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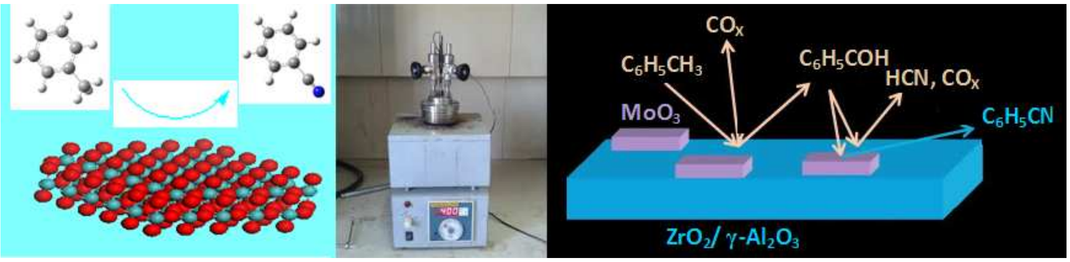

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Characterization and catalytic properties of molybdenum oxide catalysts supported on ZrO_2-γ-Al_2O_3 for ammoxidation of toluene

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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_2O_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_2O_3 was dependent on the catalyst compositions and reaction temperature. MoO_3 (20.0 wt. %) ZrO_2-γ-Al_2O_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 benzaldhyde 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

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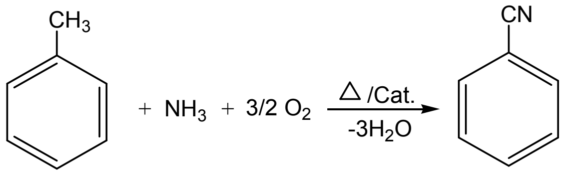
Introduction

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_2O_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-γ-Al_2O_3supported catalysts have been found to show better catalytic properties than catalysts supported on pure oxides [24,25]. The combination of Al_2O_3 and ZrO_2 provides greater mechanical strength, resulting in improved resistance to attrition [26, 27]. In recent times, ZrO_2-γ-Al_2O_3 based materials have been employed as catalysts in various catalytic applications [28, 29]. The advantages of Al_2O_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_2O_5/ZrO_2-γ-Al_2O_3 [70, 71], V_2O_5/γ-Al_2O_3 [72], Mo-V-P/γ-Al_2O_3 [73], vanadium-containing catalysts [74, 75], Fe_2O_3-based catalysts [76], ZrO_2-γ-Al_2O_3 [77], and SiO_2-supported molibdate 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-γ-Al_2O_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.



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 sheild NMR and DMSO-d6 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 Kα° (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 $MoO_3/\gamma\text{-}Al_2O_3$ catalysts were prepared by impregnation of $\gamma\text{-}Al_2O_3$ 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 ˚C for 6h before use.

A series of MoO_3/ $ZrO_2/\gamma\text{-}Al_2O_3$ 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_4OH 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 ˚C. Then the catalysts were dried at 85-90 ºC for about 4h and calcined at 500 ˚C for 6h before use.

Ammoxidation of toluene

A stainless steel cylindrical micro reactor (i.d. 4.8cm; 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 ˚C 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 ˚C, calcined at 400 ˚C 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 K_α 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 = $K.\lambda/W.\cos\theta$, where $W=W_b-W_s$ and W_b is the broadened profile width of experimental sample and W_s is the standard profile width of reference silicon sample.

Fig. 1A shows the XRD patterns of MoO_3, MoO_3/ZrO_2 and $MoO_3/\gamma\text{-}Al_2O_3$ samples. The peaks presented at 2θ=20-30° are attributed to the pure MoO_3, Fig. 1A (a). The XRD pattern of MoO_3/ZrO_2 showed peaks at 2θ = 30, 50 and 60, which were obviously the characteristics of the tetragonal ZrO_2. The X-ray diffraction pattern of $MoO_3/\gamma\text{-}Al_2O_3$ exhibit broad peaks at 2θ = 45 and 66°, which were attributed to $\gamma\text{-}Al_2O_3$, Fig. 1A (c).

X-ray diffraction patterns of the catalysts with different loadings of molybdena catalysts supported on Al_2O_3–ZrO_2 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 ZrO_2 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 $MoO_3/\gamma\text{-}Al_2O_3$ 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_2O_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-γ-Al_2O_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_2O_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.% $MoO_3/ZrO_2/\gamma\text{-}Al_2O_3$ catalysts might be because of the less availability of active MoO_3 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 ^{o}C, while the selectivity to benzonitrile was 58.6 % with the toluene conversion of 64.6% at 300 ^{o}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 $ZrO_2/\gamma\text{-}Al_2O_3$ by mixed oxides formed from the decomposition of molybdate or the solid-state reaction between the supporting oxides and the dispersed active oxides [79–81]. Table 2 shows the BET surface area values of the catalysts. The surface area and pore volume of the $MoO_3/ZrO_2\text{-}\gamma\text{-}Al$ catalysts were in the range of 48–116 $m^2 \cdot g^{-1}$ and 0.50–0.62 cm^3/g, respectively. A gradual decrease in surface area was observed for the catalysts with an increase in the loading of molybdena supported on $ZrO_2/\gamma\text{-}Al_2O_3$, but an increase in the average pore diameters. This phenomenon might be due to two reasons. One refers to MoO_3 particles deposited in the pores of $ZrO_2\text{-}\gamma\text{-}Al_2O_3$ 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/nm^2). Surface areas decreased only slightly with increasing MoO_3 loading; therefore, the Mo surface density increased almost linearly with increasing MoO_3 concentration. In addition it has been noted that for Mo/Al_2O_3 system, formation of a polymolybdate monolayer on Al_2O_3 at surface densities of 4.8 Mo/nm^2 occur.[82] As you can see, the loading 6.6 % MoO_3 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 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. % MoO_3/ ZrO_2-γ-Al_2O_3 catalyst.

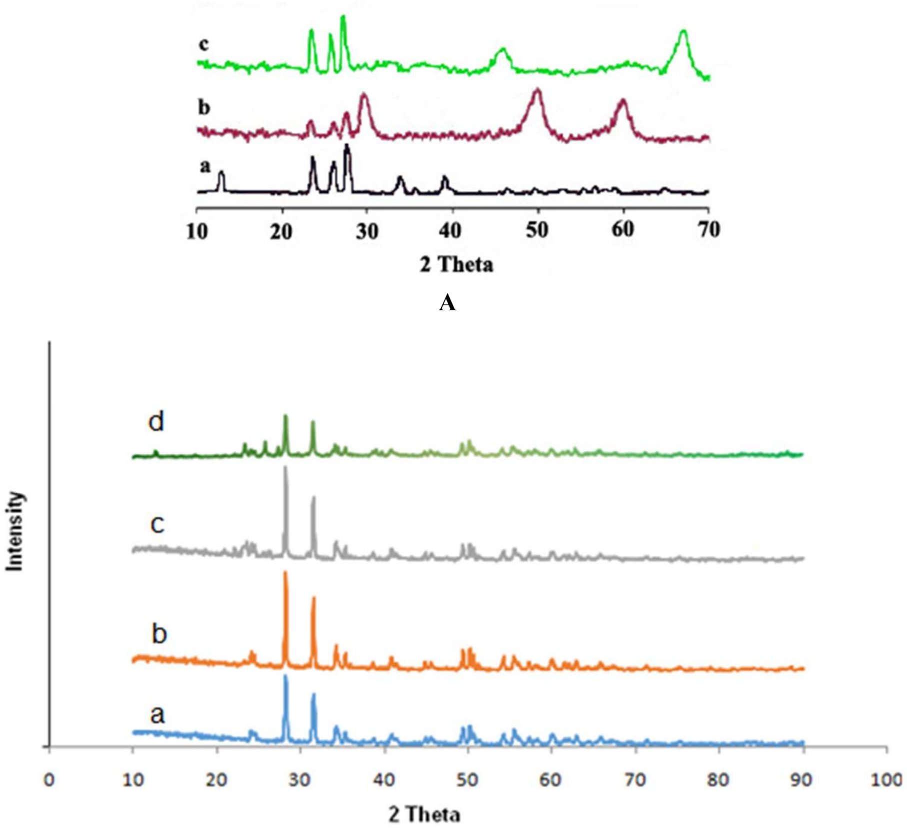
Table 1 Effect of MoO_3 content in the support on the catalyst activity and product selectivity of different MoO_3/ ZrO_2-γ-Al_2O_3 catalysts for toluene ammoxidation.

MoO_3 loading	T (^oC)	Toluene conversion (%)	Product selectivity (%)		
			benzonitrile	benzene	benzaldehyde
6.6%	200	28.6	40.7	≤1	20.5
	300	44.5	46.2	1.3	23.7
	400	44.2	63.5	2	24.4
12.5%	200	32.5	46.3	≤1	20.5
	300	48.4	50.4	1.3	23.7
	400	56.6	66.4	2	24.4
20.0%	200	44.2	40.3	1.3	23.7
	300	64.6	58.6	2	24.4
	400	68.5	68	≤1	24.4%
25.0%	200	30.3	35.9	≤1	20.5
	300	43.7	47.5	1.3	23.7
	400	48.6	67.6	2	24.2

Table 2 Nitrogen adsorption characteristics of Molibdate supported catalysts.

Catalyst	BET surface area (m^2g^{-1})	Surface Density Mo/nm^2	Pore volume (cm^3 g^{-1})	Average pore diameter (nm)
6.6 % MoO_3/ZrO_2–γ-Al_2O_3	116.26	2.37	0.78	6.22

12.5 % MoO_3/ZrO_2–γ-Al_2O_3	78.13	6.69	0.74	6.23
20.0 % MoO_3/ZrO_2–γ-Al_2O_3	66.32	12.61	0.68	6.25
25.0 % MoO_3/ZrO_2–γ-Al_2O_3	48.46	21.57	0.64	6.34



A

B

Fig. 1 (A)- XRD patterns of a) MoO_3; b) MoO_3/ZrO_2; c) MoO_3/γ-Al_2O_3. (B)- XRD patterns of MoO_3/ZrO_2–γ-Al_2O_3 catalysts with different MoO_3 loadings: a) 6.6 wt.%; b) 12.5 wt.%; c) 20.0 wt.%; d) 25.0 wt.%.

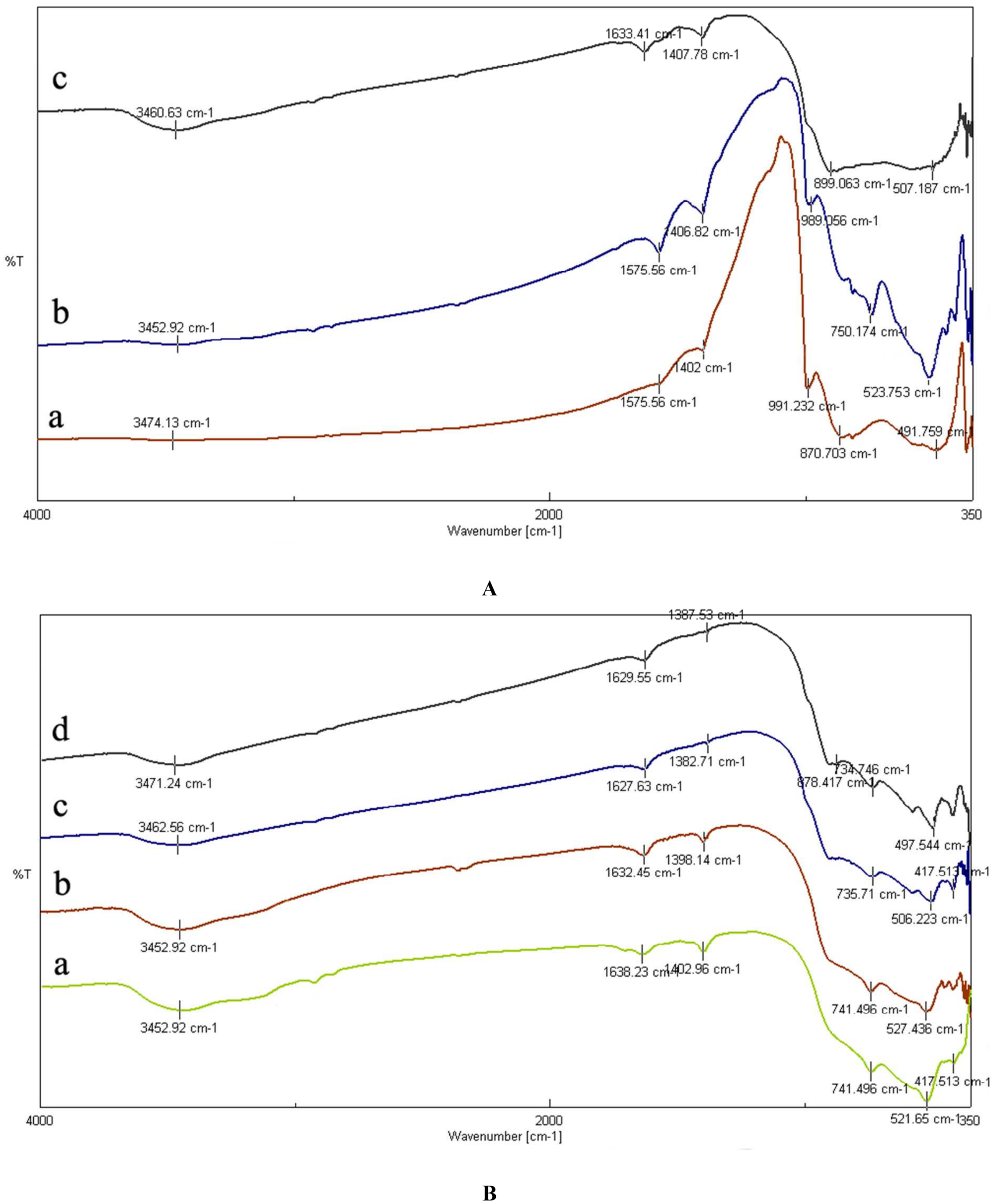
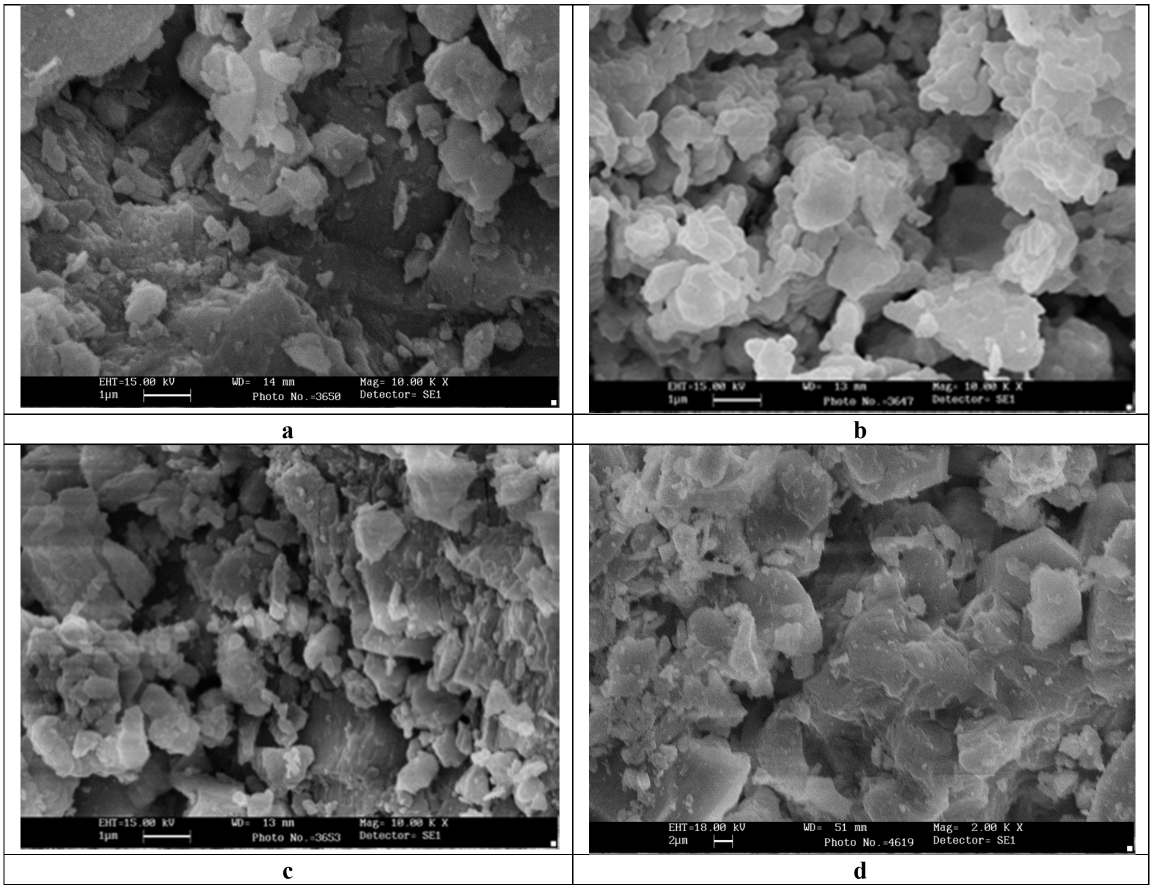


Fig. 2 (A)- FTIR spectra of the a) MoO_3; b) MoO_3/ZrO_2; c) $MoO_3/\gamma\text{-}Al_2O_3$. (B)-FTIR spectra of the $MoO_3/ZrO_2–\gamma\text{-}Al_2O_3$ catalysts with different MoO_3 loadings: a) 6.6 wt.%; b) 12.5 wt.%; c) 20.0 wt.%; d) 25.0 wt.%.



a b

c d

Fig. 3 SEM images of the Molibdate supported catalysts (a) 6.6% wt. MoO_3/ZrO_2-γ-Al_2O_3, (b) 12.5 wt.% MoO_3/ZrO_2-γ-Al_2O_3, (c) 20.0 wt.% MoO_3/ZrO_2-γ-Al_2O_3, (d) 25.0 wt.% MoO_3/ZrO_2-γ-Al_2O_3

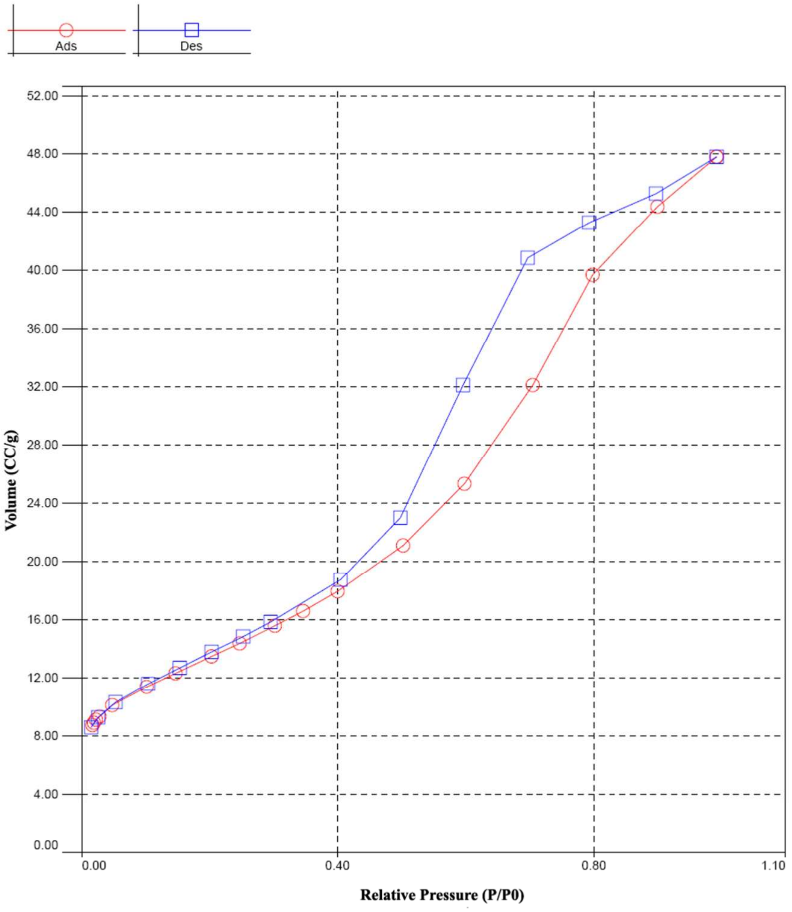


Fig. 4 N_2 adsorption–desorption isotherm of the MoO_3 (20.0 %Wt.)/ ZrO_2-γ-Al_2O_3

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).

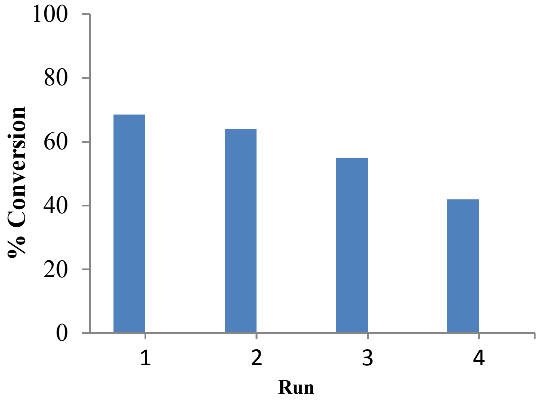


Fig. 5 The results obtained from catalyst reuse in the product formation

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 [83].

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.

□

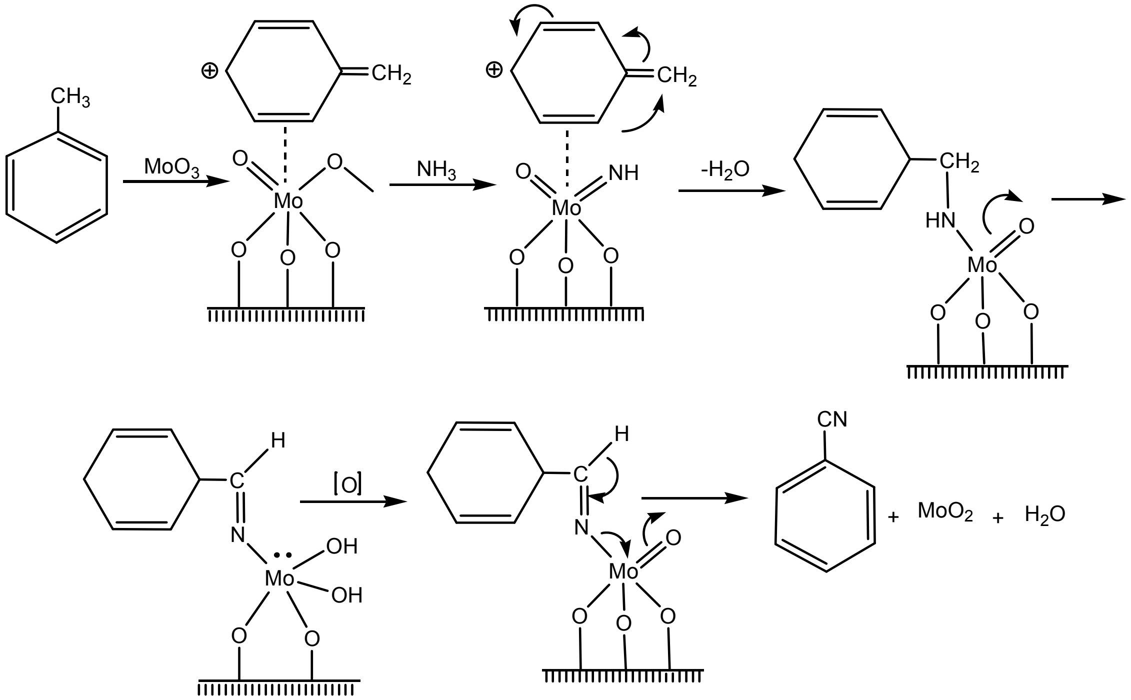


Fig. 6 A plausible mechanism for toluene ammoxidation over MoO_3/ZrO_2-γ-Al_2O_3 catalysts.

The results of ammoxidation of toluene on various MoO_3/ZrO_2-γ-Al_2O_3 catalysts at 400ºC are plotted in Fig. 7. The conversion and selectivity were increased with an increase in MoO_3 loading up to 20.0wt% and beyond this loading, the activity was decreased slightly due to the formation of MoO_3crystallites on the surface of ZrO_2-γ-Al_2O_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 onmixed oxide alumina–zirconia catalysts have been compared in Table 3. It clearly shows that molybdena was well dispersed on MoO_3/ZrO_2-γ-Al_2O_3 support, with more acidic sites per m^2 surface of the support.

Thus, it can be inferred that20.0 wt. % MoO_3/ZrO_2-γ-Al_2O_3 catalyst can be more active in ammoxidation reaction compared to a time when it is supported on alumina–zirconia catalysts.

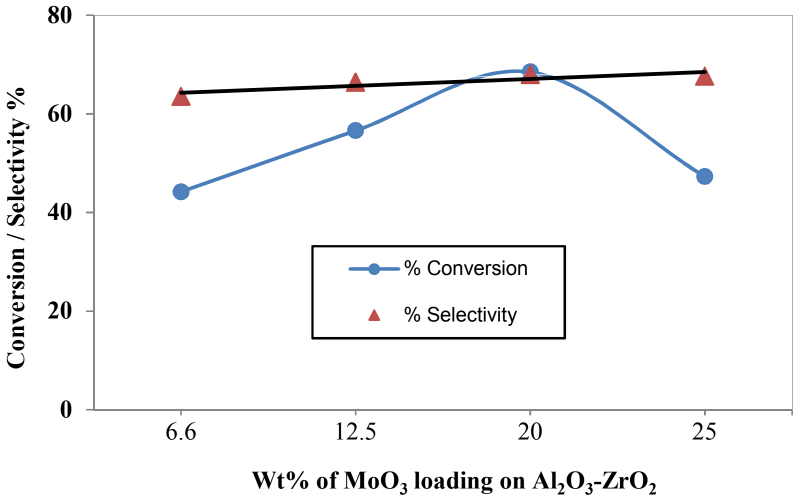


Fig. 7 Ammoxidation of toluene over various $MoO_3/ZrO_2–Al_2O_3$ catalysts (reaction temperature of 400 °C).

benzonitrile Charactrization

FTIR (KBr, cm^{-1}): 3116, 3064, 2256, 1662, 1098, 625 cm^{-1}; ^1H NMR (400 MHz, DMSO-d6): δ 7.383–7.412 (m, 2H), 7.518–7.561 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d6): δ 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-γ-Al_2O_3 exhibited excellent catalytic performance in toluene ammoxidation with benzonitrile as the main product. The Al_2O_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-γ-Al_2O_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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