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Research Article

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Esterification of acetic acid with ethylene glycol over environmentally benign mixed oxide solid acid catalysts

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ABSTRACT

Catalysis of several mixed oxide solid acid catalysts for esterification of acetic acid with ethylene glycol has been described. In esterification reaction influence of catalyst amount, reaction time and promoter used in preparation of supported catalysts has been studied. All the supported catalysts were prepared using wet impregnation technique. The X-ray diffraction profiles of zirconia based samples exhibited presence of tetragonal ZrO_2 *phase. It was testified that the* Mo/ZrO_2 *catalyst was effective catalyst for esterification of acetic acid with ethylene glycol. Higher activity of* Mo/ZrO_2 *is attributed to presence of greater amount of tetragonal phase of* ZrO_2*and higher surface acidity.*

Key words: Zirconium dioxide; tetragonal phase; esterification; solid acid.

INTRODUCTION

Environmental protection is global concern. The green chemistry is invention, design and application of chemical products and process to reduce or eliminate the use and generation hazardous substances. The laws governing the emission and their control have become stringent. Economic considerations and environmental evaluations have pushed the chemical industry to adopt new ecofriendly cleaner technologies with minimum disposal [1]. Catalysis in environmental application is attaining greater importance nowadays. Recent developments in heterogeneous catalysis meet the objectives of refining and chemical processes targeted at creating better environment tomorrow. The development of new organic catalytic procedures and catalysts is one of the major goals in the contemporary catalysis research [2].

Esters are useful as solvents, artificial flavors, plasticizers, essences and are perfumery industry. Traditionally esters are prepared using H_2SO_4 as catalyst [3]. The use of H_2SO_4 often causes problems such as corrosion and pollution for environment by producing large amounts of byproducts. In view of environmental concern, there is global effort to replace conventional catalysts by solid acids which are easily separable from products, less toxic and reusable. Esterification is carried out under batch and flow conditions over cerium ammonium nitrate [4], iodine [5], niobium(V)oxide [6], molecular sieves using higher alcohols [7], ionic liquids [8] and heteropolyacids [9]. Promoted metal oxide catalysts offer several advantages over the above catalysts. They are active over wide range of temperatures and more resistant to thermal excursions.

The chemical and physical properties of zirconia based catalysts make them very attractive catalytic materials that may compete with other ones in industry like zeotypes, clays and oxides. This presents clean efficient method to prepare solid catalysts selective and active for the transformation of organic compounds. Innovative aspects are the development of new acid catalysts is within the frame work of the discovery of new solid acid catalyst to improve the yield and selectivity towards the target product. The synthetic method is easy providing zirconia with different degree of acidity depending on reaction requirement, which makes it potential catalyst for industry devoted to organic transformation. Zirconia based solid acid catalysts for catalyzing several reactions is described by Arata and Hino et al [10]. Among solid super acid catalysts reported, sulfated zirconia received much attention due to its high activity to catalyze many reactions at low temperature [11]. It is known that mixed oxides often show enhanced acidity and thermal stability than their constituent single oxides. Therefore we undertook investigations to prepare solid acid catalysts of Nb, Mo or W oxide doped zirconia and comparing the activity of these catalysts with some other mixed oxide catalysts for esterification of ethylene glycol with acetic acid.

EXPERIMENTAL SECTION

2.1. Catalyst preparation

Zirconia based solid acid catalysts were synthesized by precipitation and impregnation method using zirconia source. In the first step zirconium hydroxide was prepared by hydrolyzing salt $ZrOCl_2.8H_2O$ with aqueous ammonia solution. In preparation of zirconium hydroxide about 5 gm of $ZrOCl_2.8H_2O$ (Loba chemie, GR grade) was dissolved in 40 ml of doubly distilled water. The p^H of the solution was 2. Dilute ammonia solution was added slowly until the p^H of the solution reached 7 with continuous stirring. The obtained precipitate was washed with distilled water several times until free from chloride ions and dried at 393K for 48 hrs. The oven dried sample was calcined at 873K in flow of oxygen to obtain ZrO_2. In the second step impregnation of the molybdate, tungstate and niobium promoter was carried out by dissolving requisite quantities of corresponding metal precursors in doubly distilled water to which $Zr(OH)_2$ is added and the excess water is evaporated. The obtained samples were oven dried at 393K for 48 hrs and finally calcined at 873K for 5h in flow of oxygen.

The titania-zirconia (1:1 ratio) mixed oxide was prepared by a homogeneous co precipitation method. In a typical experiment the required quantities of titanium tetrachloride and zirconium oxychloride were dissolved separately in deionized water and mixed together (pH = 2). The resulting solution was neutralized by adding dilute NH_4OHdropwise from a burette up to p^H 8. The obtained precipitate was washed several times with water until free from chloride ions, dried at 393K for 16 hrs and calcined at 1023K for 6h in air.

TiO_2 is prepared using titanium tetrachloride as the precursor as described above. The desired quantity of niobium oxide precursor was dissolved in excess water and to which the powdered hydrous titanium oxide was added. The excess water was evaporated on water bath with vigorous stirring. The obtained sample was oven dried at 383K for 12h and calcined at 1023K for 6h in air.

Commercial montimorillonite clay is used.

2.2. Catalyst characterization

A conventional all glass volumetric high vacuum system was used for BET surface area measurements. The BET surface areas were measured by nitrogen physisorption at liquid nitrogen temperature by taking 0.162 nm^2 as the area of cross section of N_2 molecule. The phase composition of the samples was determined by X-ray diffraction method. X-ray powder diffractograms were recorded on a Philips pw-1051diffractometer by using Ni-filtered CuK_α radiation.

2.3. General procedure for esterification

A mixture of acid (1g), alcohol (excess) and catalyst (0.1g) was heated at 358K for 6h in round bottom flask provided with condenser. After completion of the reaction conversion and selectivity are determined quantitatively by using gas chromatography with 10% OV-17 column and FID detector and qualitatively by NMR. After completion of the reaction catalyst was filtered, $NaHCO_3$ solution was added to the filtrate and extracted with ether. The organic layer was dried with (anhydrous) Na_2SO_4 concentrated and chromatographed on SiO_2.

RESULTS AND DISCUSSION

The XRD patterns of zirconia and promoted zirconia exhibit presence of tetragonal phase of zirconia which is active in catalyzing several organic reactions [12-15]. It is well-known from the literature that incorporation of promoter in zirconia lattice and calcination at 923^oK and above stabilizes the tetragonal phase of zirconia. Incorporation of Mo in to zirconia lattice has strong influence on transformation of monoclinic phase to tetragonal phase upon calcination compared to W and Nb incorporation. All the promoted catalysts exhibit higher surface area than that of ZrO_2. This can be attributed to formation of Mo-O-Zr linkage resulting in formation of porous material [14].

Acidity of promoted ZrO_2 catalyst is owing to an electron deficient state formed by the introduction of promoter cations Mo, W and Nb into ZrO_2 lattice. This is further supported by IR spectra of the above catalysts where pure ZrO_2 shows the presence of Lewis acidic sites and incorporation of promoter into zirconia lattice creates Bronsted acidic sites. The lattice defects caused by the incorporation of promoter in the Zr^{+4}sites appear to enhance the number and strength of the Lewis acidic sites of the catalyst. The ammonia-TPD results revealed that there are two types of different acid sites on all the investigated samples. The total amount of ammonia desorbed in the case of Mo-promoted samples was observed to be higher than that of W-promoted sample. It appears from ammonia-TPD results that molybdate promoters exhibit a strong influence on the surface acidity of zirconia [15].

The result of esterification of acetic acid with ethylene glycol over solid acid catalysts is given in Table 1. Among the catalysts studied, Mo/ ZrO_2 showed highest conversion and selectivity to glycol acetate. The conversion was low for other catalysts understudy showing the influence of acidity. The conversion was found to decrease from 63% to 17.9% for other catalysts attributed to influence of acidity of the catalysts on esterification of acetic acid.

Table 1Surface area, acidity of various catalysts and yield of glycol acetate

catalyst	Conversion% of acetic acid	Selectivity% of glycol acetate	Yield 0f glycol acetate	Surface area (m^2g^{-1})
Zro_2	21	100	21	42
9%Nb/ Zro_2	19.9	100	19.9	32
9%W/ Zro_2	22.9	100	22.9	35
9%Mo/ Zro_2	63	100	63	94
9%Nb/ Tio_2	30.8	100	30.8	51
Tio_2..Zro_2	17.7	100	17.7	161
Na-Montmorillonite	18	100	18	-

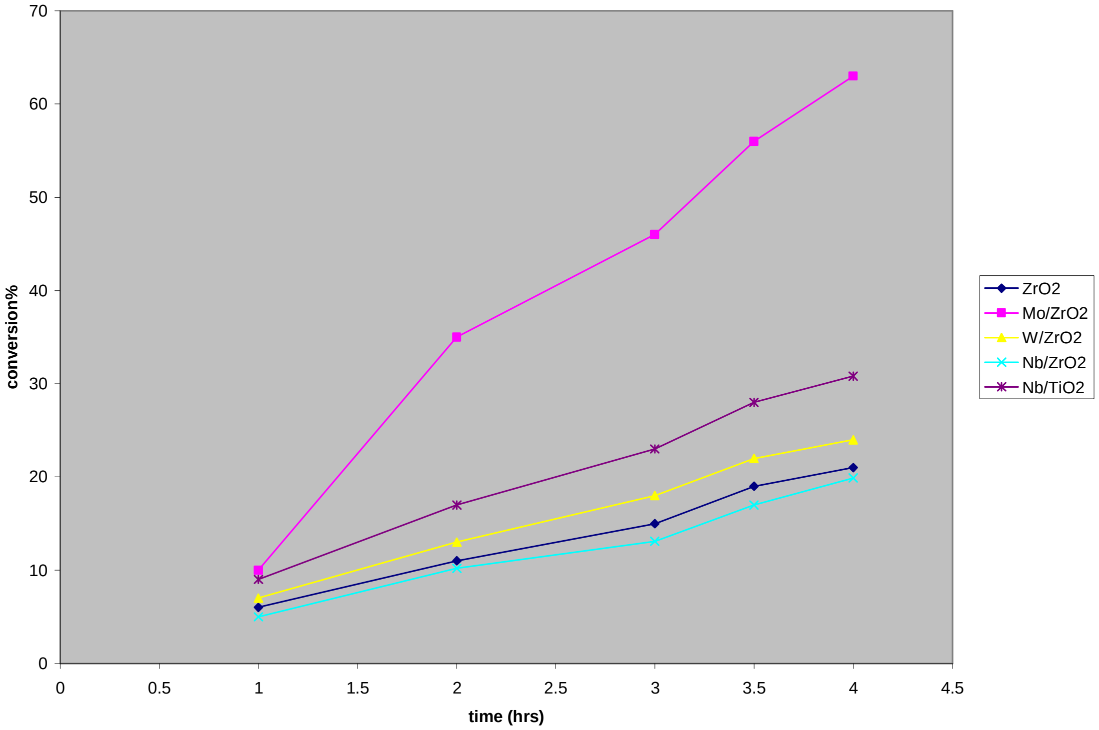

Figure 1. conversion v/s reaction time plot for esterification of acetic acid with ethylene glycol over zirconia based catalysts.

Incorporation of Mo promoter into zirconia lattice increases the Lewis acidic sites and strength of the Lewis acid sites in addition to this creates Bronsted acidic sites. Incorporation of W and Nb of same amount into zirconia lattice and calcination at the same temperature is carried out for comparison. Under similar conditions for these catalysts formation of tetragonal phase is low, surface area of the catalyst is decreasing and surface acidity also decreasing. This can be attributed to decrease in conversion of acetic acid from Mo/ ZrO_2 to Nb/ ZrO_2. For comparison sake 9% Nb/ TiO_2 is also used. Esterification over this catalyst is found to be higher than on 9% Nb/ ZrO_2 this might be due to increase in surface acidity as Nb is incorporated in to TiO_2 which creates defects.

The effect of catalyst in synthesis of glycol acetate has been studied by esterification over all catalysts by taking 0.05 and 0.1 g of each of the catalysts and refluxing up to 4 h. It has been observed that there is marginal increase in the yield of glycol acetate by increasing the amount of catalyst by two fold. In figure 1 conversion of acetic acid with respect to time is given for esterification reaction over several promoted zirconia catalysts is given. It is observed that with the increase in time there is increase in conversion of acetic acid and reaches maximum value after 4 h for all catalysts. Catalyst separated from reaction mixture and dried in oven for several hours. The catalyst was reused for several times and it was found that there is no loss in activity.

CONCLUSION

The following conclusions can be drawn from the study

- The zirconia sample calcined at 873 ^{0}K consists of mixture of monoclinic ZrO_2 phase and tetragonal phase.
- Incorporation of promoter showed significant influence on the physico chemical properties of zirconia. Incorporation of promoter transforms almost completely monoclinic phase of ZrO_2 in to tetragonal phase.

Surface area of Mo promoted ZrO_2 catalyst is higher than pure ZrO_2 and for Nb, W promoted ZrO_2 catalyst surface area is less than pure ZrO_2 catalyst.

Mo/ ZrO_2 is found to be active and selective in the formation of glycol acetate

Incorporation of any promoter leads to formation of tetragonal phase but higher activity is observed for Mo promoted catalyst this may be probably due to higher acidity of this catalyst. Further studies are essential to determine the exact nature of acidic sites present on these oxides. Although much about generation of active sites and role of redox properties of the promoter incorporated in to ZrO_2 is unresolved, the catalytic activity is reasonably good.

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REFERENCES

[1]. Chemistry of waste minimization, ed. J.H.Clark,Chapman and Hall, London, **1995**.
[2]. James H. Clark and Duncan J. Macquarrie, Chemical society reviews. **1996**, 303.
[3]. Vogels, “Text Book of Practical Organic Chemistry,” Longman Group Ltd., England, 4th edition, ELBS, **1987**, pp. 501-515.
[4]. Wen-Bin Pan, Fong-Rang Chang, Li-Mei Wei, Ming-Jung Wu and Yang-Chang Wu, Tet. Lett, **2003**, 44, 331.
[5]. K. Ramaling, K. Vijaya Lakshmi and T. N. B. Kaimal, *Tet. Lett*, **2002**, 43, 879.
[6]. Mirela Ines de Sairre, Erika Soares Bronze-Uhre and Paulo Marcos Donate, *Tet. Lett*, **2005**, 46, 2705.
[7]. L. I. Koval, V. I. Dzyuba, O. C. llnitska and V. I. Pekhnyo, *Tet. Lett*, **2009**, 49, 1645.
[8]. Dong Ziang, Yuan Yuan Wang, Ming Tu and Li Yi Dai, *Chinese. Chem. Lett*, **2008**, 19, 889.
[9]. G.Bishwa Bidita Varadwaj and K. M. Parida, *Catal. Lett*, **2011**, 141, 1476.
[10]. M. Hino, S. Kobayashi and K. Arata, *J. Am. Chem. Soc*, **1979**, 101, 6434.
[11]. Benjaram M. Reddy and Meghashyam K. Patil, *Chem. Rev*, **2009**, 109, 2185.
[12]. T. Yamagachi, *Catal. Today*, **1994**, 20, 199.
[13]. Basude Manohar, Sunkara Prasad, Sheelam Rajkumar and Paka Lingaiah, *J. Chem. Pharm. Res*, **2012**, 4(2), 1136.
[14]. B. M. Reddy, B. Choudary and P. G. Sruirniotis, *Appl. Catal.* A, **2009**, 211, 18.

[15]. Benjaram M Reddy, Pavani M Sreekanth and Vangala R Reddy, *J. Mol. Catal* A, **2005**, 225, 71.