tr>
<tr>
<td>Co$<em>{0.95}$Ir$</em>{0.05}$-CTAB [3]</td>
<td>25</td>
<td>-</td>
<td>1.6</td>
<td>7</td>
</tr>
<tr>
<td>Co$<em>{60.2}$B$</em>{39.8}$ nanospheres [4]</td>
<td>25</td>
<td>-</td>
<td>-</td>
<td>21.3</td>
</tr>
<tr>
<td>Honeycomb like Co-B [5]</td>
<td>25</td>
<td>-</td>
<td>-</td>
<td>41.8</td>
</tr>
<tr>
<td>NiPt$_{0.057}$/Al$_2$O$_3$ [6]</td>
<td>30</td>
<td>34</td>
<td>16.5</td>
<td>97</td>
</tr>
<tr>
<td>NiIr$_{0.059}$/Al$_2$O$_3$ [7]</td>
<td>30</td>
<td>38.6</td>
<td>12.4</td>
<td>&gt;99</td>
</tr>
<tr>
<td>Ni$<em>{87}$Pt$</em>{13}$/meso-Al$_2$O$_3$ [8]</td>
<td>30</td>
<td>55.7</td>
<td>50.0</td>
<td>100</td>
</tr>
<tr>
<td>Ni$<em>{85}$Ir$</em>{15}$/MIL-101 [9]</td>
<td>25</td>
<td>66.9</td>
<td>24.0</td>
<td>100</td>
</tr>
<tr>
<td>Ni$<em>{0.9}$Pt$</em>{0.1}$/Ce$_2$O$_3$ [10]</td>
<td>25</td>
<td>42.3</td>
<td>28.1</td>
<td>100</td>
</tr>
</tbody>
</table>

**This work**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction Temp. (°C)</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>TOF (h$^{-1}$)</th>
<th>$H_2$ selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoIr$_{0.081}$/γ-Al$_2$O$_3$</td>
<td>25</td>
<td>40.8</td>
<td>27.7</td>
<td>100</td>
</tr>
<tr>
<td>CoRu$_{0.11}$/γ-Al$_2$O$_3$</td>
<td>25</td>
<td>37.4</td>
<td>21.9</td>
<td>100</td>
</tr>
<tr>
<td>CoPt$_{0.034}$/γ-Al$_2$O$_3$</td>
<td><strong>25</strong></td>
<td><strong>29.1</strong></td>
<td><strong>117.8</strong></td>
<td><strong>100</strong></td>
</tr>
<tr>
<td>CoPd$_{0.093}$/γ-Al$_2$O$_3$</td>
<td>25</td>
<td>44.1</td>
<td>61.5</td>
<td>100</td>
</tr>
</tbody>
</table>

The active role of the support can be comprehended from the comparison of work done on hydrazine decomposition using bimetallic catalysts without support, Table 9.1 [1-5]. It clearly indicates that the catalytic activity of support free materials is suppressed instead of being enhanced, e.g., TOF value for hydrazine decomposition came out to be $1.6$ h$^{-1}$ for Co$_{0.95}$Ir$_{0.05}$-CTAB [3], compared to supported bimetallic catalysts, Ni$_{85}$Pt$_{13}$/meso-Al$_2$O$_3$ [8], having TOF value of $50$ h$^{-1}$.

The selectivity towards $H_2$ evolution resulted from the formation of heterometallic bonds in bimetallic samples that might tune the bonding patterns of the
catalyst surface with the reactant molecules (N$_2$H$_4$). This strong metal-metal interaction may stabilize the possible reaction intermediates leading to effective selectivity for H$_2$ generation. The catalysts composition was also optimized on the basis of activity and selectivity. Hence, CoIr$_{0.081}$/γ-Al$_2$O$_3$, CoRu$_{0.11}$/γ-Al$_2$O$_3$, CoPt$_{0.034}$/γ-Al$_2$O$_3$, and CoPd$_{0.093}$/γ-Al$_2$O$_3$ catalysts were selected as the designated compositions from each series possessing optimal properties. Moreover, the kinetic studies depicted an increase in rate of hydrogen generation with an increase in temperature. The activation energy values were also derived from Arrhenius plots for monometallic Co/γ-Al$_2$O$_3$ and optimum bimetallic composition from each series. The activation values were found much lower for bimetallic catalysts compared to Co/γ-Al$_2$O$_3$, thus showing an ease in hydrazine decomposition over bimetallic compositions.

For electrochemical studies, the catalyst powders were deposited onto glassy carbon electrode to prepare modified electrodes. The electro-oxidation of 2 mM hydrous hydrazine was carried out in 0.1 M phosphate buffer solution (pH 7.2) under ambient conditions for four series of modified electrodes. The prepared materials were one by one subjected to hydrazine electro-oxidation in the selected potential window (0.5-1.0 V). All of the modified electrodes revealed encouraging current responses via cyclic voltammetry compared to Co/γ-Al$_2$O$_3$ modified and bare GC electrodes. The prominent current response in CV studies enabled CoIr$_{0.081}$/γ-Al$_2$O$_3$, CoRu$_{0.11}$/γ-Al$_2$O$_3$, CoPt$_{0.034}$/γ-Al$_2$O$_3$, and CoPd$_{0.093}$/γ-Al$_2$O$_3$ powders as optimal compositions in each series for electro-oxidation of hydrazine. The kinetic studies on the modified electrodes revealed that the electro-oxidation was governed by diffusion control process of hydrazine to redox-active sites of the modified electrode. Fig. 9.1 presents the comparative analysis for catalytic and electrochemical activity of the optimal composition from each series. Among all catalysts, CoPt$_{0.034}$/γ-Al$_2$O$_3$ exhibited maximum performance for both model reactions. CoPt$_{0.034}$/γ-Al$_2$O$_3$ bimetallic catalyst provided TOF value of 190 h$^{-1}$ along with lowest activation energy ($E_a$) value of 29.14 kJ mol$^{-1}$ among in the optimal samples. In terms of electrochemical performance, CoPt$_{0.034}$/γ-Al$_2$O$_3$ also exhibited highest anodic peak current ($i_p$) response with 183.2 µA value. The robust performance of CoPt$_{0.034}$/γ-Al$_2$O$_3$ sample would be correlated to best synergistic effect between Co and Pt metals, high dispersion of Co-Pt alloy particles, small sized particles, improved reducibility,
and more number of active sites as confirmed by XRD, SEM, TEM, EDX, and TPR/TPO analyses.

The comparison of electroanalytical data of our modified electrodes with reported ones for hydrazine oxidation is listed in Table 9.2.

<table>
<thead>
<tr>
<th>Electrode type</th>
<th>[N₂H₄] (mM)</th>
<th>Peak potential (V)</th>
<th>Peak current (µA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NG-PVP/AuNPs modified SPCE [11]</td>
<td>0.1</td>
<td>0.003</td>
<td>85</td>
</tr>
<tr>
<td>Au/SWCNHs/GCE [12]</td>
<td>0.3</td>
<td>0.26</td>
<td>13</td>
</tr>
<tr>
<td>Co(II)BBAEDI-MWCNT-MCPE [13]</td>
<td>0.05</td>
<td>0.011</td>
<td>11.4</td>
</tr>
<tr>
<td>Au–Pd NP/GNP/GCE [14]</td>
<td>0.1</td>
<td>0.18</td>
<td>62</td>
</tr>
<tr>
<td>Ag/CNT/GCE [15]</td>
<td>10</td>
<td>0.42</td>
<td>150</td>
</tr>
<tr>
<td>FDC/GCE [16]</td>
<td>1</td>
<td>0.25</td>
<td>22</td>
</tr>
<tr>
<td>Pt NPs [17]</td>
<td>5</td>
<td>0.20</td>
<td>13</td>
</tr>
</tbody>
</table>

**Present work**

CoIr₀.₀₈₁/γ-Al₂O₃  | 2          | 0.88               | 50.3              |
CoRu₀.₁₁₁/γ-Al₂O₃ | 2          | 0.91               | 46.1              |
CoPt₀.₀₃₄/γ-Al₂O₃ | 2          | **0.85**           | 183.2             |
CoPd₀.₀₉₃/γ-Al₂O₃ | 2          | 0.90               | 59.4              |

The peak response of our modified electrodes is higher as compared to other reported modified electrodes for hydrazine electro-oxidation [11-16] thus indicating that supported bimetallic alloy compositions make facile electron transfer process.
9.2 Future perspectives

The present research work effectively established the potentiality of supported bimetallic catalysts for catalytic hydrazine decomposition and electroanalytical applications. However, additional work can be made in order to improve the performance and scope of the nanomaterials. In future, the research can be made by advancement of in situ characterization, tuning the composition of catalysts, exploring ternary systems, and adopting co-impregnation method for metal loadings. The emergence of a new generation of nanocatalysts can be exploited for low temperature on-board hydrogen production for fuel cell applications as well as electrochemical sensors which would also be of great interest for future renewable energy technologies.

Fig. 9.1: Overview of activity of prepared catalysts for catalytic decomposition and electro-oxidation of hydrazine.
References

Appendix

Fig. 1: XRD pattern of Ir/γ-Al₂O₃ catalyst.

Fig. 2: TPR profile of Pt/γ-Al₂O₃ catalyst.
Fig. 3: TPR profile Ru/γ-Al₂O₃ catalyst.

Fig. 4: CoRu₀.11/γ-Al₂O₃ catalyst before (left) and after (right) magnetic separation from the reaction mixture.
Fig. 5: Kinetic profiles for H$_2$ release from the decomposition of hydrous hydrazine (0.5 M) over (a) Co/γ-Al$_2$O$_3$ and (b) CoRu$_{0.11}$/γ-Al$_2$O$_3$ catalysts at different temperatures.
Fig. 6: TPR profiles Pd/γ-Al₂O₃ catalyst.
List of Publications


3. **Naveeda Firdous**, Naveed K. Janjua, $\gamma$-Al$_2$O$_3$ supported CoRu bimetallic nanoparticles as efficient catalysts for hydrogen generation from hydrous hydrazine (2017) (Submitted).
