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12-Tungstophosphoric acid/zirconia—a highly active stable solid acid—comparison with a tungstated zirconia catalyst†

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A highly active and stable zirconia supported 12-tungstophosphoric acid catalyst is found to be 2–3 times more active in benzylation and acylation reactions than a tungstated zirconia catalyst.

Metal oxides promoted by sulfur compounds; especially SO_x-promoted zirconia[1] containing iron and manganese oxides as promoters have recently attracted much attention owing to their catalytic performances in reactions such as hydrocarbon isomerization, alkylation, acylation, *etc*.[2] Their poor stability, tendency to form volatile sulfur compounds during catalysis and regeneration by oxidation limit their applicability.[3] Tungstated zirconia, WO_x/ZrO_2 (WZ) is found to be an alternative stable solid acid catalyst,[4,5] but has lower activity than sulfated zirconia.[6] Although Fe and Mn oxides promote catalytic activity of sulfated zirconia they do not promote tungstated zirconia.[7] Thus there is a clear need for the development of a highly active and stable solid acid catalyst.

In the present work, a series of catalysts with different 12-tungstophosphoric acid [$H_3PW_{12}O_{40}\cdot 21H_2O$ (12-TPA)] loadings were prepared by the wet impregnation method using zirconia as the support. Tungstated zirconia catalysts were prepared for comparison with 12-TPA/ZrO_2 catalysts. A direct correlation between surface structure and catalytic activity is reported.

The state of 12-TPA on the catalysts was elucidated by ^{31}P MAS NMR spectroscopy (Bruker DSX-300 spectrometer) and crystallographic identification of the samples were performed using X-ray powder diffraction with Cu-Kα radiation (Rigaku Model D/MAXIII VC, Japan, λ = 1.5418 Å). Acidity and acid strength distribution of tungstated zirconia and catalysts with different TPA loadings were measured by TPD of ammonia. Brönsted and Lewis acidity of catalysts with different TPA loadings were monitored by pyridine adsorption FT-IR spectroscopy (NICOLET MODEL 60SXB, 4 cm^{-1} resolution and averaged over 500 scans). To assay the acidity and catalytic activities of the solid acid catalysts, benzylation of phenol with benzyl alcohol ($PhCH_2OH$) and acylation of 2-methoxynaphthalene (2-MN) with acetic anhydride (Ac_2O) were used as the probe reactions.

Catalysts were prepared by wet impregnation of zirconia in a methanolic solution of 12-TPA. The zirconia support was prepared by the hydrolysis of an aqueous solution of zirconyl chloride with a 10 M ammonia solution and the precipitate was washed free of chloride and dried at 393 K for 24 h. A series of catalysts were prepared by suspending a known amount of dried zirconia in a methanolic solution of 12-TPA (4 ml methanol for 1 g of dried zirconia). This mixture was stirred in a rotary evaporator for 8–10 h followed by evaporation to dryness. The resulting samples were dried at 393 K for 24 h, powdered and calcined at 1023 K in air for 4 h. Catalysts with different TPA loadings (5–30 wt% of dried zirconia) were prepared by changing its concentration. Similarly, catalysts with optimum TPA loading (15 wt%) were prepared using different solvents as well as without solvent (neat–physical mixture). Tungstated zirconia (12.6 or 15 wt% W) was also prepared using tungstic acid dissolved in ammonia as the precursor. The properties of the catalysts with different TPA loadings prepared in methanol and that of tungstated zirconia calcined at 1023 K are presented in Table 1.

^{31}P MAS NMR spectra of 5 and 10 wt% TPA/ZrO_2 catalysts exhibit a peak at −12 ppm.‡ All other catalysts with different TPA loadings showed an additional peak at −30 ppm. The peak at −12 ppm (P–OH) is due to the presence of phosphorus in the Keggin unit[8] and the peak at −30 ppm is due to the presence of phosphorus in the decomposition product.[9]

The acidity of the catalysts with different TPA loadings and that of tungstated zirconia were measured by TPD of ammonia.§ TPD of NH_3 shows that the surface concentration of acid sites *i.e.* acidity (NH_3 nm^{-2}) increases with TPA loading and reaches its maximum for a 15 wt% TPA/ZrO_2 catalyst (Table 1). The maximum concentration of acid sites was observed at a surface density[6] of 7.2 W nm^{-2}, where a TPA monolayer completely covered the surface. Although the P–OH intensity is 100% in 5 and 10 wt% TPA/ZrO_2 and 80% in 15 wt% TPA/ZrO_2 (Table 1), the actual amount of TPA in its Keggin form is at a maximum for the latter catalyst and hence it shows the highest acidity. The acidity decreases when the TPA loading exceeds monolayer coverage (15 wt% TPA loading). Decrease in acidity is due to the decomposition of TPA into its constituent oxides as indicated by the appearance of crystalline WO_3 by

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† Electronic supplementary information (ESI) available: W and P analysis in the reaction mixtures. Fig. S1: ^{31}P MAS NMR. Fig. S2: FT-IR pyridine adsorption spectra. Fig. S3: conversion and acidity *vs.* TPA loading. See http://www.rsc.org/suppdata/cc/b2/b200722c/

Table 1 Physicochemical properties of the catalysts

No.	Catalyst (wt%)	Surface area/m^2 g^{-1}	Surface density/W nm^{-2}	Volume (%) of tetragonal ZrO_2	Acidity/ NH_3 nm^{-2}	P–OH intensity (%)
1	5 wt% TPA/ZrO_2	40.2	3.2	21.9	3.44	100
2	10 wt% TPA/ZrO_2	46.3	5.5	75.6	4.68	100
3	15 wt% TPA/ZrO_2	53.2	7.2	84.2	5.21	80
4[a]	20 wt% TPA/ZrO_2	52.3	9.8	94.6	2.65	54
5[a]	30 wt% TPA/ZrO_2	44.9	14.7	100	2.41	32
6	12.6 wt% WZ	76.0	6.2	100	2.62	—
7[a]	15 wt% WZ	44.6	12.6	100	2.16	—

[a] XRD indicates the presence of crystalline WO_3

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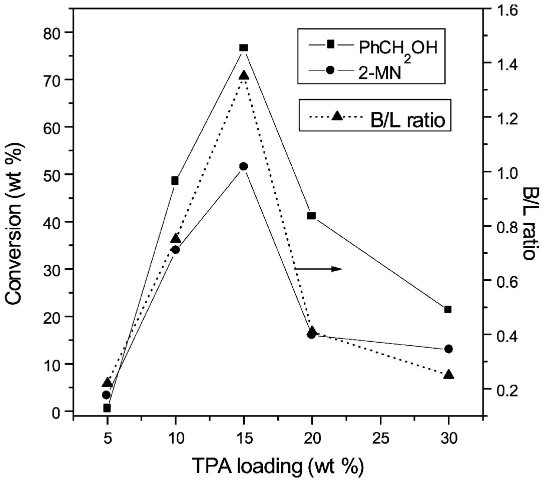

Fig. 1 Conversion and B/L ratio *vs.* TPA loading (catalyst prepared in methanol). *Reaction conditions*: benzylation: phenol = 4.2 g, $PhCH_2OH$ = 0.8 g, catalyst = 0.08 g, temp. = 363 K, time = 1 h; acylation: 2-MN = 2 g, Ac_2O = 3.86 g, catalyst = 0.2 g, temp. = 393 K, time = 12 h.

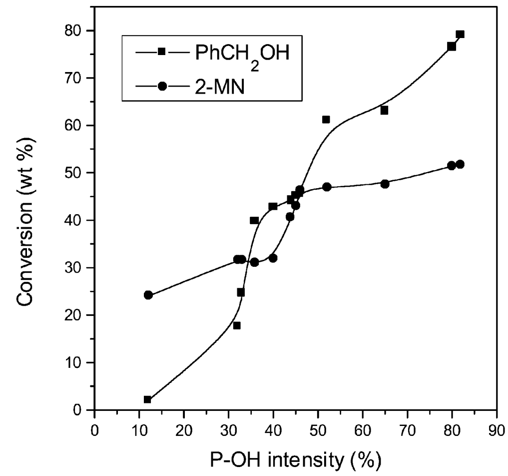

Fig. 2 Conversion *vs.* P–OH intensity of 15 wt% TPA/ZrO_2 catalyst prepared in different solvents. Order of solvents: 0.5 M aqueous ammonia, neat, diethyl ether, 1,4-dioxane, acetic acid, ethyl acetate, acetonitrile, THF, acetone, water, methanol, DMF. Reaction conditions as in Fig. 1.

XRD and phosphorus(v) oxide (a decrease in P–OH intensity) by ^{31}P MAS NMR spectroscopy (Table 1) and the accumulation of these oxides on the surface of active monolayer. However, a tungstated zirconia with similar surface density (6.2 W nm^{-2}) as that of 15 wt% TPA/ZrO_2 (7.2 W nm^{-2}) has a lower acidity.

Brönsted and Lewis acidity of catalysts with different TPA loadings prepared in methanol were measured by pyridine adsorption *in-situ* FT-IR spectroscopy.¶ FT-IR spectra of these catalysts showed Brönsted (B) acidity at 1540 cm^{-1} and Lewis (L) acidity at 1440 cm^{-1}. The B/L ratio increases with TPA loading up to 15 wt% (Fig. 1), and decreased with further loading. Thus the sample containing 15 wt% TPA is the most acidic in terms of the number of acidic sites and strength and corresponds to monolayer coverage of TPA on the surface.

Benzylation and acylation reactions were carried out in a 50 ml glass batch reactor. The reaction mixture was heated to the desired temperature and stirred for required time. The resulting solution was diluted with 5 ml *ortho*-dichlorobenzene (for acylation) and 5 ml methanol (for benzylation) and after the catalyst separation it was analyzed by GC (SE-52 packed column coupled with FID). Products of the reactions were identified using authentic samples and GC–MS analysis. Benzylation of phenol results in the formation of *ortho*- and *para*-benzyl phenol, benzyl phenyl ether and benzyl ether ($<2\%$) as the products. Acylation of 2-MN gave 1-acetyl-2-MN as the only acylated product. In the absence of catalyst no reaction was observed and catalyst removal after partial reaction results in complete stoppage of the reaction which indicates the heterogeneous catalytic nature of the reaction. The dissolution of phosphorus or tungsten species from the catalyst into solution during reaction was monitored at the end of the reaction using inductively coupled plasma-optical emission spectroscopy (ICP-OES) after catalyst filtration. This technique indicated the absence of phosphorus or tungsten in solution after reaction.

The conversion of 2-MN and benzyl alcohol with 12.6 wt% WZ are 17.9 and 38%, while with 15 wt% WZ the corresponding values are 7.1 and 19.6%, respectively. The change in conversions with TPA loading and B/L ratio is shown in Fig. 1. It is seen that conversions increases with TPA loading and is maximum for the 15 wt% TPA/ZrO_2 catalyst in both reactions. However, conversions decrease with further TPA loading. The change in conversions with TPA loading is in line with the B/L ratio and the acidity of the catalysts (Table 1). Tungstated zirconia with similar tungsten surface density as that of 15 wt% TPA/ZrO_2 prepared in methanol showed lower conversions.

Conversions for 15 wt% TPA/ZrO_2 catalyst prepared in different solvents are shown in Fig. 2. This shows that the conversions increase with P–OH intensity and is maximum for catalysts prepared in DMF or methanol as solvent. To confirm reusability, the above catalyst was recycled a few (5–6) times, with no loss in catalytic activity.

In summary, for the first time, we have prepared a highly active and stable zirconia supported 12-tungstophosphoric acid catalyst, which is more active than tungstated zirconia catalyst.

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Notes and references

‡ ^{31}P MAS NMR spectra were recorded at 121.5 MHz with high power decoupling using a Bruker 4 mm probehead. The spinning rate was 10 kHz and the delay between two pulses was varied between 1 and 30 s to ensure that a complete relaxation of the ^{31}P nuclei occurred. The chemical shifts are given relative to external 85% H_3PO_4.

§ NH_3-TPD was carried out after 0.1 g of the catalyst sample was dehydrated at 773 K in dry air for 1 h and purged with helium for 0.5 h. The temperature was decreased to 398 K under a flow of helium and then 0.5 ml NH_3 pulses were supplied to the samples until no more uptake of ammonia was observed. NH_3 was desorbed in He flow by increasing the temperature to 813 K at 10 K min^{-1} measuring NH_3 desorption using a TCD detector.

¶ Pyridine adsorption *in-situ* FT-IR spectroscopy was performed by pretreating a self-supporting wafer (10 mg) of the sample at 673 K for 1 h under a vacuum (10^{-6} mbar) followed by cooling to 373 K. Pyridine vapor was introduced into the cell followed by evacuation at 573 K for 30 min and the IR spectrum recorded. The Brönsted/Lewis acid site density ratio (B/L ratio) was determined from integration of IR bands corresponding to Brönsted acid sites (1540 cm^{-1}) and Lewis acid sites (1440 cm^{-1}).

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