



# Heteropoly acid-based supported ionic liquid-phase catalyst for the selective oxidation of alcohols

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## ABSTRACT

A supported ionic liquid strategy has been applied for the immobilization of a heteropolyacid, molybdovanadophosphoric acid, onto ionic liquid-modified mesoporous silica SBA-15. The immobilized catalyst demonstrated high activity in the aerobic oxidation of primary and secondary alcohols to aldehydes and ketones, respectively. No overoxidation of the primary alcohols to carboxylic acids was observed. Secondary alcohols were chemoselectively oxidized to ketones in the presence of primary alcohol, hetero atom, and allyl groups. This catalyst could be recycled five times without obvious loss of activity.

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## 1. Introduction

Catalysts played a vital role in establishing the economic strength of chemical industry in the first half of the twentieth century. The use of heterogeneous catalysts in liquid phase offers several advantages over homogeneous ones, including ease of recovery and recycling, atom utility, and enhanced stability [1]. For the improvement, insoluble bulk materials [2–5], impregnation of homogeneous catalysts onto inert solid supports such as metal hydroxides [6–13] and polymers [14–17], and attachment of active species through covalent or ionic bonds with supports have been used [18–24]. But these systems have some disadvantages, including decreased activity, leaching of active species into the reaction medium, early decomposition of the oxidant due to support interaction, and poor accessibility of substrate and oxidant due to either hydrophilicity or low surface area of the supports [25,26]. Considering these facts, we attempted to design a catalyst system dissolving active species in ionic liquid functionalized in mesoporous silica. This provides a catalyst system with high surface area, high accessibility of substrate and oxidant, and no leaching of active species in the reaction media.

The use of ionic liquids, composed entirely of ions with a melting point below 100 °C, has become one of the most prolific areas of research, due to their unique properties, including low volatility, high polarity, and good stability over a wide temperature range, as

well as selective dissolving capacity with proper selection of cation and anion [27,28]. Moreover, because ionic liquids are expensive, it is desirable to minimize the amount of ionic liquid used in usual biphasic reaction systems. Dissolving organometallic complexes in supported films of ionic liquids (SILP) has recently been introduced as a strategy to immobilize molecular catalysts [29–31]. This allows fixing molecular catalysts in a widely tailorable environment.

The improvement of selective oxidation processes constitutes a dynamic area of academic and industrial research [32]. In view of their importance as intermediates in organic synthesis, several methods for oxidation of alcohols to aldehydes and ketones have been reported [33,34]. Swern oxidation has been shown to be a good method for the oxidation of alcohols [35]; however, this method suffers from the formation of dimethyl sulfide as a byproduct and low chemoselectivity. On the other hand, many of the most commonly used methods suffer from the use of a stoichiometric oxygen donor, such as chromate or permanganate, but these reagents are expensive and have serious toxicity issues. In many cases, aldehydes are obtained only from activated alcohols in which the carbon bears a phenyl group, such as benzyl alcohol. Sheldon et al. obtained good yields from a biphasic system for the catalytic conversion of pentan-1-ol to the aldehyde, but found that acid was produced in the case of hexan-1-ol [36]. From economic and environmental standpoints, catalytic oxidation processes are important, particularly those using molecular oxygen or air due to their lower cost, greater abundance, and improved safety [37–46]. Unfortunately, these protocols still suffer from low substrate conversion or high catalyst loadings, or require acidic media [47–49]. Au nanocrystals have been shown to be active for the oxidation of

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alcohols with O<sub>2</sub> in an aqueous base, particularly diols and triols; but under these conditions, the product is the corresponding acid, not the aldehyde [50–53]. Kaneda et al. found that hydroxyapatite-supported Pd nanoclusters gave high turnover frequencies for the oxidation of phenylethanol and benzyl alcohol but showed limited activity for the oxidation of primary alkyl alcohols [54]. Corma et al. found similar results by the addition of Au nanocrystals to CeO<sub>2</sub> with a stoichiometric oxidant [55]. Huchtings et al. [56] investigated the TiO<sub>2</sub>-supported Au–Pd catalysts for the oxidation of benzyl alcohol with O<sub>2</sub> as an oxidant. The catalysts were active for this reaction with good selectivity to benzaldehyde and benzyl benzoate as the sole byproduct. Nonetheless, ample scope exists for developing methodologies for the aerobic oxidation of alcohols.

In the past few decades, the use of polyoxometalates (POMs) and POM-based compounds as catalysts has become a significant area of research. In particular, POMs have received much interest in the area of acid and oxidation catalysis because of their acidic and redox properties, which can be controlled at the molecular or atomic level [57–59]. Vanadium-containing heteropolyacids are well known for aerobic oxidation reaction [60], and in previous studies, we found that vanadium-containing heteropolyacids immobilized in amine-functionalized SBA-15 [61,62] are very effective for oxidation reaction. Moreover, SBA-15 is a better mesoporous support due to its high hydrothermal stability and substantially larger pore sizes. Several studies have investigated using ionic liquid-modified silica for the design of catalysts for oxidation processes [63,64]. Recently, Chungu Xia et al. reported phosphotungstic acid immobilized in ionic liquid-modified polymer for the heterogeneous oxidation of alcohols using H<sub>2</sub>O<sub>2</sub> as an oxidizing agent [65]. Herein we report an effective method for the aerobic oxidation of primary and secondary alcohols to aldehydes and ketones under mild conditions with good to excellent conversions, using imidazolium cation-exchanged H<sub>5</sub>[PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub>].32.5H<sub>2</sub>O (V2) immobilized on to ionic liquid-modified SBA-15 by the SILP strategy (V2ILSBA) as a catalyst. Furthermore, we demonstrate the possibility of recycling and reusing the V2ILSBA catalyst, which makes the system ecofriendly and cost-effective.

## 2. Experimental

### 2.1. Materials and methods

All the solvents, procured from Merck, India (AR grade), were distilled and dried before use. All chemicals were purchased from Aldrich Chemicals and used as received. V and Mo content in the resulting solids was estimated by inductively coupled plasma-optical emission spectroscopy (ICP-AES). The elemental analysis (C and N) was carried out with a Carlo Erba Instruments EA1108 elemental analyzer. Nitrogen adsorption and desorption isotherms were measured at –196 °C on a Quantachrome Autosorb 1 sorption analyzer. The samples were outgassed for 3 h at 250 °C under vacuum in the degas port of the adsorption analyzer. The specific surface area was calculated using the BET model. The pore size distributions were obtained from the adsorption branch of the nitrogen isotherms by the BJH method. The XRD patterns of the samples were collected on a Philips X'Pert Pro 3040/60 diffractometer using CuK $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ), iron as the filter, and X'celerator as the detector. A Shimadzu FTIR-8201PC unit in DRS mode was used to obtain FTIR spectra of solid samples. Diffuse reflectance UV–vis (DRUV–vis) spectra of catalyst samples were obtained using a Shimadzu UV-2101 PC spectrometer equipped with a diffuse-reflectance attachment, with BaSO<sub>4</sub> as the reference. The <sup>31</sup>P MAS NMR spectrum of the catalyst was recorded using a Bruker DSX-300 spectrometer at 121.5 MHz with high-power decoupling using a Bruker 4-mm probe head. The spin-

ning rate was 10 kHz, and the delay between the two pulses was varied between 1 and 30 s to ensure complete relaxation of the <sup>31</sup>P nuclei. The chemical shifts were given relative to external 85% H<sub>3</sub>PO<sub>4</sub>. Thermogravimetric and differential thermal analysis (TG–DTA) measurements were performed on a pyris TG–DTA apparatus from room temperature to 1000 °C in flowing nitrogen (ca. 10 ml/min). In most cases, the products were analyzed without any chromatographic purification by gas chromatography (GC) (Shimadzu 14B) and GC-mass spectroscopy (Shimadzu GC-17A and QP-5000) with identical columns to obtain >99% conversions. All known reaction products gave satisfactory GC chromatograms and GCIR (Perkin-Elmer system 2000) spectra compared with those obtained from authentic samples. NMR spectra were recorded on a DRX-300 spectrophotometer (300 MHz for <sup>1</sup>H and 75.5 MHz for <sup>13</sup>C) using CDCl<sub>3</sub> as the solvent and Me<sub>4</sub>Si as the internal standard. Column chromatography was performed on silica gel (60–120 mesh) using ethyl acetate (or diethyl ether) and hexane as the eluent.

### 2.2. Catalyst preparation

#### 2.2.1. Preparation of SBA-15 and H<sub>5</sub>[PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub>].32.5H<sub>2</sub>O

SBA-15 and H<sub>5</sub>[PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub>].32.5H<sub>2</sub>O synthesis was carried out as described previously [61].

#### 2.2.2. Synthesis of ionic liquid-modified H<sub>5</sub>[PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub>] (1)

[C<sub>4</sub>mim]<sup>+</sup> salt of [PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub>]<sup>5-</sup> was precipitated from acetone solutions of [PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub>]<sup>5-</sup> by the addition of excess [C<sub>4</sub>mim]Br. The yellow waxy solid was collected, washed thoroughly with H<sub>2</sub>O, and dried. <sup>13</sup>C NMR  $\delta$  (ppm) = 137, 124, 123 (aromatic), 50 (CH<sub>2</sub>N), 37 (NCH<sub>3</sub>), 32 (CH<sub>2</sub>), 19 (CH<sub>2</sub>), 13 (CH<sub>3</sub>). This compound is soluble in DMSO at room temperature.

#### 2.2.3. Synthesis of 1-(3-trimethoxysilylpropyl)-3-methylimidazolium-chloride (2)

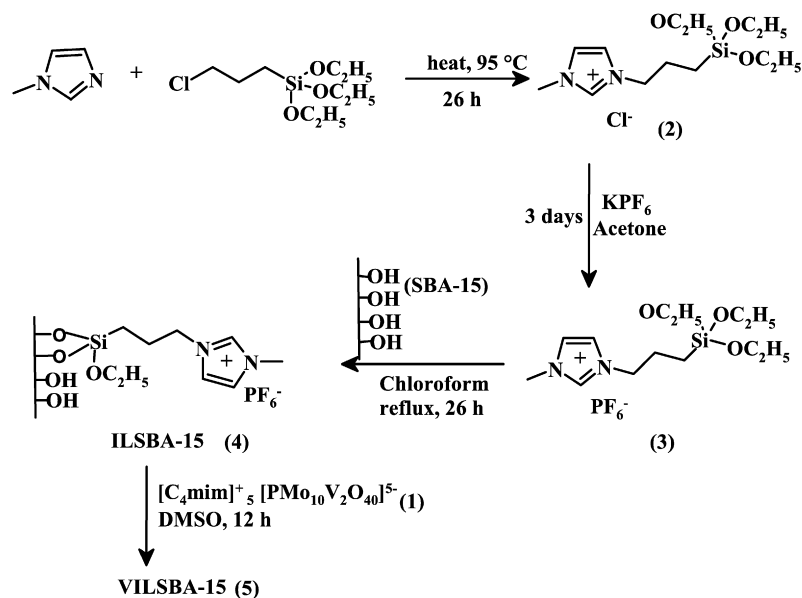
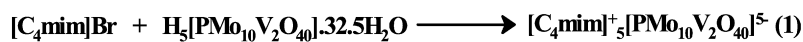
A mixture of 1-methylimidazole (3.36 g, 40 mmol) and 3-chloropropyltrimethoxysilane (9.63 g, 40 mmol) was heated under an argon atmosphere at 95 °C for 24 h. After cooling, viscous oil was formed. This viscous oil was used immediately in the next step. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) = 8.53 (s, 1H), 8.34 (d, 1H), 8.26 (d, 1H), 4.49 (t, 2H), 4.11 (s, 3H), 3.40–3.52 (m, 6H), 1.85–1.91 (m, 2H), 1.25–1.33 (t, 9H), 0.71–0.78 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) = 136.1, 124.3, 122.8, 52.2 (CH<sub>2</sub>N), 51.4 (CH<sub>2</sub>O), 36.4 (NCH<sub>3</sub>), 25.1 (CH<sub>2</sub>), 11.2 (CH<sub>3</sub>), 7.0 (SiCH<sub>2</sub>) [66].

#### 2.2.4. Synthesis of 1-(3-trimethoxysilylpropyl)-3-methylimidazolium-hexafluorophosphate (3)

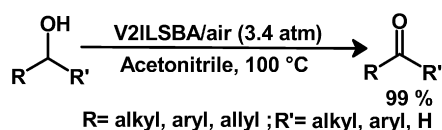
To a solution of the above, salt (3.2 g, 10 mmol), in acetone (15 mL) and potassium hexafluorophosphate (1.9, 10.5 mmol) were added in a single portion. The resulting mixture was stirred for 3 days at room temperature. Then the mixture was filtered, and the solvent was evaporated under reduced pressure to give **3**. <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  (ppm) = 8.90 (s, 1H), 7.58 (d, 1H), 7.55 (d, 1H), 4.39 (t, 2H), 4.15 (s, 3H), 3.59–3.71 (m, 6H), 1.88–1.94 (m, 2H), 1.27–1.35 (t, 9H), 0.61–0.70 (m, 2H), <sup>13</sup>C NMR (CDCl<sub>3</sub>),  $\delta$  (ppm) = 136.3, 124.0, 122.4, 51.5 (CH<sub>2</sub>N), 51.3 (CH<sub>2</sub>O), 36.0 (NCH<sub>3</sub>), 24.9 (CH<sub>2</sub>), 10.2 (CH<sub>3</sub>), 6.9 (SiCH<sub>2</sub>), <sup>31</sup>P NMR (CDCl<sub>3</sub>),  $\delta$  (ppm) = 143.6 [66].

#### 2.2.5. Synthesis of ILSBA-15 (4)

The ionic liquid **2** (2.81 g, 6.5 mmol) was dissolved in chloroform (50 mL) and treated with mesoporous silica (dried under vacuum and heated at 180 °C overnight, 4.00 g). The mixture was heated under reflux (65 °C) for 26 h. After cooling to room temperature, the solid was isolated by filtration and washed with chloroform (50 mL) and diethyl ether (50 mL), then dried under



Scheme 1. Synthesis of V2ILSBA.



Scheme 2. Oxidation of alcohols to aldehydes and ketones.

reduced pressure to give a powder.  $^{13}\text{C}$  NMR  $\delta$  (ppm) = 136.39, 124.0, 122.4 (aromatic), 63 ( $\text{CH}_2\text{N}$ ), 47–51 ( $\text{CH}_2\text{O}$ ), 36.0 ( $\text{NCH}_3$ ), 22 ( $\text{CH}_2$ ), 14 ( $\text{CH}_3$ ), 8.4 ( $\text{SiCH}_2$ ).  $^{29}\text{Si}$  MAS NMR: (59.7 MHz)  $\delta$  (ppm) = –110 ( $\text{Q}^4$ ), –102 ( $\text{Q}^3$ ), –68 ( $\text{T}^3$ ), –60 ( $\text{T}^2$ ) [66]. Elemental analysis revealed 850  $\mu\text{mol/g}$  ionic liquid per gram of SBA-15 (0.72 ionic liquid fragment/ $\text{nm}^2$ ).

### 2.2.6. Preparation of ionic liquid-modified $\text{H}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]\cdot 32.5\text{H}_2\text{O}$ catalyst supported on ILSBA-15 (V2ILSBA) (5)

ILSBA-15 (1 g) was stirred vigorously with (0.4 g) of  $[\text{C}_4\text{mim}]^+$  salt of a  $[\text{PMo}_{10}\text{V}_2\text{O}_{40}]^{5-}$  in 50 mL of DMSO at room temperature for 12 h. The solid was then filtered off, washed with a large amount of DMSO, and dried in vacuum to give V2ILSBA (Scheme 1).  $^{13}\text{C}$  NMR  $\delta$  (ppm) = 136.3, 124.0, 122.1 (aromatic), 63 ( $\text{CH}_2\text{N}$ ), 47–51 ( $\text{CH}_2\text{O}$ ), 36.0 ( $\text{NCH}_3$ ), 22 ( $\text{CH}_2$ ), 14 ( $\text{CH}_3$ ), 8.4 ( $\text{SiCH}_2$ ).  $^{29}\text{Si}$  MAS NMR: (59.7 MHz)  $\delta$  (ppm) = –110 ( $\text{Q}^4$ ), –102 ( $\text{Q}^3$ ), –68 ( $\text{T}^3$ ). The loading amount of  $\text{H}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]\cdot 32.5\text{H}_2\text{O}$  was 173  $\mu\text{mol/g}$ . After incorporation of  $[\text{PMo}_{10}\text{V}_2\text{O}_{40}]^{5-}$ , the solvent was analyzed by ICP-AES, which revealed no trace of V or Mo. This finding indicates exchange of the  $[\text{PMo}_{10}\text{V}_2\text{O}_{40}]^{5-}$  ion with the  $\text{PF}_6^-$  anion.

### 2.3. Typical procedure for oxidation of alcohols

Alcohol (1 mmol) and catalyst (V2ILSBA) (100 mg, 0.02 mol% eq. V2) were stirred at ca. 100 °C in acetonitrile (20 mL) under air pressure (3.4 atm) in a Parr autoclave (pressure reactor), using  $\alpha, \alpha$ -azobisisobutyronitrile (AIBN) or *tert*-butylhydroperoxide (TBHP) as a radical initiator (Scheme 2). After the catalyst was filtered, the filtrate was analyzed by GC and passed through a short pad of silica gel using ethyl acetate and hexane (1:19) as the eluent

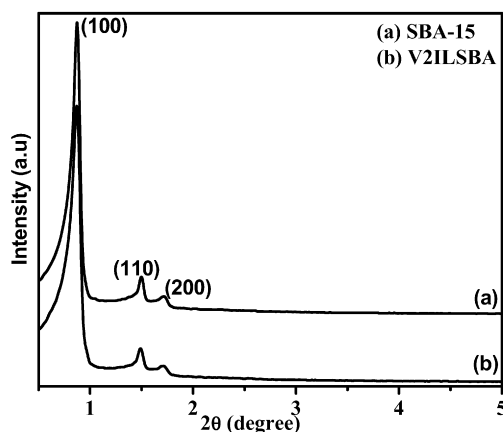


Fig. 1. Small angle XRD of (a) SBA-15 and (b) V2ILSBA.

or distilled to provide the 100% analytically pure aldehydes and ketones. 2-Methylnaphthylketone:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  (ppm) = 8.45 (s, 1H), 7.85–8.05 (m, 4H), 7.5–7.63 (m, 2H), 2.71 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 52.32 MHz)  $\delta$  (ppm) = 200.5, 136.7, 132.6, 132.6, 128.3, 127.7, 31.5, 7.9.

## 3. Results and discussion

### 3.1. Catalyst characterization

#### 3.1.1. ICP/AES analysis

ICP-AES found an estimated molybdenum content of 4.15 ppm and vanadium content of 21.5 ppm in V2ILSBA (40) (40% of  $\text{H}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]$  immobilized in ionic liquid (1-(3-trimethoxysilylpropyl)-3-methylimidazolium hexafluorophosphate).

#### 3.1.2. Low-angle XRD

Low-angle powder X-ray diffraction patterns of SBA-15 and V2ILSBA (40) are depicted in Fig. 1. SBA-15 patterns showed an

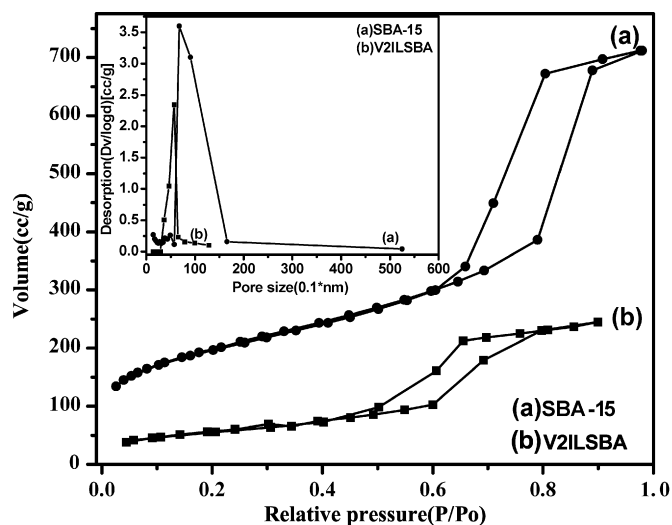


Fig. 2.  $N_2$  sorption isotherms of (a) SBA-15 and (b) V2ILSBA.

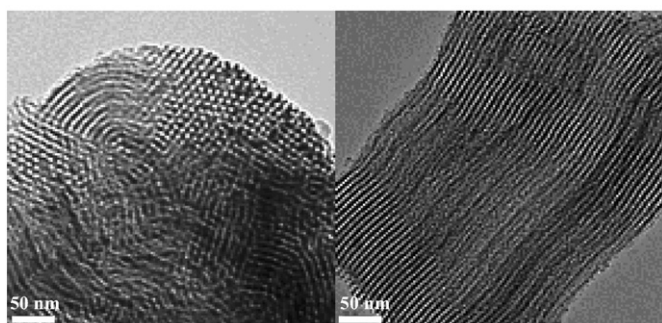


Fig. 3. HRTEM pictures of V2ILSBA.

intense peak assigned to reflections at (100) and two low-intensity peaks at (110) and (200), indicating a significant degree of long-range ordering in the structure and a well-formed hexagonal lattice. The V2ILSBA (40) sample showed a decrease in the intensities of all the aforementioned peaks with a marginal shift toward lower  $2\theta$  values, demonstrating functionalization inside the mesopore channels of SBA-15 and the induction of a relatively high number of POM anions inside the SBA-15; however, the mesoporous structure of the support remained intact under the conditions used for functionalization.

### 3.1.3. Surface area

$N_2$  adsorption–desorption isotherms of SBA-15 and V2ILSBA (40) are depicted in Fig. 2. BET surface areas and BJH distributions were calculated using  $N_2$  adsorption at 77 K. Functionalization and introduction of POM anions significantly affected the surface area and pore distribution of the modified samples. The samples displayed a type IV isotherm with H1 hysteresis and a sharp increase in pore volume adsorbed above  $P/P_0 \sim 0.7$   $cm^3/g$ , characteristic of highly ordered mesoporous materials. The textural properties of SBA-15 were substantially maintained over ionic liquid functionalization and on subsequent anchoring of vanadium-modified POM. The parent SBA-15 sample showed a maximum pore diameter (6.8 nm) and surface area (714  $m^2/g$ ). Functionalization and introduction of POM of mesoporous silica shifted the pore maximum to smaller diameter (5.7 nm) and decreased the surface area (209  $m^2/g$ ). HRTEM findings supported the mesoporous structure of V2ILSBA (Fig. 3).

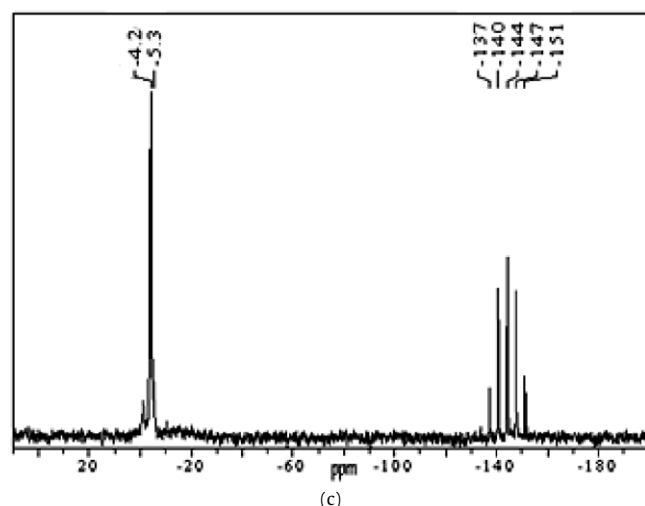
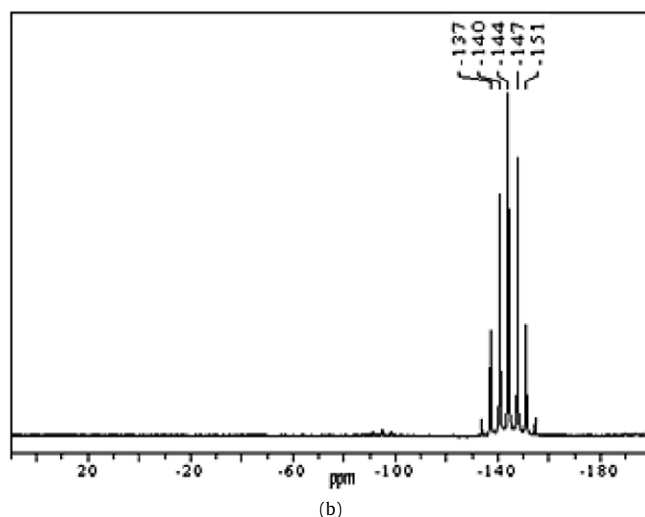
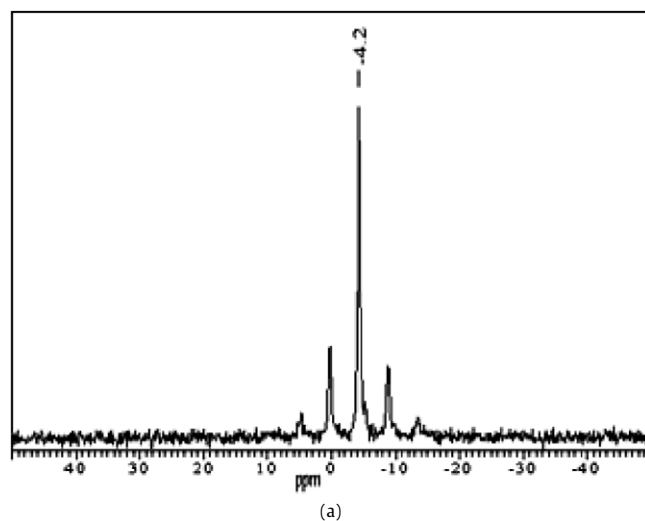


Fig. 4.  $^{31}P$  CP MAS NMR of V2ILSBA.

### 3.1.4. $^{31}P$ and $^{51}V$ CP-MAS NMR

Due to the nature of the ionic liquid-modified  $H_5[PMo_{10}V_2O_{40}] \cdot 32.5H_2O$  (relatively viscous), we were not able to achieve good rotation; thus, the  $^{31}P$  one showed numerous spinning sidebands at around 4.2 ppm (Fig. 4a). The  $^{31}P$  NMR spectra of ILSBA-15 show that the resonance signal at  $-150$  ppm corresponds to the formula  $BMIM^+ \cdot PF_6^-$  (Fig. 4b). The phosphorus spectrum of

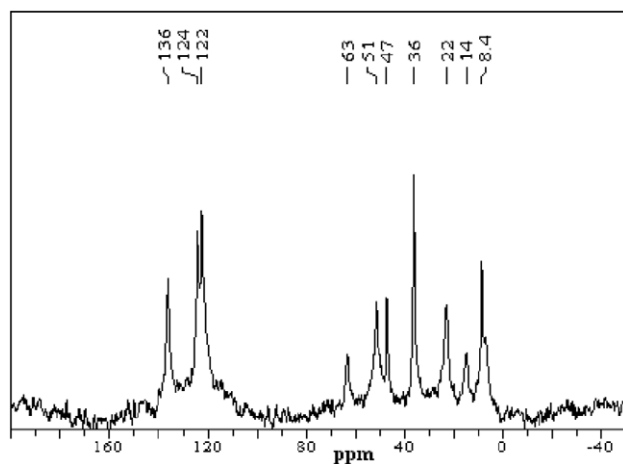
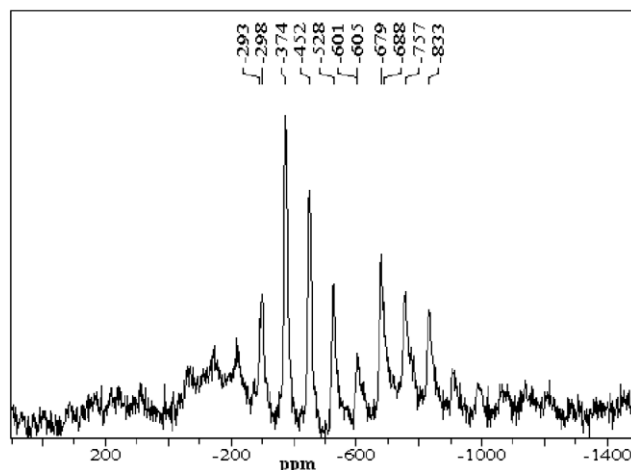
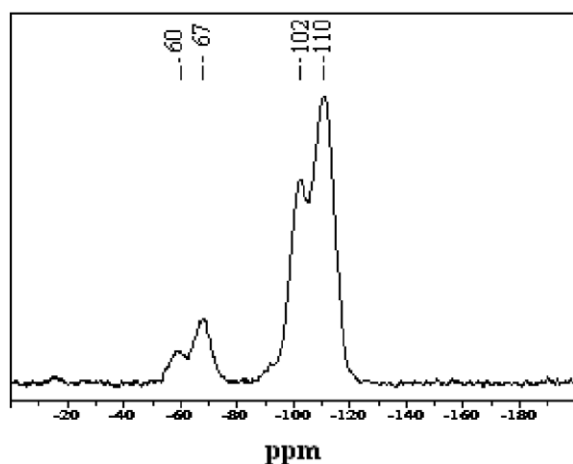
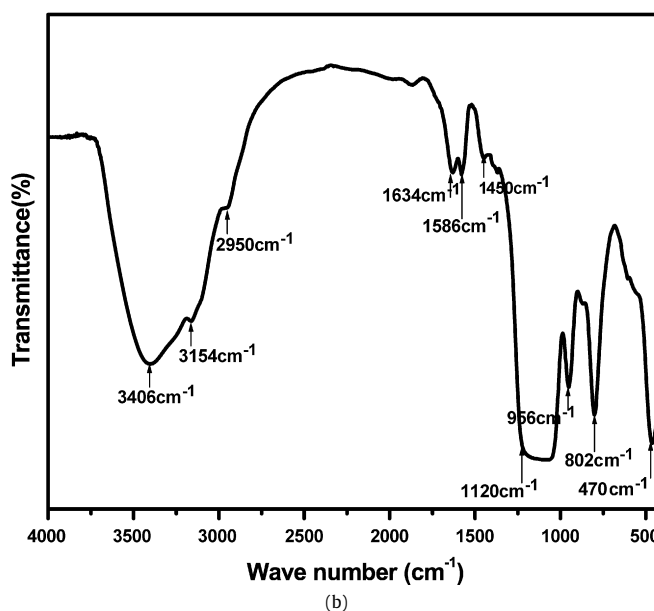
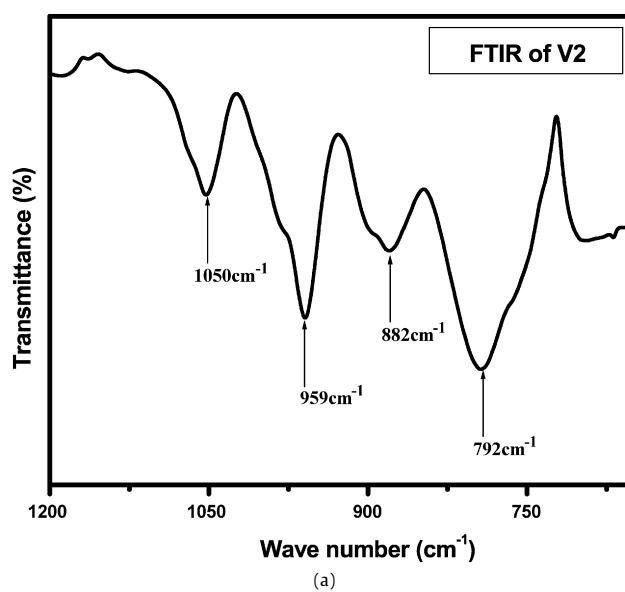
Fig. 5.  $^{13}\text{C}$  CP MAS NMR V2ILSBA.Fig. 7.  $^{51}\text{V}$  MAS NMR of V2ILSBA.Fig. 6.  $^{29}\text{Si}$  CP MAS NMR of V2ILSBA.

Fig. 8. FTIR spectra of V2ILSBA.

ionic liquid-modified  $\text{H}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]\cdot 32.5\text{H}_2\text{O}$  catalyst supported on V2ILSBA shows the two signals at 4.2 ppm and 150 ppm of the heteropolyanion and  $\text{PF}_6^-$  (the multiplet corresponds to the P–F couplings) (Fig. 4c). The  $^{13}\text{C}$  MAS NMR spectrum is depicted in Fig. 5. The  $^{29}\text{Si}$  MAS NMR spectrum of ILSBA-15 showed two signals at  $-110$  and  $-102$  ppm corresponding to  $\text{Q}^4$  and  $\text{Q}^3$  species of the silica framework, respectively ( $\text{Q}^n = \text{Si}(\text{OSi})_n(\text{OH})_{4-n}$ ) (Fig. 6) Additional signals appeared at  $-68$  and  $-60$  ppm, assignable to  $\text{T}^3$  and  $\text{T}^2$  organosilica species, respectively ( $\text{T}^n = \text{RSi}(\text{OSi})_n(\text{OEt})_{3-n}$ ).

The vanadium-51 spectra showed the presence of numerous spinning side band envelopes centered at  $-400$  ppm, attributed to the various stereoisomers possibly present (Fig. 7). In fact, from the  $^{51}\text{V}$  NMR spectra, we could not make a clear distinction between different isomers, but we could see that vanadium was octahedrally distorted.

### 3.1.5. FTIR

FTIR bands of V2 are depicted in Fig. 8a. The characteristic bands of heteropolyion was observed at 1054, 959, 882, and  $792\text{ cm}^{-1}$ . The typical FTIR bands due to siliceous material Si–O–Si are observed for V2ILSBA (Fig. 8b): a main band at  $1120\text{ cm}^{-1}$  due to asymmetric Si–O–Si stretching modes and symmetric stretching at 960, 802, and  $470\text{ cm}^{-1}$ . A broad, asymmetric feature was seen at  $3400\text{ cm}^{-1}$  due to O–H vibrations of silanols and water. Additional bands at 2950, 3154, and  $1450\text{ cm}^{-1}$  were due to C–H stretching and deformation vibrations, confirming the functionalization of ionic liquid into the material. The bands at 1586 and



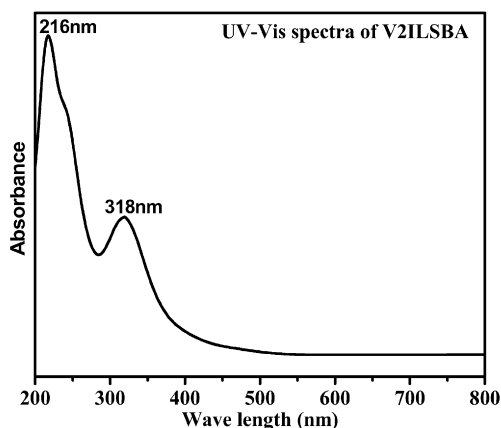


Fig. 9. UV-vis spectra of V2ILSBA.

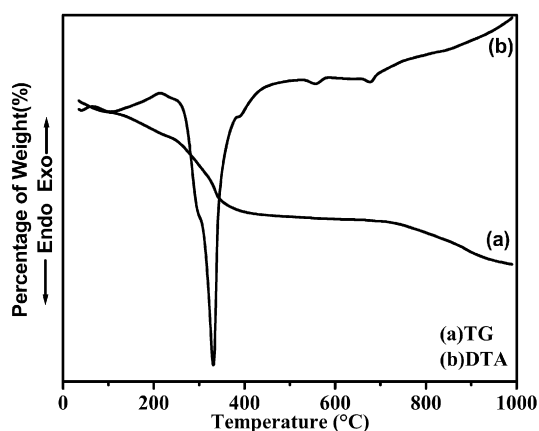


Fig. 10. TG and DTA of V2ILSBA.

$1634\text{ cm}^{-1}$  are due to C=N and C=C ring vibrations of the imidazole part of the ionic liquid. Because of the low concentration of V2 in the catalyst system, the characteristic bands of V2 were masked by the bands of SBA-15 and ionic liquid.

### 3.1.6. UV-vis

UV-vis spectra of V2ILSBA are shown in Fig. 9. Because V2 exhibited characteristic absorption bands in the UV-vis region, diffuse-reflectance UV-vis spectroscopy is commonly used to characterize their structures. V2ILSBA exhibited certain features of LMCT; the characteristic bands were observed at around 216 and 318 nm. The bands were shifted slightly with respect to neat V2, possibly due to interactions between V2 and ionic liquid in the constraining environment of mesoporous silica.

### 3.1.7. TG-DTA

The thermal behavior of V2ILSBA was determined by TG-DTA. Fig. 10 shows the TG-DTA curves of V2ILSBA from 25–100 °C. Evident weight loss was observed at 300 °C. The sample showed endothermic peaks on heating. V2ILSBA was stable up to 295 °C and decomposed rapidly above 330 °C.

## 3.2. Catalytic activity studies

The catalytic activity was studied by the following method. Alcohol (1 mmol) and V2ILSBA catalyst (100 mg, 0.02 mmol (40 wt%  $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$  supported on IL-SBA-15)) were stirred at ca. 100 °C in acetonitrile (20 mL) under air pressure (3.4 atm) in a Parr autoclave (pressure reactor) (Scheme 2). Two experiments were performed to optimize the reaction condition for this newly syn-

Table 1

Effect of reaction parameter on oxidation of 1-(naphylen-2-yl) ethanol<sup>a</sup>

Reaction parameter	Yield (%)
Effect of pressure (atm)	
2	60
2.7	93
3.4	99
Effect of temperature (°C)	
80	79
90	92
100	99
Effect of V2 loading (%)	
20	26
30	58
40	99
50	99
60	91

<sup>a</sup> Reaction conditions: catalyst V2ILSBA, substrate (1 mmol) and catalyst (V2-ILSBA) were stirred in acetonitrile (20 mL) under air pressure in Parr autoclave, GC yield.

thesized catalyst V2ILSBA (Table 1). In the first experiment, the reaction was carried out using 1-(naphylen-2-yl) ethanol as a model substrate and AIBN or TBHP as a radical initiator at 1 atm air pressure at 100 °C in a Parr autoclave with the active catalyst in acetonitrile solvent, which gave only 40% yield. Product yield increased with a pressure increase from 2 to 3.4 atm (60% to 99%). In the second experiment, we studied the effect of temperature. We found no reaction between alcohol and molecular oxygen of air at 50 °C. Alcohol yield increased with increasing temperature to 80–100 °C (79–99%). Based on these findings, we can conclude that the maximum yield can be obtained at 100 °C and 3.4 atm. To investigate the effect of V2 loading on alcohol oxidation, immobilized catalysts were prepared with various V2 loadings (20–50%) on SBA-15 and tested in alcohol oxidation; the results showed an increase in yield with increasing V2 loading (Table 1). At higher V2 loading (60%), alcohol conversion decreased, possibly due to changes in the morphology of the support (mesopore diameter and volume). Moreover, higher loadings may have acted as an inhibitor rather than as a catalyst by capturing active radicals. V2ILSBA (40%) exhibited the highest activity, due to the ease of diffusion constraints; thus, we used this catalysts for further studies. The catalytic activity of V2ILSBA was compared with that of the corresponding  $\text{H}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]\cdot 32.5\text{H}_2\text{O}$  dissolved in ionic liquid under the same reaction conditions. The product yields obtained from using liquid-dissolved  $\text{H}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]\cdot 32.5\text{H}_2\text{O}$  (90%) were only slightly lower than those from using V2ILSBA.

To evaluate the scope of this protocol, we studied the oxidation of other alcohols. As shown in Table 2 (entries 2–6), secondary alcohols such as diphenylmethanol, cyclohexanol, phenylethanol, 2-hexanol, and 2-phenylpropanol oxidized to the corresponding ketones in high yields. Similar reactivity was observed in the oxidation of substrates with electron-withdrawing and donating groups in the aromatic ring (i.e., 4-methoxy-, 4-methyl-, 4-chloro-, 4-bromo- and 4-nitro-phenylethanol) to corresponding ketones in good yields (Table 2, entries 7–11). The oxidation also proceeded effectively with some complicated alcohols, such as benzoin, menthol, [1,7]trimethylbicyclo[2,2,1]heptan-2-ol, and 3,5,5-trimethylcyclohex-2-enol, in high yields (Table 2, entries 12–15). Benzylalcohol was oxidized to benzaldehyde within 12 h with excellent yield (Table 2, entry 16).

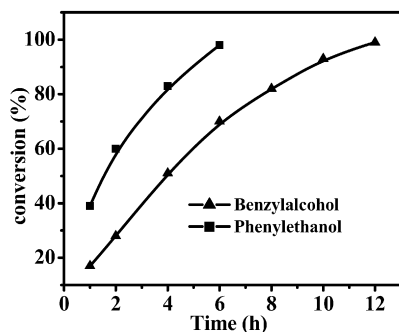
Catalysts designed for the transformation of biomolecules must be able to selectively transform only one out of several different functional groups in the same molecule, ideally without protection of the remaining other groups. Carbohydrates are multifunctional biomolecules that contain both primary and secondary alcohol groups. Thus, protection and deprotection of hydroxyl groups that

**Table 2**  
Aerobic oxidation of alcohols to aldehydes and ketones<sup>a</sup>

Entry	Substrate	Product	t (h)	Yield <sup>b</sup> (%)
1	1-(Naphylen-2-yl) ethanol	2-Methylnaphthylketone	7	99
2	Diphenylmethanol	Benzophenone	7	99
3	Cyclohexanol	Cyclohexanone	6	99
4	Phenylethanol	Acetophenone	6	99
5	2-Hexanol	2-Hexanone	5	98
6	2-Phenyl propanol	Propiophenone	7	93
7	4-Methoxy phenylethanol	4-Methoxy acetophenone	6	98
8	4-Methyl phenylethanol	4-Methyl acetophenone	6	96
9	4-Chloro phenylethanol	4-Chloro acetophenone	6	98
10	4-Bromo phenylethanol	4-Bromo acetophenone	6	98
11	4-Nitro phenylethanol	4-Nitro acetophenone	6	94
12	Benzoil	Benzil	7	95
13	Menthol	Menthone	6	96
14	[1,7,7]Trimethylbicyclo [2,2,1]heptan-2-ol	Camphor	8	95
15	3,5,5-Trimethylcyclohex-2-enol	3,5,5-trimethylcyclohex-2-enone	7	94
16	Benzyl alcohol	Benzaldehyde	12	98
17	1, 3-Butanediol	4-hydroxybutane-2-one	8	83
18	Geraniol	Geraniol	10	97
19	Cinnamyl alcohol	Cinnamaldehyde	13	98
20	Pyridine-2-methanol	2-Pyridine carboxaldehyde	11	96

<sup>a</sup> Reaction conditions: catalyst V2ILSBA, substrate (1 mmol) and catalyst (V2-ILSBA) (100 mg, 0.02 mol% of V2) were stirred at ca. 100 °C in acetonitrile (20 mL) under air pressure (3.4 atm) in Parr autoclave.

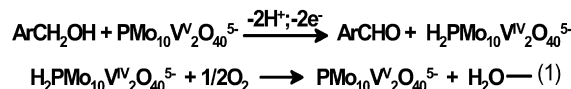
<sup>b</sup> GC yield.



**Fig. 11.** Progress of the oxidation of benzyl alcohol and phenylethanol.

must remain unchanged are required before the application of conventional oxidation methods. Therefore, we investigated the rate of oxidation of secondary and primary alcohols under the same reaction conditions. The oxidation profile of a 1:1 mixture of benzyl alcohol and phenyl ethanol (Fig. 11) shows a faster oxidation rate of the secondary alcohol (phenyl ethanol) than of the primary alcohol (benzyl alcohol). In another experiment, we used 1,3-butenediol as a substrate to check the reactivity (Table 2, entry 17) and, surprisingly, found that 4-hydroxybutane-2-one was the only product after 8 h with a 83% product yield, resulting from the oxidation of secondary alcohol. Thus, the V2ILSBA-15 catalyst preferentially oxidized secondary alcohol over the primary hydroxyl group functionality. Similarly, allylic alcohols, such as geraniol and cinnamyl alcohol, were oxidized to aldehydes without oxidation of the carbon-carbon double bonds (Table 2, entries 18 and 19). Furthermore, pyridine-2-methanol was oxidized to corresponding aldehydes in high yields (Table 2, entry 20). No oxidation was observed with the heteroatom.

The selective oxidations of primary and secondary alcohols to aldehydes and ketones, respectively, without overoxidation of the aldehydes found for heteropolyoxometallates were electron-



**Scheme 3.** Possible mechanism of oxidation of alcohols.

**Table 3**  
Recyclability of catalyst V2ILSBA for oxidation of 1-(naphylen-2-yl) ethanol to methylnaphthylketone<sup>a</sup>

Run	1	2	3	4	5
Yield (%)	99	99	98	96	95

<sup>a</sup> Reaction conditions: Substrate (1 mmol) and catalyst (V2ILSBA) (100 mg, 0.02 mol% of V2) were stirred at ca. 100 °C in acetonitrile (20 mL) under air pressure (3.4 atm) in Parr autoclave.

transfer redox-type oxidations using molybdenum–vanadium mixed-addenda Keggin anions [67]. As reported in the literature, such reactions are thought to proceed by the generalized mechanism, shown in Scheme 3.

The product yields obtained by the use of V2ILSBA were comparable to those of the homogeneous analogue  $\text{H}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}] \cdot 32.5\text{H}_2\text{O}$  under the same reaction conditions. This clearly indicates that the homogeneous catalyst can be heterogenized with the retention of the  $\text{H}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}] \cdot 32.5\text{H}_2\text{O}$  species by supporting on ILSBA-15.

The regenerability and recyclability of a catalyst system are very important for any catalytic reaction. After completion of the reaction, the reaction mixture was filtered, washed with hexane, dried, and recharged with fresh substrate and oxidant, and then the reaction was continued for the specified time. ICP-AES analysis confirmed that no vanadium or molybdenum species were present in the filtrate, and similar catalytic activity was observed in all five recyclings with only a slight decrease after the fourth recycling (Table 3). The results can rule out any involvement of vanadium or molybdenum species that leached out from the catalyst into the reaction medium, and thus the observed catalysis was truly heterogeneous in nature.

#### 4. Conclusion

Here we have presented a novel and efficient protocol for a broad range of benzylic, allylic, and aliphatic alcohol oxidation under mild conditions with a high degree of chemoselectivity using a V2ILSBA catalyst system and air as an oxidant. The benzylic and allylic alcohols were oxidized with excellent conversions, whereas aliphatic alcohols were less reactive. The activities and product selectivities were comparable to those of the homogeneous analogue, demonstrating that the homogeneous catalysis could be heterogenized successfully. The oxidation rate was faster for the secondary alcohols than for the primary alcohols. The high catalyst activity and ease of catalyst recovery and reuse raise the prospect of using this type of simple supported catalyst for organic syntheses and the industrial oxidation of alcohols.

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#### References

- [1] M. Dusi, T. Mallat, A. Baiker, *Catal. Rev.* 42 (2000) 213.
- [2] M.V. Vasylyev, R. Neumann, *J. Am. Chem. Soc.* 126 (2004) 884.
- [3] M. Musawir, P.N. Davey, G. Kelly, I.V. Kozhevnikov, *Chem. Commun.* (2003) 1414.
- [4] K. Yamaguchi, N. Mizuno, *New J. Chem.* 26 (2002) 972.
- [5] T. Okuhara, *Chem. Rev.* 102 (2002) 3641.

- [6] B.F. Sels, D.E. De Vos, M. Buntinx, F. Pierard, A.K.D. Mesmaeker, P.A. Jacobs, *Nature* 400 (1999) 855.
- [7] B.F. Sels, D.E. De Vos, P.A. Jacobs, *J. Am. Chem. Soc.* 123 (2001) 8350.
- [8] T. Matsushita, K. Ebitani, K. Kaneda, *Chem. Commun.* (1999) 265.
- [9] K. Yamaguchi, K. Mori, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Am. Chem. Soc.* 122 (2000) 7144.
- [10] K. Yamaguchi, K. Mori, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Am. Chem. Soc.* 124 (2002) 11572.
- [11] K. Yamaguchi, N. Mizuno, *Angew. Chem. Int. Ed.* 41 (2002) 4538.
- [12] C. Nozaki, C.G. Langmuir, A.T. Bell, T.D. Tilley, *J. Am. Chem. Soc.* 124 (2002) 13194.
- [13] K.L. Fudjara, I.J. Drake, A.T. Bell, T.D. Tilley, *J. Am. Chem. Soc.* 126 (2004) 10864.
- [14] Y. Uozumi, R. Nakao, *Angew. Chem. Int. Ed.* 42 (2003) 194.
- [15] N.E. Leadbeater, M. Marco, *Chem. Rev.* 102 (2002) 3215.
- [16] C.A. McNamara, M.J. Dixon, M. Bradley, *Chem. Rev.* 102 (2002) 3275.
- [17] D.E. Bergbreiter, *Chem. Rev.* 102 (2002) 3345.
- [18] A.L. Villa, B.F. Sels, D.E. De Vos, P.A. Jacobs, *J. Org. Chem.* 64 (1999) 7267.
- [19] D. Hoegaerts, B.F. Sels, D.E. De Vos, F. Verpoort, P.A. Jacobs, *Catal. Today* 60 (2000) 209.
- [20] R. Neumann, M. Cohen, *Angew. Chem. Int. Ed.* 36 (1997) 1738.
- [21] T. Sakamoto, C. Pac, *Tetrahedron Lett.* 41 (2000) 10009.
- [22] R. Neumann, H. Miller, *J. Chem. Soc. Chem. Commun.* (1995) 2277.
- [23] G. Gelbard, T. Gauducheu, E. Vidal, V.I. Parvulescu, A. Crosman, V.M. Pop, *J. Mol. Catal. A Chem.* 182/183 (2002) 257.
- [24] J. Ichihara, S. Yamaguchi, T. Nomoto, H. Nakayama, K. Iteya, N. Naitoh, Y. Sasaki, *Tetrahedron Lett.* 43 (2002) 8231.
- [25] N.M. Okun, T.M. Anderson, C.L. Hill, *J. Am. Chem. Soc.* 125 (2003) 3194.
- [26] N.M. Okun, T.M. Anderson, C.L. Hill, *J. Mol. Catal.* 197 (2003) 283.
- [27] T. Welton, *Chem. Rev.* 99 (1999) 2071.
- [28] D. Zhao, M. Wu, Y. Kou, E. Min, *Catal. Today* 74 (2002) 157.
- [29] A. Riisager, R. Fehrmann, S. Flicker, R. Van Hal, M. Haumann, P. Wassercheid, *Angew. Chem. Int. Ed.* 44 (2005) 815.
- [30] M. Gruttadauria, S. Riela, C. Aprile, P.L. Meo, F. D'Anna, R. Noto, *Adv. Synth. Catal.* 348 (2006) 82.
- [31] C.P. Mehnert, *Chem. Eur. J.* 1 (2004) 50.
- [32] M.B. Smith, J. March, *March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, fifth ed., Wiley-Interscience, New York, 2001, p. 1514.
- [33] R.A. Sheldon, J.K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, 1984.
- [34] M. Hudlicky, *Oxidations in Organic Chemistry*, ACS Monograph, vol. 186, Am. Chem. Soc., Washington, 1990.
- [35] A.J. Mancuso, D. Swern, *Synthesis* (1981) 165.
- [36] G. ten Brink, I.W.C.E. Arends, R.A. Sheldon, *Science* 287 (2000) 1636.
- [37] G.W. Parshall, S.D. Ittel, *Homogeneous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*, second ed., Wiley-Interscience, New York, 1992.
- [38] C. Marchal, A. Davidson, R. Thouvenot, G. Herve, *J. Chem. Soc. Faraday Trans.* 89 (1993) 3301.
- [39] M. Ai, E. Muneyama, A. Kunishige, K. Ohdan, *Bull. Chem. Soc. Jpn.* 67 (1994) 551.
- [40] W. Partenheimer, *Catal. Today* 23 (1995) 69.
- [41] K. Weissermel, H. Arpe, *Industrial Organic Chemistry*, third ed., VCH, Weinheim, 1997.
- [42] N. Mizuno, M. Misono, *Chem. Rev.* 98 (1998) 199.
- [43] R.A. Sheldon, I.W.C.E. Arends, A. Dijkman, *Catal. Today* 57 (2000) 157.
- [44] R. Ben-Daniel, P. Alsters, R. Neumann, *J. Org. Chem.* 66 (2001) 8650.
- [45] A. Dijkman, A. Marino-Gonzalez, A.M.I. Payeras, I.W.C.E. Arends, R.A. Sheldon, *J. Am. Chem. Soc.* 123 (2001) 6826.
- [46] G.T. Ten Brink, I.W.C.E. Arends, R.A. Sheldon, *Science* 287 (2000) 1636.
- [47] J.A. Osborn, K.S. Coleman, C.Y. Lorber, *Eur. J. Inorg. Chem.* (1998) 1673.
- [48] S.V. Ley, R. Lenz, *J. Chem. Soc. Perkin Trans. 1* (1997) 3291.
- [49] A. Cecchetto, F. Fontana, F. Minisci, F. Recupero, *Tetrahedron Lett.* 42 (2001) 6651.
- [50] L. Prati, M. Rossi, *J. Catal.* 176 (1998) 552.
- [51] F. Porta, L. Prati, M. Rossi, G. Scari, *J. Catal.* 211 (2002) 464.
- [52] S. Carretin, P. McMorn, P. Johnston, K. Griffin, G.J. Hutchings, *Chem. Commun.* (2002) 696.
- [53] F. Porta, L. Prati, *J. Catal.* 224 (2004) 397.
- [54] K. Mori, T. Hara, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Am. Chem. Soc.* 126 (2004) 10657.
- [55] A. Abad, P. Conception, A. Corma, H. Garcia, *Angew. Chem.* 44 (2005) 4066.
- [56] D.I. Enache, J.K. Edwards, P. Landon, B. Solsona-Espriu, A.F. Carley, A.A. Herzog, M. Watanabe, C.J. Kiely, D.W. Knight, G.J. Hutchings, *Science* 311 (2006) 362.
- [57] T. Okuhara, *Chem. Rev.* 102 (2002) 3641.
- [58] I.V. Kozhevnikov, *Chem. Rev.* 98 (1998) 171.
- [59] T. Okuhara, N. Mizuno, M. Misono, *Adv. Catal.* 41 (1996) 113.
- [60] M. Vazyliev, D. Sloboda-Rozner, A. Haimov, G. Maayan, R. Neumann, *Top. Catal.* 34 (2005) 93.
- [61] A. Bordoloi, F. Lefebvre, S.B. Halligudi, *J. Catal.* 247 (2007) 166.
- [62] A. Bordoloi, A. Vinu, S.B. Halligudi, *App. Catal. A* 333 (2007) 143.
- [63] F. Shi, Y. Gu, Q. Zhang, Y. Deng, *Catal. Surv. Asia* 8 (2004) 179.
- [64] F. Shi, Q. Zhang, D. Li, Y. Deng, *Chem. Eur. J.* 11 (2005) 5279.
- [65] X. Lang, Z. Li, C. Xia, *Synth. Commun.* 38 (2008) 1610.
- [66] K. Yamaguchi, C. Yoshida, S. Uchida, N. Mizuno, *J. Am. Chem. Soc.* 127 (2005) 530.
- [67] R. Newmann, M. Levin, *J. Org. Chem.* 56 (1991) 5707.