Acetylation of anisole on TPA/ZrO$_2$

R Sakthivel$^2*$ & E Kemnitz$^1$

$^1$Institut für Chemie, Humboldt-Universität zu Berlin, Brook Taylor Str.2, 12489, Berlin, Germany
$^2$Institute of Minerals and Materials Technology, Bhubaneswar 751 013, India

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Zirconia loaded with 5-20 wt% of tungstophosphoric acid (TPA) were prepared by suspending solid hydrous zirconia in methanolic TPA solution followed by evaporation of methanol and calcination at 400°C for 4 h. The product were characterized by X-ray diffraction, photoacoustic FTIR spectroscopy, and NH$_3$-TPD. XRD results show the formation of single tetragonal phase of ZrO$_2$ only for the sample loaded with 5wt% of TPA (5-TPA/ZrO$_2$), whereas the samples loaded with 10, 15 and 20wt% of TPA show two separate phases; cubic phase of hydrogen tungstenate hydrate and tetragonal phase of ZrO$_2$. The photoacoustic FTIR- spectra of pyridine chemisorbed catalysts show the existence of both Brønsted (BC) and Lewis (LC) acid sites. The intensity of Brønsted acid sites band (at 1535 cm$^{-1}$) and the intensity ratios of Brønsted to Lewis acid site bands increase with increased loading of TPA from 5 to 15 wt% and decrease with 20 wt% loading of TPA. This is correlating with catalytic yields (4- and 2-methoxy acetophenone) obtained for catalysts loaded with 5-20 wt% of TPA for the acetylation of anisole reaction with acetic anhydride. The results suggest that only the Brønsted acid sites of catalyst take part in the acetylation of anisole reaction. The NH$_3$-TPD curves of above catalysts show that the ‘strong’ acid sites which are in the >450°C region participate in the reaction.

Keywords: TPA: 12-tungstophosphoric acid, B/L ratio, Brønsted acid sites

Solid acid catalysts are attractive due to their easy handling and eco-friendly nature in comparison to the hazardous and difficult to handle liquid acids like HNO$_3$, HCl, HBr, HClO$_4$, HF, H$_2$SO$_4$ etc. SO$_4$/ZrO$_2$ has been considered to be the best example of solid acid catalyst, which substitutes these liquid acids$^1$. It performs high catalytic activity for many organic reactions, such as alkylation, acylation, isomerisation of various hydrocarbons, etc. into value added products$^1$. However, due to its thermal instability and generation of volatile sulphur compounds during catalysis its application is limited$^4$. Therefore, there is a need for development of thermally stable and active catalysts to overcome such problems. WO$_3$/ZrO$_2$ (tungstated zirconia)$^7$ is thermally stable and has been found as an alternative to SO$_4$/ZrO$_2$. But, it shows relatively low activity$^2$ in comparison with SO$_4$/ZrO$_2$. Since the activity of such catalyst depends mainly on its acidity in acid catalyzed reaction, much important and continuous efforts are being made to develop strong acid catalysts to achieve high activity.

Timofeeva$^{10}$ described the application of heteropoly acids (HPAs) in various acid catalyzed reactions. These acids have shown strong acidity and high catalytic activity in both homogeneous and heterogeneous reactions as compared to the conventional acid catalysts such as sulphuric acid, silica-alumina and others. Since the bulk HPAs cannot be used as such due to low stability and surface area$^1$, these are usually supported on acidic or neutral solid matrices$^{12-14}$ like active carbon, SiO$_2$ and ZrO$_2$. Between tungstophosphoric and molybdophosphoric acid supported zirconia, tungstophosphoric acid supported zirconia shows higher activity in esterification of acetic acid$^{11}$. Recently, 12-tungstophosphoric acid supported zirconia (12-TPA/ZrO$_2$) has been reported$^{15}$ as a highly active and stable solid acid in comparison with WO$_3$/ZrO$_2$, and it has been observed that as sulphate and tungstate, TPA also stabilizes zirconia in a tetragonal phase. Further, activity of TPA/ZrO$_2$ not only depends on its acidity but also on the various preparation methods, calcination temperature etc. Hence, the present investigation focuses on preparation of different 12-TPA/ZrO$_2$ samples and the evaluation of their catalytic activity for acetylation of anisole reaction. Activities of TPA/ZrO$_2$ samples are correlated with their Brønsted acid sites.

**Experimental Procedure**

**Preparation of zirconia**

Hydrated zirconia powder was prepared by dropwise addition of 12.5% aq. NH$_3$ into the aq. solution
of ZrOCl₂·8H₂O (99%, Fluka Chemie, Germany) until the pH of precipitate became 9 under stirring condition. After filtration, precipitate was washed with hot distilled water till it was free from chloride. Then the precipitate was oven dried at 120°C for 24 h.

**Impregnation**

Oven dried hydrous zirconia powder was impregnated with tungstophosphoric acid, H₃P(W₃O₁₀)₄×H₂O (83% Merck) dissolved in methanol. For each 1 g of zirconia 4 mL of methanol was used. This mixture was stirred in a rotary evaporator for 8 h for effective impregnation. Then methanol was removed by evaporation under vacuum. The impregnated product was oven dried at 120°C for overnight and finally calcined at 400°C for 4 h. The samples with 5, 10, 15 and 20 wt% of TPA loading on zirconia were prepared by changing its concentrations.

**XRD and BET surface area**

The X-ray powder diffractometer (XRD) RD7 (Rich, Seifert & Co., Freiberg) having Cu target was used to obtain the powder diffraction patterns of all samples. ASAP 2010 Micromeritics instruments and Barrett-Joyner-Halenda (BJH) method was used to conduct nitrogen adsorption experiments at 77 K to determine the BET surface area (S_BET), pore volume (V_p), and pore diameter (D_p).

**FTIR photoacoustic spectroscopy (FTIR-PAS)**

FTIR-photoacoustic spectrophotometer equipped with FTIR system 2000 (Perkin-Elmer) and MTEC cell was used to semiquantify the concentration of Lewis (LC) and Brønsted (BC) acid sites present on the surface of the catalyst before and after chemisorptions of pyridine. About 200 mg of catalyst was pretreated at 150°C for 30 min in Ar stream. Half of the catalyst was taken out for recording room temperature spectrum (400-4000 cm⁻¹). The remaining catalyst was treated twice with 30 μL of pyridine at 150°C with an interval of 5 min. After Ar flushing at the same temperature for 15 min, its spectrum was recorded as above. The spectra were normalized²⁸ and Lewis (LC) and Brønsted (BC) acid sites bands were identified at 1444 and 1530 cm⁻¹, respectively. The band observed at 1485 cm⁻¹ is contribution of both Lewis (LC) and Brønsted (BC) acid sites. Since one-third intensity of 1444 cm⁻¹ band attributed to Lewis acid site (LC) appears at 1485 cm⁻¹ also, its intensity was subtracted to get the exact Brønsted (BC) acid site band intensity.

**NH₃-TPD**

Quantitative determination of acid strength of catalysts and its distribution were done by temperature programmed desorption of ammonia (NH₃-TPD). About 200 mg of granulated catalyst (~0.5 mm) in a quartz reactor was pretreated at 500°C for 1 h under Ar stream. After the catalyst was cooled down to 120°C, it was treated with mixed stream of Ar and NH₃. The physisorbed NH₃ was removed by Ar flushing, and then cooled down to 80°C. The NH₃-TPD program was run with a heating rate of 10°C/min from 80 to 500°C and held at 500°C for 30 min. FTIR system was used to measure the intensity of desorbed NH₃ band at 930 cm⁻¹. The amount of desorbed NH₃ collected in an excess amount of H₂SO₄ was determined by backtitration with standard NaOH.

**Catalytic acetylation**

The activity of catalyst was evaluated for acetylation of anisole with acetic anhydride. To the mixture of anisole (Fluka, ≥ 99%) and acetic anhydride (Fluka, ≥ 99%) in the mole ratio of 10:1, and n-dodecan C₁₂ (0.3 mmol, Fluka, 95% as an internal standard), the pretreated catalyst (~300 mg) was added and maintained at a reaction temperature of 50°C for 3 h. After separation of catalyst, the liquid portion was analysed through gas chromatography. A Varian 3400 GC (Restec Corp., USA) with a wide pore column DB 5 (length 15 m, inner diameter 0.53 mm), FID: 340°C, injector: 320°C, temperature program: 120 (3 min) to 220°C (20°C/min), 0.3 μL sample. The main products of 4- and 2-methoxy acetophenone (99:1) and by-product of acetic acid were found.

**Results and Discussion**

**Phase characterization and surface properties**

The X-ray powder diffraction patterns of ZrO₂ loaded with 5, 10, 15 and 20 wt% of TPA and pure TPA calcined at 400°C are shown in Fig. 1. The diffraction patterns show the formation of single tetragonal phase of ZrO₂ [JCPDS. No. 42-1164] only for the sample loaded with 5 wt% of TPA (5-TPA/ZrO₂), whereas the samples loaded with 10, 15 and 20 wt% of TPA show two separate phases, cubic phase of hydrogen tungsten phosphate hydrate [JCPDS. No. 50-0304] and tetragonal phase of ZrO₂ [JCPDS. No. 42-1164]. The intensity of diffraction lines pertaining to hydrogen tungsten phosphate
hydrate increases with increasing loading of TPA from 10-20 wt%.

The BET specific surface area, pore volume and pore size of various samples are given in Table 1. The data show that the samples loaded with 5, 10, 15 and 20 wt% of TPA have the specific surface area of 105, 97, 84 and 73 m²/g and pore volume of 0.1084, 0.0937, 0.0819 and 0.0770 cm³/g respectively. Both specific surface area and the pore volume show the decreasing trend with increasing TPA loading from 5-20 wt%. However, the pore sizes remain almost similar, in the range of 39 to 42 Å.

Catalytic activity

The results of catalytic activities of TPA/ZrO₂ samples tested for acetylation of anisole reaction with acetic anhydride are given in Table 1. It shows 10, 48, 51 and 36% of conversion of acetic anhydride and 0.3, 38, 40 and 26% of catalytic yields (4- and 2-methoxy acetophenon) for 5, 10, 15 and 20 wt% of TPA loaded ZrO₂ samples, respectively. Both the conversion of acetic anhydride and catalytic yields increase with TPA loading from 5 to 15 wt%, and then decrease with further loading of TPA of 20 wt% (Fig. 2). This indicates that catalytic activity of TPA supported zirconia is TPA concentration dependent. Among all the samples, the sample with 15 wt% TPA loading shows the highest activity at 50°C, while for the same reaction, Sawant et al. have observed best results with 15 wt.%TPA/22.4 wt.%ZrO₂/SBA-15 at 90°C, i.e. at higher temperature (Table 1).

Acidic properties and correlation with catalytic activity

The acid site concentrations of TPA/ZrO₂ samples and their distribution determined by TPD of NH₃ are
given in Table 1 and Fig. 3, respectively. The samples loaded with 5, 10, 15 and 20 wt% of TPA have the acid site concentrations of 279, 310, 240 and 280 μmol/g, respectively. The acid site concentration increases initially from 279 to 310 μmol/g, from there it decreases to 240 μmol/g, and again increases to 280 μmol/g when the TPA loading increases from 5, 10, 15 and 20 wt%. This observation does support the results obtained by Shanbhag et al., which showed that the acid concentration increased with increasing TPA loading from 5 to 15 wt%, and decreased with higher loading and it was correlated with catalytic activity. However, in this investigation, the acid concentration increases (279-310 μmol/g) with increasing TPA loading 5 and 10 wt% and it correlates with catalytic activity; showing that high acid site concentration results in high catalytic activity. Although, the sample with 15 wt% of TPA has relatively low acid site concentration (240 μmol/g) in comparison to other samples, it shows high catalytic activity, indicating that factors other than acid site concentration influence the catalytic activity. To understand the acid site distribution, area under the NH3-TPD curve is divided into three temperature zones, <250, 250 to 450, and >450°C, which can be considered of being representative for “weak”, “medium”, and “strong” acid sites of catalyst (Fig. 4), respectively. The samples with 5, 10, and 15 wt% of TPA have nearly identical concentration of “weak” acid site distribution (29.4, 29.8 and 31.9%) whereas it is comparatively low (25.1%) for the 20 wt% of TPA loaded sample. The concentration of “medium” acid site distribution decreases (65.4 to 56.8%) with increasing TPA loading from 5 to 15 wt%, and thereafter it does not change much. However, the “strong” acid site distribution increases with increasing loading of TPA from 5 to 20 wt%. A good correlation has been seen between the concentration of “strong” acid site distribution and catalytic activity up to 15 wt% of TPA loading indicating that the “strong” acid sites take part in the acetylation of anisole reaction. Similarly, such correlation is not found for sample with 20 wt% of TPA although it has high “strong” acid site distribution, and shows low catalytic activity instead of high. This observation leads to an inference that possibly the nature of “strong” acid sites of the sample, which are participating in the reaction changes (probably from Brønsted to Lewis) beyond 15 wt% of TPA loading and is in agreement with data obtained from photoacoustic FTIR spectra.
Photoacoustic FTIR spectra and the details of chemisorbed pyridine complexes of various catalysts are shown in Fig. 4 and Table 1. They show the presence of both Lewis and Brønsted acid sites in all the samples. The Lewis (L), combined Brønsted and Lewis (B+L) and Brønsted (B) acid sites bands are observed at 1444, 1485 and 1530 cm\(^{-1}\) respectively. The intensity of Brønsted (B) acid site band (1530 cm\(^{-1}\)) increases with increasing loading of TPA from 5-15 wt% and decreases with further loading, whereas the intensity of Lewis acid site band (1444 cm\(^{-1}\)) decreases with increasing TPA loading of 5-10 wt% and thereafter increases up to 20 wt% TPA loading. The B/L ratio, intensity ratio of Brønsted to Lewis acid sites band, (shows relative Brønsted acidity- obtained with respect to the bands observed at 1485 and 1444 cm\(^{-1}\)) and catalytic activity increase with increasing TPA loading of 5-15 wt% and thereafter decreases with higher loading of TPA (20 wt%). This agrees with the reported literature\(^5\). Further, it reveals that the Brønsted acid sites of the catalyst catalyses the acetylation of anisole reaction. This supports the similar observations made on WO\(_3\)/ZrO\(_2\) catalyst for the same reaction\(^8\) and similar kind of reaction (bezoylation of anisole)\(^16,19\) made on SO\(_4\)/ZrO\(_2\) and SO\(_4\)/Zr\(_{1-x}\)Sn\(_x\)O\(_2\).

When the B/L ratio and concentration of strong acid sites observed in NH\(_3\)-TPD are compared together with increasing TPA loading from 5-20 wt%, it can be inferred that “strong” acid sites which are showing increasing trend up to 15 wt% of TPA loading can be attributed to Brønsted acid sites and beyond 15 wt% it can be ascribed to Lewis acid sites.

Conclusions
The following conclusions are drawn from the above observations,

(i) By supporting TPA on ZrO\(_2\) a considerable amount of Brønsted acid sites could be generated.

(ii) Both B/L ratio and catalytic yield increase with increasing TPA loading from 5-15 wt% and decrease with further loading which indicates that the acetylation of anisole reaction is catalysed by the Brønsted acid sites of catalyst.

(iii) Higher loading of TPA (20 wt%) on ZrO\(_2\) leads to generation of relatively higher amount of Lewis acid sites (FTIR spectra) which do not catalyze the reaction as a consequence decreased catalytic yield has been obtained.

References