Zirconia supported undecatungstophosphate: synthesis and characterization of a bifunctional catalyst†

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The synthesized supported undecatungstophosphate has been proven to be successful for acid catalyzed as well as oxidation reactions, especially, in obtaining 98.5% conversion of styrene and 100% selectivity for benzaldehyde.

In recent times, the use of polyoxometalates (POMs) has become a very important research area. Lacunary POMs ($XM_{11}O_{39}{}^{(n+4)-}$, $XM_{10}O_{32}{}^{(n+5)-}$, where X = Si, P; $n = 4, 3$; M = Mo(VI), W(VI)), which are formed by the removal of one or more of the MO octahedra from the fully occupied POMs ($XM_{12}O_{40}{}^{n-}$) have also gained much attention in the area of acid and oxidation catalysis.

The catalytic evaluation of the lacunary POMs has been reported by Neumann *et al.*[1] as well as Hill and co-workers.[2] Especially, detailed studies have been carried out on oxidation reactions[3–6] using lacunary silicotungstates by Mizuno *et al.* The acid catalysis over silicotungstates has also been reported by the same group.[6] Thus, most of the work has been reported on lacunary silicotungstates, and studies on the lacunary phosphotungstates[7] are very scarce. Moreover, it has been also observed that no literature is available on the catalytic aspects of supported lacunary polyoxometalates.

In the present communication, for first time, we report the synthesis, characterization and bifunctional catalysis of novel mono lacunary undecatungstophosphate, $(PW_{11}O_{39})^{7-}$ (LPW), supported on zirconia (ZrO_2). Its bifunctional catalytic activity has been evaluated for acid catalyzed as well as oxidation reactions.

The synthesized sodium salt of LPW has been characterized by TGA, DSC, FT-IR and ^{31}P solution as well as ^{31}P MAS NMR.‡ The frequencies of the FT-IR bands (Fig. S3, ESI†) are in good agreement with those previously reported.[7d] The solution ^{31}P NMR spectra of the undecatungstophosphate shows a chemical shift value of −10.6 ppm which is in good agreement[7a] with the formula $[PW_{11}O_{39}]^{7-}$ and indicates the formation of the Keggin structure with a vacancy created by the removal of one of the corner as well as the edge shared tungstate octahedra. ^{31}P MAS NMR spectra for the LPW shows an intense peak at −11.30 ppm. The observed shift in MAS NMR as compared to that of solution NMR is as expected.

The synthesized catalyst was studied for its chemical stability and it did not show any leaching. The FT-IR spectra for the ZrO_2, LPW, LPW_2/ZrO_2 are shown in Fig. S3 of the ESI.† The FT-IR spectra for the ZrO_2 (Fig. S3 (a), ESI†) show all the expected bands as reported earlier by us.[8] The FT-IR spectra of LPW_2/ZrO_2 (Fig S3 (b), ESI†) shows bands at 746 cm^{-1}, 952 cm^{-1}, and at 1097 and 1048 cm^{-1} corresponding to the symmetric stretching of W–O–W, W=O and P=O bonds respectively. The positions are in good agreement with those of LPW, which has been reported earlier[7d] confirming the presence of these groups in the synthesized materials.

The ^{31}P MAS NMR for LPW_2/ZrO_2 reveals two resonances, one at −3.98 ppm and another at −11.95 ppm. The peak at −3.98 ppm reveals the presence of a strongly adsorbed highly fragmented Keggin unit, while peak at −11.95 ppm indicates the presence of an adsorbed, partially fragmented Keggin unit. This observation agrees well with the related previous report.[9]

TGA of LPW shows 8% weight loss in the temperature range 100–150 °C due to the loss of crystalline water. It also shows 2% weight loss at 400 °C. This may be due to the decomposition of the Keggin structure. TGA of LPW_2/ZrO_2 shows 16% weight loss in the temperature range 70–100 °C due to loss of adsorbed water. It does not show any weight loss up to 475 °C, indicating the synthesized catalyst is stable up to 475 °C. The DSC of LPW_2/ZrO_2 shows an endothermic peak at 100 °C indicating the loss of adsorbed water. It also shows an exothermic peak at 470 °C which may be due to some phase change or decomposition of the Keggin ion. The TGA and DSC studies show an increase in the stability of LPW after being supported on ZrO_2.

The XRD pattern of LPW_2/ZrO_2 shows the amorphous nature of the materials indicating that the crystallinity of the LPW is lost on supporting it onto ZrO_2. Further, it does not show any diffraction lines of lacunary LPW indicating a very high dispersion of solute as a non-crystalline form on the support surface. The increase in the value of the BET surface area for the LPW_2/ZrO_2 (260.6 m^2 g^{-1}) as compared to that of ZrO_2 (170.0 m^2 g^{-1}) is as expected.

The synthesized catalyst was evaluated for esterification as well as for oxidation reactions. The esterification reaction of *n*-butanol with acetic acid (mole ratio 1 : 4.4) 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. The resultant mixture was heated at 80 °C for 4 h. Dean–Stark apparatus was attached to a round bottom flask to separate the water formed during the reaction. The same reaction was carried out by changing the corresponding acid concentration with different amounts of the catalyst. For esterification of isobutanol, 2-butanol and cyclohexanol the used mole ratio of alcohol to acid was 1 : 4.4, 1 : 4.4 and 1 : 3, respectively. The obtained esters were analysed on a Gas Chromatograph (Nucon-5700) using a Carbowax 20 column.

Fig 1 shows the results for the % conversion of n-butyl acetate. LPW indicates the amount of the active species on the catalyst, which is 25 mg, 41.6 mg and 81.3 mg for the corresponding 0.15 g, 0.25 g and 0.5 g catalyst. It is seen that LPW_2/ZrO_2 is the best of

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† Electronic supplementary information (ESI) available: Fig. S1: TGA; Fig. S2: DSC; Fig. S3: FT-IR; Fig. S4: solution ^{31}P NMR; Fig. S5: ^{31}P MAS NMR; Fig. S6: XRD. See DOI: 10.1039/b804788j

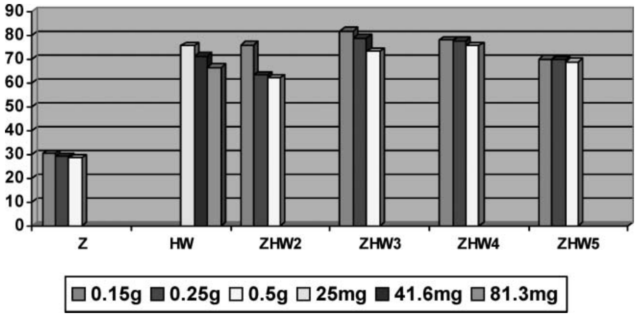


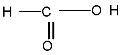
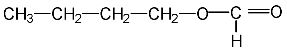
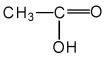
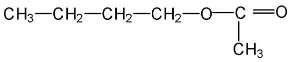
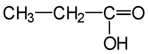
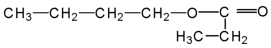
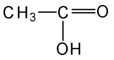
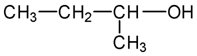
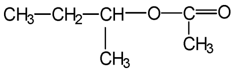
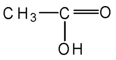
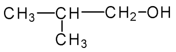
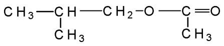
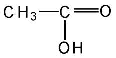
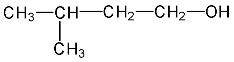
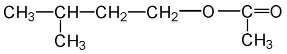
Fig. 1 Percentage (%) conversion of butyl acetate with different catalysts with different amounts and % loading. Mole ratio of alcohol to acid is 1 : 4.4. Z= ZrO_2, HW = LPW, ZHW_2= LPW_2/ZrO_2, ZHW_3 = LPW_3/ZrO_2, ZHW_4 = LPW_4/ZrO_2, ZHW_5 = LPW_5/ZrO_2.

all. The study on the effect of mole ratio of alcohol to acid was also carried out and it was found that the 1 : 4.4 mole ratio gives optimum results. The esterification of all other alcohols has been carried out under optimized conditions. The % yield for all esters is presented in Table 1.

A study has also been carried out to see the effect of temperature on the catalyst structure as well as the catalytic activity. The catalyst was calcined and characterized for FT-IR to see any structural change of supported LPW species as well as the effect of calcinations on catalytic activity. The FT-IR spectra of LPW_{22}/ZrO_2, LPW_{23}/ZrO_2, LPW_{24}/ZrO_2 are also shown in Fig. S3 (b), ESI.† The position of all the bands is almost at the same frequency as in catalyst LPW_2/ZrO_2 indicating that the LPW keeps its Keggin type structure up to 400 °C. In order to see the effect of calcination on catalytic activity all calcined catalysts have been evaluated for esterification of n-butanol and acetic acid under optimized conditions. The %yield is 75.4%, 73% and 72.6%

Table 1 Catalytic activity evaluation for LPW_2/ZrO_2

Acid catalyzed esterification reaction[a]

Acid	Alcohol	Ester	%Yield/TON
 $H-\underset{\| \atop O}{C}-O\,H$	$CH_3-CH_2-CH_2-CH_2-OH$	 $CH_3-CH_2-CH_2-CH_2-O-\underset{H}{C}=O$	68.24/8384.47
 $CH_3-\underset{OH}{C}=O$	$CH_3-CH_2-CH_2-CH_2-OH$	 $CH_3-CH_2-CH_2-CH_2-O-\underset{CH_3}{C}=O$	76.31/9376.36
 $CH_3-CH_2-\underset{OH}{C}=O$	$CH_3-CH_2-CH_2-CH_2-OH$	 $CH_3-CH_2-CH_2-CH_2-O-\underset{H_3C-CH_2}{C}=O$	50.35/6186.60
 $CH_3-\underset{OH}{C}=O$	 $CH_3-CH_2-\underset{CH_3}{CH}-OH$	 $CH_3-CH_2-\underset{CH_3}{CH}-O-\underset{CH_3}{C}=O$	41.56/5106.56
 $CH_3-\underset{OH}{C}=O$	 $CH_3-\underset{CH_3}{CH}-CH_2-OH$	 $CH_3-\underset{CH_3}{CH}-CH_2-O-\underset{CH_3}{C}=O$	73.71/9056.90
 $CH_3-\underset{OH}{C}=O$	 $CH_3-\underset{CH_3}{CH}-CH_2-CH_2-OH$	 $CH_3-\underset{CH_3}{CH}-CH_2-CH_2-O-\underset{CH_3}{C}=O$	66.42/8161.15

Oxidation of alkenes[b]

Substrate	Products	% Conversion	% Selectivity/TON
Styrene	Benzaldehyde	98.50	100.0/7273.37
Cyclohexene[c]	—	No significant conversion	—
cis-cyclooctene[c]	—	No significant conversion	—

[a] Amount of the catalyst = 0.15 g; alcohol : acid ratio = 1 : 4.4; reaction temperature = 80 °C; reaction time = 4 h; amount of the active LPW on the support = 0.025 g. [b] Amount of the catalyst = 25 mg; alkene : H_2O_2 = 1 : 3; reaction temperature = 80 °C. [c] 50 °C; reaction time = 48 h; amount of active LPW on the support = 4.16 mg.

Table 2 % Yield of different esters with the recycled catalysts

	% Yield						
Catalyst	Butyl formate	Butyl acetate	Butyl propionate	Isobutyl acetate	Sec-butyl acetate	Isoamyl acetate	Cyclohexyl acetate
Fresh catalyst	68.24	76.31	50.35	73.71	41.56	66.42	43.20
1st cycle	67.90	76.04	49.91	73.22	40.94	66.11	43.02
2nd cycle	65.1	73.4	46.7	70.61	38.38	63.05	40.10
3rd cycle	65.06	73.00	46.03	70.06	38.13	63.01	40.05
4th cycle	65.00	73.02	46.07	70.01	38.11	63.01	40.03

for LPW_{22}/ZrO_2, LPW_{23}/ZrO_2 and LPW_{24}/ZrO_2 respectively. No appreciable change in % yield indicates the stability of the catalyst up to 400 °C.

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 filtration, washed with conductivity water till the filtrate was free from the acid, dried at 100 °C in an oven for 5 h and the recovered catalyst was charged for the further run. The obtained results are as shown in Table 2. It can be seen that the catalyst can be used for up to four cycles without any appreciable change in the % yield.

In order to study the bifunctional nature of the synthesized catalyst, the oxidation reaction was considered to be an ideal one. Oxidation of alkenes was carried out in a three necked flask provided with a double walled condenser containing catalyst, alkene (10 mmol) and aqueous H_2O_2 (30 mmol) at 80 °C with constant stirring for 48 h. The temperature was maintained at 80 °C in an oil bath. The reaction was carried out by varying different parameters such as mole ratio of alkene to H_2O_2, amount of catalyst, temperature and reaction time to optimize the conditions. After completion of the reaction, the catalyst was removed and the product extracted with dichloromethane. The product was dried with magnesium sulfate and analyzed on a Nucon Gas Chromatograph using a SE-30 column. Products formed after completion of reactions were analyzed by gas chromatography using a SE-30 column. Product identification was done by comparision with authentic samples and finally by combined gas chromatography mass spectrometry. The conversion as well as selectivity under optimized conditions is presented in Table 1. The present study indicates that the synthesized catalyst is selective for oxidation of styrene.

The Na salt of LPW is expected to exist in the dissociated form in aqueous solution *i.e.* as Na^+ and anionic LPW. This Na^+ is replaced by H^+ from the aqueous medium *in situ*. Apart from H^+, tungsten can also contribute to the acid catalyzed reactions. The role of tungsten in acid catalyzed reactions has also been reported by Mizuno *et al.*[6]

In conclusion, we have introduced a novel bifunctional solid catalytic system comprising mono lacunary undecaphosphotungstates and zirconia. The catalyst has been proved to be successful for acid catalyzed as well as oxidation reactions. The superiority of the present catalyst lies, especially, in obtaining 98.5% conversion of styrene and 100% selectivity for benzaldehyde. Further, the amount of active species required is very small (4.16 mg) for the same reactions. The introduced catalyst is not only selective, for oxidation of styrene, but is also a promising alternative for traditional acid catalysts.

Acknowledgements

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Notes and references

‡ Catalyst synthesis has been carried out in three steps. The first and second step involves the synthesis of the mono lacunary undecatungstophosphate (LPW)[7c] and hydrous zirconia (ZrO_2)[8] following the methods reported previously. The third step involves the supporting of the LPW on ZrO_2. A series of catalysts containing 20–50% LPW were synthesized by impregnating ZrO_2 (1 g) with an aqueous solution of LPW (0.2–0.5 g in 20–50 mL of conductivity water) and dried at 100 °C for 10 h. The obtained materials were designated as LPW_2/ZrO_2, LPW_3/ZrO_2, LPW_4/ZrO_2 and LPW_5/ZrO_2. (The numerical subscript after W corresponds to the % loading of LPW onto the surface of support, *e.g.* LPW_2/ZrO_2 means 20% loading of LPW onto zirconia.) The selected best catalyst (LPW_2/ZrO_2) was calcinated at 200, 300 and 400 °C in air for 5 h and designated as LPW_{22}/ZrO_2, LPW_{23}/ZrO_2 and LPW_{24}/ZrO_2 respectively. The synthesized LPW as well as the catalysts have been characterized by TGA, DSC, FT-IR, solution ^{31}P NMR and ^{31}P MAS NMR, BET surface area and XRD.

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