Selective oxidation of toluene to benzaldehyde by H$_2$O$_2$ with mesoporous silica KIT-6 supported VOHPO$_4$ 0.5H$_2$O catalyst

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ABSTRACT

Highly ordered and rosebud like KIT-6 silica materials containing different amounts of vanadium phosphate have been synthesized using nonionic surfactant P123 as a structure-directing agent. The unique properties of KIT-6 such as three-dimensional cubic Ia3d symmetry, high surface area, large pore volume and large pore size enabled good dispersion of vanadium phosphorus oxide (VPO) species in crystalline form. The structure and morphology of the samples were systematically characterized by XRD, N$_2$ physisorption, SEM/EDX, elemental mapping, TEM, ICP-AES, UV-vis and FT-IR spectroscopy techniques. Various VPO loadings showed a clear influence on catalytic activity and selectivity. Within the studied range, the optimum conditions to improve toluene conversion and selectivity towards benzaldehyde over vanadium phosphorus oxide catalyst was performed in the presence of 17 wt% catalyst VPO-loading at 75 °C with 1:1.4 (toluene:H$_2$O$_2$) molar ratio, in acetonitrile as the solvent. Under these reaction conditions, 17.76% toluene conversion and 69.24% selectivity for benzaldehyde were observed after 10 h of reaction time. Finally, the recyclability of the catalysts was studied through five consecutive catalytic runs.

1. Introduction

Toluene is a typical aromatic hydrocarbon with three primary C–H bonds that is unfavorable to the environment and can be oxidized to different beneficial chemical intermediates, such as benzyl alcohol, benzaldehyde, benzoic acid and benzoate [1]. Among these products, benzaldehyde is the most desirable and value-added product due to its enormous importance in our life [2]. In the pharmaceutical industries, it is used for the manufacture of intermediates for amphiilinic, ephe-drine, chloramphenicol, etc. [3,4]. It is also an important intermediate for preparing the certain aniline dyes, processing the perfume and corrosion and production of toxic acidic waste [7]. The Rhodia, Dow and Snia-Viscosa processes were used as industrial realization of the liquid phase oxidation of toluene with homogeneous metal salt catalysts, but the halogen ions and acidic solvents were involved in these processes [8–10].

Exploration of a true heterogeneous catalyst with recyclability and ease of separation is considered to be highly interesting. There have been many attempts to find a proper oxidation catalyst, such as cobalt [11], copper and manganese [12,13], but they did not perform well, even at temperatures higher than 190 °C. Antonietti et al. reported oxidation of toluene and its derivatives using two different systems. One was B-doped polymeric carbon nitride (graphitic phase) with H$_2$O$_2$ as an oxidant [1] and the other was mesoporous nano-structured carbon nitride with O$_2$ as an oxidant [14]. Although, they obtained a high selectivity for benzaldehyde (~99%), but the conversion of toluene was low (around 2.7%). Moreover, mesoporous solids for different organic conversions, TiO$_x$/Sepolite supported vanadium catalysts and Fe-containing catalysts were used to achieve better conversion and product selectivity [15,16]. Mesoporous materials have drawn a significant attention as catalyst supports owing to huge surface area accompanied the hydrothermal stability, well-defined pores having a narrow diameter distribution, large pore volume and diameter that are expected to hinder the agglomeration and to increase the stability of the metal and metal oxide nanoparticles [17]. Among the mesoporous materials developed so far, KIT-6 has shown lots of superiority. It is notable that, the proficiency of KIT-6 is indebted to the highly ordered mesoporous structure with three-dimensional cubic Ia3d symmetry consisting of two interpenetrating continuous networks of chiral channels [18,19]. In principle, KIT-6 mesoporous silica is suitable as a template to supply a highly opened porous host with easy access for gest species [20–22].
Vanadium phosphorus oxide (VPO) catalysts are very well known for industrial n-butane oxidation to maleic anhydride [23] and ammoxidation of picoline [24]. Apart from being environmentally friendly and less expensive, VPO catalysts are also efficient to selective oxidation process [25].

In order to further improve the selective oxidation of toluene to benzaldehyde using a more efficient, easily separable and reusable catalyst for the oxidation process, the physicochemical property of VPO dispersed on the unique KIT-6-templating was investigated. The reason for KIT-6-templating to be chosen for this study was the facilitated diffusion or inclusion throughout the pore channels with mitigated pore blockage for KIT-6-templating. The catalysts have been characterized by XRD, 
\[ \text{N}_2 \] -adsorption-desorption, SEM, TEM, FT-IR and UV–vis techniques. This highly stable and recyclable catalyst was evaluated for catalytic toluene oxidation using environmentally friendly oxidants (\( \text{O}_2 \) or \( \text{H}_2\text{O}_2 \)).

2. Experimental

2.1. Materials

Hydrogen peroxide (35 wt% in water) was purchased from Merck KGaA, Darmstadt, Germany. Toluene (purity > 99.9%), acetonitrile (HPLC grade) ethylacetaet, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), acetone were purchased from Sigma-Aldrich Co. All the chemicals were used without further purification. No impurities were found in toluene by GC analysis before use.

2.2. Catalyst preparation

2.2.1. Synthesis of KIT-6 silica

The synthesis of mesoporous KIT-6 silica with cubic Ia3d symmetry was performed according to the literature procedure reported elsewhere [26]. Typically, 9.5 g of pluronic P123 was dissolved in 343.6 g of distilled water and 18.7 g of HCl solution (35 wt%) under vigorous stirring at 35 °C to form a clear solution, into which 9.5 g of n-butanol (99.4 wt%) was added. Following further stirring for 1 h, 20.4 g of tetraethyl orthosilicate was added immediately. Subsequently, the mixture was left stirring at the same speed for 24 h at 35 °C and transferred into an autoclave for hydrothermal treatment (HTT), which was sealed and maintained at 100 °C for another 24 h under static conditions. The resulting solid white product was filtered and dried at 100 °C overnight. After a brief ethanol/HCl washing, (though often in preparations of KIT-6s, washing step that was applied in this work to eliminate residue HCl (to avoid corrosion of equipment) was found not to prevent the formation of Ia3d mesostructures), the final sample was dried at 80 °C and calcined at 550 °C for 6 h in air.

2.2.2. Synthesis of VPO-functionalized KIT-6

The VPO precursor was prepared according to the procedure reported previously [27]. Required 0.5 g of \( \text{V}_2\text{O}_5 \) was suspended in a mixture of 2-butanol (3 mL) and of benzyl alcohol (2 mL), then the suspension was stirred continuously under reflux at 140 °C for 5 h. The instant orange color was changed to greenish due to the metal reduces to the +4 oxidation state. Then, PEG 6000 (0.1 g) and KIT-6 materials were introduced in suitable amounts (0.4, 0.6 and 0.8 g). One hour later, phosphoric acid (85%) (0.63 g) as phosphorous source, was added dropwise to reach a P/V atomic ratio of 1. After another 6 h of refluxing, the suspension was filtered and the solid was washed with iso-butanol and acetone, respectively. The sample was turned to light blue color and dried in air at 120 °C for 24 h. The VOHPO\( \text{X}_2\cdot\text{H}_2\text{O} \) catalyst phase was obtained. In order to compare the catalyst activity, we used both calcinated and non calcinated catalysts in the reaction. For this purpose, the dried precursor (VOHPO\( \text{X}_2\cdot\text{H}_2\text{O} \)) was heated from room temperature to 500 °C with 2 °C min\(^{-1}\) increments for 3 h in air to be calcinated.

2.3. Catalyst characterization

The Fourier transformed-infrared spectroscopy (FT-IR) spectra of the catalysts were recorded by a Jasco-680 spectrophotometer in the range of 400–4000 cm\(^{-1}\). The presence of acid sites on the surface of catalyst was investigated with pyridine adsorptions monitored by FT-IR spectroscopy. Samples were activated at 120 °C for 4 h under vacuum. Then cooled to 25 °C and samples were exposed to pyridine (50 μL). They were sealed and maintained at room temperature for 24 h under static condition. Afterward, the samples were heated at 120 °C for 4 h under vacuum condition for extracting excess amounts of pyridine. Subsequently, the spectra were recorded and analyzed by FTIR spectroscopy. The structure of the catalysts was studied by X-ray diffraction (XRD) spectroscopy obtained on Asenware XDM-300 diffractometer using Ni-filtered Cu Kα (K = 0.154 nm) radiation. Peaks were identified by search match technique using XPert High score software with reference to the ICDD database. The scanning electron micrograph (SEM) images were obtained using a VEGA/TESCAN-LMU instrument and energy dispersive X-ray spectroscopy (EDX) was used in connection with SEM for the elemental analysis. The elemental mapping was also collected with the same spectrophotometer. The transmission electron micrograph (TEM) images were collected on a Philips CM-120 electron microscope operated at an acceleration voltage of 150 kV. Nitrogen adsorption–desorption isotherms were collected at 77 K using a PHS-1020(PHSCHINA) instrument. UV–vis spectra were recorded by JASCO V-570 (Japan) spectrometer in spectral range between 200 and 800 nm. Inductively coupled Plasma Atomic Emission Spectroscopic (ICP-AES) analysis was carried out by using a sequential scanning inductively coupled plasma-atomic emission spectrometer; model: GBC INTEGRA XL, Australia.

2.4. Oxidation of toluene

The liquid phase oxidation of toluene with hydrogen peroxide was carried out in a double neck round bottom flask at 75 °C in an oil bath connected with a spiral condenser using 0.10 g catalyst, 10 mL acetonitrile as the solvent and 3.5 mL of toluene as well as 4 mL H\(_2\text{O}_2 \) (35% aq. solution) (toluene:H\(_2\text{O}_2 \) molar ratio 1:1.4 ratio). To avoid the immediate decomposition of hydrogen peroxide, addition was achieved in small portions. Small aliquots of the sample were withdrawn from the reaction mixture at regular intervals for analysis using a syringe. At the end of the reaction, the solid particles (catalyst) were separated by filtration and the products were analyzed by gas chromatography (GC, Agilent 7890) connected with a HP5 capillary column (30 m length, 0.25 mm ID, BPX5 0.25 μm) and flame ionization detector (FID) (Fig. 1(A)). The nature of the products was also determined by GC-MS (Agilent, 5975C) analysis (Figs. 2 and 3). Conversion of toluene was calculated based upon the GC-FID using cyclohexane as internal standard, where toluene conversion = [moles of toluene reacted]/[initial moles of toluene used] × 100 and selectivity of products calculated by [total moles of product formed]/[total moles of toluene converted] × 100. For the reusability test, after completion of the reaction, the catalyst was recovered from the reaction mixture by filtration and washed thoroughly with aceton and reused as such for multiple circles.

For evaluation of effect of \( \text{O}_2 \) as the oxidant, a series of reaction carried out at atmospheric pressure. For this purpose, catalytic reactions were carried out in a two neck round bottom flask according to the following procedure: a mixture of catalyst (0.03 g) and toluene (6 mL) was stirred under \( \text{O}_2 \) atmosphere with a condenser at 110 °C for 5 h (GC analysis is shown in Fig. 1(B)).

3. Results and discussion

To evaluate the effect of active sites that contribute to conversion and selective oxidation of toluene to benzaldehyde, three types of same family of VPO catalysts supported on mesoporous KIT-6 material were
synthesized and characterized by impregnation method. Based on amount of KIT-6 mesoporous material (0.4, 0.6, and 0.8 g) which was added to the vanadium phosphate solution, three catalysts were denoted as (0.4)KIT-6-VPO, (0.6)KIT-6-VPO, and (0.8) KIT-6-VPO, respectively. These catalysts were used as prepared without calcination.

3.1. Catalyst characterization

3.1.1. ICP-AES analysis

The amount of vanadium present in the samples was estimated by ICP-AES. The results are given in Table 1. Under the synthesis conditions used, it was found that the highest percentage of vanadium was 17% related to (0.4)KIT-6-VPO catalyst, which has the typical composition of VOHPO40.5H2O structure.

3.1.2. XRD diffractions

Fig. 4, illustrates well-resolved Bragg reflections in the low angle powder XRD patterns of KIT-6 and KIT-6-VPO samples of different VPO loadings. The pure KIT-6 sample (Fig. 4(a)) exhibits a sharp intense peak around 2θ of 0.95° corresponding to the (211) plane and a hump ordered is indexable as (220) reflection at around 2θ = 1.10°, which are characteristic of a highly ordered mesoporous structure with the cubic Ia3d symmetry [28]. Obviously, it shows that the KIT-6 silicate was carefully synthesized. As can be clearly seen from Fig. 4(b–d), after

Fig. 1. GC analysis of (A) catalytic oxidation reaction of toluene in present of H2O2, (B) catalytic oxidation reaction of toluene under O2 atmosphere.


Fig. 2. GC-MSS analysis of catalytic oxidation reaction of toluene in present of H2O2. (Mass spectra of (A) Toluene, (B) Acetamide, (C) Benzaldehyde, (D) o-Cresol, (E) p-Cresol).
VPO loading onto the KIT-6, the \( d_{220} \) peak was gradually disappeared, conforming that the VPO nanoparticles should successfully anchor onto the KIT-6 while the cubic \( Ia3d \) symmetry of the support is synchronously preserved.

The wide angle X-ray diffraction patterns of KIT-6-VPO catalysts with different VPO loadings (before the calcination process) are presented in Fig. 5. It is evident that the supported VPO species exhibited the presence of vanadyl hydrogen phosphate hemihydrate phase.
3.1.3. FT-IR analysis

The FT-IR spectra of catalysts are shown in Fig. 6. Spectrum of pristine KIT-6 (Fig. 6a) indicates that the band appears at 960 cm\(^{-1}\) is due to the stretching frequency of terminal silanol (Si–OH) groups. The bands at 1078 and 810 cm\(^{-1}\) indicate the asymmetric and symmetric stretching vibrations of framework Si–O–Si bridges, respectively. The bending vibration of Si–O–Si can be seen at 456 cm\(^{-1}\). The band at 3443 cm\(^{-1}\) can be attributed to the stretching mode of water hydroxyl group at support surface. The FT-IR spectra (Fig. 6b–d) of VOHPO\(_4\).0.5H\(_2\)O show the characteristic P=O and V=O stretching frequencies in the region of 900–1200 cm\(^{-1}\) with bands centered at 930, 977, 1049, 1105 and 1198 cm\(^{-1}\) [30]. The 977 cm\(^{-1}\) band can be assigned to the stretching vibration of V=O group whereas the 1049 cm\(^{-1}\), 1105 cm\(^{-1}\) and 1198 cm\(^{-1}\) bands can be ascribed to the asymmetric stretching of PO\(_3\). Another band appeared at 419 cm\(^{-1}\) and 643 cm\(^{-1}\) are due to δ-OPO and (δ\(_{oop}\) (P–OH)) vibration respectively.

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>(S_{\text{BET}}) (m(^2) g(^{-1}))</th>
<th>(V_p) (cm(^3) g(^{-1}))</th>
<th>(r_p) (nm)</th>
<th>Vanadium(^{\text{a}}) %</th>
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<tbody>
<tr>
<td>KIT-6</td>
<td>493</td>
<td>0.747</td>
<td>5.866</td>
<td>–</td>
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<tr>
<td>(0.4)KIT-6-VPO</td>
<td>150</td>
<td>0.255</td>
<td>2.377</td>
<td>17</td>
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<tr>
<td>(0.6)KIT-6-VPO</td>
<td>278</td>
<td>0.427</td>
<td>2.443</td>
<td>15</td>
</tr>
<tr>
<td>(0.8)KIT-6-VPO</td>
<td>301</td>
<td>0.467</td>
<td>2.373</td>
<td>14</td>
</tr>
<tr>
<td>After 5 times reused(^{\text{b}})</td>
<td></td>
<td></td>
<td></td>
<td>10</td>
</tr>
</tbody>
</table>

\(^{a}\) Specific surface area.
\(^{b}\) Pore volume.
\(^{c}\) Pore diameter.
\(^{d}\) From ICP-AES.
\(^{e}\) Recycling of (0.4)KIT-6-VPO catalyst.
In this case, increase in the VPO loading on KIT-6 contributed to the increase in the intensity of the peak. At lower loadings, only one broad peak is observed at 1105 cm\(^{-1}\) and it does not provide any information about VPO species. It might be due to the active VPO phase present in the highly dispersed state in the pores of the KIT-6 support or the detected peaks are over shaded by the most intense bands of the pure support. Hence FT-IR spectra are good tool for supporting the evidence of results obtained from XRD on the formation of VPO phase.

In the hydroxyl stretching region, the band at 3373 cm\(^{-1}\) which is due to water molecule coordinately bonded to the vanadium in the lattice opposite to the vanadyl oxygen is clearly distinguishable, while the two weak bands at 1637 and 1726 cm\(^{-1}\) can be assigned to the bending modes of water molecules. After the calcination of catalyst, it is evident from Fig. 6 that the band corresponding to the stretching mode of coordinated water at 3370 cm\(^{-1}\) is obviously eliminated and peak intensity of hydroxyl group considerably decreased. FT-IR spectrum of (0.4)KIT-6-VPO catalyst, after 5 times recycling, is showed in Fig. 6f. No changes were detected in structure of catalyst and the functional groups supported on VPO are preserved.

Lewis and Brønsted acid sites play different roles in the selective oxidation, and the strength of respective acid sites strongly affects the catalytic performance [31]. The acidic properties of the samples were determined by FT-IR spectroscopy of adsorbed pyridine after thermal treatment (Fig. 7). The samples show peaks at around 1445, 1485, 1540 cm\(^{-1}\) which is due to pyridine coordinated bond to the unsaturated surface V\(^{4+}\). As for the peak at 1540 cm\(^{-1}\), it is related to the pyridinium ions which formed due to the protonation of its nitrogen by the Brønsted acid sites. The co-existence of Brønsted and Lewis acid sites is confirmed by the characteristic peak at 1485 cm\(^{-1}\). Consequently, results indicate that catalysts possess both Brønsted and Lewis acid sites. It is found that the increase in the amount of V resulted in the more intense peak for Brønsted acid sites, indicating that vanadium is a very strong Brønsted acid center. The acidic property (0.4)KIT-6-VPO catalyst, after 5 times recycling is investigated by FT-IR spectroscopy of adsorbed pyridine. No changes are certainly detected in situation of pecks. However, peaks intensity slightly decrease. This is due to the leaching of active sites.

3.1.4. \(N_2\) adsorption-desorption analysis

The nitrogen adsorption–desorption isotherms of KIT-6 and KIT-6-VPO samples of different VPO loadings are shown in Fig. 8a. These isotherms are classified as type IV, with a sharp capillary condensation step at high relative pressure (in the 0.5–0.7 \(P/P_0\) range) and H1 hysteresis loop. This demonstrates, clearly, the presence of large channel-like pores in a narrow range of size distribution.

No changes are detected in the nature of isotherm or in the shape of the hysteresis loop indicating that the support pore structure is preserved after VPO loading. But the height of the hysteresis loop decreases due to decrease in the pore volume resulting from VPO loading in the mesopores.

A narrow pore-size distribution with mean value 2.2 nm is calculated from the adsorption isotherm using BJH method as shown in Fig. 8b. The BET surface area, pore volume and pore diameter of the materials are presented in Table 1. As VPO loading of KIT-6 support increase, significant decrease in surface area and pore volume are observed and also the average pore diameters of samples decrease. The obtained results clearly indicate that VPO nanoparticles are well trapped in the KIT-6 pores. This is also confirmed by the profile of pore size distribution shown in Fig. 8b.

3.1.5. TEM analysis

Fig. 9(c, d) and (a, b) presents the TEM images of the KIT-6 and (0.4)KIT-6-VPO catalyst, respectively. TEM is performed to analyze the mesoporous structure of the samples and dispersion of VPO particles on the support. A well-ordered cubic 3D array of mesoporous channels is observed for these samples and confirmed that (0.4)KIT-6-VPO sample possesses 13\(\times 3d\) cubic structure as the structure observed for KIT-6. The small dark spots in TEM image (Fig. 9b) could be ascribed to VPO particles dispersed well-uniformed shape without any significant VPO agglomerates on KIT-6 surface [32].

3.1.6. SEM/EDX and elemental mapping analyses

The morphological SEM images are shown in Fig. 10. The samples are sputtered with a thin film of gold (5 nm thick) to minimize the charging effects. The SEM pictures of KIT-6 are shown in Fig. 10(a). Images exhibit nearly the same dense aggregates of rock-like morphology. There is no definite shape shown for any particles but the edges appear to be sharp after loading different amounts of VPO on the KIT-6 template (Fig. 10(b–d)).

Obviously, three catalysts show platelet crystals, which are agglomerated into the characteristics of rosebud shape clusters. The amount of the platelet in the characteristic rosebud shaped agglomerates is discerned to be different for all catalysts. The unique morphology of rosebud is likely to be a result of adding PEG in the catalyst preparation. The presence of PEG in the synthesis medium would lower interfacial surface energy. As a result of uniform nucleation leads to the generation of fine particles. Energy dispersive X-ray spectroscopy (EDX) results are also shown in Fig. S1 (a) of Supporting information. Through the qualitative local EDX analysis, we can verify that the nanoparticles dispersed on the support are composed of vanadium and phosphorous which form a uniform over-layer on the KIT-6. When the electron beam is incident to KIT-6-VPO sample, which is the vertical to the basal plane, spots are obtained. As shown in Fig. S1 (b) of SI, elemental mapping analysis for this sample is confirmed that vanadium and phosphorous finely dispersed on the KIT-6.

3.1.7. UV–vis spectra analyses

As shown in Fig. 11, the spectrum of KIT-6 is transparent throughout the UV–vis light region. In order to obtain the information of the vanadium oxidation state in VPO particles located on KIT-6 template, the UV–vis spectra VOHPO\(_4\). \(0.5\)H\(_2\)O phase was carried out. The two transmittance bands near to 280 and 310 nm are too strong and energetic to be \(d\)-\(d\) transition, and fall into the ultraviolet region. They are assigned as \(O^2-\) to \(V^{4+}\) charge transfer bands. From the literature [33] it is clear that \(V^{4+}\) exhibits the charge transfer absorption band at around 220 nm. Furthermore, they overlap the \(B_2\) to \(2A_1\) electronic transit that appears like a shoulder. Another transition band from 700 nm in the catalyst indicates the presence of \(V^{4+}\) species in this catalyst. This region is characteristic for \(d\)-\(d\) transitions of \(V^{4+}\). These
3.2. Activity of the catalysts

In the first attempt we started oxidation of toluene by hydrogen peroxide in the absence of catalyst. The results showed a poor toluene conversion indicating the catalytic effect of VPO catalysts. In addition, when pristine KIT-6 material used as catalyst, 0.14% toluene conversion was observed (See Table 2).

In order to improve reaction progress, we also addressed the oxidation of toluene using H$_2$O$_2$ as green oxidant under new condition. It is evident from the catalytic results presented in Table 2 that the amount of VPO loading has an important effect as the higher the VPO loading is the more the conversion of toluene will be but at the same time the selectivity to benzaldehyde decreases due to the formation of para- and ortho-isomers of cresol. In this regard, the catalytic activity of (0.4)KIT-6-VPO was investigated in different amounts (see Table 2). An amount of 100 mg of (0.4)KIT-6-VPO was chosen as the optimum amount in this particular toluene oxidation system.

The effect of run time on toluene conversion and benzaldehyde selectivity by using H$_2$O$_2$ as the oxidant are shown in Table 3. It was observed that the toluene conversion increases with increasing in reaction time. However, the selectivity of benzaldehyde slightly decreases due to the formation of para- and ortho-isomers of cresol. Therefore, 10 h reaction time was chosen as the optimum time.

For more evaluation of optimum condition for the toluene oxidation, effect of different solvents on reaction was examined. Of the various solvents examined (Table 4), acetonitrile is found to be the most suitable solvent for oxidation of toluene in present of H$_2$O$_2$ as oxidant under reflux condition. It is also found that acetonitrile activates H$_2$O$_2$ by forming a perhydroxyl anion (HOO$^-$, nucleophile) which attacks the nitrile to generate a peroxycarboximidic acid intermediate, a good oxygen transfer agent [34]. Moreover, acetonitrile has a comparatively good solubility power for both the organic substrate as well as the
Fig. 10. SEM images of (a) template-free mesoporous KIT-6, (b) (0.4)KIT-6-VPO, (c) (0.6)KIT-6-VPO, (d) (0.8)KIT-6-VPO.

Fig. 11. UV–vis spectra of KIT-6 and KIT-6-VPO with different amounts of VPO.

Table 2

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion%</th>
<th>Selectivity%</th>
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<tbody>
<tr>
<td></td>
<td>Benzaldehyde</td>
<td>α-Cresol</td>
</tr>
<tr>
<td>No Catalyst</td>
<td>˃99.9</td>
<td>–</td>
</tr>
<tr>
<td>KIT-6</td>
<td>7.52</td>
<td>74.14</td>
</tr>
<tr>
<td>(0.4)KIT-6-VPO</td>
<td>7.37</td>
<td>68.47</td>
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<td>(0.4)KIT-6-VPO</td>
<td>17.76</td>
<td>69.24</td>
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<tr>
<td>(0.8)KIT-6-VPO</td>
<td>10.83</td>
<td>85.20</td>
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Table 3

<table>
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<tr>
<th>Time (h)</th>
<th>Conversion%</th>
<th>Selectivity%</th>
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<tbody>
<tr>
<td></td>
<td>Benzaldehyde</td>
<td>α-Cresol</td>
</tr>
<tr>
<td>5</td>
<td>6.70</td>
<td>67.90</td>
</tr>
<tr>
<td>8</td>
<td>11.07</td>
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<td>22</td>
<td>23.68</td>
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Table 2 and Table 3 describe the variation of toluene conversion and selectivity of products with different amounts of KIT-6-VPO catalyst by using H₂O₂ as the oxidant. The reaction conditions include a solvent of acetonitrile = 10 mL, toluene = 3.5 mL, toluene:H₂O₂ mole ratio = 1:1.4; temperature = 75 °C, and Time = 10 h.
Table 4
Effect of solvents on conversion of toluene and selectivity of products in presence of H₂O₂.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Conversion%</th>
<th>Selectivity%</th>
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<tr>
<td></td>
<td></td>
<td>Benzaldehyde</td>
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<tr>
<td>No Solvent</td>
<td>0.15</td>
<td>~99.9</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>17.76</td>
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</tr>
<tr>
<td>Acetone</td>
<td>2.40</td>
<td>72.29</td>
</tr>
<tr>
<td>MBK</td>
<td>–</td>
<td>–</td>
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<tr>
<td>EtOAc</td>
<td>0.67</td>
<td>&gt; 99.9</td>
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<td>MEK</td>
<td>1.22</td>
<td>87.81</td>
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</table>

Reaction Condition: toluene = 3 mL; solvent = 10 mL; toluene: H₂O₂ mole ratio = 1:1.4; temperature = 75 °C; time = 10 h.

Table 5
Effect of toluene: H₂O₂ molar ratios on conversion of toluene and selectivity of products in presence of H₂O₂.

<table>
<thead>
<tr>
<th>Toluene:H₂O₂</th>
<th>Conversion%</th>
<th>Selectivity%</th>
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</tr>
<tr>
<td>1:1.4</td>
<td>17.76</td>
<td>69.24</td>
</tr>
<tr>
<td>1:2.66</td>
<td>8.33</td>
<td>58.08</td>
</tr>
<tr>
<td>1:3.5</td>
<td>3.50</td>
<td>90.03</td>
</tr>
<tr>
<td>1:5.32</td>
<td>2.94</td>
<td>77.06</td>
</tr>
</tbody>
</table>

Reaction Condition: toluene = 3.5 mL; catalyst weight = 0.1 g; temperature = 75 °C; time = 10 h.

aqueous H₂O₂. The detection of acetamide in the reaction mixture was confirmed by GC–MS analysis (Fig. 3(B)) supports the formation of peroxycarboximidic acid intermediate in the reaction mixture. In addition, conducting the reaction in various other solvents does not show any satisfactory conversion. It seems that polarity of the solvent does not play significant role in this reaction. Although, the selectivity of benzaldehyde was ~99% in ethylacetate, the conversion of toluene was extremely poor in ethylacetate and methylmethylethylketone.

In addition, we examined the molar ratio of toluene:H₂O₂ and results are shown in Table 5. In fact when toluene: H₂O₂ molar ratio was adjusted to 1:1.4, the conversion of toluene was 17.76% with benzaldehyde selectivity ~69.24%. However, when the toluene:H₂O₂ molar ratio increased to 1:3.5, the toluene conversion decreased to 3.50% with 90% benzaldehyde selectivity. The reactant molecules are hindered from close contact with the catalyst due to water present in medium created from the decomposition of hydrogen peroxide.

For evaluation of effect of oxidant on toluene oxidation, we examined the solvent free liquid phase oxidation of toluene to formation of benzaldehyde at atmospheric pressure using O₂ as the oxidant. In the first attempt, the effect of amount of VOHPO₄·0.5H₂O catalyst was studied. As shown in Table 6, no toluene conversion was observed in the absence of catalyst. However, an amount of 30 mg of (0.4)KIT-6-VPO catalyst in this particular atmospheric toluene oxidation system gave toluene conversion of 2.75% with more than 99% benzaldehyde selectivity. In addition, with the catalyst loading increasing, the toluene conversion decreased. Sheldon observed that sometimes transition metal complexes, especially in low polarity media such as neat hydrocarbons, often act as catalysts at low loadings, but as inhibitors at high loadings [35]. As can be seen in Table 2, the catalytic activity of (0.4) KIT-6-VPO was the best.

Moreover, the effect of vanadium phosphate phase on its catalytic activity was evaluated by calcination of VOHPO₄·0.5H₂O supported on KIT-6 mesoporous material. For this purpose, the (0.4)KIT-6-VPO catalyst was calcined at 500 °C. The XRD pattern of catalyst is shown in Fig. 12. It was observed that supported VPO catalyst composed of (VO)₂P₂O₇ and a certain amount of VOPO₄. Then, the catalytic activity of (0.4)KIT-6-VPO calcinated catalyst was performed on oxidation of toluene under the optimum conditions. The obtained results indicated 4.11% toluene conversion and 65.34% benzaldehyde selectivity. At the same time, the selectivity of ortho- and para-isomers of cresol increased from 16.41% and 14.35% to 19.03% and 15.61%, respectively. It has been reported that the performance of supported VPO catalysts is closely related to the phase composition of the VPO component. The presence of VOPO₄ phase can notably decline both activity and selectivity in the supported VPO catalysts [36]. The results of the present study also suggest that the existence of VOPO₄ phase display significantly lower activity and benzaldehyde selectivity.

3.3. Reusability of the catalyst

One of the most important advantages of heterogeneous catalysts over the homogeneous ones is the possibility of recycling and reusing them by simple filtration, without significant loss of activity. Recycling and reusability of the catalyst is examined by introducing the used catalyst subsequently 5 times to carry out the catalytic oxidation reaction under the optimum conditions. After the first reaction cycles, the solid catalyst is recovered by a centrifugation and dried with acetone and dried for the next reaction cycle (in air oven at 120 °C for 12 h). The catalyst is effective enough in each cycle (Fig. 13), which demonstrates that no structural modification like sintering could have hardly hampered the activated phase; hence recovered catalyst could be reused several times, establishing the recyclability of the catalyst. It is noteworthy to mention that the activity of catalyst is found to be approximately the same for the first three reaction cycles, however, slightly decreases. This is due to the leaching of active sites. We also observe that the amount of V present in the catalyst after 5 catalytic cycles is estimated by ICP-AES confirming the true heterogeneity of the catalyst (Table 1). Furthermore, FT-IR and pyridine test analyses are shown in Figs. 6 f and 7 e, respectively and XRD plot of the catalyst after reusing the recovered catalyst in 5 consecutive runs (Figs. S2 of SI) ascertain that the main characteristics of the catalyst are preserved without any changes.

![Fig. 13. Recyclability tests of KIT-6-VPO catalyst for the oxidation reaction of toluene to benzaldehyde.](image)
Based on the above experimental results, the probable reaction mechanism of toluene oxidation over KIT-6-VPO catalyst is presented in Fig. 14. The activated toluene is adsorbed on the surface of the catalyst via a chelating configuration α-complex, in which abstraction of one H atom from methyl group, with concerted formation of σ-bond between C aromatic and vanadium, the other one, formation of 6-Bond on C methyl group ∼ C ppm (ene reaction). In the next step, [2,3]sigmatropic rearrangement occurred so that the molecule is anchored long enough for the reaction to be completed. The chelating configuration can explain why no other partial oxidation products are detected for toluene oxidation. There may be formation of trinuclear oxide complex among oxygen-vanadium-carbon species, which undergo cyclic transformation to form the benzaldehyde as major product.

4. Conclusions

In this study, we have developed ordered mesoporous KIT-6 catalysts containing different amounts of vanadium for selective oxidation of toluene. Based on TEM and elemental mapping analysis it is evident that a uniform and highly dispersed VPO containing catalyst successfully constructed. The results of XRD patterns show the supported VPO species exist in the form of VOHPO₄·0.5H₂O. In order to find out the possible leaching of catalyst during reaction, the fresh and used catalysts were subjected to elemental analysis by ICP-AES technique. The results show the amount of V in the fresh (0.4)KIT-6-VPO catalyst is 17% but after 5 recycles the V amount decreased to 10%, while the catalytic activity remained good. In general, oxidation of toluene by molecular oxygen and in atmospheric pressure did not show desired toluene conversion yields. However, toluene oxidation with (0.4)KIT-6-VPO and by the H₂O₂ as the oxidant, offers about 17.76% conversion and 69.24% selectivity for benzaldehyde in the optimum reaction condition (10 h over 17%wt vanadium phosphorous oxide supported on novel KIT-6 mesoporous). It is evident that the nature of the supported (KIT-6) on which VPO is dispersed has a profound influence on catalytic performance. Also, the solvent effect in this process is important and the best results were observed when acetonitrile is used as the solvent. The catalyst can be easily reused several times without any significant loss of its activity, indicating its heterogeneous nature.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jece.2017.07.019.

References


