

Heteropolyacid supported onto neutral alumina: characterization and esterification of 1° and 2° alcohol

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Abstract

Heteropolyacids (HPAs) which are freely soluble in H₂O could be made insoluble solid acid by supporting onto suitable supports. The supported HPAs thus obtained catalyzed the water participating reaction of esterification more efficiently. A series of the solid acid catalyst containing 20–70% of heteropolyacid, 12-tungstophosphoricacid, supported onto neutral alumina was synthesized. All amorphous materials were characterized by chemical stability, ion exchange capacity, TGA, DSC, FT-IR, XRD and surface area measurement (Brunner–Emmett–Teller (BET) method). The above studies indicate the increase in the stability of 12-tungstophosphoricacid after supporting onto support and the supported structure does not get destructed. The catalytic activity of these materials was evaluated by carrying out liquid phase esterification of 1° alcohol (*n*-butanol) and 2° alcohol (cyclohexanol). Based on the above experimental findings, catalytic performance was optimised with a loading of 30% 12-tungstophosphoricacid onto neutral alumina (AH₃). AH₃ was calcinated at 300 and 500 °C, designated as AH₃₃ and AH₃₅ and characterized for FT-IR and DRS. FT-IR and DRS studies indicate that the 12-tungstophosphoricacid keeps its Keggin type structure unaltered up to 500 °C when supported onto neutral alumina. Total acidity of AH₃, AH₃₃ and AH₃₅ was determined by chemisorption of ammonia. The particle size distribution for the three mentioned samples was also studied. The catalytic activity of AH₃₃ and AH₃₅ was examined by carrying out same esterification reactions under same conditions. The results indicate that the catalyst containing 30% 12-tungstophosphoricacid and calcinated at 500 °C (AH₃₅) is the best.

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1. Introduction

The esterification reaction is one of the important reaction in synthetic organic chemistry and usually carried out by use of various conventional mineral acids such as H₂SO₄, HF, H₃PO₄, HCl, etc. The growing awareness of the unacceptability of this conventional liquid catalyst and the resulting legislation give a major impetus to the search for cleaner technology. Cleaner technology could be possible by making use of environment friendly catalyst involving the use of solid acids.

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. The major disadvantages of HPAs, as catalyst lies in their low thermal stability, low surface area (1–10 m²/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. Major factors contributing to the catalytic activity are nature of support, loading and conditions of pre-treatment.

Various supports like silica [1–6], titania [3,6], active carbon [6–10], MCM-41 [11–13], acidic ion exchange resins [14] have been used for supporting HPAs. In our laboratory, detail studies have been carried out on 12-tungstophosphoricacid supported onto hydrous zirconia [15,16]. Since hydrous zirconia is acidic in nature, it was therefore thought of interest to make use of neutral support.

In the present contribution, we have synthesized a series of catalyst comprising 20–70% of 12-tungstophosphoricacid (PW) onto neutral alumina and characterized by various spectral, thermal and physicochemical techniques. The techniques used were chemical stability, ion exchange capacity,

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TGA, DSC, FT-IR, XRD and surface area measurement (Brunner–Emmett–Teller (BET) method). Their catalytic properties were evaluated for the esterification of 1° alcohol (*n*-butanol) and 2° alcohol (cyclohexanol). Further, the selected material was calcinated at 300 and 500 °C. The study on FT-IR, DRS, total acidity and particle size distribution was carried out for the calcinated materials. Their catalytic activity was also examined by carrying out same esterification reaction under the same conditions. Based on these observations, the best catalyst among all is proposed.

2. Experimental

2.1. Materials

All chemicals used were of A.R. grade. $H_3PW_{12}O_{40}\cdot nH_2O$ (Qualigens), neutral active Al_2O_3 , *n*-butanol, cyclohexanol, formic acid, acetic acid, and propionic acid were used as received from Merck.

2.2. Synthesis of the catalyst ($H_3PW_{12}O_{40}\cdot nH_2O$ supported onto neutral alumina)

The catalyst is synthesized by impregnation method. A series of catalysts containing 20–70% 12-tungstophosphoric acid (PW) were synthesized by impregnating 1 g of Al_2O_3 with an aqueous solution of 12-tungstophosphoric (PW) (0.2–0.7 g/20–70 ml of conductivity water) with stirring for 35 h and dried at 100 °C for 10 h. The obtained materials were designated as AH₂, AH₃, AH₄, AH₅ and AH₇. Further calcinations of AH₃ were carried out at 300 and 500 °C in air for 5 h and the resulting samples were designated as AH₃₃ and AH₃₅, respectively.

2.3. Characterization

Chemical stability of the material was checked in different mineral acids and alcohols. The ion exchange capacity was determined by column method using the following formula:

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

The thermo gravimetric analysis of the samples were performed on Shimadzu thermal analyzer model DT 30 at a heating rate of 10 °C/min. Differential scanning calorimetric of the samples were done on Mettler Toledo DSC 822°. The FT-IR spectra of the samples were obtained by using KBr wafer on Perkin-Elmer. The XRD pattern was obtained by using Rigaku Denki Co. Ltd., Japan. The conditions used were: Cu K α radiation (1.5417 Å), scanning angle from 5° to 60°. Adsorption–desorption isotherms of samples were recorded on a Carl Erba Sorptomatic Series 1800 at –196 °C. From the adsorption–desorption isotherm, specific surface area was calculated using BET method. The DRS spectra of AH₃, AH₃₃ and AH₃₅ were recorded

on a Shimadzu PR 1 instrument using barium sulphate as a reference. The total acidity of the AH₃, AH₃₃ and AH₃₅ was measured by chemisorption of ammonia. The study on particle size distribution for AH₃, AH₃₃ and AH₃₅ was carried out on Malvern particle size analyser, Mastersizer 2000.

2.4. Acidity measurement

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

2.5. Catalytic reaction

The esterification of *n*-butanol with formic acid, acetic acid and propionic acid was carried out in round bottom flask provided with a double walled condenser containing catalyst, *n*-butanol (1 mol) and corresponding acid (2 mol) at 80 °C with stirring for 4 h. The same reactions were carried out by changing the concentration of the corresponding acid. The esterification reactions were carried out for whole series with varying amount of the catalyst. For esterification of 2° alcohol, cyclohexanol (1 mol) and the acetic acid (3 mol) were taken and catalyst was then added in the required amount. Reaction was carried out at 80 °C with stirring for 4 h. AH₃, AH₃₃ and AH₃₅ were also evaluated for the esterification of *n*-butanol and cyclohexanol under the same conditions. The product esters were analyzed on a Shimadzu gas chromatograph using Carbowax 20 column.

3. Result and discussion

Any leaching of the catalyst from the support would make the catalyst unattractive for reusing. So it is necessary to study the stability of HPA onto neutral alumina as well as leaching of HPA from the support in order to reuse the catalyst. HPA can be quantitatively characterized by the

Table 1
Ion exchange capacity of all materials

Material	Ion exchange capacity (meq/g)
Al ₂ O ₃	0.00
AH ₂	0.72
AH ₃	1.06
AH ₄	1.22
AH ₅	1.52
AH ₇	1.98

heteropoly blue colour, that is observed when it is reacted with a mild reducing agent such as ascorbic acid [17]. 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-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 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 AH₃ with 10 ml *n*-butanol was refluxed for 4 h. Then 1 ml of the supernatant solution was treated with 10% ascorbic acid. There is no any development of blue colour indicating no leaching. The same procedure repeated with cyclohexanol, formic acid, acetic acid, propionic acid and the filtrate of the reaction mixture after reaction and no leaching was found. The above studies indicate the presence of chemical interaction between the HPA and the support. It also confirm the stability of AH₃ 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 the material. It is an indirect way to determine the acidity of the material. It is seen from the table that the value of ion exchange capacity increases as the amount of heteropolyacid supported onto neutral alumina increases.

The TGA of 12-tungstophosphoric acid shows 3–6% weight loss within a temperature range of 100–180 °C and continuous weight loss up to 350 °C. There is a break at 350 °C which may be due to the decomposition of heteropolyacid and this is in good agreement with reported one [18]. The TGA of supported 12-tungstophosphoric acid onto neutral Al₂O₃ show about 3% weight loss within the temperature range of 80–150 °C due to a loss of adsorbed water molecule and no appreciable change in weight till 600 °C indicating increase in the stability of 12-tungstophosphoric acid after supporting onto neutral alumina. This may be due to the formation of intermolecular hydrogen bonding between the support and heteropolyacid and indicates the presence of chemical interaction between the support and heteropolyacid. The DSC of supported heteropolyacid shows an exothermic peak at 80 °C which may be due to the loss of adsorbed H₂O molecules, after that there is no any endothermic peak indicating no

Table 2
Surface area measurement (BET method)

Materials	Surface area (m ² /g)
Al ₂ O ₃	81
AH ₂	98
AH ₃	109
AH ₄	88
AH ₅	90
AH ₇	89

decomposition of the supported material. The result is in good agreement with TGA analysis.

The values of surface area for all materials are listed in Table 2. It is seen from Table 2 that the value for the surface area for AH₃ is highest and is in good agreement with earlier results [16]. Almost the same value of surface area for AH₄, AH₅ and AH₇ indicates the stabilisation/blocking of the sites for the high loading.

The XRD pattern of AH₃ shows no crystalline structure. This may be due to a high dispersion of solute on the support surface. This is further supported by particle size distribution study which shows uniform distribution of particles on the surface of the support. All particles fall in the range of 1–20 μm.

The FT-IR spectra of AH₂, AH₃, AH₄, AH₅ and AH₇ show bands at 803, 1077 cm⁻¹ and a shoulder at 910 cm⁻¹ corresponding to the symmetric stretching of (W–O–W), (P–O) and (W = O), respectively. These are in good agreement with those reported earlier [18] confirming the presence of these groups in the prepared materials. The peak at 1070 cm⁻¹ does not appear to be split into components at 1085 and 1040 cm⁻¹ assigned to [PW₁₁O₃₉]²⁻ ion. There is a slight shift in the FT-IR bands of AH₃₃ and AH₃₅ as compared to that of AH₃ indicating that the 12-tungstophosphoric acid keeps its keggin type structure up to 500 °C.

Electronic absorption spectra give information about the non-reduced heteropolyanion [19] due to ligand (oxygen) to metal charge transfer [20]. The DRS spectra of AH₃, AH₃₃, AH₃₅ are shown in Fig. 1. The spectra shows λ_{max} at 260 nm, which is in good agreement as reported earlier [18] suggesting the presence of the undegraded H₃PW₁₂O₄₀ species. In other words, the Keggin phase remains unaltered up to 500 °C.

3.1. Catalytic reaction

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 [21]. 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.

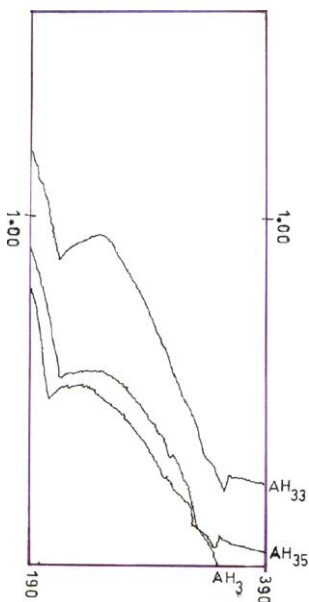


Fig. 1. DRS of AH₃, AH₃₃ and AH₃₅.

3.1.1. Esterification of *n*-butanol

The calculated percentage yield of butyl acetate with different molar ratio of alcohol to acid and with different amount of catalysts is shown in Tables 3 and 4.

The esterification of *n*-butanol with formic acid and propionic acid using AH₃, AH₄ and AH₅ is carried out under the same reaction conditions. The percentage yields of butyl formate and butyl propionate with different molar ratio of alcohol to acid are shown in Table 5.

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

butyl formate > butyl acetate > butyl propionate

Table 3
Percentage yield of butyl acetate

Name of catalyst	Amount of catalyst (g)	Percentage yield of butyl acetate ^a
AH ₂	0.25	22
	0.5	24
	1.0	33
AH ₃	0.25	42
	0.5	42
	1.0	49
AH ₄	0.25	28
	0.5	32
	1.0	35
AH ₅	0.25	40
	0.5	43
	1.0	47
AH ₇	0.25	45
	0.5	49
	1.0	54

Molar ratio of alcohol to acid is 1:2.

^a Yield based on alcohol.

Table 4
Percentage yield of butyl acetate

Name of catalyst	Amount of catalyst (g)	Percentage yield of butyl acetate ^a
AH ₂	0.25	40
	0.5	43
AH ₃	0.25	80
	0.5	80
AH ₄	0.25	60
	0.5	61
AH ₅	0.25	80
	0.5	82
AH ₇	0.25	80
	0.5	80

Molar ratio of alcohol to acid is 1:4.4.

^a Yield based on alcohol.

The percentage yield can be explained on the basis of the size of reacting acids. As the size/bulkyness 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 product. In case of formic acid the percentage yield of the ester is higher compared to the acetic acid and propionic acid. The presence of –CH₃ and –C₂H₅ groups in the latter two acids result in the decrease in the yield.

It is seen from Table 6 that AH₃ is the best among all.

Same reactions were carried out under same condition using AH₃₃ and AH₃₅. The percentage yield of butyl formate, butyl acetate and butyl propionate are listed in Table 6.

3.1.2. Esterification of cyclohexanol

The percentage yield of cyclohexyl acetate using AH₃, AH₃₃ and AH₃₅ are also listed in Table 6. It is seen from the table that AH₃₅ gives maximum yield.

The percentage yield of all esters, the value for surface area, total acidity, average particle diameter and total pore volume are listed in Table 7.

Increase in the average particle size and total pore volume of AH₃₃ as compare to that of AH₃ may be due to the loss of crystalline water from the structure of HPA anion by expanding the lattice. This loss takes place without any major change in the structure of supported heteropoly an-

Table 5
Percentage yield of butyl formate and butyl propionate

Name of catalyst	Yield of butyl formate ^a (%)		Yield of butyl propionate ^a (%)	
	1:2 ^b	1:4.4 ^b	1:2 ^b	1:4.4 ^b
AH ₃	54	85	32	32
AH ₄	54	68	26	28
AH ₅	54	83	33	33

Amount of the catalyst is 0.25 g.

^a Yield based on alcohol.

^b Molar ratio of alcohol to acid.

Table 6

Percentage yield (based on alcohol) of butyl formate, butyl acetate, butyl propionate and cyclohexyl acetate

Name of catalyst	Butyl formate ^a		Butyl acetate ^a		Butyl propionate ^a		Cyclohexyl acetate ^b	
	Yield (%)	TOF (min ⁻¹)	Yield (%)	TOF (min ⁻¹)	Yield (%)	TOF (min ⁻¹)	Yield (%)	TOF (min ⁻¹)
AH ₃	85	136	80	128	33	52.8	51	82.5
AH ₃₃	87	139	80	128	31	49.6	52	84.3
AH ₃₅	89	142	88	141	46	73.7	67	108.7
AH ₄	68	83.3	60	73.5	28	34.3	–	–
AH ₅	83	80.4	80	77	33	31.9	–	–

Amount of catalyst = 0.25 g.

^a Molar ratio of alcohol to acid is 1:4.4.^b Molar ratio of alcohol to acid is 1:3.

Table 7

Percentage yield of all esters, the value for surface area, total acidity, average particle diameter and total pore volume

Catalyst	Yield of esters (%)				Surface area (m ² /g)	Total acidity (mmol/g)	Average particle diameter (μm)	Total pore volume (cc/g)
	BF ^a	BA ^a	BP ^a	CA ^b				
AH ₃	85	80	33	51	109	0.76	4.2	0.186
AH ₃₃	87	80	30	52	112	0.68	5.4	0.188
AH ₃₅	89	87	46	68	83	1.14	5.2	0.134

Amount of catalyst = 0.25 g. BF: butyl formate; BA: butyl acetate; BP: butyl propionate; CA: cyclohexyl acetate.

^a Molar ratio of alcohol to corresponding acid is 1:4.4.^b Molar ratio of alcohol to corresponding acid is 1:3.

ion which is in good agreement with TGA which does not show any break/weight loss up to 600 °C. Due to the loss of crystalline water, the total acidity decreases which is expected. On strong heating (AH₃₅) there may be generation of Lewis acidity on alumina which results in an increase in the total acidity. It is seen from Table 7 that the total acidity of AH₃₅ is almost double than that of AH₃ but percentage yield of esters are not doubled. This may be due to the fact that esterification reactions are mainly catalysed by Bronsted acidity. It is also found that there is decrease in the pore volume as well as average particle diameter of AH₃₅. This may be due to the contraction of the empty lattice of supported HPA. It is also observed from the table that catalytic activity is proportional to the total acidity and it is not related to the surface area of the catalyst. This is in good agreement with the pseudoliquid-bulk I type catalyst in which catalytic activity is proportional to the total acidity of the catalyst [22].

The optimum conditions for the present reactions using AH₃₅ are as follows:

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

The catalyst (AH₃₅) 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 use of AH₃₅ as a solid acid catalyst has advantages of better activity, short reaction time, simple distillation of ester products, low reaction temperature and without requirement of post treatment, no corrosion and no

contamination. Besides the catalyst can be regenerated and reused.

4. Conclusion

FT-IR and electronic spectra shows that the 12-tungstophosphoric acid keeps its Keggin type structure when supported onto neutral alumina. TGA and DSC studies indicate that the supported structure does not get disturbed up to 600 °C. It is found that the catalyst containing 30% PW and calcinated at 500 °C (AH₃₅) is best among all. The catalyst AH₃₅ has been proved to be successful and useful catalyst in the esterification of 1° and 2° alcohol under mild conditions as compared to that of traditional liquid catalyst. The catalytic activity of the catalyst is correlated with the total acidity. It can be concluded that the present catalyst is not 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 catalytic activity is directly proportional to the total acidity of the catalyst.

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