CHAPTER 9

SUMMARY AND CONCLUSION

Abstract

Heterogeneous catalysis is one of the most important processes in the petroleum and the chemical industries. Today, almost 70% of all chemicals that are produced have been in contact with a catalyst somewhere in their synthesis process. This number stresses the importance of the role of catalysis in the chemical industry. Without a catalyst, processes are less clean and sometimes impossible to perform. To be able to screen catalysts at high throughput will dramatically improve performance and reduce costs. With this background the main building blocks of the present venture includes preparation, characterization and catalytic activity of supported vanadia catalysts. Rare earth oxides ceria and praseodymia were used as the support material. Silica synthesized from rice husk has been used as a promoter for the support materials in order to enhance the surface and catalytic properties. Catalysts were successfully utilized in industrially important oxidation of aromatics after a detailed investigation of physico-chemical characteristics by various instrumental techniques.
9.1 SUMMARY

Selective oxidation is a very important industrial process that is used to manufacture a variety of chemicals. Vanadium pentoxide catalysts are widely used as the selective catalysts for the oxidation of aromatic hydrocarbons. Various promoters are frequently added to vanadium pentoxide to improve the selectivity and activity to produce the desired products. In search of active catalysts one starts with simple oxides and looks for possible in terms of composition and sample preparation methods. The utilization of silica from an agrowaste rice husk in catalysis is very promising in the era of green chemical world. The development for ecologically friendly technologies is certainly one of the major present goals of research in chemistry. This is especially true in the field of oxidation of organic compounds where there is an urgent need to replace highly effective but wasteful and toxic stoichiometric oxidants with a more preferred technology based on catalytic oxygen transfer using ‘clean’ oxygen donors such as hydrogen peroxide.

Chapter 1 dealt with a brief literature review on catalysis by supported vanadia oxides and rare earth oxides. The role played by vanadia catalyst in chemical transformation processes is described. The attempts for the production of silica from an agrowaste rice husk and its current application are also discussed in detail.

In chapter 2 the importance of heterogeneous catalytic oxidation together with various mechanisms are discussed. It also envisages the redox behaviour of ceria and praseodymia due to its lattice defect structure and the importance of redox catalysis played by vanadia.
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Chapter 3 focused on the building block chemicals of present thesis work and the various instrumental techniques adopted for the characterization of all the catalysts prepared. The preparation methods of catalysts are discussed in detail. The experimental procedures used for the oxidation activity of aromatics along with gas chromatograph analysis conditions are also presented in the same chapter.

Chapter 4 described in detail the results of various characterization methods applied for the surface as well as bulk characterization of supports and supported vanadia catalysts. Surface characterization was done by BET surface area and pore volume analysis, crystal nature by X-ray diffraction and chemical composition from energy dispersive X-ray analysis. Thermal analysis, TGA/DTA was confirmed the thermal stability. Surface morphology was collected on scanning electron microscope. Information regarding the coordination and oxidation state of the vanadia and rare earth metal ions is obtained from UV-vis DRS. Various spectroscopic technique have been applied to discriminate between the surface and bulk structures on the supported oxides. Vibrational absorption by FT-IR helped to confirm the structure assignments together with FT-Raman spectroscopy which was used to identify changes in the structure of dispersed V_2O_5 in dependence on its loading and the nature of the support. EPR measurements investigated the influence of vanadia loading on the coordination geometry of vanadium oxide structures and the electron delocalization of rare earth oxides supported vanadia catalysts under room and liquid nitrogen temperatures. Solid-state nuclear magnetic resonance methods (^{29}\text{Si} and ^{51}\text{V MAS NMR}) illustrated the difference in local environment of a nucleus under study and suited for the
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structural analysis of various Si-O-Si units and surface vanadium oxide phases mainly the existence of CeVO_4 respectively. Redox behaviour of the catalysts was examined by TPR using hydrogen. TPD of ammonia together with cyclohexanol decomposition gave surface acidic properties.

Chapter 5 dealt with the activity of the catalysts tested towards liquid-phase benzene oxidation reaction. The oxidation was conducted under a condition after checking the influence of various reaction parameters such as temperature, catalyst weight, solvent and volumes of substrate, solvent and oxidant in order to get product selectively with high yield. The activity and selectivity of the supported catalysts was correlated to the difference in structural species as observed by characterization techniques.

In chapter 6 the activity of the catalysts tested towards liquid-phase ethylbenzene oxidation reaction is presented. Reaction was conducted in a selected condition after verifying the influence of reaction parameters in detail. The product formation and selectivity could correlate with the difference in structural properties associated with vanadia catalysts supported on various support materials.

Chapter 7 describes the oxidation activity of catalysts for naphthalene as substrate in liquid phase. Influence of reaction parameters like temperature, solvent, catalyst weight and volume of acetonitrile, H_2O_2 and naphthalene were also tested. Catalytic activity was correlated with the structural environment of by various species obtained by characterization techniques.

In chapter 8 the activity of the catalysts in oxidative dehydrogenation of ethylbenzene done was explained. Catalytic activity and selectivity of all the
catalysts were conducted at selected conditions after optimization of reaction conditions in order to get products selectively with high conversion rate.

Chapter 9 illustrates the summary, conclusion and future outlook of the present thesis work.

9.2 CONCLUSION

The major conclusions that can be drawn from the present thesis work are the following:

High surface area amorphous silica with high purity could be prepared from rice husk by an acid leaching process. Application of this silica as promoter of rare earth oxides ceria and praseodymia improved the surface area and dispersion properties.

Supported vanadia prepared with various wt. % of V₂O₅ (2-10) on silica promoted rare earth oxides and rare earth oxides.

Structural and physico-chemical characterization of catalysts were carried out with different techniques like XRD, EDAX, BET SA, TGA/DTG/DTA, SEM as well as spectroscopic techniques such as UV-vis DRS, FT-IR, FT-Raman, EPR, $^{29}$Si and $^{51}$V MAS NMR. Acidity obtained by TPD-NH₃ and vapour phase cyclohexanol decomposition and redox behaviour by TPR-H₂.

Catalytic activity of catalysts was tested towards oxidation of aromatics such as benzene, ethylbenzene and naphthalene in liquid phase with H₂O₂ as oxidant and CH₃CN as solvent. Oxidative dehydrogenation of ethylbenzene tested in vapour phase with air as the oxidant.
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Silica promoted rare earth oxides and vanadia on those supports exhibited relatively high surface area. Chemical composition gave an idea about the atom % of V loaded. XRD pattern results cubic form of ceria and praseodymia.

For low vanadia loading, highly dispersed vanadia species on the support surface obtained. As vanadia loading exceeds monolayer coverage, formation of orthovanadate type structure evidenced for ceria support alone while this phase is highly dispersed over the silica promoted supports owing to its higher surface area and peaks obtained only after high temperature treatment.

In praseodymia containing catalysts, higher loading introduced the formation of pyrovanadate type structure.

Coordinatively unsaturated V-oxides sites and oxygen vacancies are the locations for oxidation of aromatics. High oxidation activity of ceria containing catalysts can be related to the high reducibility and structure of vanadia on the support. Higher dispersion provides the necessary isolation of active sites, which is one fundamental factor in selective oxidation.

Lower oxidative dehydrogenation activity of ceria systems is caused by the progressive formation of ceriumorthovanadate.

The activity behaviour of praseodymia containing catalysts in oxidation reactions is found very different from that of ceria supported vanadia.

Rice husk can pose as a potential alternative for supported catalysts systems since it has high silica content and replace the conventional silica due to its enhanced properties like small particle size and high specific surface area.
FUTURE OUTLOOK

Structural properties and catalytic activity studies of rare earth oxides need more insight. Other transition metal oxides supported rare earth oxides can be studied in the same way. Application of rice husk silica to other metal oxides as a promoter is an interesting and promising approach since it can impart an amorphous nature and high surface area. Since the activity of few oxidations of aromatics were only estimated, further research is needed to obtain the more accurate catalytic route into the mechanism of reaction over the studies on supported vanadia catalysts. The study can be extended to other metal oxides especially to redox centre oxides.