

Tungstophosphoric acid supported onto hydrous zirconia: Physicochemical characterization and esterification of 1° and 2° alcohol

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Abstract. The Keggin type heteropolyacid, 12-tungstophosphoric acid (PW), was supported onto hydrous zirconia (Z) by impregnation method and designated as ZH₃. The ZH₃ was calcinated at 300°C and 500°C and designated as ZH₃₃ and ZH₃₅, respectively. The resulting materials were characterized by FTIR, diffuse reflectance spectroscopy (DRS), XRD, surface area measurement (BET method) and particle size distribution. The surface morphology was studied by scanning electron microscopy. The acidity of all materials was evaluated by carrying out chemisorption of ammonia and esterification of 1° alcohol (*n*-butanol) with different acids like formic acid, acetic acid and propionic acid and 2° alcohol (cyclohexanol, iso-butanol) with acetic acid. Above studies show the high dispersion of HPA in a non-crystalline form on the support as well as uniform distribution of particles of ZH₃ which contains 30% 12-tungstophosphoric acid. It also shows that when ZH₃ was calcinated at 500°C, it possesses highest acidity for both chemisorption of NH₃ as well as esterification reactions.

Keywords. Hydrous zirconia; heteropolyacid; morphology; particle size; acidity.

1. Introduction

Catalysis by heteropolyacids (HPAs) of the Keggin's structure is one of the most important and growing areas of research in recent years. They have been used in both homogeneous and heterogeneous catalysis (Misono *et al* 1982; Izumi *et al* 1983; Misono and Nojiri 1990; Hill and Posser-McCarthy 1995; Kozhevnikov *et al* 1995; Blasco *et al* 1998; Chu *et al* 1998; Mizuno and Misono 1998). The importance, characterization and properties of various HPAs have been reviewed in the literature (Misono 1987; Kozhevnikov 1995; Okuhara *et al* 1996). They are better active catalysts for various reactions in solution than conventional mineral acids (Kozhevnikov and Matveev 1983; Kozhevnikov 1987, 1994, 1995; Izumi *et al* 1992; Okuhara *et al* 1994, 1996; Wu *et al* 1996). The main disadvantage of HPAs lies in their low efficiency due to low surface area, rapid deactivation and poor stability. Furthermore, they suffer from the same traditional problem of separation from the reaction mixture when used in polar solvents.

Supporting of HPAs onto suitable support can overcome/improve the above mentioned disadvantages. The support provides an opportunity for HPAs to be dispersed over a large surface area. A variety of supports such as silica (Rocchiccioli–Deltcheff *et al* 1990; Nowinska *et al* 1991;

Schwegler *et al* 1992; Swanml *et al* 1997; Tatibouet *et al* 1997; Faming *et al* 1998; Misono 1998; Pizzio *et al* 1998; Hu *et al* 1999; Molnar *et al* 1999; Vazquez *et al* 1999; Choi *et al* 2000; Dutenhefner *et al* 2001; Kozhevnikov *et al* 2001; Gao and Moffat 2002; Bielanski *et al* 2003a,b; Damyanova *et al* 2003; Haber *et al* 2003; Ivanov *et al* 2003; Okuhara 2003; Pizzio *et al* 2003), alumina (Wu *et al* 1996; Hu *et al* 1999; Vazquez *et al* 1999; Bielanski *et al* 2003a,b; Pizzio *et al* 2003), titania (Wu *et al* 1996; Damyanova and Fierro 1998; Pizzio *et al* 1998; Knifton and Edwards 1999; Vazquez *et al* 1999; Bielanski *et al* 2003a, b), carbon (Izumi *et al* 1983; Schwegler *et al* 1990, 1992; Dupont *et al* 1995; Dupont and Lefebve 1996; Wu *et al* 1996; Pizzio *et al* 1998, 2003; Mukai *et al* 2003), MCM-41 (Blasco *et al* 1998; Verhoef *et al* 1999; Siahkali *et al* 2000; Jalil *et al* 2001; Nowinska *et al* 2003), acidic ion exchange resins (Nomiya *et al* 1986; Ivanov *et al* 2003) and clay (Wu *et al* 1996; Yadav and Bokade 1996; Yadav and Kirthivasan 1997; Knifton and Edwards 1999; Yadav *et al* 1999; Yadav and Doshi 2000, 2002) have been used for supporting HPAs and different reactions have been carried out. Supported HPAs have a number of advantages like high catalytic activity and selectivity, possibility of their repeated use, easy separation from reaction mixture, high surface area, high thermal stability and most of all there is no problem in the disposal of used catalyst. Since the supported catalysts are more active than the unsupported ones, it is important to understand the nature of interaction between the HPA and the supports. These interactions

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depend on the central and addenda atom of heteropolyanion, loading as well as dispersion of heteropolyacid onto the support, nature of the support and pre-treatment (Clark *et al* 1992). The difference in the performance of the supported catalyst can be explained by considering the change in acidity.

Various methods such as titration with hammet indicators, temperature-programme desorption (TPD), adsorption microcalorimetry, catalyst probe reactions and NMR have been used to probe solid acidity. A commonly used technique to study solid acidity is TPD of adsorbed bases such as NH_3 or pyridine. The catalytic performance can also be used to rank solid acidity.

In the previous paper (Patel *et al* 2003), a series of catalysts containing 12-tungstophosphoric acid and hydrous zirconia were synthesized and characterized in detail. It was found that the species present on hydrous zirconia was the heteropolyanion, $[\text{PW}_{12}\text{O}_{40}]^{3-}$, with undegraded keggin structure. Based on all studies, the catalyst containing 30% 12-tungstophosphoric acid supported onto hydrous zirconia (ZH_3) was found to be the best. The objective of this paper is to study the effect of temperature (calcination) on the supported keggin structure, alternation of surface of the support, particle size distribution and acidity.

In the present paper, the calcination of ZH_3 was carried out at two different temperatures, 300°C and 500°C and catalysts were designated as ZH_{33} and ZH_{35} , respectively. All materials were characterized for chemical stability, FTIR, DRS, XRD, surface area measurement (BET method) and particle size distribution. The surface morphology was studied by scanning electron microscopy (SEM). The acidity of all materials was determined by chemisorption of ammonia as well as by evaluating the catalytic activity for esterification of 1° alcohol (*n*-butanol) with different acids like formic acid, acetic acid and propionic acid and of 2° alcohols (cyclohexanol and isobutanol) with acetic acid. Among them ZH_{35} was found to be the best catalyst with maximum acidity.

2. Experimental

2.1 Materials

All chemicals used were of A.R. grade. $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}$ and $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$ (Lobachemie, Mumbai) were used as received. *n*-Butanol, cyclohexanol, iso-butanol, formic acid, acetic acid, propionic acid and ascorbic acid were obtained from E. Merck, Mumbai and used as received.

2.2 Synthesis of catalyst

The hydrous zirconia support was synthesized by the method reported earlier (Patel *et al* 2003). Catalyst containing 30% 12-tungstophosphoric acid (PW) was synthesized by

impregnating 1 g of hydrous zirconia with an aqueous solution of PW (0.3 g/30 ml of conductivity water) followed by drying at 100°C for 10 h. The material thus obtained was designated as ZH_3 . Further calcination of ZH_3 was carried out at 300°C and 500°C in air for 5 h and the resulting samples were designated as ZH_{33} and ZH_{35} , respectively.

2.3 Characterization

The test for leaching of HPA from the surface of the support was carried out to check the chemical stability of the catalysts.

The FTIR spectra of the samples were obtained by using KBr wafer on Perkin-Elmer. The DRS spectra of samples were recorded on a Jasco DR-UV-VIS spectrophotometer (model V-550) instrument using barium sulphate as a reference. The XRD pattern was obtained using PW3040/60 X'pert PRO console. The condition used was: $\text{CuK}\alpha$ radiation (1.5417 Å). The specific surface area was calculated using BET method from adsorption-desorption isotherm on Micromeritics ASAP 2010 surface area analyser. The surface morphology of the support and supported HPAs was studied by SEM. Scanning electron micrographs of Z, ZH_3 , ZH_{33} and ZH_{35} were taken on a Jeol SEM instrument (model JSM-5610 LV) with a scanning electron electrode at 15 kV. Scanning was done at 1mm range and images taken at a magnification of 100×, 500× and of single particle at 500×. Particle size distribution of all materials was determined using a Malvern particle size analyser, Mastersizer 2000. The acidity of Z, ZH_3 , ZH_{33} and ZH_{35} was determined by carrying out chemisorption of ammonia and esterification reactions.

2.4 Acidity measurements

2.4a Chemisorption of ammonia: The chemisorption of ammonia gas (pure) on the surface of the samples was carried out using Micromeritics Pulse Chemisorb-2705 instrument. The samples, prepared by heating at pre determined temperature, were kept in a U-shaped quartz and the tube was placed in a split furnace. The samples were first heated *in situ* at 300°C in flowing argon (99.95%) for 2 h to remove moisture. The chemisorption of pure ammonia on the preheated samples was carried out at 120°C by repeatedly injecting a pulse of pure ammonia gas till saturation was observed. The amount of ammonia chemisorbed on the sample in every pulse was detected by a thermal conductivity detector (TCD) in the form of an integrated area of the ammonia peak. From the peak areas, the acidity in terms of mmoles of ammonia chemisorbed per gram of samples were calculated at 120°C for various preheated samples. The temperature of 120°C was selected for the adsorption studies to avoid physical adsorption of ammonia.

2.4b *Esterification reactions*: The esterification of 1° alcohol (*n*-butanol) with formic acid, acetic acid and propionic acid was carried out in a round bottom flask provided with a double-walled condenser containing catalyst, *n*-butanol (1 mole) and corresponding acid (2 mole) at 80°C with stirring for 4 h. For esterification of 2° alcohol, cyclohexanol, isobutanol (1 mole) and acetic acid (3 mole) were taken and catalyst was then added in the required amount. Reaction was carried out at 80°C with stirring for 4 h. The percentage of ester formation was determined on a Nucon Gas Chromatograph using Carbowax 20 column.

3. Results and discussion

Any leaching of the catalyst from the support makes the catalyst unattractive for reuse. So it is necessary to study the stability of HPA onto hydrous zirconia as well as leaching of HPA from the support in order to reuse the catalyst. HPA can be quantitatively characterized by the heteropoly blue colour, that is observed when it reacted with a mild reducing agent such as ascorbic acid (Yadav and Bokade 1996). In the present study, this method was used for determining the leaching of HPA from the support.

Standard samples containing 1–5% of 12-tungstophosphoric acid 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 I_{\max} of 785 cm^{-1} for its absorbance values. A standard calibration curve was obtained by plotting values of absorbance with percentage solution. 1 g of supported catalyst with 10 ml conductivity water was refluxed for 4 h. Then 1 ml of the supernatant solution was treated with 10% ascorbic acid. Development of blue colour was not observed indicating that there was no leaching. The same procedure was repeated with *n*-butanol, cyclohexanol, isobutanol, formic acid, acetic acid, propionic acid and the filtrate of the reaction mixture after completion of reaction in order to check the presence of any leached 12-tungstophosphoric acid. The development of blue colour was not observed indicating absence of leaching of 12-tungstophosphoric acid. The above studies indicate the presence of chemical interaction between the HPA and the support. It also confirms the stability of catalysts under reaction conditions.

The frequencies of absorption bands of FTIR (figure 1) are reported in table 1 and are in good agreement with

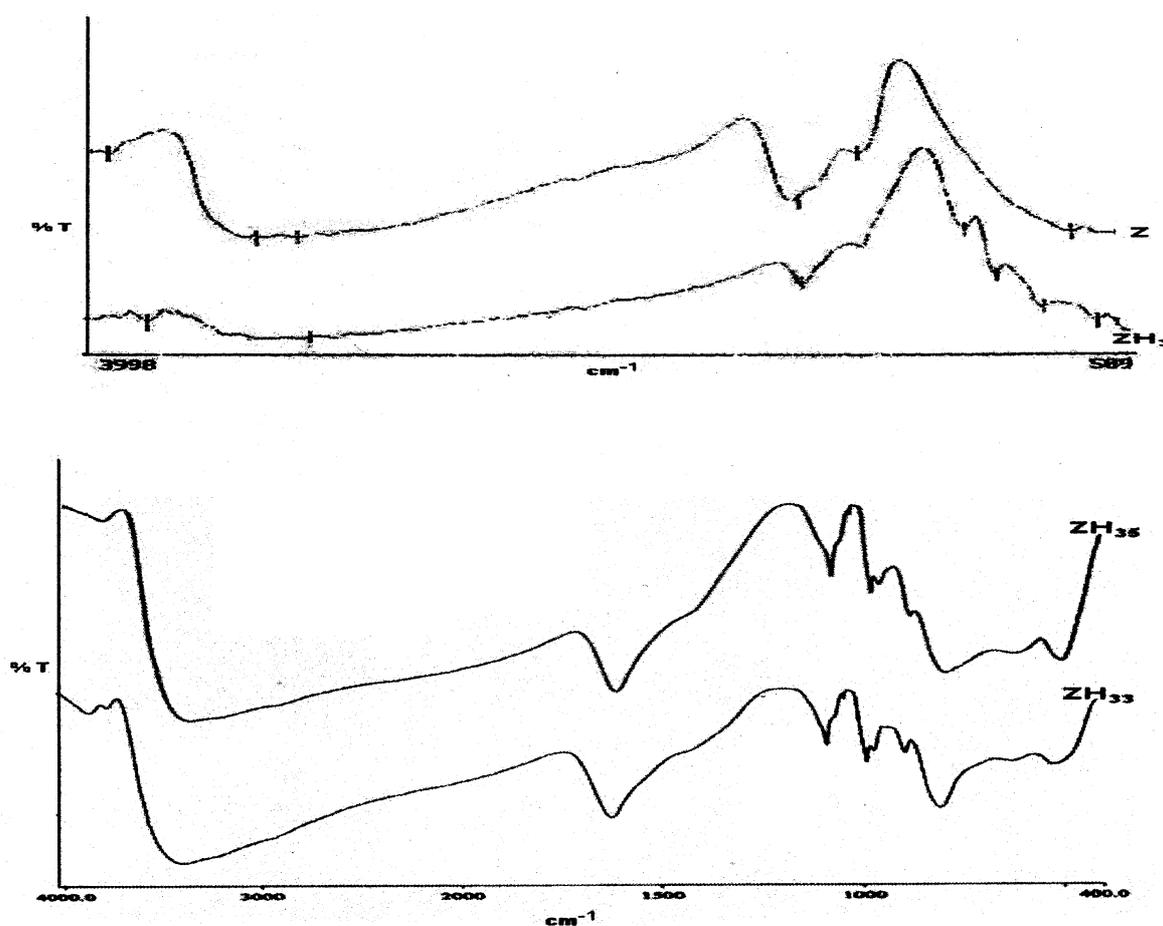
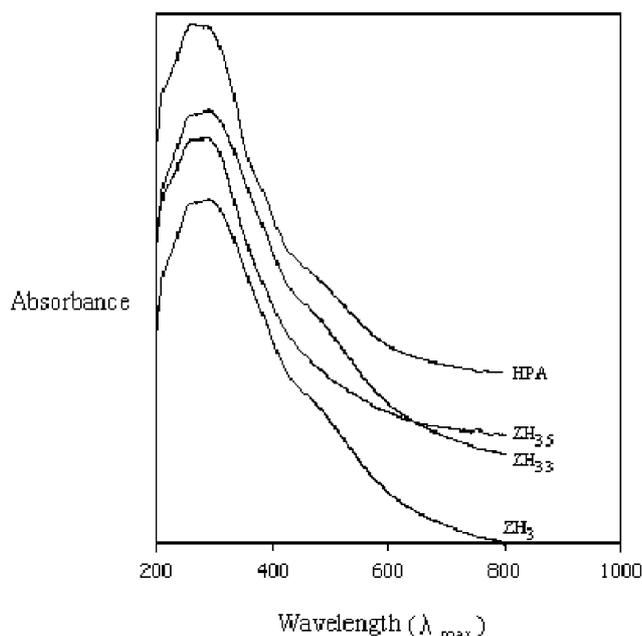


Figure 1. FT-IR of Z, ZH₃, ZH₃₃ and ZH₃₅. (Z: support (hydrous zirconia); ZH₃: catalyst prepared by 30% loading of 12-tungstophosphoric acid; ZH₃₃: catalyst ZH₃ calcinated at 300°C for 5 h; ZH₃₅: catalyst ZH₃ calcinated at 500°C for 5 h).

Table 1. Experimental absorption bands of supported catalysts and tentative band assignments.

Catalyst	Band frequency (cm ⁻¹)						
	Asym. hydroxo. and aquo (OH) str.	H-O-H	O-H-O	Z-O-H	W-O-W	W=O	P-O
Z	3400	1600	1370	600	—	—	—
ZH ₃	3400	1600	1370	600	1070	964	812
ZH ₃₃	3400	1600	1370	600	1080	964	807
ZH ₃₅	3400	1600	1370	600	1080	962	799

**Figure 2.** DRS of HPA, ZH₃, ZH₃₃ and ZH₃₅. (ZH₃: catalyst prepared by 30% loading of 12-tungstophosphoric acid; ZH₃₃: catalyst ZH₃ calcinated at 300°C for 5 h; ZH₃₅: catalyst ZH₃ calcinated at 500°C for 5 h; HPA: 12-tungstophosphoric acid).

those reported earlier (Okuhara *et al* 1996) confirming the presence of heteropolyanion in the prepared materials. The band at 1070 cm⁻¹ does not appear to be split into components at 1085 cm⁻¹ and 1040 cm⁻¹ assigned to [PW₁₁O₃₉]²⁻ ion. There is a slight shift in the FTIR bands of ZH₃₃ and ZH₃₅ as compared to that of ZH₃. Thus FTIR study indicates that the 12-tungstophosphoric acid keeps its Keggin type structure up to 500°C.

Electronic absorption spectra gives information about the non-reduced heteropolyanions due to ligand (oxygen) to metal charge transfer (Varga *et al* 1970). The DRS spectra of ZH₃, ZH₃₃ and ZH₃₅ show I_{\max} at 260 nm (figure 2) which is in good agreement with the earlier reported data (Okuhara *et al* 1996) giving evidence for the presence of the undegraded H₃PW₁₂O₄₀ species. In other words, the Keggin phase remains unaltered up to 500°C.

The XRD of Z and ZH₃ showed no crystalline structure indicating that the materials were amorphous. The XRD

pattern of ZH₃ also showed no diffraction lines of HPAs indicating a very high dispersion of solute in a non-crystalline form on the support surface. This is further supported by particle size distribution study. The graph showing average particle distribution for Z and ZH₃ is given in figure 3. It is seen from the figure that the graph (b) is more smoother as compared to graph (a). It is known that in case of particle size distribution, smoother graph contributes towards uniform distribution of particles. The graphs shown in the figure indicates that there is a non-uniform distribution of particles in case of Z and all particles fall in the range 1–200 μm while for ZH₃ uniform distribution of particles are found and all particles fall in the range 1–20 μm. The values (table 2) of specific surface area obtained from particle size distribution for Z and ZH₃ are 0.206 m²/g and 2–28 m²/g, respectively. It is well known that higher the particle size, lower is the specific surface area. The obtained values are in good agreement with this. The value of total surface area obtained from BET method (table 2) also has a similar trend i.e. the value of surface area of ZH₃ (146) is less than that of Z (170). Thus, significant decrease in average particle size diameter and increase in the specific surface area and total surface area may be due to the support of heteropolyacid as well as uniform dispersion of the heteropolyacid onto the surface of the support.

The SEM of Z and ZH₃ are shown in figure 4. It is seen from the figure that the surface of the support is distinctly altered. SEM of Z (figure 4a) shows a non-uniform distribution of particles. The SEM of ZH₃ (figure 4b) shows a uniform distribution of particles and also significant reduction in particle size as compared to that of Z. The reduction in particle size may be due to the support of heteropolyacid. Thus XRD, particle size distribution and SEM are in good agreement with each other and confirms the uniform and high dispersion of HPA in a non-crystalline form because of the interaction with the support on the support surface.

Table 2 shows the value of average particle size diameter, total acidity of materials and the value of percentage yield (%) of different esters, butyl formate, butyl acetate, butyl propionate, cyclohexyl acetate and iso-butyl acetate. It is also seen from table 2 that the value of average particle size diameter is maximum for ZH₃₅ i.e. the catalyst calcinated at 500°C. The order of value of average parti-

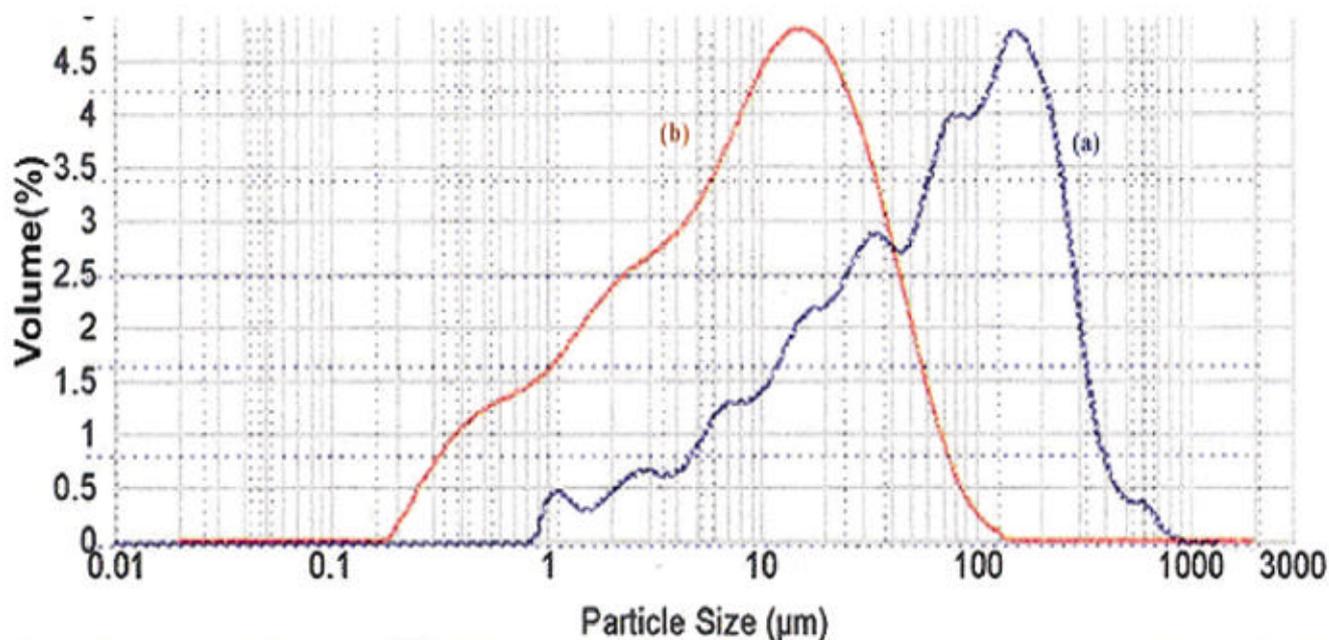


Figure 3. Average particle size distribution of (a) Z and (b) ZH₃. (Z: support (hydrous zirconia); ZH₃: catalyst prepared by 30% loading of 12-tungstophosphoric acid).

Table 2. The values of surface area, average particle size diameter and total acidity and value of percentage yield (%) of different esters: butyl formate, butyl acetate, butyl propionate and cyclohexyl acetate.

Catalyst	% Yield of butyl formate ^a	% Yield of butyl acetate ^a	% Yield of butyl propionate ^a	% Yield of isobutyl acetate ^a	% Yield of cyclohexyl acetate ^b	Total surface area (m ² /g)	Total acidity (mmol. of NH ₃ /g sample)	Average particle size diameter (μm)	Specific surface area (m ² /g)
Z	52	51	27	46	38	170	0.64	112.15	0.206
ZH ₃	75	70	47	73	68	146	0.84	9.12	2.28
ZH ₃₃	75	71	46	77	78	214	1.06	16.90	2.32
ZH ₃₅	84	78	48	81	84	126	1.24	22.16	1.68

Amount of catalyst, 0.5 g; ^amole ratio of alcohol to acid is 1 : 2; ^bmole ratio of alcohol to acid is 1 : 3.

cle size diameter ZH₃₅ > ZH₃₃ > ZH₃ can be explained as follows.

It is well known that the structure of hydrous zirconia (Clearfield 1988) is open containing water molecules in the form of OH⁻, H₃O⁺ and H₂O. It is also known that the structure of HPA contains unbonded H₂O molecules as water of crystallization inside the cages of HPA. Increase in the particle size of ZH₃₃ may be due to the loss of H₂O/H₃O⁺ from hydrous zirconia as well as loss of crystalline H₂O from the structure of heteropolyanion by expanding the lattice. This loss takes place without any major change in the structure of supported heteropolyanion and is in good agreement with our earlier results (Sharma *et al* 2004). On strong heating, i.e. calcination at 500°C, the total removal of H₂O/H₃O⁺ from hydrous zirconia is expected and hence more expansion of lattice is also expected. This may be the reason for ZH₃₅ to have maximum average particle size diameter. These observations can be very well shown in the SEM of ZH₃, ZH₃₃ and ZH₃₅. The SEM

of ZH₃, ZH₃₃ and ZH₃₅ are also shown in figures 5 and 6. The SEM of ZH₃₅ appears more shining and somewhat crystalline among all as a result of total removal of H₂O/H₃O⁺ from hydrous zirconia.

The XRD of ZH₃₃ and ZH₃₅ is shown in figure 7. The XRD pattern of ZH₃₅ indicates the presence of crystalline entities. It shows the characteristic diffraction line for tetragonal zirconia. These changes may be due to complete loss of water molecules present in the form of OH⁻, H₃O⁺ and H₂O from hydrous zirconia after calcination (500°C). The absence of characteristic diffraction line of 12-tungstophosphoric acid indicates undegraded species of HPA onto the surface of the support.

3.1 Acidity

The total acidity of the support, catalysts and % yields of different esters are shown in table 2.

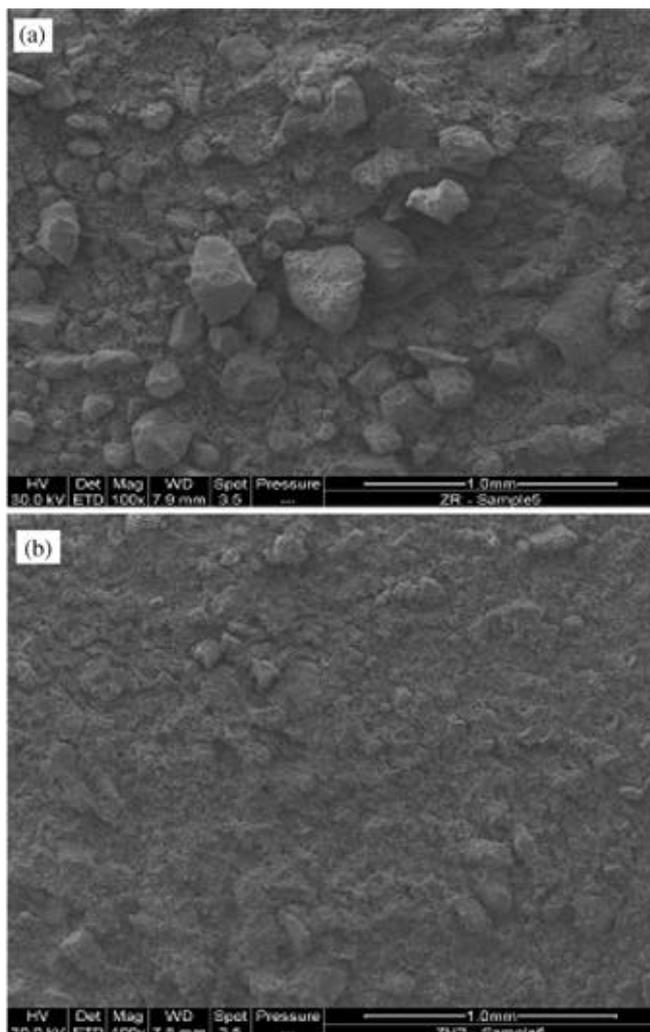


Figure 4. SEM of (a) Z (support, hydrous zirconia) and (b) ZH₃ (catalyst prepared by 30% loading of 12-tungstophosphoric acid).

The esterification is a straight forward reaction subject to general Bronsted acid catalysis. The yield can be increased by increasing the concentration of either alcohol or acid (Furnis *et al* 1994). In a practical situation when one wants to prepare an ester, it is desirable to obtain the maximum yield. For economic reasons the reactant that is usually less expensive of the two is taken in excess. In the present study, all corresponding acids were used in excess.

The % yield of above three esters are obtained in the following order:

Butyl formate > butyl acetate > butyl propionate.

The % yield can be explained on the basis of the size of reacting acids. As the size/bulkiness of the acid increases, the number of acid molecules sorbed on the surface of the catalyst will decrease and hence the number of molecules reacting in definite time will be less. This should result in decrease in the amount of the product. In case of formic acid the % yield of the ester is higher compared to the

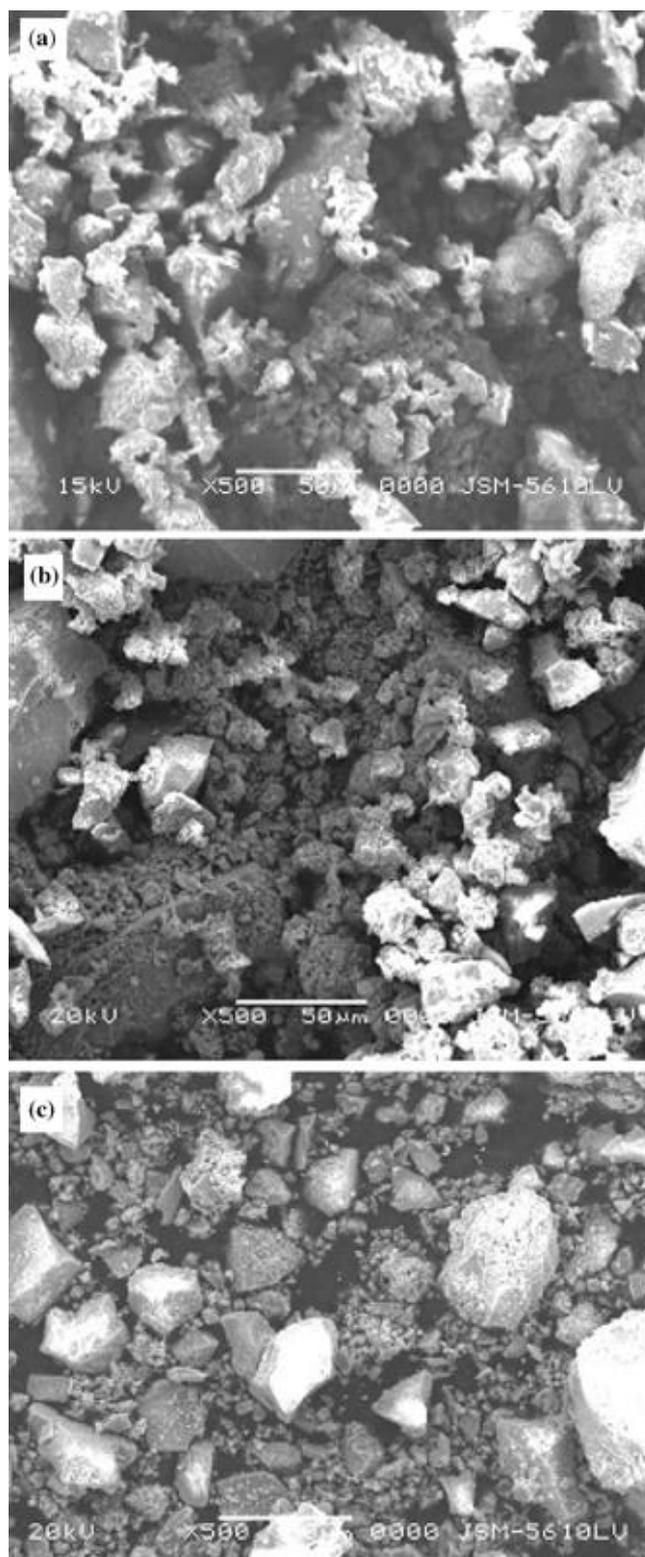


Figure 5. SEM of (a) ZH₃ (catalyst prepared by 30% loading of 12-tungstophosphoric acid (×500), (b) ZH₃₃ (catalyst ZH₃ calcinated at 300°C for 5 h) and (c) ZH₃₅ (catalyst ZH₃ calcinated at 500°C for 5 h).

acetic acid and propionic acid. The presence of -CH₃ and -C₂H₅ groups in the latter two acids results in the decrease in the yield.

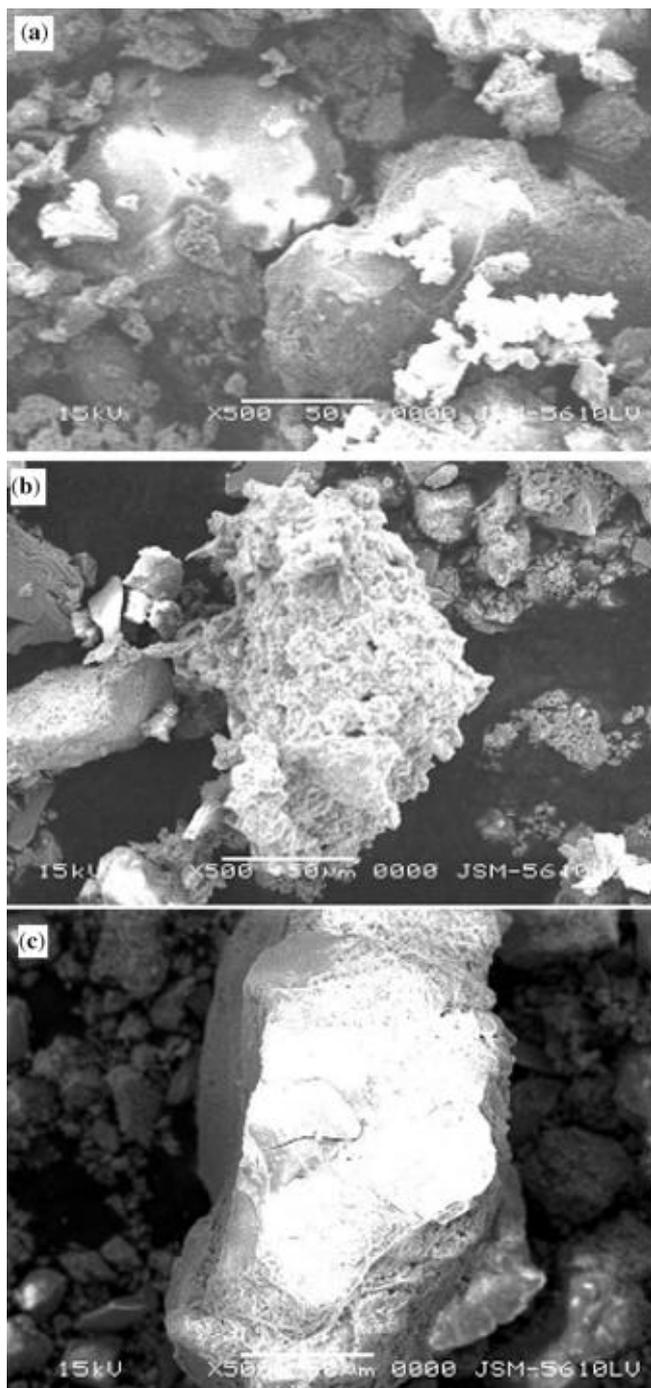


Figure 6. SEM of single particle of (a) ZH_3 (catalyst prepared by 30% loading of 12-tungstophosphoric acid), (b) ZH_{33} (catalyst ZH_3 calcinated at 300°C for 5 h) and (c) ZH_{35} (catalyst ZH_3 calcinated at 500°C for 5 h) ($\times 500$).

It is seen from table 2 that ZH_{35} has the highest total acidity. On heating (ZH_{33} and ZH_{35}) there may be increase of Lewis acidity on Z which results in an increase in the total acidity. It is also seen from table 2 that the increase in % yield of esters is not comparable with increase in total acidity. This may be due to the fact that esterification

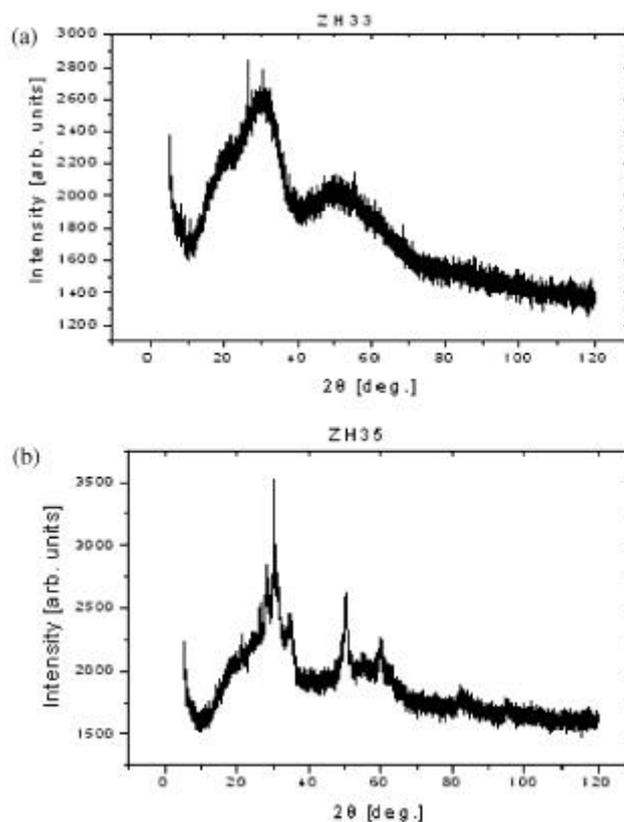


Figure 7. XRD of (a) ZH_{33} and (b) ZH_{35} . (ZH_{33} : catalyst ZH_3 calcinated at 300°C for 5 h; ZH_{35} : catalyst ZH_3 calcinated at 500°C for 5 h).

reactions are mainly catalysed by Bronsted acidity. It is also observed that the catalyst (ZH_{35}) consisting of highest total acidity gives maximum yield of esters. The optimized conditions for present reactions are: amount of the catalyst (0.5 g), refluxing temperature (80°C) and reaction time (4 h).

The catalyst (ZH_{35}) was washed with conductivity water and dried at 100°C and reused. In the regenerated sample the yield decreased by 5%. The yield becomes constant on further regeneration. The catalyst, ZH_{35} , has several advantages as a solid acid catalyst for liquid-phase reactions since it is insoluble, easily reusable and thermally more stable. Further it can be used in various types of acid catalysed liquid-phase organic reactions over a wide temperature range (500°C). They are environmentally friendly candidates by which conventional problematic corrosive acid catalysts can be replaced.

4. Conclusions

FTIR and DRS studies confirm the undegraded HPA supported onto the surface of the support up to 500°C . XRD, SEM and average particle size distribution show that the

morphology of the support, Z, is distinctly altered, exhibit considerable shining after supporting of HPA. It shows significant reduction of the particle size as well as uniform distribution of particles for ZH_3 . It also indicates that the species present onto the supported surface are highly dispersed as a non-crystalline form and after calcination at 500°C, formation of crystalline phase, probably conversion of hydrous zirconia to zirconia takes place. It was found that the catalyst calcinated at 500°C, ZH_{35} , has the highest average particle size, highest acidity, highest % yield for all esters and hence is best among all. The catalytic activity of the catalyst correlated well with the total acidity. It can be concluded that the present catalyst is not a surface type ordinary heterogeneous catalyst in which catalytic activity is directly proportional to the surface area of the catalyst, but it is pseudoliquid-bulk I type catalyst in which the catalytic activity is directly proportional to the total acidity of the catalyst.

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