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Supported Heteropolyacids: Sytnhesis, Characterization and Effect of Supports on Esterification Reactions[1]

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Abstract—12-Tungstophosphoric acid supported onto silica was synthesized by impregnation. The supports and synthesized catalysts were characterized for chemical stability, ion exchange capacity, thermogravimetric analysis, differential scanning calorimetry, FT-IR, and BET surface area. The catalytic activity was evaluated for liquid phase esterification reactions. The catalyst was regenerated and reused. The best catalyst was calcined at different temperatures and its catalytic activity was also evaluated for esterification reactions under optimized conditions. Further, obtained results are compared with 12-tungstophosphoric acid supported onto zirconia in order to see effect of acidic nature of support on catalytic activity as well as thermal stability of the catalyst.

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In recent times supported heteropolyacids (HPAs) have been gaining importance as acid catalyst, especially for reactions of esterification [1–6], alkylation [7–12] and acylation [8, 13–16], as they posses a number of advantages such as high catalytic activity and selectivity, high surface area, high thermal stability over traditional corrosive and hazardous liquid acid catalyst, easy separation from reaction mixture and possibility of their repeated use.

In case of supported HPAs, it is known that support does not play always merely a mechanical role but it can also modify the catalytic properties of the HPAs. Various supports (see [5, 6]) have been used for supporting HPAs. As a contribution towards the same, we have established the use of 12-tungstophosphoric acid (TPA) supported onto Al_2O_3 (neutral support) and ZrO_2 (acidic support) for some organic reactions such as esterification of primary and secondary alcohols [17], *tert*-butylation of phenols and cresols [18, 19]. The obtained promising results encouraged us to explore the catalytic activity of TPA supported onto SiO_2, more acidic support than ZrO_2. The main aim of present work is to see the effect of more acidic support (SiO_2) on catalytic activity as well as on thermal stability of TPA.

The present work consists of synthesis and characterization of TPA supported onto SiO_2. The support and catalysts were characterized for chemical stability, ion exchange capacity, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), FT-IR, and BET surface area. The catalytic property was evaluated for the esterification of primary alcohols (ethanol, *n*-propanol, *n*-butanol) with acetic acid. The best catalyst was calcined at different temperatures (300, 400, and 500°C) and evaluated for esterification reactions under optimized conditions. To see the effect of support, the obtained results are compared with TPA supported onto ZrO_2. The difference in the catalytic activity was correlated with the nature of support.

EXPERIMENTAL

Materials

All chemicals used were of A.R. grade. $H_3PW_{12}O_{40} \cdot nH_2O$ "Lobachemie," Mumbai) and silica (60–120 mesh size "SD Fine Chemicals," Mumbai) was used as received. Ethanol, propanol, *n*-butanol, and glacial acetic acid were obtained from "Merck" and used as received.

Synthesis of the Catalyst

TPA was supported onto SiO_2 by impregnation method. A catalyst containing 30% TPA was synthesized by impregnating 1 g of SiO_2 with an aqueous solution of TPA (0.3 g/30 ml of bidistilled water) with stirring for 35 h and dried at 100°C for 10 h. The obtained material was designated as TPA_3/SiO_2.

The same process was followed for the synthesis of series of supported TPA containing 20 and 40% of TPA (0.2 or 0.4 g, 20 or 40 ml of bidistilled water). The obtained materials were designated as TPA_2/SiO_2 and TPA_4/SiO_2, respectively. The best catalyst TPA_3/SiO_2 was calcined at 300, 400, and 500°C in air for 5 h and the resulting materials were designated as

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C_3-TPA_3/SiO_2, C_4-TPA_3/SiO_2, and C_5-TPA_3/SiO_2, respectively.

Characterization

Detail characterization of TPA_3/ZrO_2 can be found in our earlier publications [17, 20]. The present study includes detail characterization of TPA supported onto SiO_2. Different mineral acids and bases were used for checking the chemical stability of the material.

The ion exchange capacity (IEC) was determined by using the following formula:

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

Thermogravimetric analysis of the samples was carried out on METTLER TOLEDO STAR SW 7.01 instrument. Differential scanning calorimetry of the samples was carried out on METTLER S RSW810. The FT-IR spectra of the samples (fresh and calcined) were obtained by using KBr wafer on Perkin–Elmer spectrometer. Adsorption–desorption isotherms of samples were recorded on a Micromatries ASAp 2010 surface area analyzer at –196°C. From adsorption–desorption isotherms surface area was calculated using BET method.

Esterification Reactions

The esterification reaction was carried out in a 50 ml glass reactor provided with a double walled air condenser, Dean–Stark apparatus, magnetic stirrer and a guard tube. Dean–Stark apparatus was attached to a round bottom flask to separate the water formed during the reaction. The reaction mixture was heated at 80°C for 4 h. The obtained esters were analyzed on a gas chromatograph (Nucon-5700) using a Carbowax 20 column. Turnover number (TON) is defined as mole substrate reacted per mole of the catalyst and was calculated using following formula:

$$\text{TON} = \frac{\text{numbers of moles of substrate reacted}}{\text{number of moles of catalyst}}.$$

RESULTS AND DISCUSSION

Characterization of Catalysts

The catalyst comprising TPA supported onto ZrO_2 was synthesized in our laboratory and well characterized by us earlier. From our earlier study, it was found that catalyst containing 30% loading of TPA onto ZrO_2 was the best. The main characterization of TPA_3/SiO_2 and TPA_3/ZrO_2 like ion exchange capacity, surface area measurement and thermal stability are presented in Table 3.

Chemical stability of material plays an important role. The material having solubility in water and/or in acidic media may not be very useful as a catalyst. Therefore the chemical stability of the material has been checked in different mineral acids (HCl, H_2SO_4, HNO_3) and bases (NaOH, Na_2CO_3) up to 4 M concentration. The present catalyst TPA_3/SiO_2 shows no change in color or form indicating their stability.

Table 1. Ion exchange capacity (IEC) values of the catalysts

Catalyst	IEC, meq/g
SiO_2	0.21
TPA_2/SiO_2	0.57
TPA_3/SiO_2	0.62
TPA_4/SiO_2	0.69

Table 1 shows values of ion exchange capacity. These values give an idea about the acidity of materials. It is an indirect way to determine the Brønsted acidity of materials. It is observed from the Table 1 that value of IEC increases as the amount of TPA supported onto SiO_2 increases.

In order to check the stability, the catalyst was studied for thermogravimetric analysis. The TGA of TPA (Fig. 1) shows initial weight loss up to 210°C is due to loss of adsorbed water and water of crystallization. After that there is no weight loss up to 475°C. The weight loss between 475 to 500°C may be due to the decomposition of TPA. The TGA of TPA_3/SiO_2 shows 6.6% weight loss within 50–100°C temperature range which is due to loss of adsorbed water and there is no appreciable change in weight till 500°C indicating increase in the stability of the TPA. This decrease in percentage weight loss indicates the presence of chemical interaction between the support, SiO_2 and TPA.

This can be further supported by DSC. DSC of TPA_3/SiO_2 (Fig. 2) shows an endothermic peak in the region of 80–100°C indicating the loss of adsorbed water molecule. The DSC of TPA_3/SiO_2 did not show any endothermic peak up to 500°C indicating no decomposition of supported material. TGA and DSC

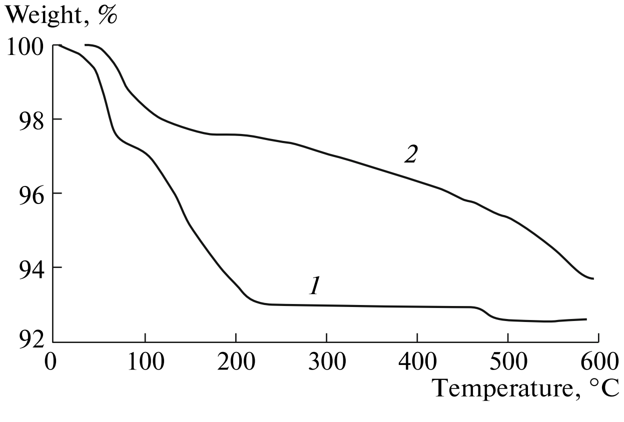

Fig. 1. TGA of TPA (*1*) and TPA_3/SiO_2 (*2*).

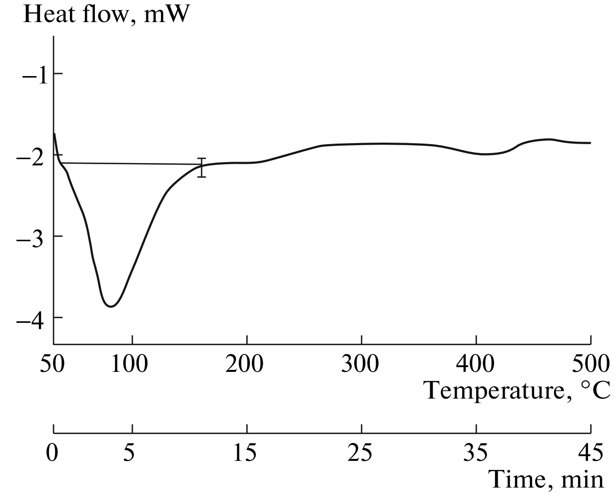

Fig. 2. DSC of TPA_3/SiO_2.

indicate that TPA is thermally stable up to 500°C when supported onto silica.

FT-IR spectrum of SiO_2 (Fig. 3a) shows broad band at of 3464 cm^{-1} attributed to asymmetric hydroxo (–OH) stretches and two bending vibrations at 1636 and 1370 cm^{-1} corresponding to H–O–H and O–H–O, respectively. In addition to these bands, FT-IR spectrum of TPA_3/SiO_2 (Fig. 3a) shows bands at 1088, 987 and 800 cm^{-1} which correspond to W–O–W bending, W–O and P–O symmetric stretching, respectively. The positions are in good agreement with those reported earlier [21, 22]. Further, no appreciable shifting in the band positions (Fig. 3b) of calcined catalyst (C_3-TPA_3/SiO_2, C_4-TPA_3/SiO_2, C_5-TPA_3/SiO_2) were observed as compared to TPA_3/SiO_2, indicating that the TPA keeps its Keggin type structure undegraded up to 500°C when supported onto SiO_2.

The values of BET surface area of SiO_2 and TPA_3/SiO_2 were found to be 500 and 234 m^2/g, respectively. It is known [23] that there may be decrease in the surface area in case of the supported catalyst in which oxides are used as supports. Decrease in surface area [24] could be explained due to support pore blocking by active phase.

Esterification Reactions

Esterification is a straight forward reaction subjected to general Brønsted acid catalysis. The yields can be increased by increasing the concentration of either alcohol or acid. In a practical means, it is desirable to obtain maximum yield for economic reasons, the reactant that is usually less expensive is taken in excess. In present study corresponding acid is taken in excess.

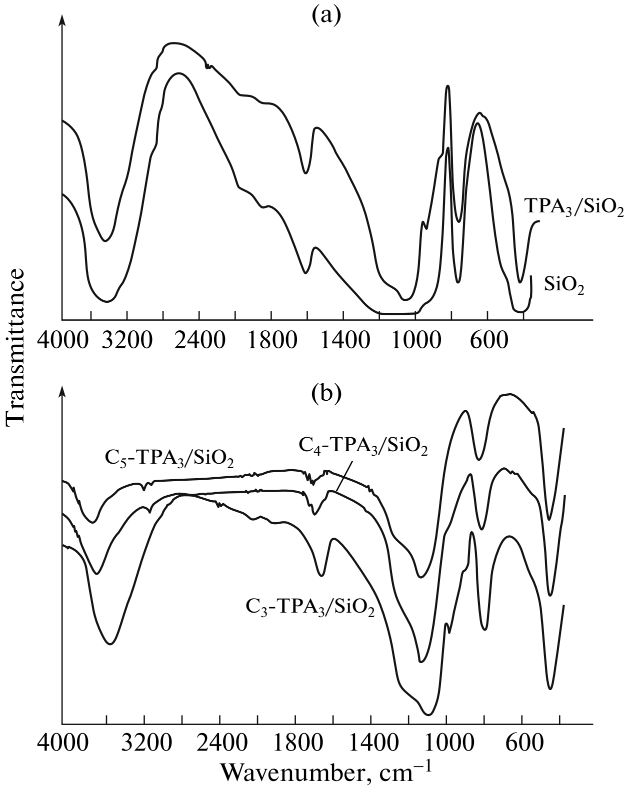

Fig. 3. (a) FT-IR spectra of SiO_2 and TPA_3/SiO_2; (b) FT-IR spectra of C_3-TPA_3/SiO_2, C_4-TPA_3/SiO_2, and C_5-TPA_3/SiO_2.

Esterification of n-Butanol

Effect of loading of TPA onto SiO_2. The esterification reaction was carried out with TPA_2/SiO_2, TPA_3/SiO_2, and TPA_4/SiO_2. The obtained results are shown in Fig. 4. It is observed from the Fig. 4 that with increase in the loading of TPA onto SiO_2, the yield also increases. For 30 and 40% loading, the difference in yields is not that much appreciable. This may be due to the blocking of active sites. Hence, the catalyst containing 30% of TPA was used for the detail study.

Effect of molar ratio of *n*-butanol to acetic acid. The reaction was carried out by varying molar ratio of *n*-butanol to acetic acid, with 0.25 g of the catalyst for 4 h at 80°C. It is observed that with increase in concentration of acid the yield of the product increases. With 1 : 2 molar ratio of *n*-butanol to acetic acid the yield of butyl acetate was found to be 52% while with 1 : 4.4 molar ratio was found to be 70%. Hence, further reactions were carried out in 1 : 4.4 molar ratio of alcohol to acid.

Effect of amount of catalyst (TPA_3/SiO_2). To study the effect of the amount of the catalyst, the reaction was carried out with different amounts of the catalyst keeping the molar ratio of alcohol to acid 1 : 4.4 for 4 h at 80°C. The yield of butyl acetate is reported in Fig. 5. It is seen that initially the activity increases with an

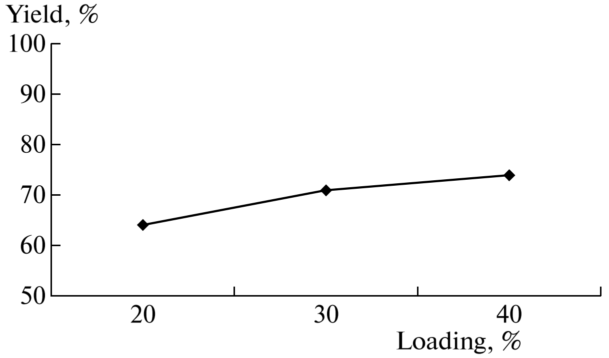

Fig. 4. The yield of butyl acetate with different catalysts (molar ratio of alcohol to acid is 1 : 4.4).

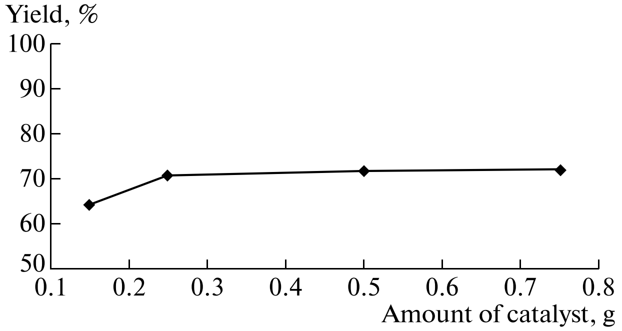

Fig. 5. The yield of butyl acetate with TPA_3/SiO_2 catalyst (molar ratio of alcohol to acid is 1 : 4.4).

increase in the amount of the catalyst. On further increase with the amount from 0.25 to 0.75 g of the catalyst, almost 71–72% yield of ester was obtained. The effect of the amount of the catalyst was studied keeping all other parameters (temperature, reaction time, molar ratio of alcohol to acid) constant. Under these conditions, no increase in the yield with increase in amount of catalyst indicates the attainment of the maximum equilibrium. The obtained results are as expected. Hence, 0.25 g is the optimized amount of the catalyst.

The optimum conditions for esterification of *n*-butanol using TPA_3/SiO_2 are: molar ratio of alcohol to acid is 1 : 4.4; amount of catalyst, 0.25 g; reaction temperature, 80°C and reaction time, 4 h.

The butyl acetate yield over the calcined catalysts C_3-TPA_3/SiO_2, C_4-TPA_3/SiO_2, and C_5-TPA_3/SiO_2 under optimized conditions was 74, 76, and 78%, respectively.

Recycling of the catalyst. The catalyst was recycled in order to test its activity as well as stability. The catalyst was separated from the reaction mixture only by simple filtration, washed with conductivity water till the filtrate is free from the acid, dried at 100°C and the recovered catalyst was charged for the further run. There is no appreciable change in the yield of butyl acetate using regenerated catalyst up to four cycles. Hence, the catalyst can be reused and regenerated.

Esterification of Various Alcohols Using TPA_3/SiO_2 As Catalyst

The esterification of other alcohols such as *n*-propanol and ethanol with acetic acid was also carried out under optimized conditions and the yields of corresponding esters are shown in the Table 2.

The order of catalytic activity is ethyl acetate < propyl acetate < butyl acetate. The activities of alcohols were increased as the carbon chain of the alcohols grew longer. This could be explained due to the effect of OH-group location in long chain alcohols which is more exposed towards active sites of the catalyst. In terms of turnover number, it is also seen from Table 2 that TPA_3/SiO_2 was proved to be more efficient catalyst for long chain alcohols.

Effect of the Support

TPA was supported onto two different supports, SiO_2 and ZrO_2. As the active species, TPA is the same, same catalytic activity is expected. But it is seen from Table 3 that TPA supported onto SiO_2 is more active as compared to that of ZrO_2. The obtained difference in catalytic activity may be due to the nature of support. It is known that IEC is an indirect method of measuring Brønsted acidity and it involves exchange of ions on the surface. The IEC values for SiO_2 and ZrO_2 were found to be 0.21 and 0.16, respectively. It is interesting to note that even though SiO_2 is more acidic than ZrO_2 the IEC for TPA_3/SiO_2 and TPA_3/ZrO_2 is the same (Table 3) at equal concentration of TPA. This may be due to the fact that exchange of ions occurs only from the same surface species, i.e., from TPA for both supports.

Esterification reactions are purely Brønsted acid catalyzed reactions. As mentioned earlier, support may also play a role in modifying the catalytic activity of HPAs. As SiO_2 is more acidic than ZrO_2, higher catalytic activity is expected in case of TPA_3/SiO_2. The results are as expected. The turnover numbers measured also suggested that TPA_3/SiO_2 was more active

Table 2. The yields of different esters using TPA_3/SiO_2^*

Name of alcohol	Name of ester	Yield of ester, %	TON
Ethanol	Ethyl acetate	60	2985
n-Propanol	Propyl acetate	66	3280
n-Butanol	Butyl acetate	71	3545

* Amount of catalyst 0.25 g, molar ratio 1 : 4.4, reaction temperature 80°C, reaction time 4 h.

Table 3. Main characteristics of TPA_3/SiO_2 and TPA_3/ZrO_2

Catalyst	Thermal stability (TGA), °C	IEC, meq/g	Surface area, m^2/g	Yield of butyl acetate, %	TON
TPA_3/SiO_2	500	0.62	234	71	3545
TPA_3/ZrO_2	430	0.62	146	53	2650

catalyst than TPA_3/ZrO_2 since higher TON are expected for more efficient catalyst.

Surface area of catalyst also plays an important role in catalytic reactions. The surface area of SiO_2 is higher than that of ZrO_2. Increase in surface area may be due to the nature of support. The higher value of surface area for TPA_3/SiO_2 as compared to that of TPA_3/ZrO_2 is also responsible for higher catalytic activity.

Thermal stability of the catalyst at higher temperature decides its applicability in extreme conditions. The thermal stability of TPA increases from TPA_3/ZrO_2 to TPA_3/SiO_2 as observed from TGA and DSC results. This increased thermal stability of TPA on SiO_2 could be explained due to the nature of support.

Thermal study shows that the TPA keeps its Keggin structure undegraded up to 500°C when supported on SiO_2. The present catalyst is proved to be successful in esterification of primary alcohols under mild conditions as compared with the traditional liquid acid catalyst. The TPA_3/SiO_2 was found to be more active as compared to TPA_3/ZrO_2. The difference in the catalytic activity may be due to the more acidic nature of SiO_2 than ZrO_2.

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