STUDIES ON CATALYSIS BY MESOPOROUS CERIA MODIFIED WITH TRANSITION METALS

Thesis submitted to

Cochin University of Science and Technology

in partial fulfillment of the requirements

for the award of the degree of

Doctor of Philosophy

in

Chemistry

Under the faculty of Science

by

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June 2012

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...

Acknowledgements

My work would not have been possible without the support of many people who contributed their time and knowledge to me.

First of all, I would like to express my sincere appreciation to my guide Dr. S.Sugunan, Department of Applied Chemistry, Cochin University of Science and Technology, Kochi, for his intelligent insight, generosity and for guiding me through challenging research field. With deep regards and profound respect, I avail this opportunity to express my deep sense of gratitude and indebtedness to him for introducing the present research topic and for his inspiring guidance, constructive criticism and valuable suggestions throughout my research work.

I would like to acknowledge my deep sense of gratitude to Dr. K. Sreekumar, Head, and Dr. Prathapachandra Kurup and Dr. Girish Kumar, former heads, Department of Applied Chemistry, Cochin University of Science and Technology, Kochi, for their valuable advices and constant encouragement. With all sincerity and high regards, I wish to thank all the faculty members & all staff members of the Department of Applied Chemistry for their support and help during the research work.

I also thank my doctoral committee member, Dr. K. K. M. Yusuff, Department of Applied Chemistry, Cochin University of Science and Technology, Kochi, who has generously provided his time, energy and valuable suggestions to both my thesis and my academic life from my MSC study onwards in this university.

I am grateful to my lab mates and friends Dr. Rajesh, Dr. Ambili, Reni, Cimi, Dhanya, Soumini, Sandhya, Nissam, and Mothi who helped me a lot in various needs. I thank them sincerely for their friendship and help. Thanks to all my senior research scholars of physical lab, especially Dr. Maya, Dr. Radhika, Dr. Binitha, Dr. Ajitha, Dr. Joyes, Dr. Reshmi, Dr. Bolie and Satheesh for their help and co-operation.

I also extend a special word of thanks to all research scholars of other research labs and students of the department for their help and warm wishes. Acknowledge STIC, CUSAT for providing various analysis part of the work. I also express my sincere thanks to my student Jithesh for doing TEM and TG/DTA analysis for me and Leena for doing low angle XRD analysis from NCL, Pune.

My sincere thanks to the Principal Dr. Edwin Xavier, former principal Prof. P. J. Roy, Manager Fr. Alex Chakalackal and former manager Fr. Douglus Pinhero of St. Paul's College, Kalamassery for granting me leave for completing my research work when FIP fellowship was awarded to me. I would also like to thank Prof. George John, head and Dr.V.Nanadanan former head of the department of Chemistry, St. Paul's College and all the staff members of the department for their help and warm wishes. I acknowledge all my friends of St. Paul's college.

This work would not have been fruitful without the encouragement and support of my husband Marshal who has been with me to support and encourage me when I was in tensions related to the research work. I remember my dearest daughters Sruthy, Smruthy and Shraddha who have been the lights of my life and God given gifts to me.

I am very much indebted to my parents Mr. K. V. Joseph and Mrs. Mary Joseph and all the members of my family for their love, patience and interest in my studies. I am very much thankful to God Almighty for helping me to complete my research work and thereby fulfilling the dream of my grandfather late Mr. K. D. Varkey. I remember with gratitude both my uncles Prof. K.V. Thomas and Dr. K.V. Peter who have been always a source of strength, support and inspiration in my life. At this moment of joy I also remember my parents in law late Mrs and Mr. K.A. Joseph and all the family members.

I acknowledge University Grant Commission for awarding the teacher fellowship for doing PhD.

Above all, I believe that what so ever I am, it is because of ***God Almighty,*** *the creator of all.*

Rose Philo K.J

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_2 adsorption/desorption studies), TG/DTA, EDX, ICP-AES, SEM, TEM, UV-Vis. DRS and TPR of H_2. 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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