



# Aluminium exchanged heteropoly tungstate supported on titania catalysts: The generation of Lewis acidity and its role for benzylation reaction

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## ABSTRACT

Aluminium exchanged heteropoly tungstate (AITPA) supported on titania catalysts were prepared and characterized by FT-Infra red, X-ray diffraction, Laser Raman, temperature programmed desorption of ammonia and X-ray photo electron spectroscopy. The catalytic properties of the catalysts were evaluated for benzylation of anisole with benzyl alcohol. The catalysts showed high activity for anisole benzylation and the catalyst with 20 wt% of AITPA exhibited highest activity. The presence of Al resulted in generation of Lewis acidic sites. Acidic property and chemical structure of AITPA on different supports also evaluated by supporting AITPA on Nb<sub>2</sub>O<sub>5</sub>, ZrO<sub>2</sub> and SnO<sub>2</sub>. The catalytic activity of these catalysts is in the order of AITPA/TiO<sub>2</sub> > AITPA/SnO<sub>2</sub> > AITPA/ZrO<sub>2</sub> > AITPA/Nb<sub>2</sub>O<sub>5</sub>. The benzylation activity and selectivity towards benzylation product also depends on the reaction temperature, catalyst weight and anisole to benzyl alcohol ratio.

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## 1. Introduction

Heteropoly acids (HPAs) have been widely investigated as catalysts for acid-catalyzed and oxidation reactions due to their strong acidity and high oxidation potential [1–4]. Tungstophosphoric acid (TPA) is the usual catalyst of choice for acid catalyzed reactions, because of its high acidic strength and thermal stability among the Keggin type HPAs. However, certain drawbacks are associated with the use of HPAs as catalysts due to their low surface area (5–8 m<sup>2</sup>/g), solubility in polar solvents. HPAs can be made heterogeneous catalyst by exchanging their protons with metal ions [5,6] or by supporting them on suitable supports [7].

Metal exchanged HPA can be classified into two groups: group A are the HPAs which protons are exchanged with small metal ions like Na<sup>+</sup> and Cu<sup>2+</sup> and group B are those HPAs containing large metal ions like Cs<sup>+</sup>. The group A salts usually possess: (i) low surface area (ii) high solubility in water and (iii) absorption capability of polar or basic molecules in the solid bulk. On the other hand, the group B salts are: (i) with high surface area, (ii) insoluble in water and (iii) unable to absorb molecules [8].

The formation of certain HPA salts of metal ions (M<sup>n+</sup>) of PW<sub>12</sub>O<sub>40</sub><sup>3-</sup> (M<sub>3/n</sub>PW<sub>12</sub>O<sub>40</sub>) show Lewis acidity [9–13], originating from the metal cation as electron pair acceptor apart from the

characteristic Bronsted acidity of HPAs generated from dissociation of coordinated water under the polarizing effect of the cation.

Friedel–Crafts alkylation of aromatic compounds is important process in both petroleum and chemical industries [14]. Alkylated anisole compounds are constituents of lubricants with improved and interesting properties as, for example, thermal oxidation and hydrolytic stabilities [15]. Conventional Friedel–Crafts alkylation reactions generally require stoichiometric amounts of Lewis or Bronsted acid reagents. These conditions afford the concomitant production of hydrogen halides that often induces side reactions and many byproducts. As an alternative, moisture-tolerant homogeneous Lewis acid catalysts (Lanthanide and actinide triflates) and transition metal complexes (Fe, Bi, Mo, Ir, and Au complexes) have been reported to be effective for Friedel–Crafts like alkylations using alcohols, ethers, styrene or benzylic acetates [16–18]. Various types of heterogeneous catalysts, such as zeolites, metal oxides like niobium oxide, MoO<sub>3</sub>, clay and resin have been reported as an environmentally benign catalyst for the benzylation of arenes by alcohols and styrenes [13,19–28].

HPAs are also used as catalysts for Friedel–Crafts alkylation in both homogeneous and heterogeneous systems [29,30]. We have been working on the modification of HPAs to use for acid catalyzed reactions [6,7]. HPAs are modified by exchanging its protons with metal ion and supporting them on different supports to enhance acidity, thermal stability and surface area. These modified HPA catalysts are used for preparation of indole derivatives, benzylation, Friedel–Crafts acylation, regioselective ring opening of epoxides, esterification, hydro amination and other reactions [7,31–35].

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In the present work, aluminium exchanged tungstophosphoric acid (AITPA) supported on titania with different TPA contents (5–25 wt%) were prepared and their catalytic activity was evaluated for benzylation of anisole with benzyl alcohol. Titania, a widely used catalyst as well as support [36], is known to enhance the activity in many cases due to the strong interaction of the active phase [37]. The present study is focused to know about the generation of Lewis acidity with the formation of AITPA Keggin ion on titania. The role of surface and structural properties of the catalysts and their influence on the catalytic activity in benzylation is also one of the aims of the study.

## 2. Experimental

### 2.1. Catalyst preparation

Preparation of Al exchanged TPA (AITPA) supported on TiO<sub>2</sub> involves two steps. In the first step, AITPA was prepared by exchanging the protons of TPA with Al<sup>3+</sup>. The required quantity of TPA dissolved in minimum amount of distilled water and to this the calculated amount of aqueous Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O was added drop wise. The resulting mixture was aged for 1 h at 80 °C. The excess water was evaporated to dryness and obtained catalyst mass was oven dried at 120 °C for overnight and calcined at 300 °C for 2 h.

In the second step, a series of catalysts with varying amounts of AITPA supported on titania were prepared by impregnation method. The calculated amount of AITPA dissolved in distilled water was added to titania with continuous stirring. The resultant mixture was allowed to stand for 3 h and the excess water was evaporated on a water bath. The dried catalyst masses were kept overnight for further drying in an air oven at 120 °C and calcined at 300 °C for 2 h. The catalysts are represented as x% AITPA/TiO<sub>2</sub>. Where x represents the weight percentage of AITPA. The amount of Al exchanged with the proton of TPA are calculated by atomic absorption spectroscopy (AAS) analysis. The protons present in TPA are partially exchanged with Al ion. Based on these results the AITPA is in the form of Al<sub>2.33</sub>H<sub>0.67</sub>TPA.

### 2.2. Characterization of catalysts

X-ray powder diffraction patterns were recorded on a Rigaku Miniflex diffractometer using Cu K<sub>α</sub> radiation (1.5406 Å) at 40 kV and 30 mA and secondary graphite monochromatic. The measurements were obtained in steps of 0.045° with count times of 0.5 s, in the 2θ range of 10–80°.

The FT-IR spectra were recorded on a Bio-Rad Excalibur series spectrometer using the KBr disc method.

Confocal Micro-Raman spectra were recorded at room temperature in the range of 200–1200 cm<sup>-1</sup> using a Horiba Jobin-Yvon Lab Ram HR spectrometer with a 17 mW internal He-Ne (Helium-Neon) laser source of excitation wavelength of 632.8 nm. The catalyst samples in powder form (about 5–10 mg) were usually loosely spread onto a glass slide below the confocal microscope for measurements.

The acidity of the catalysts was measured by temperature programmed desorption of ammonia (TPD-NH<sub>3</sub>). In a typical experiment, 0.1 g of catalyst was loaded and pretreated in He gas at 300 °C for 2 h. After pretreatment the temperature was brought to 100 °C and the adsorption of NH<sub>3</sub> is carried out by passing a mixture of 10% NH<sub>3</sub> balanced He gas over the catalyst for 1 h. The catalyst surface was flushed in He gas at the same temperature for 2 h to flush off the physisorbed NH<sub>3</sub>. TPD of NH<sub>3</sub> was carried with a temperature ramp of 10 °C/min and the desorption of ammonia was monitored using thermal conductivity detector (TCD) of a gas chromatograph.

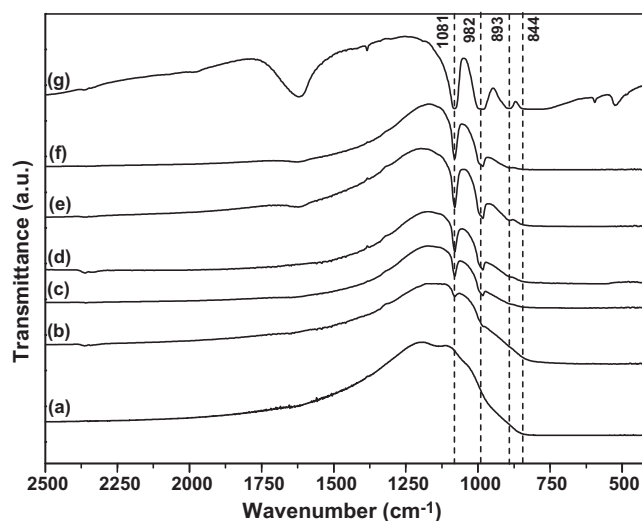


Fig. 1. FT-IR spectra of (a) TiO<sub>2</sub>, (b) 5% AITPA/TiO<sub>2</sub>, (c) 10% AITPA/TiO<sub>2</sub>, (d) 15% AITPA/TiO<sub>2</sub>, (e) 20% AITPA/TiO<sub>2</sub>, (f) 25% AITPA/TiO<sub>2</sub> and (g) AITPA catalysts.

X-ray photo electron spectroscopy (XPS) measurements were conducted on a KRATOS AXIS 165 with a DUAL anode (Mg and Al) apparatus using Mg K<sub>α</sub> anode. The non-monochromatized Al K<sub>α</sub> X-ray source ( $h\nu = 1486.6$  eV) was operated at 12.5 kV and 16 mA. Before acquisition of the data each sample was out-gassed for about 3 h at 100 °C under vacuum of  $1.0 \times 10^{-7}$  T to minimize surface contamination. The XPS instrument was calibrated using Au as standard. For energy calibration, the carbon 1s photoelectron line was used. The carbon 1s binding energy was taken as 285 eV. Charge neutralization of 2 eV was used to balance the charge up of the sample. The spectra were deconvoluted using Sun Solaris Vision-2 curve resolver. The location and the full width at half maximum (FWHM) value for the species were first determined using the spectrum of a pure sample. Symmetric Gaussian shapes were used in all cases. Binding energies for identical samples were, in general, reproducible within  $\pm 0.1$  eV.

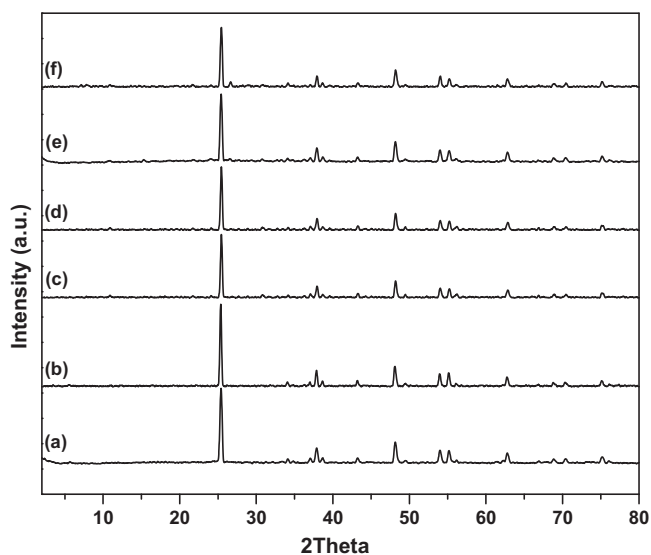
### 2.3. General alkylation procedure

The alkylation reaction was carried out in a 50 ml three necked round bottom (RB) flask provided with a reflux condenser, a nitrogen gas inlet and a septum for sample removal. In a typical run, 10 g of anisole and 3.37 g of benzyl alcohol (15:5 molar ratio) were taken in RB flask and 0.1 g catalysts were added. The reaction was carried out at a reaction temperature of 120 °C under atmospheric pressure. The reaction mixture was withdrawn at different intervals and analyzed by gas chromatograph (VARIAN GC-3800) equipped with SE-30 column and flame ionization detector. The oven temperature was programmed from 100 to 250 °C with a temperature ramp of 20 °C/min to separate the products. The products were identified by GC-MS (SHIMADZU-2010) analysis.

## 3. Results and discussion

### 3.1. Characterization of catalysts

FT-IR patterns of AITPA supported on TiO<sub>2</sub> catalysts are shown in Fig. 1. The catalysts showed four characteristic bands in the region of 1100–500 cm<sup>-1</sup>. The main peaks observed at 1081, 982, 893 and 844 cm<sup>-1</sup> are related to the asymmetric stretching vibrations of P–O, W=O<sub>t</sub>, W–O<sub>c</sub>–W and W–O<sub>e</sub>–W respectively of characteristic Keggin ion [7]. The catalysts with low AITPA content showed mainly bands related to P–O and W=O<sub>t</sub> vibration. The intensity of

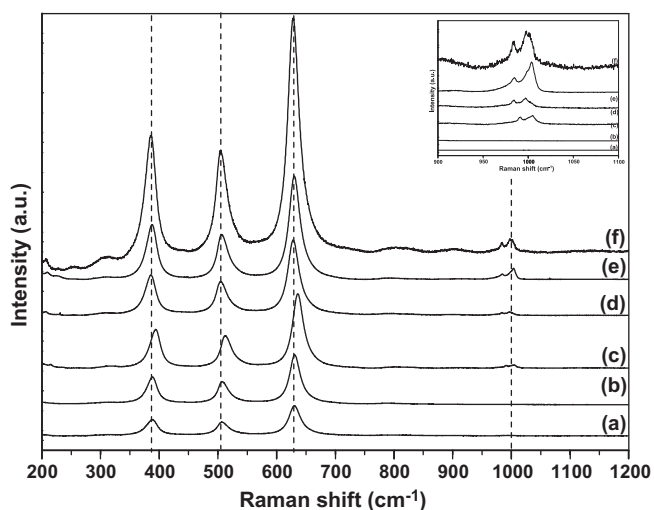


**Fig. 2.** XRD patterns of (a) TiO<sub>2</sub>, (b) 5% AITPA/TiO<sub>2</sub>, (c) 10% AITPA/TiO<sub>2</sub>, (d) 15% AITPA/TiO<sub>2</sub>, (e) 20% AITPA/TiO<sub>2</sub>, and (f) 25% AITPA/TiO<sub>2</sub> catalysts.

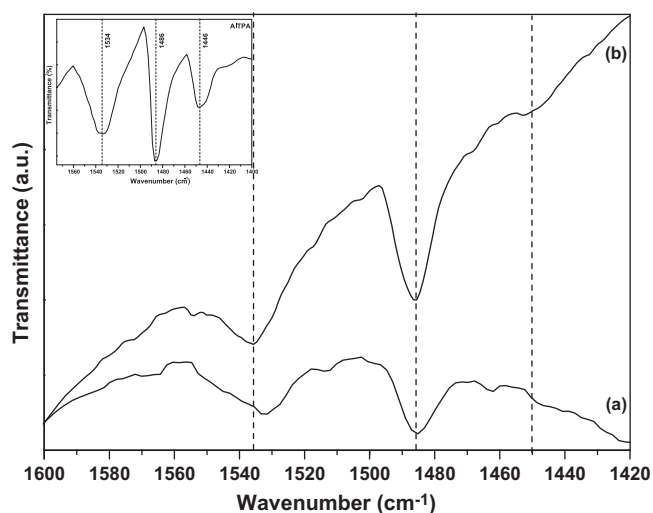
these bands increased with AITPA content and the catalyst with high content showed all the major vibrations of Keggin ion. FT-IR analysis indicates that the Keggin structure of AITPA remained unaltered when supported on TiO<sub>2</sub>.

The X-ray patterns of the AITPA/TiO<sub>2</sub> catalysts are shown in Fig. 2. The diffraction patterns of anatase titania are seen at  $2\theta$  of 25.52°, 37.84°, 48.07°, 53.88°, 55.04° and 62.71° corresponding to (1 0 1), (0 0 4), (2 0 0), (1 0 5), (2 1 1) and (2 0 4) reflection planes of crystal anatase titania respectively [38,39]. The XRD patterns related to Keggin AITPA are seen for the catalysts with above 20 wt% of AITPA on titania. This result reveals that AITPA is highly dispersed on the surface of the catalyst at lower loading. Crystalline phase of AITPA Keggin are present when its content is  $\geq 20$  wt% suggests the attainment of bulk nature of AITPA on support.

Fig. 3 shows the Raman spectra of the catalysts. The Raman spectra were dominated by the band related to titania. The predominant band at 388, 507 and 629 cm<sup>-1</sup> originates from the anatase phase of TiO<sub>2</sub> are seen for all the samples [40,41]. The Keggin ion characteristic bands are shown in the inset of the Fig. 3 for the sake of



**Fig. 3.** Raman spectra of (a) TiO<sub>2</sub>, (b) 5% AITPA/TiO<sub>2</sub>, (c) 10% AITPA/TiO<sub>2</sub>, (d) 15% AITPA/TiO<sub>2</sub>, (e) 20% AITPA/TiO<sub>2</sub>, and (f) 25% AITPA/TiO<sub>2</sub> catalysts. Inset figure: Raman spectra of AITPA/TiO<sub>2</sub> catalysts in the Raman shift range of 900–1100 cm<sup>-1</sup>.



**Fig. 4.** FT-IR spectra of pyridine adsorbed on (a) 20% TPA/TiO<sub>2</sub>, (b) 20% AITPA/TiO<sub>2</sub> catalysts. Inset figure: FT-IR spectra of bulk AITPA.

clarity. The catalysts showed Raman bands at 1005 and 990 cm<sup>-1</sup> related to symmetric and asymmetric stretching vibration of W = O<sub>T</sub> of intact Keggin ion. The characterization results from FT-IR, XRD and Laser Raman suggest the presence of crystalline anatase phase of titania. These spectral studies also reveals that AITPA Keggin ion was well dispersed at lower loading and present in crystallite form at higher contents.

FT-IR spectra of pyridine adsorbed on 20% TPA/TiO<sub>2</sub>, 20% AITPA/TiO<sub>2</sub> catalysts are shown in Fig. 4. The TPA with Al and without Al are compared to distinguish the difference in the nature of acidity. AITPA supported on TiO<sub>2</sub> catalysts contain both Bronsted and Lewis acid sites, as evidenced by the presence of strong IR bands at 1534 and 1446 cm<sup>-1</sup> respectively [6]. The band at 1486 cm<sup>-1</sup> is a combined band originates from pyridine bonded to both Bronsted and Lewis acid sites. The Lewis acidity arises due to the exchange of aluminium with the protons of TPA. The intensity of combined band at 1486 cm<sup>-1</sup> is high for 20% AITPA/TiO<sub>2</sub>, when compared to 20% TPA/TiO<sub>2</sub> catalyst. 20% TPA/TiO<sub>2</sub> catalyst shows Lewis acidity due to the coordinately unsaturated Ti<sup>4+</sup> species on the surface. These results suggest the generation of more Lewis acidity by the modification of heteropoly tungstate with aluminium.

The ammonia adsorption–desorption technique enables for determination of strength of acid sites and together with total acidity of catalysts. The TPD profiles of the catalysts are shown in Fig. 5 and the acid strength distribution calculated based on the TPD-NH<sub>3</sub> are presented in Table 1. All the samples showed unresolved, broad desorption peaks. The acidity values depended on the amount of AITPA and increased with increase in AITPA loading. When compared to all other catalysts 20% AITPA/TiO<sub>2</sub> catalyst poses more acidity. Further increase in AITPA content there was no appreciable increase in acidity. The catalysts with high AITPA loading showed a low temperature desorption peak around 110–350 °C and two high

**Table 1**  
Acid strength distribution of AITPA/TiO<sub>2</sub> catalysts.

S.No.	Catalyst	Acidity (mmol/g)		
		Weak	Moderate/strong	Total
1.	5% AITPA/TiO <sub>2</sub>	0.0517	0.0484	0.100
2.	10% AITPA/TiO <sub>2</sub>	0.0642	0.0566	0.121
3.	15% AITPA/TiO <sub>2</sub>	0.0987	0.0581	0.157
4.	20% AITPA/TiO <sub>2</sub>	0.1316	0.0624	0.194
5.	25% AITPA/TiO <sub>2</sub>	0.1294	0.0626	0.192
6.	20% TPA/TiO <sub>2</sub>	0.0351	0.1252	0.160

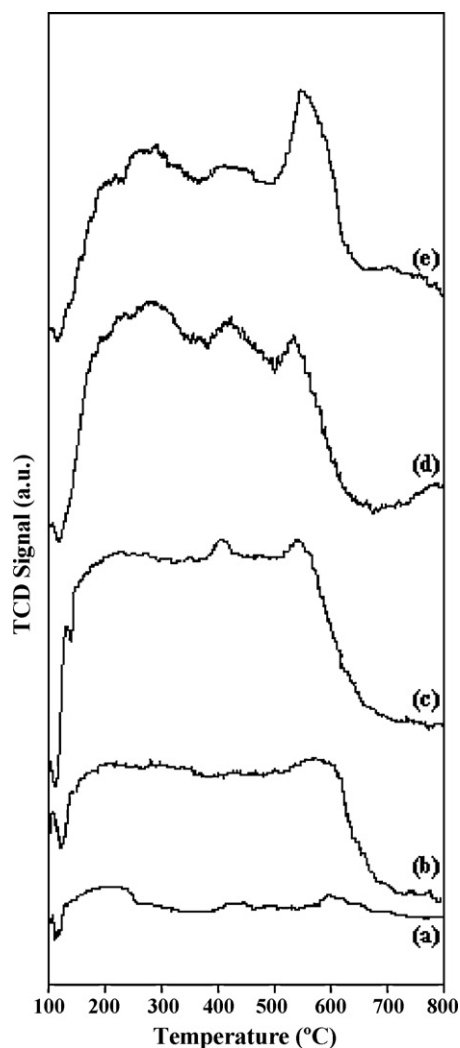


Fig. 5. TPD patterns of (a) 5% AITPA/TiO<sub>2</sub>, (b) 10% AITPA/TiO<sub>2</sub>, (c) 15% AITPA/TiO<sub>2</sub>, (d) 20% AITPA/TiO<sub>2</sub>, and (e) 25% AITPA/TiO<sub>2</sub> catalysts.

temperatures desorption peaks in the range of 360–650 °C. The low temperature desorption peak originates from the weak acidic sites of the support. The intensity of the high temperature desorption peak is increasing as the AITPA content increased.

Fig. 6(A) and (B) shows the XPS spectra of TPA/TiO<sub>2</sub> and AITPA/TiO<sub>2</sub> catalysts respectively. TPA supported on titania shows O 1s binding energy at 530.5 eV. The O 1s of pure titania shows peak at 529.7 eV. The binding energy of 530.5 eV may be attributed to Ti–O–W linkage. Whereas in the case of 20% AITPA/TiO<sub>2</sub> catalyst (Fig. 6(B)) binding energy value of O 1s is 531.8 eV. This suggests that Al is combined on to surface of titania, forming a Ti–O–Al bond. The electronegativity of Al is slightly greater than that of Ti, the O 1s peak for 20% AITPA/TiO<sub>2</sub> has a chemical shift of +1.3 eV.

The binding energy Ti 2P for the 20% TPA/TiO<sub>2</sub> is observed at 457.9, 463.6 eV corresponding to Ti 2P<sub>3/2</sub>, 2P<sub>1/2</sub> respectively. These bands are shifted to higher binding energy values for 20% AITPA/TiO<sub>2</sub> catalyst as they found at 458.6, 464.4 eV. This may be due to interaction of AITPA with support and formation of Ti–O–Al bond. Increase in binding energy value may be due to decrease of the electron density around titania atom, which results from the greater electronegativity of Al via O acting on Ti. The XPS of P 2p binding energy is observed at 133.7, 132.5 eV for 20% TPA/TiO<sub>2</sub> catalyst due to spin orbit coupling. Whereas for 20% AITPA/TiO<sub>2</sub> catalyst the P 2p binding energy observed at 133.4 eV.

The W 4f XPS spectrum of 20% TPA/TiO<sub>2</sub> showed two binding energy values at 35.5, 36.6 eV assigned to W 4f<sub>7/2</sub> and W 4f<sub>5/2</sub> respectively. These are related to characteristic band of Keggin ion due to spin–orbit splitting. These values are in agreement with literature data [42]. There is no change in the binding energy values in case of 20% AITPA/TiO<sub>2</sub> catalyst. The Al containing catalyst shows Al 2P<sub>3/2</sub> binding energy at 74.4 eV suggesting the existence of Al species in 20% AITPA/TiO<sub>2</sub> catalyst. The XPS characterization data confirms the presence of Al<sup>3+</sup> exchanged with the protons of TPA and its interaction with support.

### 3.2. Catalysts activity for benzylation of anisole

#### 3.2.1. Effect of AITPA loading on benzylation of anisole

The insoluble nature of AITPA/TiO<sub>2</sub> catalyst in polar media makes this catalyst attractive for application in benzylation of aromatic compounds. The catalytic performances of 5–25% AITPA/TiO<sub>2</sub> catalysts were evaluated for benzylation of anisole with benzyl alcohol and the results are presented in Fig. 7. The analysis of the products showed that the reaction resulted in the formation of o- and p- benzylated product and dibenzylether. From the figure it was observed that benzyl alcohol conversion increased with increase in AITPA loading and attained maximum for 20 wt% AITPA/TiO<sub>2</sub> catalyst and remained same with further increase in AITPA content. The activity of the catalyst increased considerably when the AITPA content increased from 10 to 15 wt%. TPD of NH<sub>3</sub> results showed a substantial increase in moderate acidic sites for 15 and 20% AITPA/TiO<sub>2</sub> catalyst. The catalyst with high AITPA content (25%) showed similar activity that of 20 wt% due to attainment of bulk nature of AITPA on TiO<sub>2</sub>. The results suggest that the activity is related to the amount of AITPA on TiO<sub>2</sub>. The surface–structural properties derived from XRD, IR, acidity measurements can through light for the observed catalytic activity of the catalyst. The XRD result supports the well dispersed AITPA on titania. The acidity values suggest the presence of well distributed moderate and strong acidic sites for the catalyst with 20 wt% AITPA on titania. The presence of highly dispersed AITPA and high acidity with reasonable amount of Lewis acidic sites of the catalyst is responsible for its high benzylation activity.

In order to know the influence of AITPA, the catalytic activity of most active 20% AITPA/TiO<sub>2</sub> catalyst was compared with 20% TPA (without Al) supported on different supports like Nb<sub>2</sub>O<sub>5</sub>, SnO<sub>2</sub>, ZrO<sub>2</sub> along with TiO<sub>2</sub> are studied and the results are shown in Fig. 8. The 20% AITPA/TiO<sub>2</sub> showed higher activity compared to 20% TPA/TiO<sub>2</sub>. The results suggest that, when AITPA is highly dispersed on support, it exhibit maximum benzylation activity. The TPA without Al dispersed on different supports exhibited low activity compared to AITPA/TiO<sub>2</sub> catalyst. The catalysts particularly TPA supported on Nb<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub> showed reasonable conversion. However, they are mainly selective to para benzylated product. These results suggest that the exchange of Al resulted in the increase of total acidity along with the generation of more Lewis acidic sites. The presence of Lewis acidic sites for the AITPA catalyst is clearly seen from the FT-IR pyridine adsorption spectra as shown in Fig. 4. Pyridine adsorbed FT-IR spectra of these catalysts suggest the generation of Lewis acidic sites with Al ions present in AITPA Keggin ion. The presence of Lewis acidity alters the selectivity of the benzylation product compared the catalysts with more number of Bronsted acidic sites.

#### 3.2.2. Effect of support in benzylation activity

In order to know the support role in benzylation of anisole, catalysts with 20 wt% of AITPA supported on Nb<sub>2</sub>O<sub>5</sub>, ZrO<sub>2</sub>, and SnO<sub>2</sub> were prepared by the same method as reported in Section 2.

The catalytic activity of AITPA supported on different supports for benzylation of anisole with benzyl alcohol shown in Fig. 9. Compared to all other catalysts, AITPA supported on TiO<sub>2</sub> catalyst

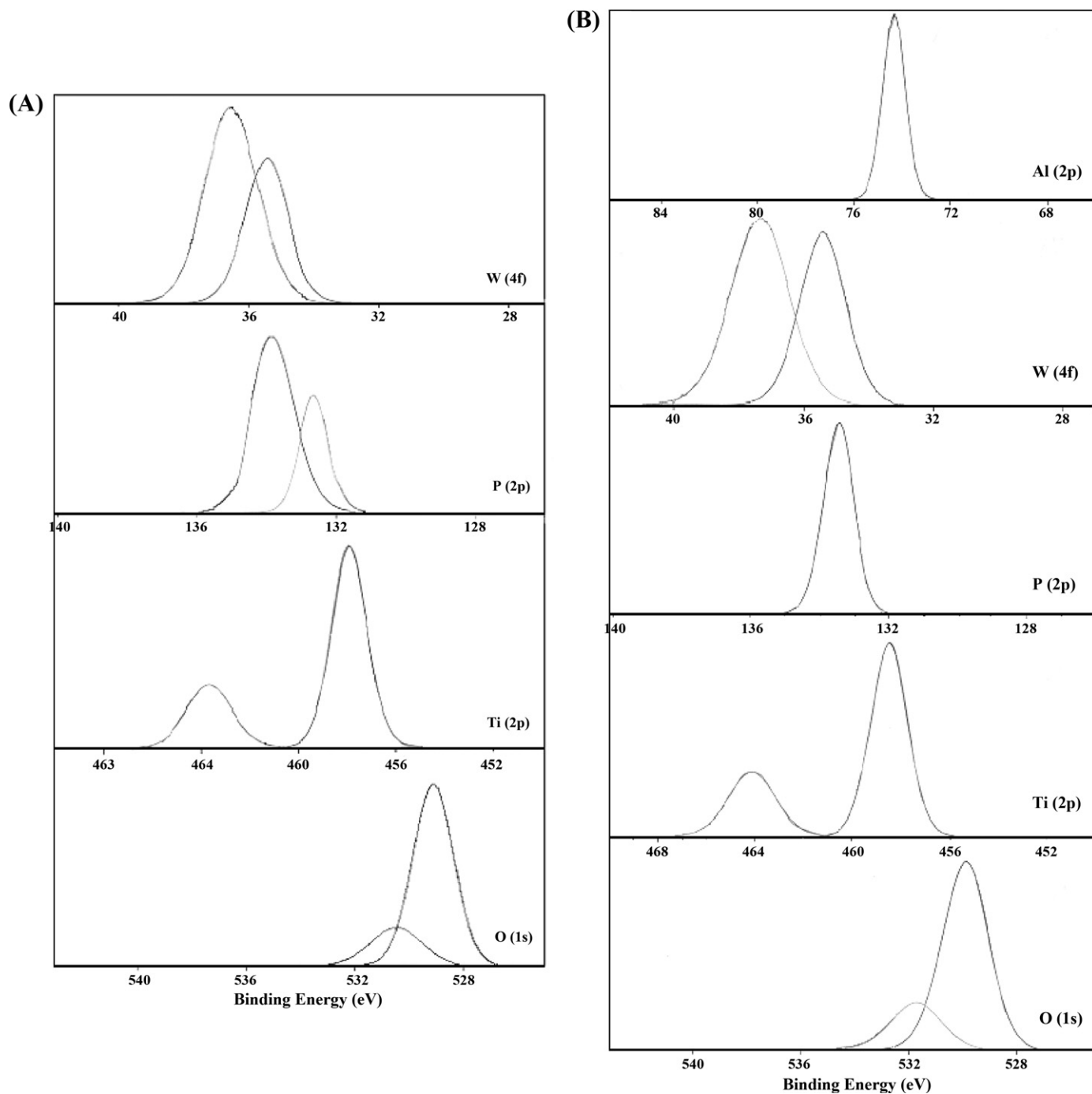


Fig. 6. (A) XPS spectra of 20%TPA/TiO<sub>2</sub> and (B) 20%AITPA/TiO<sub>2</sub> catalyst in the O 1s, Ti 2p, P 2p, W 4f binding energy regions.

showed high conversion of benzyl alcohol. Benzylation activities of these catalysts are in the following order: 20% AITPA/TiO<sub>2</sub> > 20% AITPA/SnO<sub>2</sub> > 20% AITPA/ZrO<sub>2</sub> > 20% AITPA/Nb<sub>2</sub>O<sub>5</sub>. The selectivity towards benzylated products are also followed the same order.

These catalysts were characterized by TPD of ammonia to know the acidity of the catalysts and there by its relation to observed benzylation activity. Fig. 10 shows the TPD-NH<sub>3</sub> profiles of AITPA supported on TiO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>, ZrO<sub>2</sub> and SnO<sub>2</sub> catalysts. All the catalysts showed three types of desorption peaks in the range of 110–650 °C, except 20% AITPA/Nb<sub>2</sub>O<sub>5</sub> catalyst. It showed only a broad desorption peak ranging from 110 to 450 °C related to weak and moderate acidic sites along with a small desorption peak at

500 °C related to strong acidic sites. All other catalysts showed desorption peak around at 250 °C originating from the acidic sites of the supports. When compared to ZrO<sub>2</sub> and SnO<sub>2</sub> supported systems, 20% AITPA/TiO<sub>2</sub> showed a broad desorption peak. The desorption peaks at 430 °C and 550 °C corresponds to moderate and strong acidic sites. As discussed earlier, the desorption peak at 430 °C may be related to Lewis acidic sites present on the support. Compared to all other catalysts 20% AITPA/TiO<sub>2</sub> contains more number of acidic sites which are might be generated by interaction of AITPA with titania.

The high benzyl alcohol conversion for 20% AITPA/TiO<sub>2</sub> catalyst can be related to the amount of Lewis and Bronsted acidity originating from AITPA and TiO<sub>2</sub>.

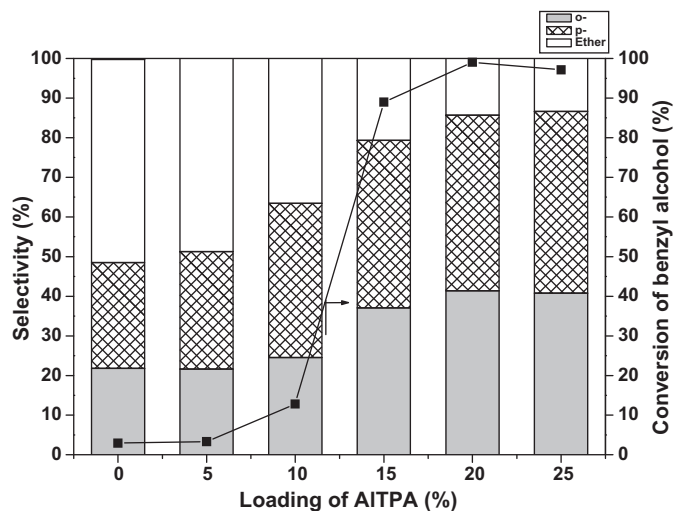


Fig. 7. Effect of AITPA loading on benzylation activity.

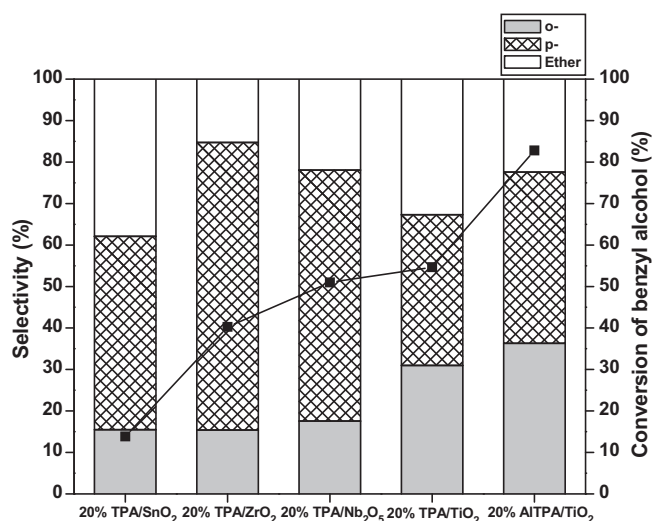


Fig. 8. Comparison of catalytic activity of 20% AITPA/TiO<sub>2</sub> with TPA supported on different supports.

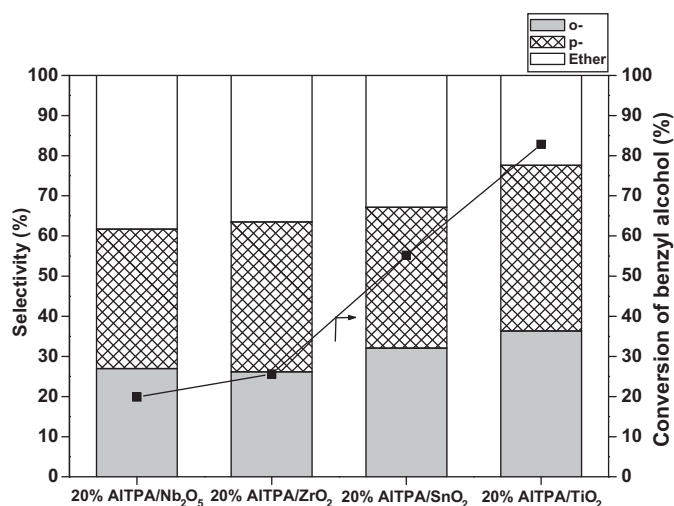


Fig. 9. Benzylation activity of AITPA on different supports.

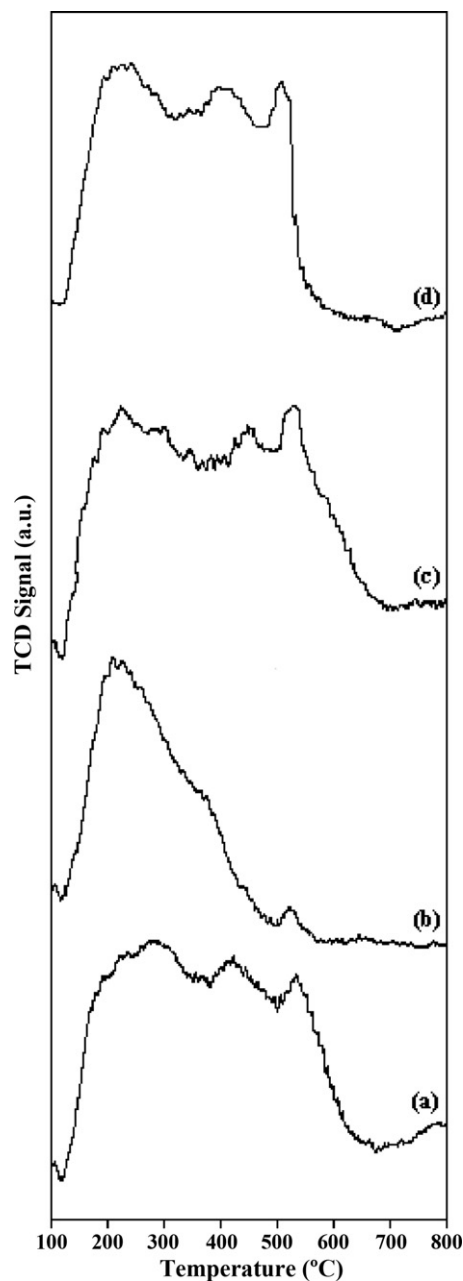


Fig. 10. TPD patterns of (a) 20% AITPA/TiO<sub>2</sub>, (b) 20% AITPA/Nb<sub>2</sub>O<sub>5</sub>, (c) 20% AITPA/SnO<sub>2</sub>, and (d) 20% AITPA/ZrO<sub>2</sub>.

### 3.2.3. Effect of reaction temperature

In order to optimize the reaction conditions, the benzylation of anisole was carried out at different reaction temperatures ranging from 80 to 140 °C and the results are shown in Fig. 11. From the figure it is observed that the percentage yield of benzylated products is low at 80–100 °C and the activity increased when reaction temperature increased to 120 °C. Further increase in temperature there is only marginal change in the conversion. The selectivity towards benzylated product increased with increase in reaction temperature. Formation of ether is not observed at reaction temperature of 140 °C. These results suggest that a reaction temperature of 140 °C is optimum for benzylation of anisole over 20% AITPA/TiO<sub>2</sub> catalyst.

### 3.2.4. Effect of catalyst weight

Influence of catalyst weight on the benzylation activity was studied and the results are presented in Fig. 12. From the figure it

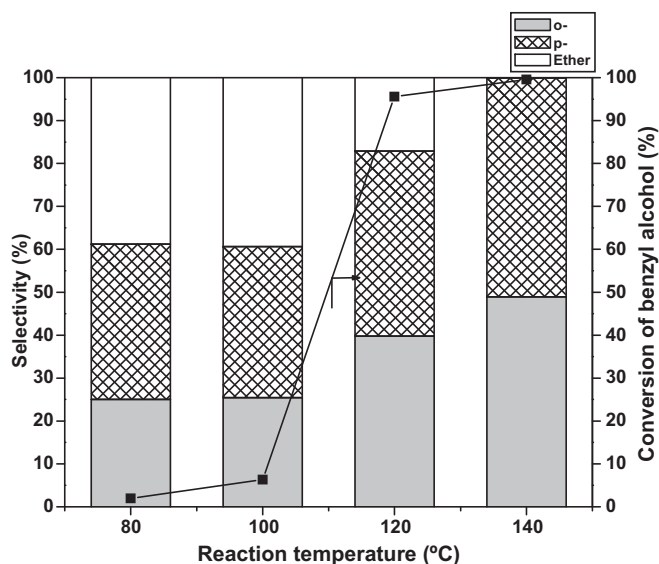


Fig. 11. Effect of reaction temperature on the conversion of benzyl alcohol.

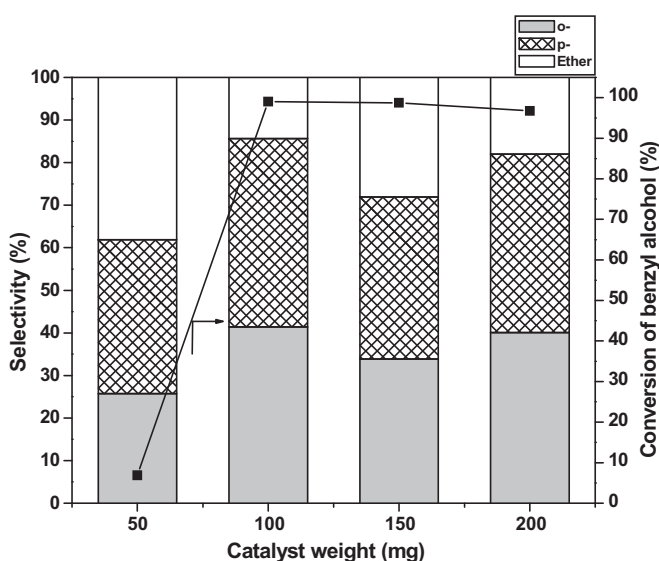


Fig. 12. Effect of catalyst weight on the benzylation of anisole.

can be concluded that benzylation product increased with increase in catalyst weight up to 0.1 g and further increase in catalyst weight there is no much change in overall activity. Product selectivity was more or less consistent with variation in catalyst amount. These results reiterate the high activity of the catalysts.

### 3.2.5. Effect of molar ratio of anisole to benzyl alcohol

Table 2 shows the effect of anisole to benzyl alcohol ratio on the benzylation activity. The conversion of benzyl alcohol increased with increase in molar ratio from 1.5 to 15. Selectivity towards benzylation product also improved with increase in anisole to benzyl

**Table 2**  
Effect of anisole to benzyl alcohol molar ratio on benzylation of anisole.

Anisole to benzyl alcohol ratio	Conversion of benzyl alcohol (%)	Selectivity (%)		
		o-	p-	Ether
1.5	13.0	19.5	27.1	53.5
3	90.6	37.1	41.6	21.3
15	98.2	47.1	48.8	4.1

alcohol molar ratio. Formation of dibenzylether is expected with high benzyl alcohol concentration due to relatively low rates of benzylation compared to that of dehydration.

### 3.2.6. Stability/leaching of the catalyst

After completion of the reaction where the conversion of benzyl alcohol is complete, the catalyst was separated from the reaction mixture by centrifugation. To the reaction mixture (filtrate) calculated amount of benzyl alcohol was added and the reaction is carried out (without addition of catalyst) to check whether any leaching of the active content (AITPA) from the support in to reaction mixture. The reaction was continued for a period of 4 h. There was no conversion of benzyl alcohol. This study reiterates that there was no leaching of active component during the reaction and the reaction is taking place on the surface of the catalyst.

## 4. Conclusions

Al exchanged TPA supported on TiO<sub>2</sub> catalysts were prepared with retention of Keggin ion structure of AITPA. Exchange of TPA protons with Al ions results in the generation of Lewis acidic sites. Benzylation activity of anisole depends on the acid strength distribution and total acidity of the catalysts which related to the content of AITPA on support. The optimum loading of AITPA was 20 wt% for high benzylation activity. Role of support in benzylation activity also studied by supporting AITPA on different supports and their activity was in the following order: 20% AITPA/TiO<sub>2</sub> > 20% AITPA/SnO<sub>2</sub> > 20% AITPA/ZrO<sub>2</sub> > 20% AITPA/Nb<sub>2</sub>O<sub>5</sub>. The catalyst was stable during reaction without any leaching of active content. The benzylation activity and selectivity towards benzylation products also depend on the reaction temperature, catalyst weight and particularly on the anisole to benzyl alcohol ratio.

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## References

- [1] I.V. Kozhevnikov, *Appl. Catal. A: Gen.* 256 (2003) 3–18.
- [2] K. Na, T. Okuhara, M. Misono, *J. Mol. Catal. A: Chem.* 115 (1997) 449–455.
- [3] K. Na, T. Okuhara, M. Misono, *J. Catal.* 170 (1997) 96–107.
- [4] C. Travers, N. Essayem, M. Delage, S. Quelen, *Catal. Today* 65 (2001) 355–361.
- [5] K.-I. Shimizu, H. Furukawa, N. Kobayashi, Y. Itaya, A. Satsuma, *Green Chem.* 11 (2009) 1627–1632.
- [6] Ch. Ramesh Kumar, K.T. Venkateswara Rao, P.S. Sai Prasad, N. Lingaiah, *J. Mol. Catal. A: Chem.* 337 (2011) 17–24.
- [7] Ch. Ramesh Kumar, P.S. Sai Prasad, N. Lingaiah, *Appl. Catal. A: Gen.* 384 (2010) 101–106.
- [8] H. Niiyama, Y. Saito, E. Echigo, *Proceedings of the seventh International Congress on Catalysis, 1980, Kodansha, Tokyo; Elsevier, Amsterdam, 1981, p. 1416.*
- [9] T. Baba, H. Watanabe, Y. Ono, *J. Phys. Chem.* 87 (1983) 2406–2411.
- [10] T. Baba, J. Sakai, Y. Ono, *Bull. Chem. Soc. Jpn.* 55 (1982) 2657–2658.
- [11] A.K. Gosh, J.B. Moffat, *J. Catal.* 101 (1986) 238–245.
- [12] K. Shimizu, K. Niimi, A. Satsuma, *Catal. Commun.* 9 (2008) 980–983.
- [13] K. Shimizu, K. Niimi, A. Satsuma, *Appl. Catal.* 349 (2008) 1–5.
- [14] G.A. Olah, *Friedel–Crafts and Related Reactions. Part I, vol. II, Wiley-Interscience, New York, 1964.*
- [15] S. Chu, M.M.-S. Wu, Y. Xiong, L.B. Yang, (Mobil corporation, USA) *Jpn. Kokai Tokyo Koho*, 1999, p. 9. CODEN: JKXXAF JP 11181456 A 2 19990706, Application: JP 1997-304443 19971106.
- [16] S.I. Fukuzawa, T. Tsuchimoto, T. Hiyama, *J. Org. Chem.* 62 (1997) 151–156.
- [17] T. Tsuchimoto, K. Tobita, T. Hiyama, S.I. Fukuzawa, *J. Org. Chem.* 62 (1997) 6997–7005.
- [18] M. Noji, T. Ohno, K. Fuji, N. Futaba, H. Tajima, K. Ishii, *J. Org. Chem.* 68 (2003) 9340–9347.
- [19] T. Yamato, C. Hideshima, G.K.S. Prakash, G.A. Olah, *J. Org. Chem.* 56 (1991) 2089–2091.
- [20] K. Motokura, N. Nakagiri, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Org. Chem.* 72 (2007) 6006–6015.

- [21] B.M. Choudary, B.P.C. Rao, N.S. Chowdari, M.L. Kantam, *Catal. Commun.* 3 (2002) 363–367.
- [22] B.M. Devassy, G.V. Shanbhag, F. Lefebvre, W. Bohringer, J. Fletcher, S.B. Halligudi, *J. Mol. Catal. A: Chem.* 230 (2005) 113–119.
- [23] K. Okumura, K. Yamashita, M. Hirano, M. Niwa, *J. Catal.* 234 (2005) 300–307.
- [24] Y. Rao, M. Trudeau, D. Antonelli, *J. Am. Chem. Soc.* 128 (2006) 13996–13997.
- [25] M.H.C. de La Cruz, M.A. Abdel-Rehim, A.S. Rocha, J.F.C. da Silva, A.C. Faro Jr., E.R. Lachter, *Catal. Commun.* 8 (2007) 1650–1654.
- [26] T. Shishido, T. Kitano, K. Teramura, T. Tanaka, *Catal. Lett.* 129 (2009) 383–386.
- [27] K. Mantri, K. Komura, Y. Kubota, Y. Sugi, *J. Mol. Catal. A* 236 (2005) 168–175.
- [28] F. Wang, W. Ueda, *Chem. Eur. J.* 15 (2009) 742–753.
- [29] I.V. Kozhevnikov, *Chem. Rev.* 98 (1998) 171–198.
- [30] S.M. Kumbar, G.V. Shanbhag, F. Lefebvre, S.B. Halligudi, *J. Mol. Catal. A: Chem.* 256 (2006) 324–334.
- [31] H. Firouzabadi, N. Iranpoor, A.A. Jafari, *J. Mol. Catal. A: Chem.* 244 (2006) 168–172.
- [32] H. Firouzabadi, N. Iranpoor, F. Nowrouzi, *Tetrahedron* 60 (2004) 10843–10850.
- [33] H. Firouzabadi, N. Iranpoor, A.A. Jafari, S. Makarem, *J. Mol. Catal. A: Chem.* 250 (2006) 237–242.
- [34] K. Srilatha, N. Lingaiah, B.L.A. Prabhavathi Devi, R.B.N. Prasad, S. Venkateswar, P.S. Sai Prasad, *Appl. Catal. A: Gen.* 365 (2009) 28–33.
- [35] N. Lingaiah, N. Seshu Babu, K. Mohan Reddy, P.S. Sai Prasad, I. Suryanarayana, *Chem. Commun.* 27 (2007) 8–279.
- [36] C.N. Satterfield, *Heterogeneous Catalysis in Industrial Practice*, 2nd ed., McGraw-Hill, New York, 1991.
- [37] M. del Arco, A. Caballero, P. Malet, V. Rives, *J. Catal.* 113 (1988) 120–128.
- [38] M. Balaraju, V. Rekha, B.L.A. Prabhavathi Devi, R.B.N. Prasad, P.S. Sai Prasad, N. Lingaiah, *Appl. Catal. A: Gen.* 384 (2010) 107–114.
- [39] Y. Le, Y. Shuai, S. Liyi, Z. Yin, F. Jianhui, *Microporous Mesoporous Mater.* 134 (2010) 108–114.
- [40] G. Lu, X. Li, Z. Qu, Q. Zhao, H. Li, Y. Shen, G. Chen, *Chem. Eng. J.* 159 (2010) 242–246.
- [41] X.L. Yang, W.L. Dai, H. Chen, Y. Cao, H.X. Li, H.Y. He, K.N. Fan, *J. Catal.* 229 (2005) 259–263.
- [42] L. Xu, W. Li, J. Hu, K. Li, X. Yang, F. Ma, Y. Guo, X. Yu, Y. Guo, *J. Mater. Chem.* 19 (2009) 8571–8579.