



Room temperature selective oxidation of toluene over vanadium substituted polyoxometalate catalysts

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ARTICLE INFO

Article history:

Received 1 September 2008

Received in revised form

29 December 2008

Accepted 6 January 2009

Available online 9 January 2009

Keywords:

Selective oxidation

Toluene

Vanadium

Molybdophosphoric acid

Niobia

ABSTRACT

Selective oxidation of toluene at room temperature was carried on vanadium containing molybdophosphoric acid supported on niobia catalysts using *t*-butyl hydrogen peroxide (TBHP) as oxidant. The catalysts were characterized by FT-IR, X-ray diffraction (XRD), ³¹P MAS NMR, Laser Raman spectroscopy and N₂ adsorption. The characterization data reveals the incorporation of vanadium and retention of intact Keggin ion on the support. The catalyst activity is related to the presence of vanadium in Keggin ion. The effect of TBHP–toluene concentration on the conversion and selectivity during toluene oxidation was also studied. A plausible reaction mechanism for the selective formation of benzaldehyde was proposed. The present catalyst is highly active, selective towards benzaldehyde and reusable with out any appreciable loss in activity and selectivity.

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1. Introduction

The catalytic oxidation of C–H bonds of hydrocarbons to oxygenated products under mild reaction condition is a major challenge in view of industrial aspects [1,2]. The oxygenated products are the required intermediates for many chemical feedstocks, agrochemicals, fragrances, pharmaceuticals and polymers. The traditional homogeneous catalytic oxidation methods often require stoichiometric amounts of metal complexes such as Cr(VI), Mn(VII) or Os(VIII) that generate large quantities of toxic metal waste [3]. These wastes can be eliminated if the vapor phase oxidation using a heterogeneous catalyst is employed. However, this requires excess temperature or pressure and also need specialized equipment [4]. Moreover, the selectivities to the desired oxygenated products are always less. Thus, the selective catalytic oxidation of inactive hydrocarbons to industrially important oxygenated derivatives is still remains a major challenge [5–7]. Among various hydrocarbons, toluene is an important one that can be converted into oxidation products such as benzyl alcohol, benzaldehyde and benzoic acid. Among these products, benzaldehyde is the most desirable product. However, benzaldehyde is easily over oxidized to benzoic acid. Traditionally, benzaldehyde is produced by side-chain chlorination of toluene and saponification of the resulting dichloromethyl group to form the aldehyde. The product still contains the chlorinated

impurities, does not meet food and drug grade specifications. The vapor phase oxidation of toluene with oxygen generally carried at high pressure (0.5–2.5 MPa) and seems too harsh for improving the selectivity of benzaldehyde [8]. There exists lot of difficulties in vapor phase oxidation of toluene such as control of over oxidation or combustion that leads to the formation of carboxylic acids, phenols or decomposition to carbon oxides (CO₂ and CO) and tar [9]. There are only few reports on the selective oxidation of toluene is carried out at low temperatures using different oxidants like *tert*-butyl hydrogen peroxide, O₂, etc. Peroxides are very attractive, relatively cheap and waste-avoiding oxidants only when it is used in a controlled manner without organic solvents and other toxic compounds [10]. Brutchey et al. have reported the toluene oxidation on Co-SBA-15 catalyst by using TBHP as an oxidant [11]. This catalytic system showed maximum toluene conversion of 8% with 64% benzaldehyde selectivity at 80 °C in 24 h. Ruthenium-based catalysts are extensively studied for oxidation reactions with TBHP [12–14]. However, these catalysts are expensive.

In this regard, a more environmentally benign, economically feasible and selective catalytic process is desirable. Metal supported heterogeneous catalysts that can operate in combination with an acquiescent oxidant in liquid phase are advantageous, due to mild reaction conditions, catalyst recovery and have minimal environmental impact [15,16]. In this context, Keggin type heteropoly acids (HPAs) are widely used in various oxidation reactions [17,18]. HPAs like 12-molybdophosphoric acid and vanadium containing molybdophosphoric acid are used for oxidation of alcohols. These catalysts

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are soluble in most of the solvents. Efforts are being made to overcome the solubility problem by supporting them on solids [19,20]. The acid–base and redox properties of Keggin ion can be tuned by substituting one or more Mo atoms with other metal atoms such as vanadium [21,22].

As part of our investigation of vanadium containing Keggin type heteropoly acids we report a conveniently developed method that can efficiently oxidize toluene to benzaldehyde at room temperature in atmospheric pressure using heterogeneous vanadium containing molybdophosphoric acid supported on niobia catalyst.

2. Experimental

2.1. Catalyst preparation

The 12-molybdophosphoric acid (MPA) was supplied by Loba Chemie, India, and the Nb₂O₅ support was obtained from CBMM, Brazil. Vanadium incorporated molybdophosphoric acid catalysts H₄PMo₁₁V₁O₄₀ (MPAV₁) and H₅PMo₁₀V₂O₄₀ (MPAV₂) are prepared according to the reported procedure [23]. In the synthesis of the MPAV₁, 7.1 g of disodium hydrogen phosphate dissolved in 100 ml of hot water and 6.1 g sodium metavanadate taken in 100 ml of distilled water were mixed together thoroughly. The mixture was cooled and acidified with 5 ml of concentrated sulfuric acid. To this mixture 133 g sodium molybdate dihydrate dissolved in 200 ml of distilled water was added. Then, 80 ml of concentrated sulfuric acid was slowly added while stirring, following the color change from dark red to light red. The MPAV₁ formed was extracted with diethyl ether, as the heteropoly acid was present in the middle layer as heteropoly etherate. Subsequently the ether was removed by passing air through the solution. The orange solid obtained was dissolved in water and concentrated until the crystals appeared. MPAV₂ catalyst is prepared in the same way as that of MPAV₁ except by taking the required amount of sodium metavanadate and sodium molybdate.

Niobia supported catalysts were prepared by impregnation method. The required quantity of MPAV₁/MPAV₂ dissolved in minimum amount of water and this solution was added to support with constant stirring. The excess water was removed on the water bath and the catalyst masses were dried in an air oven at 120 °C for 12 h and finally calcined in air at 350 °C for 4 h. These catalysts were denoted as MPAV₁/Nb₂O₅ and MPAV₂/Nb₂O₅, respectively. In these catalysts, 20 wt% of active component (MPAV₁ and MPAV₂) was supported.

2.2. Catalyst characterization

BET surface areas of the catalysts were determined on a Micromeritics (Auto Chem-2910) instrument with nitrogen physisorption at 77 K, taking 0.169 nm² as the cross-sectional area of dinitrogen. FTIR spectra of catalysts were taken on a DIGILAB (USA) IR spectrometer by the KBr disc method. XRD patterns were measured on a RIGAKU MINI FLEX diffractometer using Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). The 2θ angles were scanned from 2° to 80° at a rate of 2° min⁻¹. Elemental analysis of the heteropoly acid samples were estimated by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The samples were digested using aqua-regia and the elements to be analyzed are phosphorus, molybdenum and vanadium are analyzed.

The ³¹P MAS NMR spectra of solids were recorded on a 400 MHz Bruker spectrometer. A 4.5 μ s pulse (90°) was used with repetition time of 5 s between pulses in order to avoid saturation effects. Spinning rate was 5 kHz. The measurement was carried at room temperature using 85% H₃PO₄ as standard reference.

The Raman spectra of the samples were collected with a Horiba-Jobin Yvon LabRam-HR spectrometer equipped with a confocal microscope, 2400/900 grooves/mm gratings, and a notch filter. The

visible laser excitation at 532 nm (visible/green) was supplied by a Yag doubled diode pumped laser (20 mW). The scattered photons were directed and focused onto a single-stage monochromator and measured with a UV-sensitive LN₂-cooled CCD detector (Horiba-Jobin Yvon CCD-3000V).

2.3. Preparation of TBHP–toluene mixtures

In a one-liter single neck flask required quantity of tertiary-butyl hydrogen peroxide (in water) and analytical grade dry toluene was taken. The resulting solution is turbid and then refluxed slowly with fabric mantle using a Dean-Stark apparatus upon continuous stirring. The water associated with TBHP solution will form an azeotrope with toluene and gets collected in the side arm of the Dean-Stark condenser and removed periodically. The reflux should be continued for 6–8 h till the solution become clear. By varying the TBHP and toluene concentrations 4 M, 3 M, 2 M and 1 M TBHP–toluene solutions were prepared. These oxidation systems are designated as 4 M TBHP–TL, 3 M TBHP–TL, 2 M TBHP–TL and 1 M TBHP–TL, respectively.

2.4. Catalyst evaluation

Oxidation of toluene was carried out in liquid phase at room temperature under inert atmosphere. A mixture of freshly prepared 4 M TBHP–TL (2 ml, 8 mmol of TBHP and 10 mmol of toluene is present) and catalyst (50 mg) was added into a 10 ml double neck round bottom flask. The oxidation was conducted with continuous stirring at room temperature. The progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was separated by filtration and the reaction mixture was pored into a 10% aqueous Na₂SO₃ solution and slowly extracted with ethyl acetate and dried with anhydrous Na₂SO₄. The products were analyzed by gas chromatography using DB-5 capillary column. All the yields are calculated based on the calibration of all reactants and products.

3. Results and discussion

The surface areas of bulk and supported heteropoly acid catalysts are shown in Table 1. The pure support niobia showed the surface area of 140 m²/g. The comparative decrease in the surface area of supported catalysts may be due to pore blockage by active MPAV Keggin ions.

The elemental analysis of these catalysts was estimated by ICP-AES. Keggin units have one central atom, 12 transition metal atoms and an appropriate number of charge balancing protons or cations. The Mo/P ratio of the standard (ideal formula H₃PMo₁₂O₄₀) was 12.6, indicating a pure phase of heteropolyacid. The Mo/P ratio in our synthesized MPAV₁ and MPAV₂ catalysts are 11.1 and 10.2, respectively. The pure MPAV₁ and MPAV₂ catalysts contain slightly lower contents of Mo in the Keggin units due to partial substitution of Mo by V cation. Indeed, the V/P ratios in these samples are 0.92 and 1.86, respectively. The Mo/P ratios for MPAV₁/Nb₂O₅ and MPAV₂/Nb₂O₅ were 10.8, 9.7, respectively. Since elemental anal-

Table 1
Surface area of pure MPA and its modified supported catalysts.

Catalyst	Surface area (m ² /g)
MPA	3.0
MPAV ₁	7.0
MPAV ₂	8.5
MPAV ₁ /Nb ₂ O ₅	48.0
MPAV ₂ /Nb ₂ O ₅	56.0
Nb ₂ O ₅	140.0

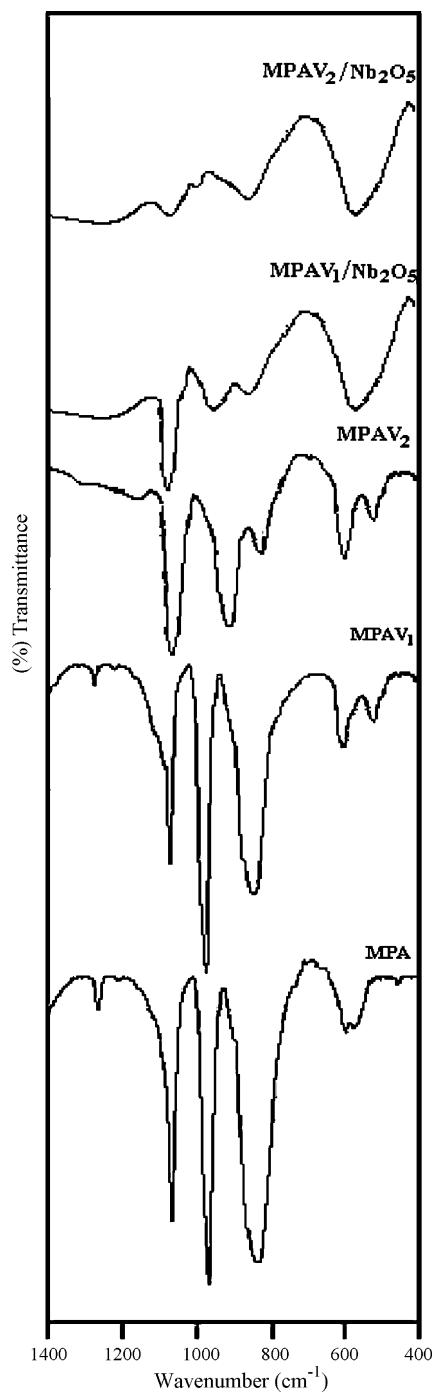


Fig. 1. FT-IR patterns of modified supported MPA catalysts.

ysis of the bulk solids cannot provide information on the phases present in the solid, different characterization techniques such as XRD and FT-IR are used to obtain additional structural insights for the supported catalysts.

The FTIR spectra of the samples are presented in Fig. 1. The intense IR bands for all the samples observed at 1064, 946, 864 cm^{-1} and a broad band at 785 cm^{-1} , attributed to Keggin ion characteristic stretching vibrations of P–O_d, Mo=O_t, Mo–O_b–Mo and Mo–O_c–Mo, respectively [24]. It is interesting to note that the characteristic bands of Keggin ion for vanadium containing samples are shifted to lower wave numbers (blue shift) proportional to the number of introduced vanadium atoms in its primary structure. This shift is due to the influence of vanadium on the M–O bond and

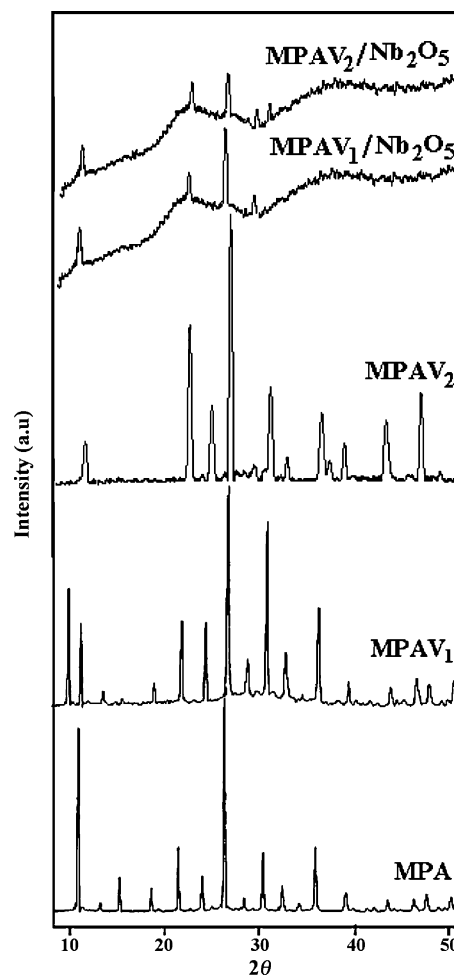


Fig. 2. XRD patterns of modified supported MPA catalysts.

there by change in the structure symmetry [25]. This shift suggests that vanadium has entered into the primary structure of Keggin anion of MPAV catalysts. A shoulder in the P–O stretching vibration is noticed for the MPAV₁ and MPAV₂ catalysts. The splitting of P–O_d band was reported for the samples with the presence of vanadium in the Keggin structure. It is known that the introduction of a metal other than Mo in the Keggin ion induces a decrease in the Mo–O_t stretching frequency and a possible splitting of the P–O_d band [26]. This splitting suggests the incorporation of V into the Keggin ion. The vibrations of V–O bonds are marked by the very strong absorption of Mo–O bonds in supported catalysts [27]. A broad band at around 580 cm^{-1} in supported catalysts is ascribed due to Nb₂O₅.

To investigate further the structural stability with the incorporation of vanadium into the primary structure of Keggin ion, the samples are characterized by XRD and the patterns of the samples are shown in Fig. 2. The strong characteristic peaks at 2 θ values of 10.5°, 23.7°, 26.1°, 30.2° and 35.6° are assigned to Keggin structure of MPA [JCPDS File 1-32]. These characteristic peaks are observed in all the samples. The XRD patterns suggest that the Keggin structure is intact even with the incorporation of vanadium into the primary structure and also when supported on niobia.

The ³¹P NMR spectra of the representative samples (MPA, MPAV₂ and MPAV₂/Nb₂O₅) are shown in Fig. 3. The NMR spectra of MPA showed a single peak at –1.13 ppm related to H₃PMo₁₂O₄₀·9H₂O. The vanadium containing bulk MPAV₂ catalyst exhibited a single resonance peak at –4.45 ppm. The presence of single peak reveals that the catalyst is in undissociated phase after the incorporation of vanadia in to MPA. The MPAV₂ supported on Nb₂O₅ showed a

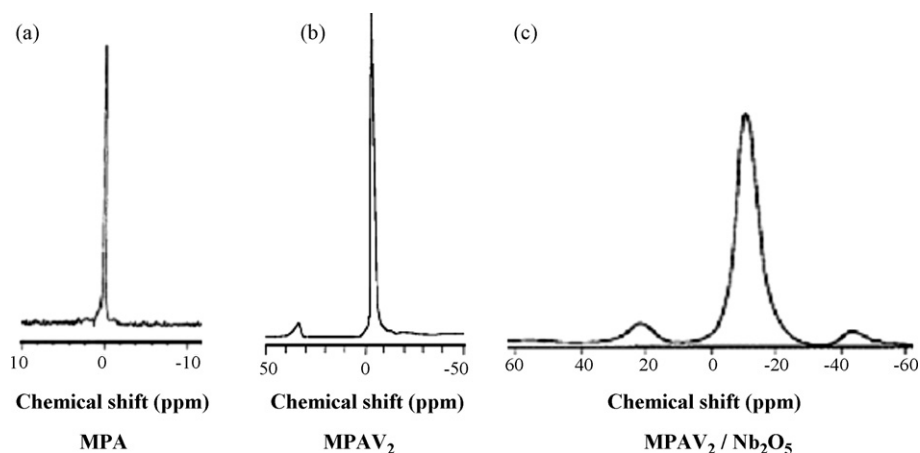


Fig. 3. ^{31}P NMR spectra of MPA, MPAV_2 and $\text{MPAV}_2/\text{Nb}_2\text{O}_5$ catalysts.

broad single peak at -13 ppm. The shift in NMR signal by supporting the MPAV_2 is due to the interaction of Keggin ion with support. The single peak for $\text{MPAV}_2/\text{Nb}_2\text{O}_5$ catalyst indicates that the Keggin structure was intact after impregnation and calcinations process [28].

In order to know the stability and the incorporation of V into the Keggin ion of MPA, the samples are characterized by Laser Raman spectroscopy and the spectra are shown in Fig. 4. The Raman spectra of MPA, MPAV_2 and $\text{MPAV}_2/\text{Nb}_2\text{O}_5$ catalysts are presented for clarity. The Raman spectra of the samples exhibit the characteristic bands of the MPA Keggin structure with bands at 998, 983, 890, 620 and 248 cm^{-1} . The strong band at 998 cm^{-1} with a shoulder at 983 cm^{-1} arise from the symmetric and asymmetric stretching modes of the $\text{Mo}=\text{O}_t$ bond, respectively. The broad bands ~ 890 and $\sim 620\text{ cm}^{-1}$ are from the asymmetric $\text{Mo}-\text{O}_b-\text{Mo}$ and symmetric $\text{Mo}-\text{O}_c-\text{Mo}$ stretching modes, respectively. The strong band at 248 cm^{-1} corresponds to $\text{Mo}-\text{O}-\text{Mo}$ bending mode of the intact Keggin. In the case of $\text{MPAV}_2/\text{Nb}_2\text{O}_5$ catalysts apart from Raman bands related to Keggin ion, a broad band at 700 cm^{-1} related to Nb_2O_5 is observed. The results suggest that the presence of Keggin ion even after incorporation of V and supporting on niobia. One important observation can be made from the Raman spectra is about the location of vanadium. The absence of 1034 cm^{-1} band related to vanadyl cation in the case vanadium containing catalyst suggests the presence of V in the primary structure of Keggin ion.

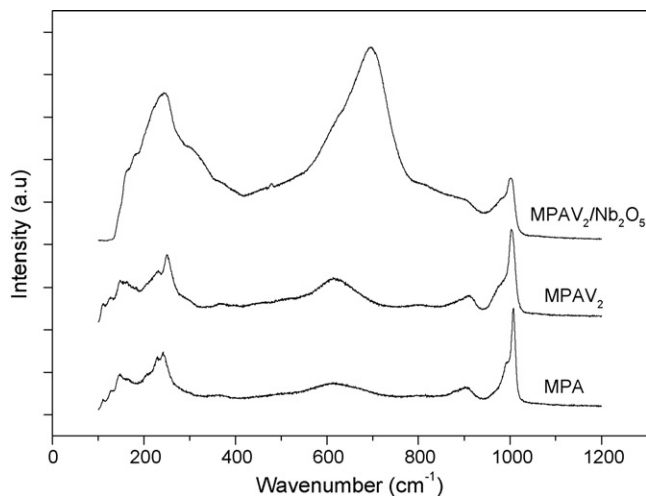


Fig. 4. Laser Raman spectra of MPA, MPAV_2 and $\text{MPAV}_2/\text{Nb}_2\text{O}_5$ catalysts.

If V is present in the secondary structure or on the support gives a characteristic band at 1034 cm^{-1} [29].

Liquid phase oxidation of toluene was conducted at room temperature and atmosphere pressure over MPA and its vanadium modified catalysts. Three different oxidant-reactant systems viz: TBHP–toluene; TBHP– H_2O –toluene, TBHP–Decane–toluene are studied over these catalysts. The results obtained over these catalysts at different oxidant-reactant systems are presented in Table 2. Toluene oxidation without catalyst does not yields any products. Among the three-oxidation systems the TBHP–TL is the best one. The pure MPA, MPAV_1 and MPAV_2 catalysts are less active towards toluene oxidation and suffering from homogeneity. The highest conversion of toluene (30%) is obtained on MPAV_2 supported on niobia catalyst. Among the supported catalysts the activity increased with increase in number of vanadium atoms in Keggin ion. The $\text{MPAV}_2/\text{Nb}_2\text{O}_5$ catalyst showed better activity compared to all other catalysts. The high activity of vanadium containing heteropoly acids might be due to the redox nature of vanadium present in the primary structure of Keggin ion.

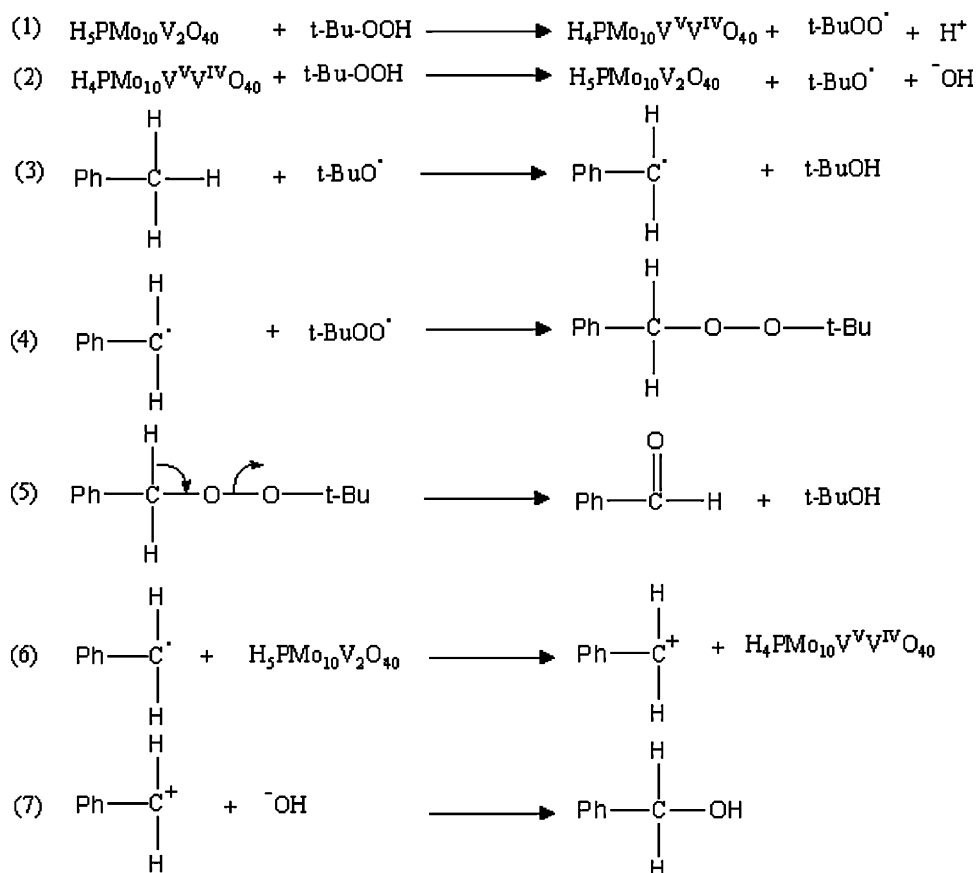
The selective formation of benzaldehyde over these vanadium containing polyoxometallate catalysts is might be due to the plausible mechanism as shown in Scheme 1. The polyoxometallate $[\text{PMo}_{10}\text{V}_2\text{O}_{40}]^{5-}$ reacts with TBHP invariably proceed with initial formation of *tert*-butyl peroxy (*t*-BuOO \cdot) and *tert*-butyloxy radicals (*t*-BuO \cdot) [30]. The *tert*-butyloxy radical reacts with toluene to form the benzyl radical. The benzyl radical combines with *tert*-butyl peroxy radical to yield benzaldehyde. The formation of benzyl alcohol proceeds via the formation of benzyl cation by the transfer of electron from benzyl radical to the catalyst. The benzyl cation reacts with hydroxyl anion to yield benzyl alcohol. The reduced catalyst is reoxidized by TBHP. One cannot ruled out the formation of benzaldehyde from the benzyl alcohol over these catalysts. It is reported that for the vanadium containing polyoxometallate $[\text{PMo}_{10}\text{V}_2\text{O}_{40}]^{5-}$ catalysts through transfer of two electrons and two protons from the benzyl alcohol to the catalyst to yield benzaldehyde [31]. The high activity for the supported catalysts is mainly because of the availability of well-dispersed MPAV_2 Keggin ion on niobia.

The optimum conditions required to promote the activity of toluene towards selective formation of benzaldehyde was carried using $\text{MPAV}_2/\text{Nb}_2\text{O}_5$ catalyst by changing the concentration of TBHP–TL system. The conversion and selectivities with different TBHP–TL concentrations are shown in Table 3. The conversion and selectivity is varied with change in TBHP–TL concentration. About 30% conversion of toluene obtained when 4 M TBHP–TL was used. At lower concentration it observed a high selectivity towards benzyl alcohol. However, the conversion is low (6%). Controlled

Table 2
Toluene oxidation activity of MPA and its modified supported catalysts in different TBHP–TL systems.

Catalyst	Reaction time (h)	TBHP–TL system ^a	TBHP–H ₂ O–TL system ^a	TBHP–Decane–TL system ^a
No catalyst	48	–	–	–
MPA	14	2	–	–
MPAV ₁	14	4	<1	>1
MPAV ₂	14	5	2	1
MPAV ₁ /Nb ₂ O ₅	14	20	4	3
MPAV ₂ /Nb ₂ O ₅	14	30	3	4
Nb ₂ O ₅	14	>1	–	<1

^a Conversion (%) of toluene.



Scheme 1. Plausible reaction mechanism for the formation of benzyl alcohol and benzaldehyde.

experiments showed that the high selectivity towards benzaldehyde could be obtained using 2 M concentration of TBHP.

The reaction profile during the oxidation of toluene with 4 M TBHP–TL system over MPAV₂/Nb₂O₅ catalyst has been studied. The variations of reaction products with time are measured and the results are shown in Fig. 5. The conversion of toluene increased with reaction time. The selectivity towards the three products is varied with reaction time. Initially the selectivity to benzyl alcohol

and benzaldehyde is high. The formation of benzoic acid increased substantially at prolonged reaction and at the same time selectivity of benzyl alcohol is decreases. However, the variation in selectivity towards benzaldehyde is limited. These results suggest that further oxidation of alcohol is taking place with time to yield more benzoic acid, a stable oxidation product.

Carrying the reaction with the same catalyst, which is recovered from the first cycle by simple filtration, establishes the reusability

Table 3
Product distribution during toluene oxidation over MPAV₂/Nb₂O₅ catalyst.

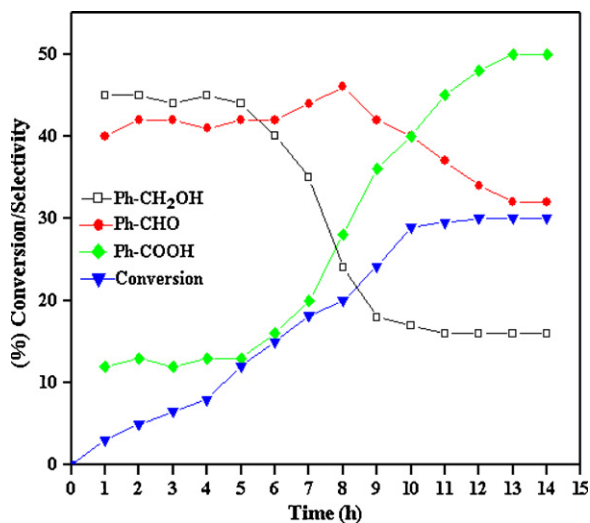
Oxidant	Conversion of (%)	Turn over number (TON)	Selectivity (%)		
			Benzyl alcohol	Benzaldehyde	Benzoic acid
4 M TBHP–TL	30	15	16	32	50
3 M TBHP–TL	23	11.5	26	52	21
2 M TBHP–TL	22, 21 ^a	11, 10.2 ^b	22	76	–
1 M TBHP–TL	14	7	71	26	–

^a Conversion (%) of toluene after third cycle.

^b Turn over number after third cycle.

Table 4A comparison of toluene oxidation activity of the MPAV₂/Nb₂O₅ catalyst with other reported catalysts.

Catalyst	Temperature/pressure	Oxidant	Conversion (%)	Selectivity (%) R-CHO	References
Cu–Mn (1:1)	190 °C/1 MPa	O ₂	17.2	20	[32]
Cu–Fe/TiO ₂	190 °C/1 MPa	O ₂	1.8	27	[33]
Co(II)TPP	150 °C/0.8 MPa	O ₂	8.9	33	[34]
CoSBA-15	80 °C/1 atm	TBHP	7.97	63.8	[11]
MPAV ₂ /Nb ₂ O ₅	RT/1 atm	TBHP	22	76	Present work

**Fig. 5.** Toluene oxidation reaction profile over MPAV₂/Nb₂O₅ using 4M TBHP-TL system.

of the catalyst. During the filtration the catalyst is washed with dry toluene and dried in air oven at 120 °C for 12 h. The catalyst was recycled for three times and the activity after third cycle is presented in Table 3. It is noteworthy to mention that the catalyst is showing similar activity even after third recycle.

In order to find out the possible leaching of catalyst during reaction the fresh and used catalysts are subjected to elemental analysis. The amount of vanadium in the fresh MPAV₂/Nb₂O₅ catalyst is 0.79 mmol/g and V in the catalyst after third recycle is estimated as 0.76 mmol/g. A negligible decrease in the amount of vanadium content is noticed. These results suggest that there is no appreciable leaching of active components during the reaction.

The present catalyst is compared with some of the heterogeneous catalysts reported in the literature for the low temperature oxidation of toluene and the details are shown in Table 4. The MPAV₂/Nb₂O₅ catalyst is comparable with the other reported catalysts and offers high catalytic activity. Toluene oxidation with Co-SBA-15 catalysts using TBHP as oxidant offered about 8% conversion and 64% selectivity towards benzaldehyde at 80 °C. The present catalyst exhibits better conversion (22%) and selectivity to benzaldehyde (76%) even at room temperature. The disclosed catalyst offers considerably high activity than most of reported the catalysts.

4. Conclusions

In summary, the present study reveals a convenient method for selective oxidation of toluene to yield benzaldehyde at room temperature. The niobia supported vanadium contain heteropoly acid is an efficient heterogeneous solid catalyst for selective oxidation

of toluene using TBHP as an oxidant. The present catalytic system is environmentally benign, economical, non-corrosive and active at room temperature. The reaction mechanism proposed explains the high selectivity towards benzaldehyde formation. The catalyst can be separated easily and recyclable with consistent activity.

Acknowledgements

The authors thank Department of Science and Technology, New Delhi for the financial support. One of the authors KTVR also thanks Council of Scientific & Industrial Research (CSIR), New Delhi for the award of Junior Research Fellowship.

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