

SUMMARY AND CONCLUSIONS

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My Ph.D. research work is concerned mainly on developing new mesoporous materials. A wide range of important organic reactions can be efficiently catalyzed by these materials, which can be designed to provide different types of acidity as well as high degrees of reaction selectivity. Industrial catalysis was developed from an art to science. A typical industrial catalyst should be regenerable, reproducible, mechanically and thermally stable and economical and should possess suitable morphological characteristics apart from its activity, selectivity, and stability.

A variety of methodologies for synthesizing mesoporous metal oxides have been investigated. Here in this work mesoporous ceria was prepared by soft templating method using the neutral surfactant hexadecyl amine. The mesoporous ceria thus prepared is modified with transition metals Cr, Fe, Mn, Cu, Co and Ni. The applications of these catalysts in industrially important reactions like ethyl benzene oxidation, alkylation of aromatics, protection and de-protection of acetone like cyclohexanone are also investigated. This chapter reviews the summary of the work detailed in the

previous chapters. The important conclusions arrived from different studies are also presented in this chapter.

8.1 Summary

Chapter I deal with the literature survey in which the introduction about the heterogeneous catalysis, detailed informations about the solid catalysts, their importance in heterogeneous catalysis and in industrial processes and the use of metal oxides as solid acids are dealt with. The new generation mesoporous solids can be obtained from various metal precursors employing different methods of preparation are discussed here.

In the field of catalysis, much effort has been spent in the preparation, characterization and application of ceria and ceria based mixed oxide materials for automotive exhaust catalysis and oxidation of environmental pollutants. The influence of the redox properties of ceria on several reactions has also been investigated systematically. Doping can improve the sintering properties of ceria, by stabilizing the ceria surface area and crystal size. The effect of modification of mesoporous ceria by transition metals in the study is discussed in this section.

Surface acidity and basicity investigations have received great attention due to its application in determining catalytic behaviour which is used to describe the effectiveness of a catalyst. The acidity of the solids plays a significant role when these are used as supports. The necessity for the determination of surface acidity and the test reaction of acidity are also discussed in this chapter. Finally the activities of prepared catalysts studied using different industrially important reactions and the importance of these reactions are discussed.

Chapter II deals with the materials and the experimental procedures used for catalyst preparation, surface acidity and catalytic activity measurements. The structural and morphological characteristics of the prepared samples were investigated by the techniques like wide and low angle XRD, BET surface area and pore volume measurements, BJH sorption studies, TEM, FT- IR, TG-DTA, SEM, EDX, ICP –AES, TPR in H₂ and UV-Vis DRS. Ammonia TPD, and cumene cracking as the test reaction for acidity are adopted for the surface acidity determination. For the activity study of the prepared systems, liquid phase reactions like oxidation of ethyl benzene using TBHP to get acetophenone as the main product, Friedel Crafts benzylation of toluene, o-xylene, anisole and benzene using benzyl chloride as the benzylating agent, acetalization and deacetalization of cyclohexanone for the protection of ketone functional group and vapour phase reaction of methylation of phenol are done.

Chapter III describes the results of physico–chemical characterization of prepared catalysts. A detailed investigation of physico-chemical characterization of the catalytic systems was performed by techniques such as wide and low angle XRD, BET surface area, pore volume and pore distribution by sorption studies of nitrogen gas, EDX, ICP-AES, SEM, TEM, thermogravimetry, UV-Vis DRS, FT-IR and TPR in H₂. Surface acidic properties of the systems were obtained from TPD of Ammonia and the results were tested by the test reaction of vapour phase cumene cracking. The results of these techniques are discussed.

Chapter IV deals with the liquid phase benzylation of toluene, o-xylene and anisole using benzyl chloride as benzylating agent. Here in this chapter, conversion of the reaction in terms of benzyl chloride is correlated with the acidities of the prepared catalysts. The various reaction parameters

like temperature, molar ratio of substrate to benzyl chloride, weight of catalyst and time of the reaction were optimized using iron loaded catalyst for toluene benzylation. Then o-xylene and anisole were also benzylated in this optimized condition.

In chapter V the synthesis of dimethyl acetals of carbonyl compound such as cyclohexanone, is successfully carried out by the reaction between cyclohexanone and methanol using different prepared catalysts are described. The strong influence of the textural properties of the catalysts such as acid amount and adsorption properties (surface area and pore volume) on the catalytic activity is interrelated in this chapter.

Chapter VI presents the investigation, about the oxidation of ethyl benzene carried out in liquid phase using the mesoporous ceria and transition metal modified ceria systems using tert.butylhydroperoxide (TBHP) as the oxidizing agent. The reaction was studied in different temperatures and using different solvents. Based on this report in the present study, we utilized mesoporous ceria modified with different transition metals as catalysts for the oxidation of ethyl benzene using TBHP as oxidant in liquid phase. The stability and reusability of the catalyst is studied using representative samples. The kinetic parameters of the reaction with Cr modified catalyst are calculated considering the reaction to be pseudo unimolecular.

In chapter VII discussions about selective C-methylation of phenol to o-cresol in high yield carried out with methanol over mesoporous ceria modified by transition metals are done. The influence of various experimental parameters on phenol conversion and product selectivity has been investigated. The catalyst was active without any deactivation showing its longer life. The catalytic activity and selectivity is correlated

with its acidity and structure. A tentative mechanism for the ortho selective methylation of phenol over the catalyst has been proposed. Phenol is adsorbed perpendicularly on Lewis acidic site by lone pair electrons of oxygen atom and is alkylated by methanol, which is possibly in the form of methyl carbonium ion. The kinetic parameters of the reaction with Fe modified catalyst are calculated considering the reaction to be pseudo unimolecular.

8.2 Conclusions

Mesoporous ceria modified with various transition metals can be successfully synthesized by template method using Hexadecyl amine as surfactant. All the samples prepared have ordered pores. Major conclusions that can be drawn from the present research work are the following.

Mesoporous ceria can be successfully prepared by surfactant route using neutral surfactant hexadecyl amine that has more surface area.

- The surface area and pore volume of the support decrease with the introduction of transition metals. Adsorption isotherms of ceria calcined at different temperatures resemble Type IV of IUPAC classification which is characteristic of mesoporous materials. The narrow pore size distribution shows uniformity of the pore.
- The XRD data of the prepared systems agree well with the standard values for the cubic fluorite structure of ceria. No additional peaks corresponding to the doped metal oxide is found for Cr, Fe, Mn, Ni & Co. This shows that metals are highly dispersed within the frame work structure. For Cu when the concentration exceeds a limit the metal peaks are found in the XRD pattern.

- From FT-IR studies it can be seen that the neutral surfactant is successfully removed at a lower calcination temperature attaining maximum surface area. It also shows large amount of surface hydroxyl groups present which are responsible for Brønsted acidity.
- From the interpretation of the total acidities of samples measured by temperature programmed desorption of ammonia gave good correlation with the cumene cracking conversion. It confirms the enhancement of surface acidity upon modification with transition metals.
 - The study on liquid phase Friedel Crafts benzylation reaction of toluene shows that they are suitable solid acid catalysts for reaction. The most efficient catalysts for Friedel Crafts benzylation among the prepared samples are iron modified ones. Exceptionally high activity in the case of iron systems proposed a free radical mechanism, which was confirmed by the effect temperature as well as the presence of an induction period for the reaction.
 - The catalysts are regenerable and can be used again. This reusability regenerability, high selectivity, 100% conversion, moderate reaction temperature, and absence of solvent, etc. make these catalyst to be used in a truly heterogeneous manner and makes the benzylation reaction an environment friendly one. Hence this solid acid catalyst can be used in efficient green chemical process for the manufacture of industrially important compounds.

- 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 introduced a mild and selective reagent for the oxidative cleavage of acetals under aqueous and heterogeneous conditions. The stability, simple work-up and high yields of the products are among the advantages of this procedure which make it an attractive supplement to the present reported methods.

The present study on liquid phase oxidation of ethyl benzene can be summarized as given below.

- Ethyl benzene can be oxidized effectively using mesoporous ceria modified catalyst using TBHP in liquid phase to get acetophenone selectively as the major product.
- Reaction variables like temperature, weight of catalyst, time, solvent and volume of the solvent have predominant effect on the % conversion and selectivity to acetophenone.
- Chromium, manganese and copper doped catalysts have more activity in the reaction and product selectivity. For the effective catalyst Cr doped ceria, the metal loading has pronounced influence on % conversion and selectivity.
- Transition metal-incorporated mesoporous materials have proved to be potential catalysts in the oxidation of alkyl arenes to

carbonyl compounds. The reactions were found to be extremely sensitive to the oxidant and solvents used. Mesoporous ceria materials appeared to be promising acid and redox catalysts and were also successfully applied as supports for active sites.

- We report herein the development of an environmentally friendly process for C-methylation of phenol derivatives with methanol using mesoporous ceria modified solid acid catalysts. In summarizing the results, the following conclusions can be deduced:
 - These systems are highly efficient for alkylating phenol in the ortho position, leading to o-cresol as the major product. Under optimized conditions, for the best catalyst among the prepared samples (CeCr10%) the total ortho selectivity was higher than 97% with a phenol conversion of 74%.

Preferential C- alkylation can be attributed to large number of weak and medium acid sites whereas preferential ortho-alkylation is due to perpendicular orientation of phenol aromatic ring on catalyst surface. The undesired side reactions such as the dealkylation to phenol and formation of poly methylated products are suppressed over these catalysts due to the unavailability of strong acid sites.

- Formation of poly methylated products is suppressed over these catalysts due to the unavailability of strong acid sites. Direct C-alkylation over the prepared catalysts is due to the higher acidity of catalysts. The catalyst is highly stable and does not deactivate even after a number of cycles.

- A tentative mechanism for the ortho selective methylation of phenol over the catalyst has been proposed. Phenol is adsorbed perpendicularly on Lewis acidic site by lone pair electrons of oxygen atom and is alkylated by methanol, which is possibly in the form of methyl carbonium ion.
- The reaction is proved to be following first order kinetics with phenol conversion with the frequency factor A and the activation energy E_a evaluated as 9.6×10^6 (kg of catalyst)⁻¹ h⁻¹ and 57.2 kJ/ mol, with (CeCr10%) catalyst. The values of E_a vary in the same range (30-130 kJ mol⁻¹) as reported recently by several authors for phenol conversion over different catalyst. The kinetic parameters like ΔH^\ddagger , ΔS^\ddagger of activation for the reaction are calculated.
- For Cr, Fe & Ni modified samples, the rate constants increases as the metal content increases. For Co & Mn loaded samples the rate constant initially decreases with metal loading up to a higher concentration then it increases. However with Cu loading, the rate constant decreases steadily. Effect of metal loading on phenol conversion may be due to the higher uniform dispersion of metal ions on ceria support as well as moderate acidity.

8.3 Future Outlook

The present study on the mesoporous ceria shows that the textural and catalytic activity of the support can be modified by the loading with various transition metals. Among the prepared systems Cr and Fe modified systems are found to be efficient for oxidation, acetalization of

cyclohexanone and Friedel Crafts benzylation and alkylation reactions. These systems can be used for further studies for acetalization of various carbonyl compounds, oxidation and Friedel Crafts alkylation various organic compounds. The improved acidities and redox properties can be utilized for the application in environmental pollution control. Cerium oxide has been identified as a potentially important catalytic support for the hydrogen production from syngas due to its ability to undergo rapid reduction/oxidation cycles. The possibility of using these prepared catalysts with improved OSC and reducibility can be studied for WGS activity.

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