Mixed Oxide Supported MoO$_3$ Catalyst: Preparation, Characterization and Activities in Nitration of o-xylene

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Abstract

TiO$_2$-ZrO$_2$ mixed oxide support was prepared and impregnated with 12 wt % MoO$_3$ and calcined at various temperatures. The resultant catalyst systems were characterized by XRD, FT-IR, BET, SEM, NH$_3$-TPD and pyridine adsorbed FT-IR methods to know the physico-chemical changes occurred in course of thermal treatment. Activities of these catalysts were tested by employing them in the nitration of o-xylene. Mostly, 500 °C calcined catalyst sample was found to be most active for nitration reaction. Catalyst calcined at higher temperatures showed the negative influence on o-xylene conversion and 4-nitro-o-xylene selectivity. Conversion can be correlated with the presence of strong Brönsted acid sites over the catalyst surface whereas change in selectivity was found attributed to the pore diameter of the catalyst. These catalysts also performed satisfactorily, when used for nitration of other aromatics. No use of corrosive sulfuric acid and efficient reusability of the catalyst make the process environmentally friendly and economic. © 2010 BCREC UNDIP. All rights reserved.

Keywords: TiO$_2$-ZrO$_2$, Mixed oxide, Nitration, O-xylene

1. Introduction

Nitration of aromatic compounds is most widely studied reaction as nitro-aromatics are greatly used as intermediates for the fine chemical industries. Mononitrated o-xylene is found useful for the production of vitamins, agrochemicals, fragrance and dyes [1]. 4-nitro-o-xylene (4-NOX) and 3-nitro-o-xylene (3-NOX) are used for the synthesis of xylidine (a starting material for the production of riboflavin, vitaminB2) and mefenamic acid (an agrochemical) respectively [2]. Therefore, nitration of o-xylene is an important chemical reaction from the industries point of view. Moreover, selectivity aspects of catalysts are equally important as 4-nitro-o-xylene needed to be produced in excess because of higher demand of riboflavin in market.

Nitration of o-xylene using conventional ‘mixed acid’, a mixture of sulphuric acid and nitric acid, as a nitrating agent gives a mixture of 4-nitro-o-xylene (31-55 %) and 3-nitro-o-xylene (45-69 %) [3]. But the poor selectivity and the problem regarding the waste disposal makes this process uneconomic and hazardous in view of environment. That is why
the research in avoiding the use of sulfuric acid and selective synthesis of desired isomer in the nitration of aromatics are of great interest to minimize the pollution caused by sulfuric acid and promote the greater yield of valuable isomer respectively. With respect to this, solid acid catalysts are potentially more attractive due to their shape selective behavior, non corrosiveness, easy recovery, reusability and environmentally friendly nature. Taking in to the account of this, zeolite beta [4, 5], ZSM-5 [5, 6], sulfated zirconia [7], sulfuric acid supported on silica [8], clay supported metal nitrates [9], metal exchanged clays [10] etc. have been used and studied for the nitration of aromatic substrates like benzene, toluene, halo-benzene, phenol, anisole and di-nitration of aromatic substrates like benzene, clays [10] etc. have been used and studied for the supported metal nitrates [9], metal exchanged [7], sulfuric acid supported on silica [8], clay zeolite beta [4, 5], ZSM-5 [5, 6], sulfated zirconia [7]. However, some of these catalysts were suffered with need of longer residence time, tedious workup procedures and above all, their expensiveness

MoO₃ based catalysts are well known and successfully tested for different applications like, trassterification of dimethyl oxide with phenol [13], thiophene hydrodesulfurization and 1-cyclohexene hydrogenation [14] and hydroprocessing applications [15]. An activity of these catalysts in the respective reactions was found related with strong acidity possessed by them. It is also found that, the type of support plays an important role on the catalytic properties and for a given reaction the activity and selectivity of the catalyst can be improved by the use of an appropriate support [16]. For example, intrinsic benign characteristics of both titania and zirconia support can be explored fully by using them in combination. Therefore the combined TiO₂-ZrO₂ mixed oxide has attracted much attention recently as a support [17-19].

As, very little literature is available regarding the use of mixed oxide supported molybdenum oxide catalysts for nitration of aromatics, in present investigation, the goal is set to evaluate the performance of MoO₃ supported on mixed TiO₂-ZrO₂ support as a catalyst in the nitration of o-xylene. In this respect, 12 wt % MoO₃ was deposited over TiO₂-ZrO₂ (1:1) binary oxide support and the catalyst was calcined at different temperatures. The resultant catalytic systems were then individually employed in liquid phase nitration of o-xylene with 69% HNO₃ to study the effect of calcination temperature of activity of catalyst and the corresponding results presented in this paper. To our knowledge this is the first study with binary oxide supported MoO₃ as a catalysts for nitration of o-xylene.

2. Materials and methods

2.1 Catalyst preparation

1:1 mole ratio of TiO₂-ZrO₂ mixed oxide support was prepared by homogeneous co-precipitation method using ammonia as a precipitating agent. Appropriate amount of cold TiCl₄ (Loba chemi, AR grade) was initially digested in cold conc. HCl and then diluted with doubly distilled water. To this aqueous solution the required quantity of ZrOCl₂·8H₂O (Loba chemi, AR grade) dissolved separately in deionized water was added, excess ammonia solution (40%) was also added to this mixture solution for better control of pH and heated to 115 °C with vigorous stirring. Instantly a white precipitate was formed in the solution. The precipitate was allowed to stand at room temperature for 24 hours to provide aging. The precipitate thus obtained was filtered off and thoroughly washed with deionized water until no chloride ion could be detected with AgNO₃ in the filtrate. The obtained sample was then oven dried at 120 °C for 16 h and finally calcined at 500 °C for 6 h in an open air atmosphere.

Molybdena (12 wt %) was deposited on 1:1 mole ratio of TiO₂-ZrO₂ mixed oxide support by adopting wet impregnation method. To impregnate MoO₃, calculated amount of ammonium heptamolybdate was dissolved in doubly distilled water and few drops of dilute NH₄OH were added to make the solution clear and to keep pH constant. Finally, powdered calcined support was then added to this solution and the excess of water was evaporated on water bath with continuous stirring. The resultant solid was then dried at 110 °C for 12 h; part of the obtained catalyst powder is again calcined at 500 °C, 600 °C, and 700 °C for 5h.

For the simplicity in discussion, catalyst with 12 wt% MoO₃ supported on TiO₂-ZrO₂ mixed oxide support, calcined at 500 °C, 600 °C, and 700 °C are coded as MTZ-5, MTZ-6, and MTZ-7 respectively and generally termed as MTZ.

2.2. Catalyst characterization

XRD analysis was carried out with Phillips Holland, XRD system, PW1710 Using Cu-κα (1.54056 Å) radiation, the diffractograms were recorded in 10-60° range of 2θ, The XRD phases present in the samples were identified with the help of JCPDS card files. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on Perkin-Elmer 1720 single beam spectrometer at ambient conditions using KBr disks, with a nominal resolution of 4 cm⁻¹. The mixed samples were pressed into a 10 mg/cm² self-
supporting wafers before measurements were conducted at room temperature in the range of 1500–400 cm⁻¹. Temperature programmed desorption of ammonia (NH₃-TPD) was carried out using Micromeritics Autochem 2920 instrument. Scanning Electron Micrograms (SEM) was obtained using Instrument, JEOL JSM-6380. BET surface area and pore size was estimated by, Quantachrome Autosorb Automated Gas Sorption System, using N₂ as a probe molecule. Gas chromatograms were recorded on Perkin-Elmer Autosystem XL, with PE-1 column.

2.3. Nitration of o-xylene

All liquid phase catalytic nitration reactions were carried out in a batch reactor adopting the procedure from Ref. [20]. In a typical run; 10 mmol o-xylene (1.06 g) in 10 ml carbon tetrachloride, 10 mmol nitric acid (0.9 g, 69 wt%) and 0.212 g freshly activated catalyst (20 wt%, based on o-xylene) were taken in a 50 ml three neck round bottom flask and the mixture was continuously stirred at 75 °C. The temperature of the reaction was maintained by using an oil bath. Water formed during the reaction was separated by Dean-Stark condenser. The samples were periodically collected, neutralized using sodium hydrogen carbonate and analyzed by gas chromatography. Products were confirmed by comparing their GC retention time with that of authentic samples.

3. Results and discussion

3.1. Catalyst surface study

3.1.1. XRD

The XRD patterns of 12 wt% MoO₃/TiO₂-ZrO₂ catalyst calcined at various temperatures from 500 °C to 700 °C are shown in Figure 1. As can be noted from the this figure, diffractogram for sample MTZ-5 (catalyst calcined at 500 °C) exhibited few characteristics lines due to TiO₂-anatase (JCPDS file no. 21-1272) phase, ZrO₂ monoclinic phase (JCPDS file no. 13-307) and ZrTiO₄ compound (JCPDS file no. 7-290). ZrTiO₄ compound is formed from the mutual interaction of TiO₂ and ZrO₂ counterparts of the support. Recently Fling and Wang [21] also reported the formation of the ZrTiO₄ compound coinciding with our observations. As no XRD lines were observed due to crystalline MoO₃ phase, it can be inferred that the impregnated molybdenum oxide is in a highly dispersed state or crystallites formed are less than the detection capacity of the XRD technique. This observation also back up the possibility that 12 wt % loading of molybdenum oxide chosen in the present investigation corresponds to the monolayer capacity of the support. When catalyst is calcined at 600 °C the small increase in the intensity of the line due to ZrTiO₄ compound was noted whereas that of due to TiO₂ and ZrO₂ was found lowered. This clearly suggests the quantitative increase in the ZrTiO₄ compound at the expense of TiO₂ and ZrO₂ species. Upon further increase of the calcination temperature from 600 to 700 °C (MTZ-7) the formation of ZrMoO₄ was noted. Evidently, according to Ref. [22] heating of stoichiometric mixtures of zirconia and molybdena at 600-700 °C resulted in crystalline ZrMoO₄. Molybdenum oxide preferably reacts with ZrO₂ portion of ZrTiO₄ producing ZrMoO₄ compound and TiO₂ releases out in rutile form [23]. Formation of the ZrMoO₄ compound can be attributed to the resemblance in the sizes of ZrO₂ and Mo⁶⁺ as suggested in literature [24]. The general scheme for the formation of ZrMoO₄ compound is shown by the equation 1 and 2.

![Figure 1. XRD pattern of calcined MoO₃/TiO₂-ZrO₂ catalyst: (▲) lines due to anatase phase; (■) ZrTiO₄; (●) ZrO₂; (○) ZrMo₂O₈; (●) rutile phase of TiO₂; (#) container](image-url)
TiO₂ + ZrO₂ → ZrTiO₄ (1)
ZrTiO₄ + 2MoO₃ → ZrMo₂O₈ + TiO₂ (rutile) (2)

In line to this, the diffraction pattern for MTZ-7 catalyst shows the evidence of formation of ZrMo₂O₈ compound and TiO₂ in rutile form (intense peak at 2θ = 27.39°, 54.2° and 31.56°). The amount of rutile phase of TiO₂ formed generally depends on preparation methods, amount of loading of MoO₃ and calcination temperature of the catalyst. The dominant intensity of the lines due to TiO₂ (rutile) along with the appearance of new lines ascribed to ZrO₂ (monoclinic) phase also provides an indication of decomposition of ZrTiO₄ compound at 700 °C temperature which is inline with the observations made by Noguchi and Mizuno [25] and Jung-Chung Wu and co-workers [26].

3.1.2. FT-IR

The FTIR spectra of MoO₃/TiO₂-ZrO₂ catalyst calcined at various temperatures are shown in Figure 2. Generally the IR spectrum of bulk MoO₃ shows absorption band at 1000 cm⁻¹ due to M=O stretching vibration mode [27]. Frausen at al. [23] reported the formation of ZrMo₂O₈ by heating ZrO₂ with MoO₃ together which showed the IR bands at 980, 920 and 800 cm⁻¹. Beside that anatase and rutile phase of titania normally exhibits the strong absorption band in the region of 850-650 cm⁻¹ and 800-650 cm⁻¹ respectively [28]. Absence of any band around 1000 cm⁻¹ confirms that Mo oxide is in highly dispersed state in to a titania zirconia mixed oxide support, which is inline with the XRD results. According to Reddy et al. [29], unsupported TiO₂-ZrO₂ calcined at 500 °C and above temperatures exhibits IR bands at 830 and 740 cm⁻¹ ascribed to ZrTiO₄ species. In our case also, ZrTiO₄ and TiO₂ (anatase) structures prominently appeared at the surface, when catalyst was calcined at 500 °C (MTZ-5) and 600 °C (MTZ-6) temperatures. But, FT-IR spectra of these samples suggest that the bands assigned to ZrTiO₄ are masked which may be due to the interaction of molybdenum phase with ZrTiO₄ in the dormant state at these temperatures. Further sample MTZ-7 (catalyst calcined at 700 °C) ideally shows the band at 976 and 902 cm⁻¹ for ZrMo₂O₈ and at 750 and 625 cm⁻¹ for TiO₂ in rutile phase. Moreover, ZrO₂ in its crystalline monoclinic form can also be identified by a small band around 430 cm⁻¹, coinciding with Ref. [30]. FT-IR results perfectly agree with the observations made from the XRD results.

3.1.3. BET surface area and Pore size analysis

The surface area, pore volume and pore size analysis of 12 wt% MoO₃/TiO₂-ZrO₂ catalyst was carried out using N₂ as a probe molecule and the corresponding results are presented in Table 1. Pure TiO₂-ZrO₂ support prepared in this investigation exhibited the surface area of 128 m²/g. As can be noted form Table, after impregnating 12 wt % MoO₃ over TiO₂-ZrO₂ support and subsequently calcined at 500 °C (MTZ-5, SA = 96 m²/g) the substantial decrease in the BET surface area was observed when compared to that of unpromoted TiO₂-ZrO₂ support. This is generally expected due to the accumulation of molybdenum oxide phase over the support material. When the catalyst was calcined at higher temperatures (600 and 700 °C), the decrease in pore volume and pore diameter was noted. This, in turn indicated the loss in surface area for the respective samples. The down trend in the surface areas of catalyst with respect to increase in calcination temperature is attributed to the formation of ZrTiO₄, ZrMo₂O₈ and other non porous species (confirmed by XRD) which narrowed the channels present inside the material and as a result, denser solid material was formed that offered lowered surface area for the

![Figure 2. FT-IR spectra of MTZ series of catalyst samples](image-url)
Table 1. Surface area and acidity measurement of the catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface area (m²/g)</th>
<th>Average pore diameter (Å)</th>
<th>Average pore volume (cm³/g)</th>
<th>Amount of NH₃ desorbed (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTZ-5</td>
<td>96</td>
<td>69.66</td>
<td>0.1507</td>
<td>0.752</td>
</tr>
<tr>
<td>MTZ-6</td>
<td>82</td>
<td>62.74</td>
<td>0.1441</td>
<td>0.473</td>
</tr>
<tr>
<td>MTZ-7</td>
<td>21</td>
<td>23.62</td>
<td>0.0124</td>
<td>0.121</td>
</tr>
</tbody>
</table>

catalysts. SEM images of the corresponding catalyst sample provide additional evidence to the above discussion.

3.1.4. SEM

Figure 3 represents the photograph for catalyst calcined at 700 °C (MTZ-7). As the temperature changes from 500 °C to 700 °C, the surface of the catalyst appeared to be rough and looks volatilized and sintered due to high calcination temperature. The average particle size for MTZ-5 sample was found increased form 5-8 µm to > 15 µm for MTZ-7 sample due to the agglomeration of small crystallites, but on this behalf no change is noted in the shape of the particles.

3.1.5. Ammonia desorption (NH₃-TPD)

MoO₃/TiO₂-ZiO₂ catalyst calcined at various temperatures were subjected to temperature programmed desorption of ammonia (NH₃-TPD) to survey the acid amount and acid strength of catalysts. In NH₃–TPD profile, peaks are generally distributed into two regions, high temperature (HT) region (T > 400 °C) and low temperature (LT) region (T < 400 °C). Peaks in high temperature (HT) region are ascribed to desorption of ammonia from strong Brønsted and Lewis acid sites, while peaks in low temperature region are assigned to desorption of ammonia from weak acid sites [31, 32]. NH₃-TPD profiles for the samples are shown in Figure 4 and amount of ammonia desorbed is given in Table 1.

It was found that the sample calcined at 500 °C (MTZ-5) has higher acidity (0.752 mmol/g) than compared with other samples. A broad desorption peak in LT region for this catalyst sample indicates the greater contribution of weak acid sites in to the total acid amount of catalyst. With increase in calcination temperature from 500 °C to 700 °C the decrease in the total acidity of catalyst was noted. This clearly suggests that the calcination temperature has great effect on textural properties and therefore the acidic properties. As proposed earlier by Zaho et al. [33, 34], MoO₃ at monolayer coverage on ZrO₂ support leads to the formation of Mo-O-Zr surface species. This Mo/Zr interaction was found responsible for the higher acidity in the respective catalyst. Further, they were also observed that with increase in calcination

Figure 3. Scanning Electron Micrographs of MTZ-7 catalyst

Figure 4. NH₃-TPD profiles for samples: MTZ-5, MTZ-6 and MTZ-7
temperature, Mo-O-Zr species transforms in to bulk ZrMo2O8 compound which eventually shows the lower acidity. Form XRD results of MTZ series of catalyst, it can be noted that MoO3 was present in highly dispersed state till the calcination temperature of 600 °C but, catalyst when calcined at 700 °C, ZrMo2O8 crystallites along with TiO2 (rutile) was developed at the surface of catalyst. Therefore, similar to the observations made by Zaho et al., the increased crystalline nature may be the reason for showing the low acidity by MTZ-7 catalyst sample. From the figure, it is clear that, the acid strength of MTZ-5 catalyst was stronger than that of MTZ-7 catalyst as was indicated by the maximum height of peak at higher desorption temperature. To understand the attribution of these strong acid sites, a survey of nature of acid sites was carried out and discussed in next section.

3.1.6. Pyridine adsorbed FT-IR

In order to obtain clear distinction between Lewis and Brønsted acid sites, FT-IR analysis of pyridine adsorbed on catalyst surface was carried out and results are displayed in Fig. 5. Pyridine adsorbed on Brønsted acid sites produce characteristic IR band around 1540 and 1638 cm⁻¹ due to vibration modes of adsorbed pyridine and bands at 1450 and 1480 cm⁻¹ are assigned to pyridine coordinated with Lewis acid sites [35].

According to Tanabe's hypothesis [36] the surface structure of TiO2-ZrO2 can be represented as (i) and (ii). Both structures contain acidic and basic sites. When MoO3 is doped into this support and subsequently calcined, molybdenum atom interacts with basic hydroxyl group of the support leads to form bidantately coordinated bridged structure as shown in Scheme 1 (iii). Hence the basic hydroxyl groups of support those are normally present more on titania rich domain, coordinates through Ti-O terminal to the Mo centre. Such hydroxyl groups are considered to be the sources of strong Brønsted acid sites. Beside this, bridged bidentate structure could strongly withdraw electrons from the neighboring Ti cations, resulting in a number of electron-deficient metal centers on the Ti cations that act as strong Lewis acid sites. Therefore Lewis acid sites may associate with Zr4+, Ti4+ and Mo6+ cationic centers arising due to unsaturation in coordination [37].

With respect to these proposals, catalyst calcined at 500 °C (MTZ-5) exhibited the bands at 1443 cm⁻¹, 1547 cm⁻¹ and 1488 cm⁻¹ indicating the presence of Brønsted as well as Lewis acid sites over its surface. Further for catalyst MTZ-6, it was observed that the intensities of bands associated with Brønsted acidity decreases as compared to that of Lewis acidity. Similar trend was also observed for MTZ-7 catalyst but the intensities of...
the respective peaks are very low due to sharp decrease in the population of total acid sites at high calcination temperature, as seen by NH3-TPD method. The decrease of strong Brönsted acid sites can be justified by the removal of surface hydroxyl groups in the form of water and subsequent formation of highly crystalline material at higher calcination temperatures.

### 3.2. Activity Measurement

#### 3.2.1. Nitration of o-xylene

Table 2 lists the result of liquid phase nitration of o-xylene over MoO3/TiO2-ZrO2 catalyst calcined at various temperatures. It shows that, among the various catalysts, MTZ-5 (calcined at 500 °C) was more active compared to the others. When reaction was performed using sulphuric acid, 17 % o-xylene conversion and 0.73 of 4/3 NOX ratio is noted which suggests the influence of heterogeneous acid catalyst in reaction. In case of MTZ-5 catalyst the greater o-xylene conversion is attributed to the presence of strong Brönsted acid sites over the surface of catalyst which promotes the generation of nitronium ion from nitric acid. The resulted nitronium ions later attack the ring of o-xylene to produce the desired nitro-aromatics in the reaction, as shown in Scheme 2. On the other hand, 4-nitro-o-xylene selectivity can be correlated to the bigger pores of this catalyst that may be suitable for the faster diffusion of 4-NOX than 3-NOX due to the difference in the kinetic diameter. Catalyst calcined at 600 °C and 700 °C temperatures (MTZ-6, MTZ-7) shows lower conversion of o-xylene which is expected due to the disappearance of Brönsted acid sites form the catalyst surface because of the thermal treatment.

Accordingly, lowered 4-NOX selectivity of these catalysts may be because of smaller pores of the catalysts compared to MTZ-5, leading to the surface reaction which results into a formation of excessive side products. This happening can also be verified from the acidity and XRD measurement that confirms the poorly acidic and non porous nature of the catalysts when calcined at respective temperatures. Water present in 69% HNO3 and formed during the generation of nitronium ion has to be removed which otherwise deactivates the catalyst. Therefore using Dean and Stark assembly, azeotropic removal of water from the reaction mixture was done and the reaction was repeated by providing 3 h of

![Scheme 2: The plausible reaction mechanism of nitration of o-xylene over MTZ](image)
residence time and studied separately. The study reviles that as the reaction progressed, after 3 h the conversion was marginally increased for MTZ-5 (27-34 %) and MTZ-6 (21-25 %) whereas no change was noticed in case of MTZ-7 (16-17 %). Beside that, it was observed that longer residence time adversely affects the 4-NOX selectivity due to the pore blocking of the catalyst by side products.

3.2.2. Nitration of other aromatics

In order to access the activities of MoO₃ supported on titania zirconia mixed oxide catalyst calcined at various temperatures, studies were extended to the nitration of some other aromatic substrates like benzene, toluene and phenol and results are summarized in Table 3. Exclusive formation of nitrobenzene, faster reaction rates and fairly good conversion of benzene are some of the advantages of carrying out the nitration using MTZ series of catalysts. When toluene was used as a substrate for nitration, higher conversion was noted with MTZ-5(90%) catalyst which falls down for MTZ-7(58%) catalyst, suggesting the influence of calcinations temperature of catalyst. Nitration of toluene over MTZ series of catalyst has advantageous for suppression of unwanted byproducts, which enhances the yield of desired nitro-aromatics. Para selective nature of the catalyst increases with the increase in calcination temperature. This may be due to reduction in pore diameter of the catalyst with respect to thermal treatment. Phenol being more polar compared to

<table>
<thead>
<tr>
<th>Aromatic substrate</th>
<th>Reaction conditions</th>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Major products (Selectivity, %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>a</td>
<td>MTZ-5</td>
<td>100</td>
<td>Nitrobenzene (100)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MTZ-6</td>
<td>96</td>
<td>Nitrobenzene (100)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MTZ-7</td>
<td>82</td>
<td>Nitrobenzene (94)</td>
</tr>
<tr>
<td>Toluene</td>
<td>b</td>
<td>MTZ-5</td>
<td>90</td>
<td>Ortho-nitro-toluene (57), Para-nitro-toluene (42)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MTZ-6</td>
<td>83</td>
<td>Ortho-nitro-toluene (44), Para-nitro-toluene (45)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MTZ-7</td>
<td>58</td>
<td>Ortho-nitro-toluene (43), Para-nitro-toluene (55)</td>
</tr>
<tr>
<td>Phenol</td>
<td>c</td>
<td>MTZ-5</td>
<td>97</td>
<td>Ortho-nitro-phenol (59), Para-nitro-phenol (40)</td>
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<td>Ortho-nitro-phenol (46), Para-nitro-phenol (47)</td>
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<tr>
<td></td>
<td></td>
<td>MTZ-7</td>
<td>71</td>
<td>Ortho-nitro-phenol (43), Para-nitro-phenol (52)</td>
</tr>
</tbody>
</table>

Table 4. Nitration of o-xylene with different solvents over MTZ-5: Reactions were performed by changing the solvents and keeping the other reaction conditions similar to that of mentioned in Table 3 notes.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Conversion of o-xylene, %</th>
<th>Selectivity, %</th>
<th>4/3 NOX ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>3-NOX</td>
<td>4-NOX</td>
</tr>
<tr>
<td>1</td>
<td>DCM</td>
<td>19</td>
<td>31</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>n-Hexane</td>
<td>7</td>
<td>52</td>
<td>49</td>
</tr>
<tr>
<td>3</td>
<td>CCl₄</td>
<td>24</td>
<td>36</td>
<td>49</td>
</tr>
<tr>
<td>4</td>
<td>DCE</td>
<td>27</td>
<td>37</td>
<td>52</td>
</tr>
</tbody>
</table>
the other aromatic substrates interacts readily with the catalyst surface. That is why higher values of conversions are recorded as compared to that of toluene. In this case also, para selectivity was found increased with the increase in calcination temperature of the catalyst. But, by products are formed in lower extent.

In general, the change in conversion and selectivity of respective nitro-derivatives of these aromatic substrates can be well correlated to the change in the acidity and pore size distribution rather than to the change in the surface area of the catalysts.

3.2.3. Effect of solvent

In order to search the best entrainer or otherway the best reaction medium, nitrations of o-xylene over MTZ-5 catalyst were performed using different solvents and their subsequent effect on o-xylene conversion and 4-nitro o-xylene selectivity was studied and details are listed in Table 4. Among the solvents used hydrocarbon solvent provided lower yields. On the other hand, chlorinated solvents CCl₄ and DCE are proved to be the best entertainers for the effective removal of water azeotropically to provide higher conversions. Di-chloromethane generates side products. Dichloroethane is found best as it gives high o-xylene conversion and 4/3NOX ratio. This was also observed by Kale and co workers for selective chlorination [38].

3.2.4. Reusability of catalysts

After completion of 3 hours of nitration of o-xylene with 69% HNO₃ over MTZ-5, catalyst is filtered off, washed with solvent and used in another batch of same reaction. In all, 4 such cycles were performed and corresponding effect on o-xylene conversion and 4-NOX selectivity was noted and presented in Fig. 6. Result indicates that activity and selectivity were retained for all 4 cycles suggesting the high stability of catalyst in acidic environment of reaction.

4. Conclusions

Greater yield of 4-NOX can be achieved by nitrating o-xylene with HNO₃ as nitrating agent, dichloroethane as an entrainer and MTZ-5 as a catalyst. High calcination temperature brings the physico-chemical changes in catalyst which correspondingly affects the conversion and selectivity of desired molecules. MTZ series of catalyst can be successfully utilized for nitrating the aromatics like benzene, toluene and phenol. These catalysts have the several advantages over conventional 'mixed acid', viz., easy separation of the catalyst by simple filtration, zero emission of effluents and non corrosive nature.

References


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