

# **STUDIES ON CATALYSIS BY MESOPOROUS CERIA MODIFIED WITH TRANSITION METALS**

*Thesis submitted to*  
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***Chemistry***  
***Under the faculty of Science***

*by*  
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# **Studies on Catalysis by Mesoporous Ceria Modified with Transition Metals**

*Ph.D Thesis*

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**Certificate**

Certified that the present work entitled “**Studies on catalysis by mesoporous ceria modified with transition metals**” submitted by Smt. Rose Philo K. J. is an authentic record of research work carried out by her under my supervision at the Department of Applied Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry of the Cochin University of Science and Technology and has not been included in any other thesis previously for the award of any degree.

***Dr. S. Sugunan***  
*(Supervising Guide)*

Kochi-22  
6-6-2012

## *Declaration*

I hereby declare that the research work entitled, “**Studies on catalysis by mesoporous ceria modified with transition metals**” is entirely original and was carried out by me independently under the supervision of Dr.S.Sugunan, Professor, Department of Applied Chemistry, Cochin University of Science and Technology, Kochi-22, India and has not been included in other thesis submitted previously for the award of any other degree.

*Rose Philo K,J*

Kochi-22

6-6-2012

*.....To my dearest parents  
and  
My husband  
for their love and constant support...*

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## *Preface*

Catalysis has wide ranging applications in chemical industry and has a major impact on the quality of human life as well as economic development. In recent years catalysis is looked up as a solution to eliminate or replace polluting processes. Solid acid catalysis is one of the most important areas of research and has assumed great relevance as an economic alternative to many homogenously catalysed, industrially important reactions. The solid acid catalysts can also be designed to give higher activity, selectivity, regenerability and longer catalyst life.

Among the different solid acid catalysts used, mesoporous materials are more widely studied nowadays. In the field of catalysis, much effort has been spent in the preparation, characterization and application of mesoporous metal oxides. Among different rare earth metal oxides studied, ceria has potential applications. Ceria and ceria based mixed oxide materials are used in automotive exhaust catalysis and oxidation of environmental pollutants. Cerium oxide is an excellent catalyst for redox reactions.

In this work mesoporous ceria is synthesized with cubic fluorite structure by templated route, using neutral surfactant hexadecylamine. The catalytic activity is enhanced by loading transition metals Cr, Fe, Cu, Co, Mn and Ni into this mesoporous network by wet impregnation method. The systems were characterized by low and wide angle XRD, FT-IR, BJH (N<sub>2</sub> adsorption/desorption studies), TG/DTA, EDX, ICP-AES, SEM, TEM, UV-Vis. DRS and TPR of H<sub>2</sub>. Ammonia TPD and cumene cracking as the test reaction for acidity are adopted for the surface acidity determination. For the activity studies of the prepared systems, liquid phase reactions - oxidation of



ethyl benzene using TBHP to get acetophenone as the main product, Friedel Crafts benzylation of toluene, o-xylene and anisole using benzyl chloride, acetalization and de-acetalization of cyclohexanone for the protection of ketone functional group and vapour phase reaction - methylation of phenol are also done.

The work is presented in 8 chapters. Chapter 1 is introduction and literature survey. Chapter 2 explains the method of preparation and characterization of the prepared catalysts. Chapter 3 contains results and discussions of physico-chemical characterization. Chapter 4, 5, 6 and 7 describe the various liquid phase reactions done for studying the catalytic activities of the prepared systems. Chapter 8 gives the summary of the work done and conclusions made on the basis of the different physico-chemical characterizations and catalytic activity studies. The most efficient catalysts for Friedel Crafts benzylation among the prepared samples are iron modified ones. The Cr loaded mesoporous ceria is found to be the most efficient among the prepared systems for oxidation of ethyl benzene using TBHP in liquid phase to get acetophenone selectively as the major product. From the study on acetalization and deacetalization of cyclohexanone it can be concluded that the prepared catalysts are successful in the protection of ketone group and afterwards the same catalysts can be used to regenerate the ketone group in the substrate by de-protection in a simple manner. We report herein the development of an environment friendly process for C-methylation of phenol with methanol using mesoporous ceria modified catalysts.

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