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Characterization and catalytic properties of molybdenum oxide catalysts supported on ZrO$_2$-γ-Al$_2$O$_3$ for ammoxidation of toluene

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ABSTRACT

Molybdenum oxide catalysts with MoO$_3$ loadings ranging from 6.6 to 25 wt% supported on ZrO$_2$-γ-Al$_2$O$_3$ (1:1 wt. %) mixed oxide were prepared by wet impregnation method. The catalytic behavior of catalysts in toluene ammoxidation reaction was investigated in a lab-scale tube reactor at 400 °C. The catalytic performance of MoO$_3$/ZrO$_2$-γ-Al$_2$O$_3$ was dependent on the catalyst compositions and reaction temperature. MoO$_3$ (20.0 wt. %) ZrO$_2$-γ-Al$_2$O$_3$ exhibited good toluene oxidation; over this catalyst, the selectivity to benzonitrile reached to 67.0 % with the toluene conversion of 68.5% at 400 °C, while the selectivity to benzaldehyde was 24.4 % with the toluene conversion of 68.5 % at 400 °C. Catalysts were characterized by various techniques, such as N$_2$ sorption, FTIR, SEM and XRD.

Keywords: Ammoxidation, Toluene, Molybdenum oxide, benzonitrile
Introduction

Ammoxidation of alkyl aromatics such as toluene to their corresponding nitriles has been the subject of numerous studies in recent times, because the nitriles are very useful organic intermediates to prepare a good number of industrially important chemicals \(^1,2\). The ammoxidation reaction generally refers to the one-step formation of nitrile compounds in a single step by the oxidation of simple olefins, aromatics and heteroaromatics in the presence of oxygen and ammonia in the gas phase \(^3-5\). Supported molybdenum oxide catalysts are well known and widely investigated as they represent an important group of catalysts for the heterogeneous oxidation and ammoxidation of hydrocarbons \(^6-17\).

Because pure MoO\(_3\) is relatively volatile, molybdena is almost always used in the presence of a second oxide, on an oxide support such as Al\(_2\)O\(_3\), TiO\(_2\), ZrO\(_2\), SiO\(_2\) and MgO \(^6,11,12,14,18-23\). The desirable inherent properties of alumina and zirconia supports can be explored by combination of both supports in a mixed oxide. The ZrO\(_2\)-\(\gamma\)-Al\(_2\)O\(_3\) supported catalysts have been found to show better catalytic properties than catalysts supported on pure oxides \(^24,25\). The combination of Al\(_2\)O\(_3\) and ZrO\(_2\) provides greater mechanical strength, resulting in improved resistance to attrition \(^26,27\). In recent times, ZrO\(_2\)-\(\gamma\)-Al\(_2\)O\(_3\) based materials have been employed as catalysts in various catalytic applications \(^28,29\). The advantages of Al\(_2\)O\(_3\)-ZrO\(_2\) as a catalyst support include moderate surface area, higher thermal stability and medium acidity. The ammoxidation of toluene \(^25,31-53\) and other alkyl aromatics \(^30,52-63\) over various supported metal oxide catalysts has been extensively studied. Iron \(^64-66\), MoO\(_3\)/MgF\(_2\) \(^67\), MoO\(_3\)/ZrO\(_2\) \(^68,69\), V\(_2\)O\(_5\)/ZrO\(_2\)-\(\gamma\)-Al\(_2\)O\(_3\) \(^70,71\), V\(_2\)O\(_5\)/\(\gamma\)-Al\(_2\)O\(_3\) \(^72\), Mo-V-P/\(\gamma\)-Al\(_2\)O\(_3\) \(^73\), vanadium-containing catalysts \(^74,75\), Fe\(_2\)O\(_3\)-based catalysts \(^76\), ZrO\(_2\)-\(\gamma\)-Al\(_2\)O\(_3\) \(^77\), and SiO\(_2\)-supported molybdate catalyst \(^78\), have also been used for the preparation of aromatic nitriles.
In the present study, we report the synthesis of benzonitrile by the vapor phase ammoxidation over highly dispersed molybdena catalysts supported on ZrO$_2$-$\gamma$-Al$_2$O$_3$ mixed oxide, as shown in Scheme 1. The catalysts were characterized by X-ray diffraction (XRD), SEM, BET specific surface area and temperature programmed desorption of N$_2$.

\[
\text{Scheme 1 Catalytic ammoxidation of toluene to benzonitrile}
\]

**Experimental section**

**Materials and Instruments**

Toluene and other agents were purchased from Merck and Aldrich and used without further purification. Products were characterized by spectroscopy data (FTIR, $^1$H NMR and $^{13}$C NMR spectra). NMR spectra were recorded on a Bruker 400 Ultra shield NMR and DMSO-d$_6$ was used as the solvent. Mass Spectra were recorded on a Shimadzu Gas Chromatograph Mass Spectrometer GCMS-QP5050A/Q P5000 apparatus.

The samples were analyzed by X-ray diffraction (XRD) using Philips X'PERT MPD X-ray diffractometer (XRD) with Cu Ka\(^{\circ}\) (1.5405 Å). Date sets were collected over the range of 5°–90° with a step size of 0.02° and a count rate of 3.0°/min. The structural morphology of the samples was evaluated using scanning electron microscope (SEM, JEOL, JSM-6300, Tokyo, Japan). A JASCO FT/IR-680 PLUS spectrometer was applied to record IR spectra using KBr pellets. The BET specific surface areas and BJH pore size distribution of the samples were determined by adsorption–desorption of nitrogen at liquid nitrogen temperature using a Series BEL SORP 18.
Catalyst preparation

The MoO$_3$/ZrO$_2$ and MoO$_3$/γ-Al$_2$O$_3$ catalysts were prepared by impregnation of γ-Al$_2$O$_3$ or ZrO$_2$ with a 2 M oxalic solution of ammonium heptamolybdate. The mixture was left in an open vessel with stirring at 60 ºC for 24 h to evaporate the excess water. The precursor was dried at 100 ºC for 12 h and calcined at 500 ºC for 6 h before use.

A series of MoO$_3$/ZrO$_2$/γ-Al$_2$O$_3$ catalysts with MoO$_3$ loadings in the range of 6.6–25.0 wt.% were prepared by wet impregnation method. To impregnate MoO$_3$, the calculated amount of ammonium heptamolybdate was dissolved in 30–40 ml doubly distilled water and reflux at 85–90 ºC for 5 h. Then, a few drops of dilute NH$_4$OH were added to make the solution clear and keep the pH constant (pH=8). After impregnation, the reaction mixture was added to a 50 ml Pyrex flask. The mixture was irradiated in the water bath of the ultrasonic at 20 kHz for 1 h within the temperature range of 25–30 ºC. Then the catalysts were dried at 85–90 ºC for about 4 h and calcined at 500 ºC for 6 h before use.

Ammoxidation of toluene

A stainless steel cylindrical micro reactor (i.d. 4.8 cm; a reactor length of 8.55 cm; volume 150 cm$^3$), was charged with toluene (3 ml), 20 mg catalyst and a magnetic stirring bar. The autoclave was purged and filled with NH$_3$ until the pressure reached 0.75 MPa. Then O$_2$ was introduced until the total pressure reached to 1.25 MPa. The reaction mixture was stirred at a controlled temperature (400 ºC for 2 h). After the reaction, the mixture was filtered. The filtrate was analyzed by GC–MS and GC using benzonitrile as an internal standard. For recycling tests, the catalyst was filtered after the reaction, washed with acetone three times and then with doubly distilled water several times. Then, it was dried at 110 ºC, calcined at 400 ºC for 4 h, and then used for the next run.

Conversion and selectivity were defined as follows.
• C (mol%) = (mol toluene reacted/mol toluene in the feed) × 100.

• Si (mol%) = (mol i formed/mol toluene reacted) × 100, where i= B, BA, BN

Results and discussion

XRD analysis

X-ray diffraction (XRD) patterns of the catalysts were obtained using Cu Kα radiation (λ=1.5405 Å). Crystallite size of the crystalline phase was determined from the peak of maximum intensity by using Scherrer formula, 46 with a shape factor (K) of 0.9, which can be described as: Crystallite size = K.λ/W.cosθ, where W=Wb−Ws and Wb is the broadened profile width of experimental sample and Ws is the standard profile width of reference silicon sample.

Fig. 1A shows the XRD patterns of MoO₃, MoO₃/ZrO₂ and MoO₃/γ-Al₂O₃ samples. The peaks presented at 2θ=20-30° are attributed to the pure MoO₃, Fig. 1A (a). The XRD pattern of MoO₃/ZrO₂ showed peaks at 2θ = 30, 50 and 60, which were obviously the characteristics of the tetragonal ZrO₂. The X-ray diffraction pattern of MoO₃/γ-Al₂O₃ exhibit broad peaks at 2θ = 45 and 66°, which were attributed to γ-Al₂O₃, Fig. 1A (c).

X-ray diffraction patterns of the catalysts with different loadings of molybdena catalysts supported on Al₂O₃–ZrO₂ and calcined at 450 °C are shown in Fig. 1B. The catalysts showed characteristic peaks at 2θ = 32.8, 37.3, 45.9, 62.3 and 66.09°that were related to the support γ-alumina. The sharp diffraction lines at 2θ = 30.4, 51.0 and 60.2°corresponded to the tetragonal ZrO₂ phase. Loading of molybdenum species led to the appearance of new peaks at 2θ =12.8, 23.9, 22.2, 25.7, 28.5, 34.2 and 39.4°.

FT-IR analysis
The FTIR spectrum for MoO$_3$ is presented for the range, 350-4000 cm$^{-1}$ in Fig. 2A (a). The bands at 991, 870, and 491 cm$^{-1}$, were assigned to the Mo=O stretching mode, the Mo-O-Mo stretching mode, and MoO$_3$ vibration mode, respectively. For MoO$_3$/ZrO$_2$ catalyst in Fig. 2A (b), FTIR band at 989 cm$^{-1}$ was due to the Mo=O stretching mode of the molybdenum oxide complex bonded to the ZrO$_2$ surface. Molybdenum oxides species was stabilized through multiple Mo-O-Zr bonds between each molybdenum oxide species and the zirconia surface. The FTIR spectrum for MoO$_3$/γ-Al$_2$O$_3$ catalyst is shown in Fig. 2A (c). The band at 899 cm$^{-1}$ characterized the stretching mode of the Mo=O bond in surface-bound Mo species. These species could be either isolated tetrahedral or octahedral polymolybdate species.

FT-IR spectra of the supports and molybdenum catalysts are shown in Fig. 2B. A broad band in the range of 350–4000 cm$^{-1}$ appeared for all catalysts related to the MoO$_3$ species (including the vibrations of Mo-O, bridging oxygen corresponding to Mo-O-Mo). The bands at 878, 734 and 497 cm$^{-1}$ corresponding to the polymolybdates species. The spectrum in Fig. 2B exhibited bands at 3450-3760 cm$^{-1}$, typical of the ν OH bands of alumina hydroxyls. The band at 3764 cm$^{-1}$ was assigned to basic hydroxyl groups bound to a single tetrahedrally coordinated aluminum atom, while the band at 3642 cm$^{-1}$ was due to bridged OH groups shared by an octahedrally and tetrahedrally coordinated aluminum cation. The appearance of the band around 1050 cm$^{-1}$ was typical for γ-alumina due to Al–O vibration mode. On the other hand, bands that appeared at 1632 and 2350 cm$^{-1}$ were related to physisorbed water and OH group free from the interaction of H bonding respectively. There was a strong absorption band at 417 cm$^{-1}$ which could be attributed to the tetragonal zirconia. At higher MoO$_3$ loading, the bands due to microcrystallites MoO$_3$ appeared at 518, 734, and 878 cm$^{-1}$. The increase in the intensity of this band with MoO$_3$ loading indicated the growth of polymolybdate species. These bands were associated with Mo–O–Al and Mo=O bond vibration in aluminum molybdate and crystalline MoO$_3$ phases, respectively.
SEM analysis

Fig. 3 shows SEM micrographs of catalysts obtained from MoO$_3$ loadings ranging from 6.6 to 25.0 wt. %. Alumina displayed an irregular texture and accumulated aggregates with a variety of particles size. This indicated that the introduction of ZrO$_2$ into Al$_2$O$_3$ largely changed the morphology of the support composites. It can be seen from Fig. 3 that the particles seemed to aggregate to form microspheres. SEM shows a regular texture with small, uniform and dispersed particles.

BET Analysis

Fig. 4 shows the N$_2$ adsorption–desorption isotherms. Surface area was calculated by applying the BET equation to the isotherm [27]. The samples were degassed under vacuum at 120 °C for 4 h, prior to adsorption measurement, to evacuate the physisorbed moisture.

The effects of catalyst composition and reaction temperature on the toluene conversion and product distribution for toluene oxidation over MoO$_3$/ZrO$_2$-$\gamma$-Al$_2$O$_3$ are illustrated in Table 1. As shown, the toluene conversion reached a maximum over the catalyst with the MoO$_3$ loading of 20.0 wt.% under each reaction temperature, while the selectivity to the main products fluctuated with the increase of MoO$_3$ loading.

The MoO$_3$/ZrO$_2$/-γ-Al$_2$O$_3$ catalysts with different MoO$_3$ contents were evaluated for the ammoxidation of toluene. The ammoxidation of toluene resulted in the formation of benzonitrile as the major product, while benzene and benzaldehyde were formed in very low amounts. The catalysts with the low loading of MoO$_3$, up to 6.6 wt.%, showed moderate activity and when the loading was increased to 20.0 wt.%, a substantial increase in activity was observed. The catalyst with 20.0 wt.% MoO$_3$ exhibited the highest activity. With further increase in the active content to 25 wt.%, the ammoxidation activity was decreased
marginally. The low catalytic activity of 6.6–20.0 wt.% MoO₃/ZrO₂/γ-Al₂O₃ catalysts might be because of the less availability of active MoO₃ compound. With the increase of the reaction temperature, the toluene conversion and the selectivity to benzonitrile and benzaldehyde were increased, while the selectivity to benzene was decreased. Over this catalyst, the selectivity to benzonitrile reached to 67.0 % with the toluene conversion of 68.5% at 400 °C, while the selectivity to benzonitrile was 58.6 % with the toluene conversion of 64.6% at 300 °C. A significant drop in surface area occurred when molybdena loading was increased from 6.6 to 20.0 wt.%. Such a decrease might be due to either the blockage of some pores of ZrO₂/γ-Al₂O₃ by mixed oxides formed from the decomposition of molybdate or the solid-state reaction between the supporting oxides and the dispersed active oxides. Table 2 shows the BET surface area values of the catalysts. The surface area and pore volume of the MoO₃/ZrO₂-γ-Al catalysts were in the range of 48–116 m²·g⁻¹ and 0.50–0.62 cm³/g, respectively. A gradual decrease in surface area was observed for the catalysts with an increase in the loading of molybdena supported on ZrO₂/γ-Al₂O₃, but an increase in the average pore diameters. This phenomenon might be due to two reasons. One refers to MoO₃ particles deposited in the pores of ZrO₂-γ-Al₂O₃ and the blocked part of the small pores.

In addition, the Mo surface density values are measured and data are presented in Table 2. The surface density is defined as the number of Mo atoms per square nanometer BET surface area (Mo atoms/nm²). Surface areas decreased only slightly with increasing MoO₃ loading; therefore, the Mo surface density increased almost linearly with increasing MoO₃ concentration. In addition it has been noted that for Mo/Al₂O₃ system, formation of a polymolybdate monolayer on Al₂O₃ at surface densities of 4.8 Mo/nm² occur. As you can see, the loading 6.6 % MoO₃ leads to formation of a molybdate monolayer on mixed oxide surface.
The other relates to the morphology of composite supports changed from big blocks into small particles (observed from SEM image), thereby forming more inter pores between the particles. All samples were mesoporous, with \( \text{N}_2 \) adsorption–desorption isotherms of type IV according to the IUPAC classification. Such isotherms are shown in Fig. 4, which shows the case of a bare support taken as a representative example for 20.0 wt. % \( \text{MoO}_3/ \text{ZrO}_2-\gamma-\text{Al}_2\text{O}_3 \) catalyst.

Table 1 Effect of \( \text{MoO}_3 \) content in the support on the catalyst activity and product selectivity of different \( \text{MoO}_3/ \text{ZrO}_2-\gamma-\text{Al}_2\text{O}_3 \) catalysts for toluene ammoxidation.

<table>
<thead>
<tr>
<th>( \text{MoO}_3 ) loading</th>
<th>( T ) (°C)</th>
<th>Toluene conversion (%)</th>
<th>Product selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>benzonitrile</td>
</tr>
<tr>
<td>6.6% ( % )</td>
<td>200</td>
<td>28.6</td>
<td>40.7</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>44.5</td>
<td>46.2</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>44.2</td>
<td>63.5</td>
</tr>
<tr>
<td>12.5% ( % )</td>
<td>200</td>
<td>32.5</td>
<td>46.3</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>48.4</td>
<td>50.4</td>
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<td></td>
<td>400</td>
<td>56.6</td>
<td>66.4</td>
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<tr>
<td>20.0% ( % )</td>
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<td>44.2</td>
<td>40.3</td>
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<td></td>
<td>300</td>
<td>64.6</td>
<td>58.6</td>
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<tr>
<td></td>
<td>400</td>
<td>68.5</td>
<td>68</td>
</tr>
<tr>
<td>25.0% ( % )</td>
<td>200</td>
<td>30.3</td>
<td>35.9</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>43.7</td>
<td>47.5</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>48.6</td>
<td>67.6</td>
</tr>
</tbody>
</table>

Table 2 Nitrogen adsorption characteristics of Molibdate supported catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET surface area (m²g⁻¹)</th>
<th>Surface Density Mo/nm²</th>
<th>Pore volume (cm³g⁻¹)</th>
<th>Average pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.6 % ( \text{MoO}_3/\text{ZrO}_2-\gamma-\text{Al}_2\text{O}_3 )</td>
<td>116.26</td>
<td>2.37</td>
<td>0.78</td>
<td>6.22</td>
</tr>
<tr>
<td>MoO$_3$/ZrO$_2$–γ-Al$_2$O$_3$ Loading</td>
<td>MoO$_3$ wt.%</td>
<td>ZrO$_2$ wt.%</td>
<td>γ-Al$_2$O$_3$ wt.%</td>
<td>2 Theta (°)</td>
</tr>
<tr>
<td>----------------------------------</td>
<td>--------------</td>
<td>---------------</td>
<td>-------------------</td>
<td>-------------</td>
</tr>
<tr>
<td>12.5 % MoO$_3$/ZrO$_2$–γ-Al$_2$O$_3$</td>
<td>78.13</td>
<td>6.69</td>
<td>0.74</td>
<td>6.23</td>
</tr>
<tr>
<td>20.0 % MoO$_3$/ZrO$_2$–γ-Al$_2$O$_3$</td>
<td>66.32</td>
<td>12.61</td>
<td>0.68</td>
<td>6.25</td>
</tr>
<tr>
<td>25.0 % MoO$_3$/ZrO$_2$–γ-Al$_2$O$_3$</td>
<td>48.46</td>
<td>21.57</td>
<td>0.64</td>
<td>6.34</td>
</tr>
</tbody>
</table>

Fig. 1 (A)- XRD patterns of a) MoO$_3$; b) MoO$_3$/ZrO$_2$; c) MoO$_3$/γ-Al$_2$O$_3$. (B)- XRD patterns of MoO$_3$/ZrO$_2$–γ-Al$_2$O$_3$ catalysts with different MoO$_3$ loadings: a) 6.6 wt.%; b) 12.5 wt.%; c) 20.0 wt.%; d) 25.0 wt.%. 
Fig. 2 (A)- FTIR spectra of the a) MoO$_3$; b) MoO$_3$/ZrO$_2$; c) MoO$_3$/γ-Al$_2$O$_3$. (B)-FTIR spectra of the MoO$_3$/ZrO$_2$–γ-Al$_2$O$_3$ catalysts with different MoO$_3$ loadings: a) 6.6 wt.%; b) 12.5 wt.%; c) 20.0 wt.%; d) 25.0 wt.%.
Fig. 3 SEM images of the Molibdate supported catalysts (a) 6.6% wt. MoO$_3$/ZrO$_2$-$\gamma$-Al$_2$O$_3$, (b) 12.5 wt.% MoO$_3$/ZrO$_2$-$\gamma$-Al$_2$O$_3$, (c) 20.0 wt.% MoO$_3$/ZrO$_2$-$\gamma$-Al$_2$O$_3$, (d) 25.0 wt.% MoO$_3$/ZrO$_2$-$\gamma$-Al$_2$O$_3$
One of the most important advantages of heterogeneous catalysis over the homogeneous counterpart is the possibility of reusing the catalyst by simple filtration, without loss of activity. The recovery and reusability of the catalyst were investigated in the product formation. After completion of the reaction, the catalyst was separated by filtration, washed first 3 times with 5 ml acetone and then with doubly distilled water several times, dried at 110 °C and calcined at 400 °C for 4 h. Then the recovered catalyst was used in the next run. The results of three consecutive runs showed that the catalyst could be reused several times without any significant loss of its activity (see figure 5).

Fig. 4 N₂ adsorption–desorption isotherm of the MoO₃ (20.0 %Wt.)/ZrO₂-γ-Al₂O₃
Fig. 5 The results obtained from catalyst reuse in the product formation

It is generally accepted that the reaction proceeds by the adsorption of toluene on the catalyst surface through the formation of a π-complex with a Lewis site of the catalyst; furthermore, we should consider H abstraction of a benzylic H-atom to form a methylene-like species with parallel formation of water, partial oxidation, N-insertion and subsequent rearrangements of the chemisorbed activated surface species, which was converted to an adsorbed imine, and desorption of the so formed benzonitrile, which was followed by oxidative reconstruction of the catalyst surface. (Fig.6.) A similar mechanism has been proposed for this reaction \(^8^3\).

This was also reflected in the catalytic activity of these catalysts. Conversion of toluene to benzonitrile was increased continuously with molybdena loading up to 20.0 wt%. It indicated that the moderate and weak acidic sites played an important role in the ammoxidation of toluene.
Fig. 6 A plausible mechanism for toluene ammoxidation over MoO$_3$/ZrO$_2$-$\gamma$-Al$_2$O$_3$ catalysts.

The results of ammoxidation of toluene on various MoO$_3$/ZrO$_2$-$\gamma$-Al$_2$O$_3$ catalysts at 400°C are plotted in Fig. 7. The conversion and selectivity were increased with an increase in MoO$_3$ loading up to 20.0 wt% and beyond this loading, the activity was decreased slightly due to the formation of MoO$_3$ crystallites on the surface of ZrO$_2$-$\gamma$-Al$_2$O$_3$ support. The increase in the ammoxidation activity of the catalysts might be attributed to the increase in the number of sites on the active molybdena phase, which could be increased with the increase in molybdena content on the surface of the support. The surface properties and catalytic activity results of 20.0 wt% MoO$_3$ supported on mixed oxide alumina–zirconia catalysts have been compared in Table 3. It clearly shows that molybdena was well dispersed on MoO$_3$/ZrO$_2$-$\gamma$-Al$_2$O$_3$ support, with more acidic sites per m$^2$ surface of the support. Thus, it can be inferred that 20.0 wt. % MoO$_3$/ZrO$_2$-$\gamma$-Al$_2$O$_3$ catalyst can be more active in ammoxidation reaction compared to a time when it is supported on alumina–zirconia catalysts.
Ammoxidation of toluene over various MoO$_3$/ZrO$_2$–Al$_2$O$_3$ catalysts (reaction temperature of 400 °C).

benzonitrile Characterization

FTIR (KBr, cm$^{-1}$): 3116, 3064, 2256, 1662, 1098, 625 cm$^{-1}$; $^1$H NMR (400 MHz, DMSO-d6): $\delta$ 7.383–7.412 (m, 2H), 7.518–7.561 (m, 3H); $^{13}$C NMR (100 MHz, DMSO-d6): $\delta$ 112.30 (1C), 118.82 (1C), 129.16 (2C), 132.05 (2C), 132.82 (1C); ESI MS (m/z): 103.08 (M$^+$).

Conclusions

The catalyst MoO$_3$/ZrO$_2$–Al$_2$O$_3$ exhibited excellent catalytic performance in toluene ammoxidation with benzonitrile as the main product. The Al$_2$O$_3$–ZrO$_2$ binary oxide was found to be an interesting support to investigate the dispersion of molybdenum oxide and catalytic properties. The catalytic performance of MoO$_3$/ZrO$_2$–Al$_2$O$_3$ was dependent on the catalyst compositions and reaction temperature. Increasing the MoO$_3$ loading from 6.6 to 25.0 wt. % enhanced the activity of the catalyst. Above 20.0 wt. %, however, it led to inactivity and performance failure of the catalyst. Over this catalyst, the selectivity to benzonitrile reached 67.0% with the toluene conversion of 68.5% at 400 °C, while the selectivity to benzonitrile was 58.6 % with the toluene conversion of 64.6% at 300 °C.
Conflict of interest
The authors declare no competing financial interest.

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Notes and references


