Chapter 11

Summary and Conclusions

Abstract

Nowadays the chemical industries are facing challenges to reduce the use of environmentally hazardous chemicals. Central to this problem, the search for a better methodology for chemical industries has been of great interest to scientists throughout the world. Catalysis is a fascinating field of science because it deals with processes, which may provide solutions for many of the key problems we face. The fundamental aspects giving prime importance to the preparation of titania and their modified analogues by particulate sol-gel route and its physico-chemical characterization are briefly reviewed in this thesis. The great versatility of the prepared catalysts for carrying out some industrially important organic reactions is also included in the thesis. This chapter deals with the summary and the conclusions of the results described in the preceding chapters of the thesis.
11.1 Summary

The present work concentrates on the preparation of the catalyst starting from a comparatively cheaper inorganic precursor like metatitanic acid through sol-gel route. The incorporation of transition metals like chromium, molybdenum and tungsten as well as rare earth metals like lanthanum, praseodymium and samarium is done in small amounts to titania, thus improving the surface characteristics, thermal stability and surface acidity of the composite catalysts and consequently their catalytic performance. It is well known that supported oxides of transition metals and rare earth metals are widely used as catalysts for various reactions. A systematic investigation of the physico-chemical characterization of the prepared catalysts is necessary considering their industrial relevance. The catalytic and photocatalytic properties of titania systems are systematically studied in this work. Thus the thesis gives emphasis to various aspects like catalyst preparation, characterization and their versatile applications in carrying out some industrially important organic transformations. The chapter wise organization of the thesis is as follows.

Chapter 1 gives an overview about solid acid catalysis carried out by titania. The importance of titania based catalysts in current environmental aspects is discussed in detail. The present chapter gives major stress to the various structural aspects of titania as well as different methods for its preparation. A brief literature survey is also included in this chapter.
Chapter 2 is devoted to a complete description of the materials used in the present work and the experimental techniques employed for the catalyst characterization. The flow chart describing the mode of preparation of the catalyst systems are also included in this chapter. The experimental details for the evaluation of catalytic activity are also incorporated in this chapter. The surface acidity determination by different techniques including the test reactions like cumene cracking and cyclohexanol decomposition is the additional features of this chapter.

Chapter 3 focuses on the physico-chemical characterization of the prepared catalytic systems. The catalyst systems were characterized by BET surface area and pore volume measurements, XRD analysis, TG/DTG studies, UV-Vis DRS and FTIR spectroscopy. The elemental composition of the systems were revealed by EDX analysis and the Scanning Electron Micrograms of the representative systems gives an insight into their surface morphology. The results obtained from ammonia TPD and thermodesorption studies using 2,6-dimethyl pyridine as probe molecule is also described in detail. Cumene conversion discriminates the Bronsted as well as Lewis acidity of the prepared systems. Cyclohexanol decomposition reaction is carried out to know the acid base properties of the catalysts prepared.

Chapter 4 discusses the applicability of titania and their modified analogues towards the epoxidation of cyclohexene. The influence of various reaction parameters like reaction temperature, flow rate, nature and amount of the solvent as well as the oxidant is investigated in detail in this section.
Chapter 5 illuminates the application of titania and their modified analogues in the hydroxylation of phenol. Here also, the variation in the catalytic activity and product selectivity with experimental parameters has been taken care of. A possible mechanism has been suggested after a critical analysis of the catalytic performance.

Chapter 6 deals with the catalytic activity of the prepared systems towards the alkylation of aromatics. Tert-butylolation of phenol as well as the methylation of aniline and anisole is carried out efficiently in a vapour phase reactor. Various factors, which influence the percentage conversion as well as the product selectivity, are also considered in detail. Attempt has been made to correlate the catalytic activity with the surface acidic properties of the catalyst systems.

Chapter 7 presents the dehydrogenation of cyclohexane and cyclohexene. The influence of reaction temperature and flow rate is investigated in detail. The dependence of surface acidity of the prepared systems on the percentage conversion is also investigated in detail.

Chapter 8 lays the foundation of photocatalysis. A brief literature review on titania as well as their modified systems are tabulated in this section showing their applications in the vast field of photocatalysis. The applications of titania based systems in today's world of growing environmental concern are also dealt in this chapter.
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Chapter 9 describes the photooxidation of benzhydrol over titania and their modified systems. The influence of various reaction parameters like irradiation time, amount of catalyst, concentration of the reactant and the nature of the solvent has been investigated. The chapter also discusses the mechanistic aspects of this reaction.

Chapter 10 narrates the photodegradation of methyl orange. The dependence of photodegradation of the dye rates on various parameters such as dye concentration, photocatalyst concentration, irradiation time and intensity of radiation were also studied in detail. The percentage degradation of various systems for this reaction is correlated with the band gap energy of the prepared systems.

Chapter 11 presents the summary and important general conclusions of the work done.

11.2 Conclusions

The following conclusions that can be drawn from the present research work are the following.

Particulate sol-gel method is found to be an efficient method for the preparation of high surface area titania systems together with their transition metal and rare earth metal analogues. The high cost of alkoxide precursor widely used in the sol-gel synthesis is avoided in the present preparation route, which adds to its economical importance.
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The enhanced anatase phase stability of the modified systems is an important consequence of metal incorporation. The high dispersion of the incorporated metals on the surface of the titania support is evident from the XRD patterns.

Modified titania systems are capable of improving the physico chemical characteristics and the surface properties of pure titania. The XRD and SEM analysis emphasizes the agreement between the increase in surface area and decrease in the crystallite size.

The high thermal stability of the prepared systems can be understood from the TG-DTG curves. The characteristic peak of pure titania is obtained from the FTIR analysis. UV-Vis DRS helped in the identification of tetrahedrally coordinated titanium ions and calculation of the band gap energy of the prepared systems.

The surface acidic properties of titania supports improve considerably upon incorporation of transition metal as well as rare earth metals. There is a good correlation between the surface acidity measured by ammonia TPD, thermodesorption of 2,6-dimethyl pyridine adsorbed samples and catalytic test reactions such as cumene cracking and cyclohexanol decomposition reaction.

The epoxidation of cyclohexene is carried out efficiently over the prepared systems with the selective formation of cyclohexene epoxide. The excellent activity and selectivity in the epoxidation of cyclohexene is due to highly dispersed Lewis acidic titanium sites. The activity of the prepared catalysts and their stability with time in the epoxidation of
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cyclohexene by tert-butyl hydroperoxide hints that it might be possible to create cleaner nylon chemistry.

The prepared systems are highly active in the hydroxylation of phenol. Selection of an optimum reaction time also demands prime importance in order to achieve maximum activity and selectivity of the products. The performance of the catalytic systems points to its potential in the degradation of phenolic wastes.

Friedel Crafts alkylation of arenes is successfully carried out over the prepared systems and thus introducing green and clean processes replacing the conventional hazardous acid catalysts. Tert-butylation of phenol gives 4-tertiary butyl phenol as the major product, which is catalyzed by medium acid sites. In the methylataion of aniline, the percentage N-methyl selectivity is more than that of C-alkylated product selectivity in all the systems. Good correlation exists between various types of acidity obtained from NH$_3$ TPD as well as percentage product selectivities, which give clear-cut evidence about the reaction mechanism. The vapour phase methylation of anisole over the prepared catalyst systems results in the selective formation of 2,6-xylenol. The acid-base properties of catalysts are responsible for the methylation of anisole.

In the catalytic dehydrogenation of cyclohexane and cyclohexene carried out over the prepared systems, benzene is obtained as the major product. The total surface acidity of the systems plays an important role in determining the catalytic activity.

The photooxidation of benzhydrol is efficiently carried out over the prepared systems resulting in the formation of benzophenone as the sole
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product. The proposed mechanism involves the reaction between a cation radical of benzhydrol formed by the oxidation of the alcohol by a hole and a superoxide radical anion produced by the transfer of a conduction band electron to oxygen.

The photochemical degradation of methyl orange occurs effectively over the prepared catalysts. The large surface area of the photocatalyst is one of the most dominating factors in achieving a high efficiency in the reaction. The percentage degradation of various systems for this reaction is correlated with the band gap energy of the prepared systems.

Future Outlook

Catalysis is a fascinating, interdisciplinary and future oriented area. Indeed the chemistry of catalysis is as varied as chemistry itself. With its versatility and excellent control over products characteristics, sol-gel processing has played an important role in catalyst preparation and no doubt will continue to do so. The use of metatitanic acid as the precursor in the preparation of high surface area titania catalysts receives special attention. From the viewpoint of green chemistry, the use of heterogeneous catalysts like modified titania is desirable. The present investigation on the catalytic activity of modified titania catalysts reveal their high efficiency for various types of reaction like epoxidation of cyclohexene as well as hydroxylation of phenol. The work can be extended in the epoxidation of other cycloolefins and the products of which are of independent significance and/or are valuable chemicals for synthesis of biologically active species. The application of the prepared catalysts makes the wet air oxidation process more attractive by
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achieving high conversion at considerably lower temperature and pressure. The higher activity and selectivity in the alkylation of aromatics carried out over the prepared systems is another important observation we got. Since the prepared catalysts are highly acidic, studies can be extended for various industrially important acid catalyzed alkylation and rearrangements of other aromatic molecules.

Good photocatalytic activity is shown by titania systems towards the photo degradation of methyl orange and photooxidation of benzhydrol. Being a photocatalyst, the work can be extended in this vast ever growing field too. The photocatalytic activity of the prepared systems can be utilized to establish an effective method for the remediation of volatile organic compounds from indoor air, which poses a significant health risk. Titania based catalysts can also be applied in the degradation of various types of dye stuffs which represent an increasing environmental problem. Their effective removal is a challenging task as environmental laws and regulations are becoming more and more stringent. The areas of application of photocatalysis to water purification and treatment of water, area selective reactions, polymer degradation and selective organic synthesis will probably gain priority as they appear to possess the potential to alter environmental and electronic scenarios.