BIFUNCTIONAL OXIDATIVE AND ACIDIC TITANIUM SILICALITE (TS-1) CATALYSTS FOR ONE POT SYNTHESIS OF 1,2-OCTANEDIOL FROM 1-OCTENE

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BIFUNCTIONAL OXIDATIVE AND ACIDIC TITANIUM SILICALITE (TS-1) CATALYSTS FOR ONE POT SYNTHESIS OF 1,2-OCTANEDIOL FROM 1-OCTENE

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A thesis submitted in fulfilment of the requirements for the award of the degree of Doctor of Philosophy

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Specially dedicated to:

My mom, dad, wife and daughters
ACKNOWLEDGEMENT

Bismillaahirrahmaanirrohiim
In the name of Allah, the most Gracious, the most Merciful

Alhamdulillaahirrabbi ‘alamin, Allaahumma sholli ala Muhammad wa ‘ala alihi wa shohbihi wa sallam. All praise must be to Allah, The supreme Lord of the world. Peace and blessing to Rasulullaah Muhammad Shollallahu ‘Alaihi Wasallam, all the prophets, his families, his close friends and all Muslims.

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ABSTRACT

New bifunctional catalysts containing both oxidative and Brønsted acidic sites have been prepared and used for the consecutive transformation of alkenes to the corresponding diols via the formation of epoxides with aqueous hydrogen peroxide as oxidant. The catalytic system was designed in order such that two kinds of active sites would allow for the epoxidation of alkenes to take place within the pore channels of titanium-containing molecular sieve while acid catalysis of the epoxides to diols occurs on the external surface of the catalyst. Based on this design, titanium silicalite (TS-1), an excellent and commercial oxidation catalyst known so far, has been chosen. The TS-1 was then modified with different acidic oxide precursors. Synthesis of the series of bifunctional catalysts was achieved by deposition of various loadings of acidic oxide precursors up to 25 wt% onto TS-1 powder. The Ti$^{4+}$ and acidic oxides in the TS-1 molecular sieve served as oxidative and acidic sites, respectively. The thus obtained bifunctional catalysts were sulfated TS-1 (SO$_4^{2-}$/TS-1), sulfated titanium oxide supported on TS-1 (SO$_4^{2-}$-Ti/TS-1), tungsten oxide supported on TS-1 (WO$_3$/TS-1), sulfated zirconia supported on TS-1 (SZ/TS-1), and niobium oxide supported on TS-1 (Nb/TS-1). The X-ray diffraction analysis revealed that TS-1 still retained the MFI structure after incorporation of the acidic oxides even when the crystallinity is lower. The infrared (IR) and ultra-violet diffuse reflectance (UV-Vis DR) spectra showed that the titanium in TS-1 was mainly in tetrahedral coordination after incorporation of acidic oxides. Results of pyridine adsorption followed by IR spectroscopy showed the presence of Brønsted acid sites in WO$_3$/TS-1, Nb/TS-1 and highly loaded SZ/TS-1 but not sulfated samples of TS-1 (SO$_4^{2-}$/TS-1 and SO$_4^{2-}$-Ti/TS-1). In the consecutive transformation of 1-octene to 1,2-octanediol through the formation of 1,2-epoxyoctane, all the catalysts showed a significant increase in the rate of formation of 1,2-epoxyoctane with respect to TS-1. The presence of acidic oxides in TS-1 was proposed to explain the increased hydrophilic character of the catalysts, which is responsible for the higher rate of formation of reactive oxo-titanium species. Moreover, the acid sites were shown to effectively catalyze the formation of 1,2-octanediol with the 10 wt% niobium oxide supported on TS-1 giving the highest yield. Comparison of the catalytic performance of the prepared bifunctional catalysts with that of the mechanical mixture comprising of TS-1 and H-ZSM-5 (Brønsted acid), showed that the bifunctional catalysts were more active; suggesting that specific location of the two active sites plays an important role in the consecutive transformation of alkenes to epoxides and then diols. The higher activity of the bifunctional catalysts was supposedly due to the location of the acidic sites in the immediate vicinity of the oxidative sites which enabled the epoxidation products to undergo hydrolysis rapidly at the Brønsted acid sites that were located on the external surface of TS-1.
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8.1 The yield of 1,2-octanediol over prepared catalysts

8.2 The ratio of the yield of 1,2-octanediol to the amount of Ti⁴⁺ in the prepared catalysts

8.3 Correlation of the selectivity of 1,2-octanediol and the amount of Brønsted acid sites in the prepared catalysts
LIST OF SYMBOL / ABRREVIATIONS

FTIR - Fourier Transform Infrared
GC - gas chromatography
GC-MSD - gas chromatography mass spectrometry detector
h - hour
NBA - niobium oxide hydrated or niobic acid
NBO - niobium oxide
SIL - silicalite
SZ - sulfated zirconia
TEOS - tetraethylorthosilicate
TEOT - tetraethylorthotitanate
TPAOH - tetrapropylammonium hydroxide
TPD-Ammonia - Temperature Programmed Desorption of Ammonia
TPR - Temperature Programmed Reduction
TS-1 - titanium silicalite - 1
UV-Vis DR - Ultra Violet - Visible Diffuse Reflectance
wt% - weight %
XRD - X-ray Diffraction
LIST OF PUBLICATIONS

International Journals:


Conference and National Publications:


CHAPTER 1

INTRODUCTION

Catalysis is an important process to improve the production of chemicals. This phenomenon can be employed in a chemical reaction that is favored thermodynamically but is very slow without the use of a catalyst. The catalyst accelerates the kinetics of the reaction to attain equilibrium without being consumed in the process. It plays an essential role in the manufacture of a wide range of products, from gasoline and plastics to fertilizers and herbicides, which would be unobtainable or expensive.

There are homogeneous and heterogeneous systems in the catalytic processes. In general, heterogeneous systems offer easier separation of catalysts from the product mixture, reusability of the catalysts and the possibility of continuous processing. On the other hand, homogeneous catalysis usually allows more efficient heat transfer and milder operating condition, as well as higher selectivity. Heterogeneous catalysts are being increasingly studied for liquid and gas phase catalysis.

1.1 Background of Study

A large segment of the modern chemical industry is based on selective catalytic oxidation processes (Centi et al., 2001). More than 60% of the chemicals and intermediates synthesized via catalytic processes are the products of oxidation.
Most of the oxidation processes are being carried out in the gas and liquid phases. Catalytic oxidation in the liquid phase is widely used in bulk chemicals manufacture and are becoming increasingly important in the synthesis of fine chemicals (Sheldon and Dakka, 1994). Catalytic oxidations in the liquid phase generally employ soluble metal salts or complexes as catalysts, oxidants such as O\textsubscript{2}, H\textsubscript{2}O\textsubscript{2}, organics hydroperoxide, and solvents (Centi et al., 2001).

An early example of the successful application of the site-isolation concept in liquid phase oxidation catalysis is the Ti(IV)/SiO\textsubscript{2} catalyst, commercialized by Shell in the 1970s for the production of propene oxide (Sheldon, 1980). Another benchmark was the development of titanium silicalite (TS-1) by Enichem scientists in the mid-eighties (Taramasso et al., 1983). Over the last decade, TS-1 has shown excellent catalytic activity in organic oxidation reactions using hydrogen peroxide as oxidant under mild conditions. In alkenes epoxidation, many works have been done to enhance the epoxide selectivity due to the industrial importance of epoxides in the synthesis of organic and pharmaceutical materials. The ability of TS-1 to catalyze a wide variety of oxidation transformations including alkenes epoxidation with 30% aqueous hydrogen peroxide has led to extensive research worldwide on the synthesis of related heterogeneous catalysts for liquid-phase oxidation (Perego et al., 2001).

Beside the oxidative catalysts, the acid catalysts also play important role in the area of catalysis. There are a number of reactions catalyzed by acid catalysts, i.e. esterification, oligomerization, alkylation, acylation, isomerization, cracking, hydrolysis, and other reactions in the synthesis of intermediates or specialty fine chemicals. Researchers have tried to substitute homogeneous catalysts (HCl, HF, H\textsubscript{2}SO\textsubscript{4} and AlCl\textsubscript{3}) by heterogeneous solid acid catalysts. The advantages of using heterogeneous acid catalysts is to overcome the problems encountered by homogeneous catalysts, i.e. corrosive, toxic, difficulties in the storage and handling, and environment problem for disposal. The heterogeneous acid catalysts include alumina, zeolites, solid phosphoric acid, cationic ion exchange resin and metal oxides. Some examples of recent successfully commercialized new solid acid catalysts have been reviewed (Mitsutani, 2002).
The two types of catalysts mentioned above are just for oxidative or acidic catalyzed reactions. It means that for a certain type of reaction, certain type of catalysts should be used. Unfortunately, two or three steps of catalytic processes are needed in the production of fine chemicals. Consequently, two reactors with different catalysts and processes should be built and run successively when the product is catalyzed by two catalysts. To overcome such problem, research has been carried out in the design of a new concept in the material catalyst, called bifunctional or multifunctional catalysts, in which two or more active sites are present in one solid material. By using this concept, the whole process is more practical and economical than the two-step processes (Hoelderich, 2000).

One of the crucial points for the development of catalysts is to design the active sites for catalytic processes. The efficiency of a catalytic process in general greatly depends on the performance of the catalyst, rendering the development of efficient catalytic materials one of the foremost challenges in catalysis research. In many of catalytic processes a stream of reactant is passed over tiny particles (atomic or cluster) of active sites on an oxide support surface. One of the challenges is to design highly-functionalized catalysts by a combination of oxidative and acidic active sites for consecutive oxidation and acid catalytic reactions. As shown by the model reaction in Figure 1.1, Ti site acts as oxidative site for oxidation of 1-octene to 1,2-epoxyoctane (as intermediate) and niobic acid acts as acidic site for transformation of 1,2-epoxyoctane to 1,2-octanediol.

Several bifunctional oxidative and acid catalysts have been prepared by incorporation of trivalent metal ions (Al$^{3+}$, B$^{3+}$, Fe$^{3+}$, Ga$^{3+}$) and titanium ion (Ti$^{4+}$) together in the framework of silica based molecular-sieves (Trong On et al., 2003; van der Wall et al., 1998; Krijnen et al., 1999). The catalysts being active both in the oxidation reactions due to the presence of tetrahedral Ti$^{4+}$ and in acid catalyzed reactions as the substitution of the trivalent cations in the framework of silica generates acid sites. In a previous study, some research groups (van der Wall et al., 1998; Davies et al., 2001; Sashidaran et al., 2002) have demonstrated that Ti-Al-beta and Ti-beta zeolites can lead to acid-catalyzed consecutive reaction. The catalysts were active in epoxidation of alcohol or bulky alkenes and selective in diol formation.
Diols products are useful intermediates in the production of pharmaceutical, pesticide, fragrance and other fine chemicals. Diols contribute to high water solubility, hygroscopicity and reactivity with many organic compounds, on usually linear and aliphatic carbon chain. 1,2-octanediol, linear diol containing two primary hydroxyl groups, has bacteriostatic and bactericidal properties which are useful in cosmetics and skin care products as a preservative, an emollient, humectants and wetting agent (Brown et al., 2003; Milbradt et al., 2005). It is also used as an ingredient in inks (Kelly-Rowley and Chatterjee, 2004).

Special 1,2-diols, e.g., ethylene glycol and propylene glycol, are manufactured on a million ton scale per annum. Worldwide production capacities for ethylene glycol in 1995: 9.7 Million ton per annum, while worldwide production of 1,2-propylene glycol in 1994: 1.1 Million ton per annum (Weissermel and Arpe, 2003). A number of 1,2-diols such as 2,3-dimethyl-2,3-butanediol, 1,2-octanediol, 1,2-hexanediol, 1,2- pentanediol, and 1,2- and 2,3-butanediol are interesting for fine chemical applications. At present they are produced in industry by a two-step sequence consisting of epoxidation of the terminal olefin with a peracid followed by hydrolysis of the resulting epoxide (Szmant, 1989; Pohl and Gaube, 1985). In addition, chiral 1,2-diols are of interest as intermediates for pharmaceuticals and agrochemicals (Kolb et al., 1994; Beller et al., 2004).

1.2 Design of Bifunctional Oxidative and Acidic Catalyst

The product selectivity of consecutive oxidation and acid catalytic reactions depends on the nature of the oxidative and acid sites which are located in the structure of zeolite. However, it is difficult to control the number of oxidative sites together with acidic sites in the framework of zeolites. Controlling the number and the location of the active sites is important since it relates to the product selectivity. We have designed an alternative way to prepare bifunctional catalyst containing certain amount of active sites as shown in Figure 1.1.
Figure 1.1: Oxidative and acidic catalyst for consecutive oxidation and acid catalytic reactions.

The use of TS-1 as a model catalytic system is an advantage because it is known as a good heterogeneous oxidation catalyst in alkene epoxidation with aqueous hydrogen peroxide as an oxidant. Our proposal is based on the idea that the epoxidation of alkene occurs in the pores of TS-1 and acid catalysis of 1,2-epoxyoctane to 1,2-octanediol takes place on the external surface of TS-1. The location of oxidative and acid sites on the internal and external surfaces of TS-1, respectively, has a beneficial effect in the consecutive oxidation and acid catalytic reactions of 1-octene to 1,2-octanediol (see Figure 1.1) since oxidation and acid reactions preferentially occur in hydrophobic and hydrophilic environments, respectively. It has been reported that the framework of TS-1 has hydrophobic properties (Drago et al., 1998). In order to maintain the hydrophobicity of the TS-1, the acid sites is placed on the external surface of TS-1 which is covered by acidic oxides.
1.3 Objectives of the Study

The objectives of the study are:
1. To prepare and characterize the bifunctional oxidative and acidic catalysts consisting of TS-1 and selected acidic oxides as oxidative and acid sites, respectively.
2. To evaluate the performance of the materials as bifunctional oxidative and acidic catalysts in the one pot synthesis of 1,2-octanediol from 1-octene as a model reaction.
3. To relate the catalytic performance and physicochemical properties of the bifunctional oxidative and acidic catalysts.

1.4 Scope of the Study

Model catalysts with well-defined structural and physicochemical properties serve for elucidating structure-activity relationships (Figure 1.2). The scope of the study is focused on the following aspects i.e. synthesis of titanium silicalite (TS-1) molecular-sieves, preparation of bifunctional oxidative and acidic catalysts, and catalytic testing.

Chapter 3 of this thesis describes the synthesis, characterization and catalytic testing of TS-1. The medium pore microporous material i.e. silicalite and TS-1 were synthesized by hydrothermal method. TS-1 was prepared with various amounts of titanium concentration i.e. 1-4 mol%. Characterizations of the obtained solids were carried out by several techniques, such as X-ray diffraction, infrared and UV-visible diffuse reflectance spectroscopy, temperature programmed desorption and pyridine adsorption followed by infrared spectroscopy.

The bifunctional oxidative and acid catalysts containing certain amount of active sites were prepared by impregnation of sulfated titania, tungsten oxide, sulfated zirconia and hydrated niobium oxide as the acidic precursors on the surface of oxidative TS-1. The structure and physicochemical properties of catalysts were
examined by X-ray diffraction, infrared and UV-visible diffuse reflectance spectroscopy, temperature programmed reduction, and pyridine adsorption. The catalytic performance and structure-activity relationship of bifunctional catalysts were carried out in the consecutive reaction of 1-octene to 1,2-octanediol through the formation of 1,2-epoxyoctane. These studies are reported in four chapters (Chapters 4 to 7).

**Figure 1.2:** Methodology of research.
REFERENCES


