Esterification of 1° and 2° alcohol using an ecofriendly solid acid catalyst comprising 12-tungstosilicic acid and hydrous zirconia

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Abstract

A series of ecofriendly solid acid catalyst was synthesized by supporting 12-tungstosilicicacid onto hydrous zirconia using impregnation method in order to contribute towards clean technology which is the most important need of the society. The support and resulting catalysts were characterized by various spectral, thermal, and physicochemical techniques. The techniques used were chemical stability, ion exchange capacity, DSC, FT-IR, electronic spectra, XRD, particle size distribution and surface area measurement (BET method). Further, the surface morphology was studied by scanning electron microscopy. The above studies indicate that the keggin structure does not get destructed after supporting. Their catalytic properties were evaluated for the esterification reaction. Esterification of 1° alcohols (*n*-butanol, iso-butanol) and 2° alcohols (2-butanol, cyclohexanol) was carried out by varying different parameters such as different amount of the catalysts, different mole ratio of acid to alcohol using the synthesized catalysts. It was found that using the present catalysts, very high activity in all esters synthesis can be obtained.
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Keywords: Hydrous zirconia; 12-Tungstosilicicacid; Solid acid catalyst; Esterification; Clean technology

1. Introduction

Among acid catalysed reactions, esterification is an important organic reaction and usually carried out by use of various conventional mineral acids such as H_2SO_4, HF, H_3PO_4, HCl, etc. The replacement of these conventional hazardous and polluting corrosive liquid acid catalysts by solid acid catalyst is one of the demands of the society. This could be possible by making use of environment friendly catalysts involving the use of solid acids. Reduction of environmentally unacceptable waste, reduction of pollution and use of catalyst as a user-friendly catalysts are the crucial factor for developing environmental friendly catalyst.

Heteropolyacids (HPAs) are typical strong Bronsted acids and catalyze a wide variety of reactions in homogeneous phase offering strong option for efficient and cleaner processing [1–5]. The major disadvantages of HPAs, as catalyst lies in their low thermal stability, low surface area ($1–10\,m^2/g$) and separation problem from reaction mixture. HPAs can be made ecofriendly insoluble solid acid with high thermal stability and high surface area by supporting them onto suitable supports. The support provides an opportunity to HPAs to be dispersed over a large surface area, which increases catalytic activity.

Various supports like silica [1–6] titania [3,6], alumina [3] active carbon [6–11], MCM-41 [12–17], acidic ion exchange resins [18], clay [19–22] have been used for supporting HPAs.

The literature survey shows that hydrous oxides have multiphase applications. Among metal oxides, especially hydrous zirconia has drawn great attention. One of the main reason that has drown great attention to the use of hydrated zirconia as a precursor of a catalyst carrier is the fact that its surface hydroxyl groups are able to undergo a chemical reaction or strong interaction with incorporated components.

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A detail study has been carried out on 12-tungstophosphoric acid supported on to different support [23–25] by us. From viewpoint of thermal stability [26–28], as well as acidic strength [26,27,29], 12-tungstophosphoric acid is the most stable HPA in keggin series. Therefore, it was thought of interest to study on 12-tungstosilicic acid, next stable HPA in the keggin series.

The present contributions consist of synthesis of amorphous new solid acid catalysts comprising 12-tungstosilicicacid (SW) and hydrous zirconia (Z). A series of catalysts containing 20–70% SW were synthesised. The support and new amorphous catalysts have been characterized by chemical analysis, chemical stability, ion exchange capacity, DSC, FT-IR, DRS, XRD, particle size distribution and surface area measurement (BET method). The surface morphology was studied by scanning electron microscopy (SEM). Their catalytic properties were evaluated for the esterification of 1° alcohol (*n*-butanol, iso-butanol) and 2° alcohol (2-butanol, cyclohexanol). Further, the selected material was calciained at 300° C and 400 °C. The study on FT-IR and DRS was carried out in order to see any decomposition of HPA species.

2. Experimental

2.1. Materials

All chemicals used were of A.R. grade. $H_4SiW_{12}O_{40} \cdot nH_2O$ (Lobachemie, Mumbai), $ZrOCl_2 \cdot 8H_2O$ (SD Fine chemicals, Mumbai) were used as received. *n*-Butanol, isobutanol, 2-butanol, cyclohexanol, glacial acetic acid, formic acid and propionic acid were obtained from Merck and used as received.

2.2. Synthesis of the catalyst

2.2.1. Synthesis of the support, hydrous zirconia (Z)

Hydrous zirconia was prepared by adding an aqueous ammonia solution to an aqueous solution of $ZrOCl_2 \cdot 8H_2O$ up to pH 8.5. The resulted precipitates were aged at 100 °C over a water bath for 1 h, filtered, washed with conductivity water until chloride free water was obtained and dried at 100 °C for 10 h. The obtained material is designated as Z.

2.2.2. Supporting of 12-tungstosilicicacid onto hydrous zirconia

12-tungstosilicicacid was supported on hydrous zirconia by impregnation method. One gram of Z was impregnated with an aqueous solution of $H_4SiW_{12}O_{40}$ (S) (0.2 g/20 ml of conductivity water). The water from the suspension was allowed to evaporate at 100 °C in an oven. Then the resulting mixture was dried at 100 °C with stirring for 10 h. Material thus obtained was designated as ZS_2. Same process was followed for the synthesis of a series of supported heteropolyacids containing 30–70% tungstosilicicacid (0.3–0.7 gm/30–70 ml of conductivity water). The obtained materials were designated as ZS_3, ZS_4, ZS_5 and ZS_7. Further calcination of ZS_3 was carried out at 300 °C and 400 °C in air for 5 h and the resulting samples were designed as ZS_{33} and ZS_{34}, respectively.

2.3. Catalytic reaction

The esterification reactions of *n*-butanol (7.4 g) with different acids such as formic acid (4.6 g), acetic acid (6 g) and propionic acid (7.4 g) were carried out in round bottom flask provided with a double walled condenser containing catalyst at 80 °C and stirring for 4 h. The mentioned amount of alcohol and corresponding acid is in 1:2 ratio. Same reactions were carried out with different amount of the catalyst. For esterification of isobutanol, 2-butanol and cyclohexanol the ratio of corresponding alcohol to acetic acid taken was 1:2 (7.4 g:12 g), 1:2 (7.4 g:12 g) and 1:3 (9.9 g:18 g), respectively. Reactions were carried out at 80 °C with stirring for 4 h. The product esters was analysed on a Nucomb gas chromatograph using Cabowax 20 column.

2.4. Characterization

Different mineral acids and alcohols were used for checking the chemical stability of the material. The ion-exchange capacity was determined by using the following formula:

$$IEC(meq/g) = \frac{\text{normality of NaOH} \times \text{volume of NaOH}}{\text{grams of material}}$$

Differential scanning calorimetry of the sample was carried out on TA INSTRUMENTS DSC-2010 instrument. Adsorption–desorption isotherms of samples were recorded on a Micromeritics ASAP 2010 surface area analyser at −196 °C. From the adsorption–desorption isotherms specific surface area was calculated using BET method. The FT-IR spectra of the samples were obtained by using KBr wafer on Perkin-Elmer. The DRS spectra of the samples were recorded on a Shimadzu PR1 instrument using barium sulphate as a reference. The XRD pattern was obtained by using PHILIPS PW-1830. The conditions used were: Cu Kα radiation (1.5417 Å), scanning angle from 5° to 60°. The study on particle size distribution for Z and ZS_3 was carried out on Malvem particle size analyser, Mastersizer 2000. The surface morphology of the support and supported HPAs was studied by scanning electron microscopy using a Jeol SEM instrument (model-JSM-5610 LV) with scanning electron electrode at 15 kV. Scanning was done at 1 mm range and images taken at a magnification of 100× for Z, 100× and single particle image at 500× for ZS_3.

3. Results and discussion

Leaching is a negative property for any catalyst. Any leaching of the catalyst from the support would make the catalyst unattractive for reusing. So, it is necessary to study

Table 1
Ion-exchange capacity of all materials

Material	Ion-exchange capacity
Z	0.16
ZS_2	0.42
ZS_3	0.45
ZS_4	0.60
ZS_5	0.64
ZS_7	0.78

Table 2
Surface area of materials

Material	Surface area
Z	170
ZS_2	190
ZS_3	208
ZS_4	200
ZS_5	171
ZS_7	114

the stability of heteropolyacid onto hydrous zirconia in order to reuse the catalyst. When heteropolyacid react with a mild reducing agent such as ascorbic acid [30], it developed blue coloration, which can be used for the quantitative characterization for the leaching of heteropolyacid from the support. In the present study, this method was used, for determining the leaching of HPA from the support.

Standard samples amounting to 1–5% of 12-tungstosilicicacid in water were prepared. To 10 ml of the above samples, 1 ml of 10% ascorbic acid was added. The mixture was diluted to 25 ml. The resultant solution was scanned at a λ_{max} of 785 cm^{-1} for its absorbance values. A standard calibration curve was obtained by plotting values of absorbance with percentage solution. One gram of ZS_3 with 10 ml n-butanol was refluxed for 4 h. Then 1 ml of the supernent solution was treated with 10% ascorbic acid. No development of blue colour indicates no leaching. The same procedure was repeated with water, isobutanol, cyclohexanol, 2-butanol, formic acid, acetic acid, propionic acid and with the filtrate of the reaction mixture after reaction. The above procedure was followed for all catalysts and no leaching was found. The study indicates the presence of chemical interaction between the HPA and the support, as well as stability of resulted catalysts under reaction conditions.

Table 1 shows the value of ion-exchange capacity. The value of ion exchange capacity gives an idea for the acidity of material. It is an indirect way to determine the acidity of the materials. It is seen from the Table 1 that the value of ion exchange capacity increases as the amount of heteropolyacid supported on to hydrous zirconia increases.

The DSC of supported heteropolyacid shows an endothermic peak at 131 °C indicating the loss of crystallization water molecules. It also shows an exothermic peak at 430 °C which may be due to some phase change/decomposition of keggin ion. The values of surface area for all materials are listed in Table 2. The values of surface area for ZS_2 and ZS_3 are greater than that of the support, which is as expected. With increase in the percent loading of HPA, the surface area decreases [24]. This may be due to the stabilization/blocking of the sites.

The FT-IR spectra of Z (Fig. 1a) shows broadband in the region of 3400 cm^{-1}. This is attributed to asymmetric hydroxo (−OH) and aquo (−OH) stretches. Two types of bending vibrations are observed at 1600 cm^{-1} and 1370 cm^{-1} indicating the presence of −(H−O−H)− bending and −(O−H−O)− bending, respectively. It also shows a

weak bending band at 600 cm^{-1} attributed to the presence of Zr−O−H bond. In addition to these bands, the FT-IR spectra of ZS_2, ZS_3, ZS_4, ZS_5 and ZS_7 shows bands at 970 cm^{-1}, 916 cm^{-1} and 799 cm^{-1}. The FT-IR spectra of ZS_3 is shown (Fig. 1b) as an example. These can be assigned to the symmetric stretching of W=O, Si−O and W−O−W, respectively, and the positions are in good agreement with those reported earlier [26] conforming the presence of these groups in the synthesized materials. The FT-IR spectra of ZS_{33} and ZS_{34} are also shown in Fig. 1b. The position of all band are almost at the same frequency as in catalyst ZS_3 indicating that the 12-tungstosilicicacid keeps its keggin type structure up to 400 °C.

The electronic spectra gives information about the non-reduced heteropoly anion [31] due to ligand (oxygen) to metal charge transfer [32]. It gives an evidence for the presences of HPA. The electronic spectra of S and ZS_3, ZS_{33}, ZS_{34} are shown in (Fig. 2). The spectra shows λ_{max} at 260 nm which
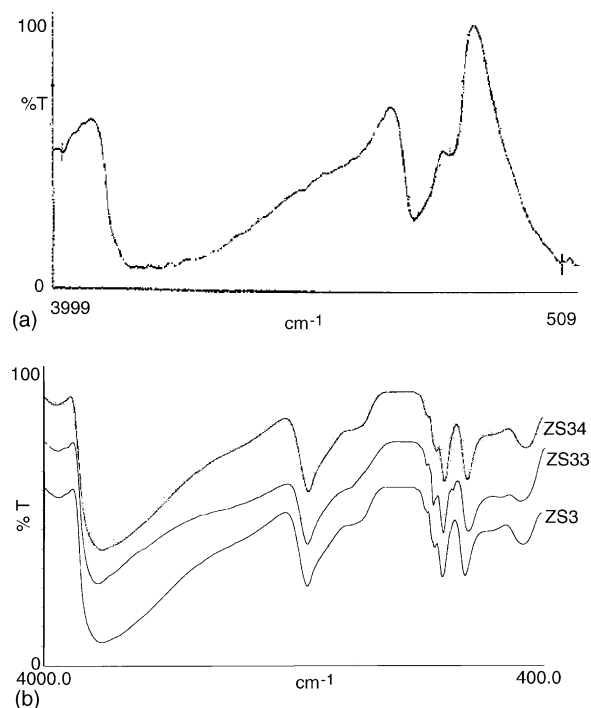
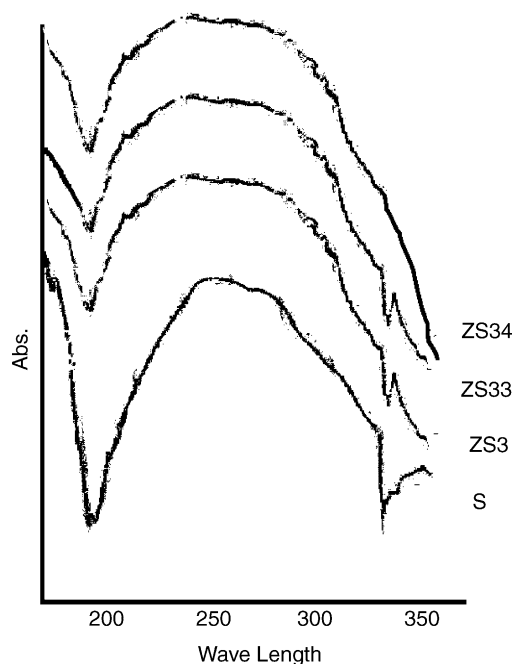Fig. 1. Fourier transform infrared spectra of (a) Z and (b) ZS_3, ZS_{33}, ZS_{34}.

Fig. 2. Electronic Spectra of S, ZS_3, ZS_{33}, ZS_{34}.

is in good agreement with reported earlier [26] and suggesting the presence of the undegraded $H_4SiW_{12}O_{40}$ species. In other words, the keggin phase remains unaltered up to 400 °C. Thus, DSC, FT-IR and DRS show no decomposition of the HPA species on the surface of the catalyst as well as presence of undegraded 12-tungstosilicicacid species.

The XRD of ZS_3 shows no crystalline structure indicating the material is amorphous. Further, it does not shows any diffraction lines of HPAs indicating a very high dispersion of solute as a non crystalline form on the support surface. This is further supported by particle size distribution study. The graph for average particle distribution for Z and ZS_3 is shown in Fig. 3. It is seen from the Fig. 3 that there is a non-uniform distribution of particles in case of Z and all particles fall in the range of 1–200 μm while for ZS_3 uniform distribution of particles are found and all particles fall in the range of 1–80 μm. The significant decrease in

the average particle size diameter of ZS_3 as compare to that of the Z may be due to the supporting of HPA as well as uniform dispersion of the HPA onto the surface of the support.

The SEM of Z and ZS_3 are shown in Fig. 4. It is seen from the figure that surface of the support is distinctly altered. It exhibits considerable surface shinning after supporting of the HPA. Picture taken at higher magnification (Fig. 4c, 500×) shows clearly the alternation and shining of the surface.

3.1. Catalytic reactions

The esterification is a straightforward reaction subject to general Bronsted acid catalysis. The yields of the ester can be increased by increasing the concentration of either alcohol or acid [33]. For economic reasons, the reactant that is usually the less expensive of the two is taken in excess. In the present study, all corresponding acids were used in excess.

3.2. Esterification of 1° alcohol

The esterification of *n*-butanol with acetic acid using whole series was carried out with molar ratio of alcohol to acid (1:2) and with different amount of catalysts. The percentage yields are shown in Fig. 5. It is seen that ZS_3 (yield is 81%) is the best among all. The same reaction was carried out with formic acid and propionic acid by taking molar ratio of alcohol to acid (1:2) with 0.5 g of the catalyst (ZS_3). The % yield of butyl formate and butyl propionate are shown in Fig. 6. Same catalyst is further used for esterification reaction of iso-butanol with acetic acid. The mole ratio of alcohol to acid taken was 1:2. The percentage yield of isobutyl acetate is shown in Fig. 6.

3.3. Esterification of 2° alcohol

The esterification reaction of cyclohexanol and 2-butanol was carried out with acetic acid using 0.5 g of ZS_3. The mole ratios of alcohol to acid were 1:3 and 1:2, respectively. The percentage yield of cyclohexyl acetate and 2-butyl acetate are presented in Fig. 6.
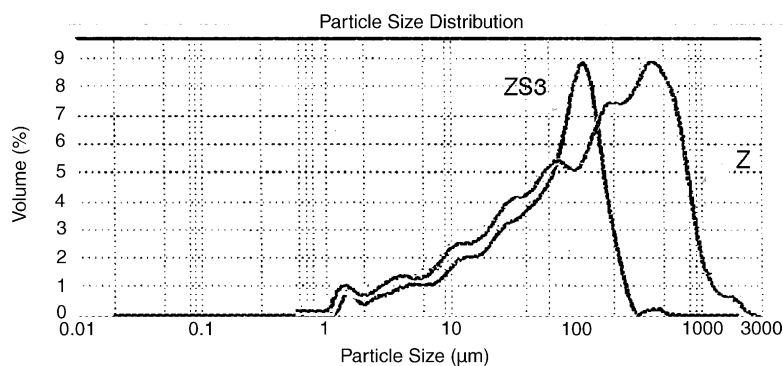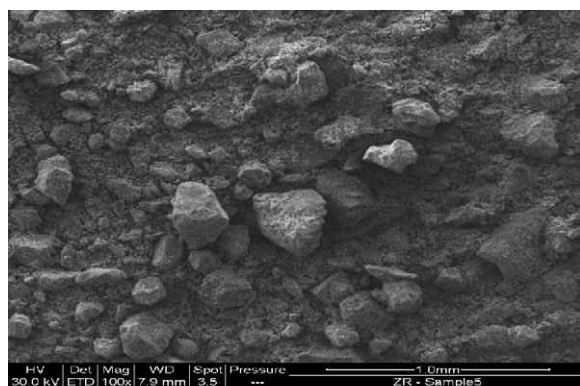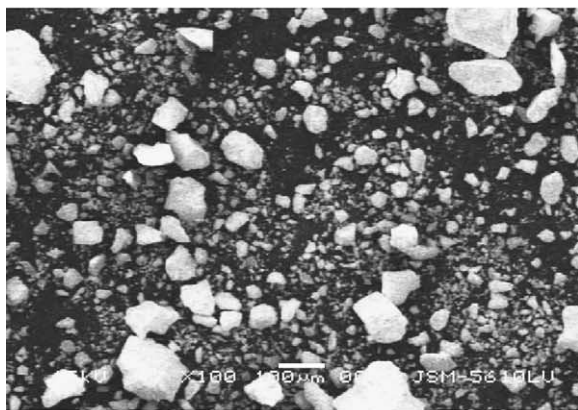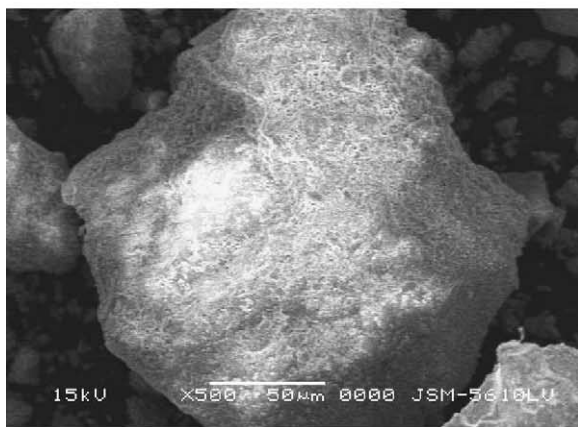

Fig. 3. Average particle size distribution of (a) Z and (b) ZS_3.

(a)

(b)

(c)

Fig. 4. SEM of (a) Z at magnification 100×, (b) ZS$_3$ at magnification 100×, and (c) ZS$_3$ single particle at magnification 500×.
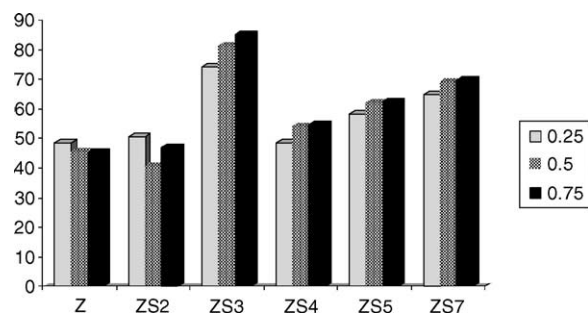

Fig. 5. Percent (%) yield of butyl acetate with different catalyst. Mole ratio of alcohol to acid is 1:2.
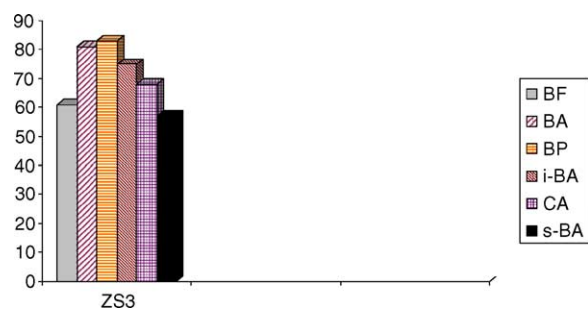

Fig. 6. Percent (%) yield of different esters with ZS$_3$. Amount of the catalyst = 0.5 g; mole ratio of alcohol to acid = 1:2; mole ratio of alcohol to acid for CA = 1:3.

The optimum conditions for all reactions using ZS$_3$ are as follows:

amount of the catalyst = 0.25 g;
temperature = 80 °C;
reaction time = 4 h.

In order to investigate the details of the deactivation, repeated use of the catalyst was examined. The catalyst was separated from the reaction mixture by simple filtaration, washed with conductivity water till filtrate is free from acid, dried at 100 °C in oven for 5 h and the recovered catalysts was charged for the further run. The results obtained are shown in Table 3.

Thus, it is seen from the table that in the regenerated sample, the yield decreased by 5%. The yield becomes constant on further regeneration.

Table 3
% yield of different esters with recovered catalysts

Cycle	Yield (%)					
	Butyl formate	Butyl acetate	Butyl propionate	Iso-Butyl acetate	Sec-Butyl acetate	Cyclohexyl acetate
1	53	70	72	65	50	52
2	49.5	65	66	61	45	46
3	49	65	65	60	45	45
4	49	65	65	60	45	45

Amount of the catalyst = 0.25 g; temperature = 80 °C; and reaction time = 4 h.

4. Conclusion

FT-IR and electronic spectra conform that the 12-tungstosilicicacid keeps its keggin type structure when supported onto hydrous zirconia. DSC study shows that the supported HPA does not get disturbed up to 430 °C. XRD, PSD and SEM studies shows the uniform dispersion of heteropoly anion onto the surface of the support. From the above experimental results, it is found that the catalyst containing 30% loading of 12-tungstosilicicacid on hydrous zirconia is best among all. The catalyst is proved to be successful in the esterification of 1° and 2° alcohol under the mild condition as compared with the traditional liquid acid catalyst.

Acknowledgements

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