“Solid acid catalysts based on supported nanocrystalline ceria”
Chapter 8- Summary and Conclusion

Summary and Conclusions:

This chapter gives a brief summary of the results discussed in previous chapters and the overall conclusions derived from the work.

In Chapter 1, it includes the introduction and importance of catalysis and mixed oxide catalysts in various fields were discussed. Development in catalytic science and technology with respect to economic growth and sustainable development can be resolved by using solid acid catalysis. It includes about nanocrystalline supported ceria and its applications.

In Chapter 2, contains brief literature review on ceria and ceria based various catalysts were included. Investigation on various literatures focused on synthesis, textural, morphological properties as well as applications of ceria and ceria based materials in different fields. This chapter contain detailed outline on acid catalyzed reactions by using ceria based materials. The combinations of metal and ceria offered good catalytic activity in various organic transformation reactions. So these mixed oxide catalysts could be used for the industrially important reactions such as oxidation, alkylation and so on. The ceria based materials were reported at high temperature reactions but studies of the reactions at mild temperature conditions have not been done well. Therefore, this study covers sustainable oxidation processes as well as acid catalyzed reactions using nano ceria supported catalysts.

In Chapter 3, the aims and objectives of the thesis was fulfilled and completed.

In Chapter 4, it include detailed discussion about materials used and the hydrothermal technique used for preparation of pure ceria and various wt. % loading of Fe (0.1, 0.3, 0.5, 0.8, 1.0) on CeO₂ mixed oxide catalysts. The hydrothermal process has been selected since particles of the desired size and shape was obtained by controlling the parameters such as solution pH, reaction temperature, reaction time and concentration.

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Well-crystallized nano-ceria and different wt. % loading of Fe (0.1, 0.3, 0.5, 0.8, 1.0) on nanocrystalline CeO₂ catalysts were obtained by hydrothermal synthesis using an oxidizer H₂O₂. This chapter also describes information about characterization techniques used for the study of prepared catalysts.

In Chapter 5, the physico-chemical characterization of pure CeO₂ and various wt. % loading of Fe on CeO₂ catalysts were carried out to obtain useful information regarding the phase purity, stability, acidity, composition, surface area and morphology. The structure of the prepared catalysts were confirmed by the FT-IR data which showed the presence of metal-oxygen bonding. From XRD data concluded that all the prepared catalysts showed nanosized crystalline nature having crystallite size in range between 9-14 nm. TGA data confirmed the strong thermal stability of prepared catalysts above 450°C. Therefore 500°C temperature was selected for the calcination of catalysts. From Raman spectra, the pure cubic CeO₂ displayed an intense peak at 462 cm⁻¹ assigned to the symmetric breathing mode of O atoms around each Ce⁴⁺ in metal oxides. As compared to pure ceria spectrum the intense band of CeO₂ at 462 cm⁻¹ slightly shifted towards 459 cm⁻¹ which confirmed the loading of metal oxide on CeO₂. FT-IR and Raman spectrum confirmed the formation of ceria based catalysts.

The BET surface area showed specific surface area and pore volume of the prepared catalysts. With increasing the loading of the Fe content on CeO₂ gave decrease in their surface area. The acidity measurements by acid-base titrimetric method confirmed the acidic nature of the prepared solid acid catalysts which responsible for the catalytic performance.

The EDX analysis data confirmed presence of Fe and Ce and O elements in the synthesized catalysts. Therefore the EDX confirmed the composition of pure CeO₂ and various wt. % Fe/CeO₂ mixed oxide catalysts. The FESEM photographs showed smaller particles size with an average particle size distribution between 9 - 18 nm. The FESEM micrograph described the spherical shaped uniform particle size distribution and mesoporous structure. The prepared mixed oxide catalysts revealed good agreement between the particle size obtained from FESEM and XRD data.
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In Chapter 6, this chapter deals with the study of catalytic activity of prepared CeO$_2$ and various wt.% loading of Fe on CeO$_2$ catalysts used for the liquid phase benzylation of benzene. The influence of various reaction parameters such as effect of temperature, catalyst amount, substrate, molar ratio and various catalysts were studied on benzylation reaction. The analysis of the product was confirmed by TLC and gas chromatography techniques. Therefore, from the optimized reaction conditions, the benzylation reaction was carried out by using 0.8 wt.% Fe/CeO$_2$ catalyst at temperature 90$^\circ$C, catalyst amount 0.2g with molar ratio 1:6 (BC:benzene) gave higher % conversion of benzyl chloride (99.94%) with 100 % selectivity of diphenylmethane as a product.

In Chapter 7, the prepared catalysts were used for detailed study for liquid phase oxidative coupling of thiophenol to disulfide. The effects of various reaction parameters were discussed with respect to conversion and selectivity. Temperature was optimized to have an accelerating effect on conversion. The effect of catalyst amount showed that, minimum quantity of the catalyst was only needed to carry out the reaction. The use of acetonitrile solvent was found to increase the conversion. Hence, the oxidative coupling of thiophenol to diphenyl disulfides carried out by using acetonitrile as a solvent over 0.8 wt. % Fe/CeO$_2$ catalyst, at 80$^\circ$C temperature, catalyst amount 0.3g gave good conversion as well as selectivity.

Overall 0.8 wt. % Fe/CeO$_2$ catalyst showed excellent catalytic activity in both the reactions. This might be due to loading of tri-valent Fe$^{3+}$ species on ceria which helps to generate more active oxygen vacancies by the conversion of Ce$^{4+}$ ions to Ce$^{3+}$ ions [31,32]. As compared to other catalysts with different loading, 0.8 wt. % Fe/CeO$_2$ catalyst revealed smaller particle size with good dispersion and more acidic strength. These parameters were helped for good conversion in catalytic reactions.

Thus, it can be concluded that the use of solid acid materials were very promising as far as both economy and environmental advantages were concerned. They minimize neutralization, disposal costs associated with liquid acids. And also they facilitate easy separation of catalysts and provide new reaction pathways and product selectivity.

Hydrothermally prepared nanocatalysts showed excellent catalytic performance and offers to develop innovative and green chemical process useful for the industry.