

**SYNTHESIS AND CHARACTERIZATION OF OXIDES OF Mn, Co  
AND Ni AND INVESTIGATION OF THEIR CATALYTIC  
ACTIVITIES FOR ORGANIC OXIDATION REACTIONS IN  
LIQUID PHASE**



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PHYSICAL CHEMISTRY,  
UNIVERSITY OF PESHAWAR  
PAKISTAN**

**2010**

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*A dissertation submitted to the University of Peshawar in partial  
fulfillment for the degree of*  
**DOCTOR OF PHILOSOPHY IN PHYSICAL CHEMISTRY**

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2010**

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Dedicated to my dear Parents  
**Dedicated to my dear Parents**



## Key Words

Manganese oxide, Cobalt oxide, Nickel oxide, Nickel hydroxide, Benzyl alcohol, Benzaldehyde, Benzoic acid, Phenol, Carbon dioxide, XRD, FTIR, SEM, Langmuir-Hinshelwood

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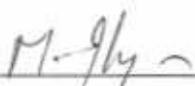
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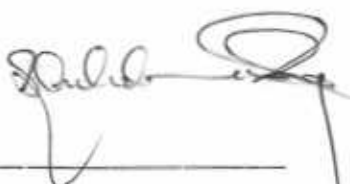
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This is to certify that this dissertation submitted by **Mr. Muhammad Saeed**, entitled **“Synthesis and Characterization of Oxides of Mn, Co and Ni and Investigation of Their Catalytic Activities for Organic Oxidation Reactions in Liquid Phase”** is accepted in its present form by the University of Peshawar, Peshawar, Pakistan as satisfying the dissertation requirement for the degree of Doctor of Philosophy in Physical Chemistry.

  
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Muhammad Saeed  
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## List of Publications

The thesis includes the following papers which were published in different journals (I and II) and presented at various conferences (III-VIII).

- I. Ilyas, M; **Saeed, M**; International Journal of Chemical Reactor Engineering, 2010, Vol. 8, A77, 1-19.
- II. Ilyas, M; **Saeed, M**; Journal of The Chemical Society of Pakistan, 2009, Vol. 31, No. 4, 526-533.
- III. M. Ilyas, **M. Saeed**, "Oxidation/dehydrogenation of benzyl alcohol in liquid phase catalyzed by oxides of nickel" 18<sup>th</sup> National Chemistry Conference, Institute of Chemistry, University of the Punjab, Lahore, 25-27<sup>th</sup> February 2008.
- IV. M. Ilyas, **M. Saeed**, "Oxidation of benzyl alcohol in liquid phase catalyzed by oxides of nickel: Kinetic Analysis" 1<sup>st</sup> National Symposium on Analytical, Environmental and Applied Chemistry, Department of Chemistry, Shah Abdul Latif University, Khairpur, 24-25<sup>th</sup> October 2008.
- V. M. Ilyas, **M. Saeed**, "MnO; An effective catalyst for oxidation of benzyl alcohol using n-octane as solvent" 19<sup>th</sup> National Chemistry Conference, Department of Chemistry, Kohat University of Science and Technology, Kohat, 09-11<sup>th</sup> June 2009.
- VI. M. Ilyas, **M. Saeed**, "Oxidation of benzyl alcohol in liquid phase catalyzed by cobalt oxide" 19<sup>th</sup> National Chemistry Conference, Department of Chemistry, Kohat University of Science and Technology, Kohat, 09-11<sup>th</sup> June 2009.
- VII. M. Ilyas, **M. Saeed**, "Oxidation of benzyl alcohol in liquid phase catalyzed by cobalt oxide: Kinetic Analysis" 8<sup>th</sup> International and 20<sup>th</sup> National Chemistry Conference, Department of Chemistry, Quaid-eAzam University Islamabad, Pakistan, 15-17<sup>th</sup> Feb 2010.
- VIII. M. Ilyas, **M. Saeed**, Mohsin Siddique, "Oxidative removal of phenol from water catalyzed by cobalt oxide and nickel hydroxide under milder reaction conditions" 1<sup>st</sup> National Conference on Physical & Environmental Chemistry (PEC-2010) at

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University of Peshawar, Peshawar, Pakistan, September 26-30, 2010.

## Abstract

Four catalysts, manganese oxide, cobalt oxide, nickel hydroxide and nickel oxide, were investigated. Manganese oxide was prepared by manganese chloride and potassium permanganate in solid state chemical reaction at room temperature. Cobalt oxide was prepared by cobalt nitrate and ammonium bicarbonate in solid state chemical reaction at room temperature. Nickel hydroxide was prepared by reaction of nickel sulfate, sodium hydroxide and sodium hypochlorite. Nickel oxide was prepared by reaction of nickel nitrate, sodium hydroxide and sodium carbonate.

Prepared catalysts were characterized by chemical and physical methods. Chemical method includes determination of oxygen content, while physical methods include nitrogen adsorption studies, XRD, FTIR, particle size and SEM analysis.

Prepared catalysts were used for oxidation of benzyl alcohol, oxalic acid and phenol in liquid phase. Oxidation of benzyl alcohol was carried out in organic solvent and in aqueous medium as well. Only nickel hydroxide was active for oxidation of benzyl alcohol in aqueous medium. In aqueous medium both benzaldehyde and benzoic acid were detected as reaction products. In organic solvents only benzaldehyde was formed in nickel hydroxide and nickel oxide catalyzed reaction, while in case of manganese oxide and cobalt oxide catalyzed reactions both benzaldehyde and benzoic acid were formed. In case of manganese oxide catalyzed oxidation reaction benzoic acid was formed after almost complete conversion of benzyl alcohol to benzaldehyde in organic solvent, showing the parallel nature of reaction. Using cobalt oxide as catalyst benzoic acid was formed after about 60% conversion of benzyl alcohol to benzaldehyde showing the consecutive nature of reaction. In aqueous medium all the three catalysts (manganese, cobalt and nickel oxides) were inactive for oxidation of benzyl alcohol. For oxidative degradation of oxalic acid in aqueous medium only manganese oxide was active catalyst. Oxalic acid was completely degraded to carbon dioxide. In all the cases Langmuir-Hinshelwood type of mechanism was operative. For oxidative degradation of phenol cobalt oxide and nickel hydroxide were active catalysts. Phenol was also degraded to carbon dioxide. First order kinetics model was applicable to the data for oxidative

degradation of phenol. Effect of various parameters like time, catalyst loading, temperature, partial pressure of oxygen, speed of agitation etc on catalytic performance was investigated. All the catalysts were heterogeneous in nature, which could be separated easily by simple filtration.



## Chapter 1

# Back Ground

### 1.1. Introduction

The oxidation of organic compounds in liquid phase is one of the most important and widely used reactions in laboratory scale organic synthesis as well as in large scale chemical industrial processes [1, 2]. Many processes with different reagents and methods are available for the oxidation of organic compounds. These methods exist and are very applicable for a laboratory scale synthesis; however most of them share common disadvantages from an industrial point of view. Stoichiometric oxidants such as peroxides or high oxidation state metal compound such as permanganate and dichromate are frequently used reagents for oxidation purposes. But these reagents are expensive, toxic and produce large amount of wastes and hence separation and disposal of the waste increases the number of steps [3, 4]. When these oxidation reactions are scaled to tons instead of grams, the use of these stoichiometric oxidants is not an attractive option. For these kinds of oxidation reactions an alternative and environment friendly oxidant is desirable. An ideal oxidant for any large-scale oxidation reaction is the one which has low price, high quality (purity), non-toxic and easy availability. Molecular oxygen is the one which qualify this criterion [5]. It is easily available as it is present in air and the only by-product produced from it is water.

There are a few points, however, which make the use of molecular oxygen challenging:

- Although molecular oxygen has a high oxidation potential, it is not very reactive towards organic molecules
- The reactions where molecular oxygen is present are often radical reactions, which are hard to control.

To make an efficient use of molecular oxygen as oxidant, an appropriate catalyst is needed, which can activate the oxygen molecules for appropriate reaction. Currently molecular oxygen is used in several large-scale oxidation reactions, catalyzed by inorganic heterogeneous catalysts. Typically, these reactions are carried out at high temperatures and high pressures, often in the gas phase. Unfortunately, these

heterogeneous oxidation methods are not suitable for large scale synthesis, where selectivity and mild reaction conditions are favored in the production of high value products. Therefore, it is required that the stoichiometric oxidants should be replaced by catalysts that are capable to activate molecular oxygen at mild reaction conditions during oxidation reactions in liquid phase. The most promising solution to this challenge is homogeneous transition metal complexes that are able to catalyze selective oxidation reactions under mild conditions using molecular oxygen as the oxidant.

Although molecular oxygen has the potential required from a good oxidant, the kinetic and thermodynamic restrictions caused by the spin conservation rule and its one electron reduction reaction pathways make it rather inert towards organic molecules [6]. Therefore, in order to get molecular oxygen to efficiently react with organic molecules, the electronic configuration of the molecular oxygen (a triplet in ground state) has to be changed to match the electronic configuration of the organic molecules (a singlet ground state). This can be done either physically with light excitation or chemically by letting the molecular oxygen react with, for example, transition metals. This is the basis for using transition metal complexes as oxidation catalysts [7]. However, with homogeneous catalytic reactions both the reactants and catalysts are present in one phase and from an engineering viewpoint, a major disadvantage of this arises from the difficulty in separating the products from the catalyst, which increases the number of steps [8, 9]. Therefore, the use of heterogeneous systems would be superior to homogeneous counterparts due to the easier separation of products and catalysts and reuse of catalysts. Metal oxides and supported metal oxides have been proposed as effective heterogeneous catalysts for oxidation of organic compounds. In many cases, alumina-supported and zirconia supported metal oxides of precious metals like Pt and Pd have shown high activity for oxidation of organic compounds. From the economical point of view, using oxides of non-precious transition metals like manganese (Mn), cobalt (Co), nickel (Ni) etc. as heterogeneous catalysts for oxidation of organic compounds, using clean oxidants such as molecular oxygen is of great importance [10, 11].