Mixed Oxide Supported MoO₃ Catalyst: Preparation, Characterization and Activities in Nitration of o-xylene

S.M. Kemdeo, V.S. Sapkal [1], G.N. Chaudhari *

Department Of Chemistry, Shri Shivaji Science College, Amravati, India.
[1] University Department Of Chemical Technology, SGB Amravati University, Amravati, India

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 ᵒC 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.
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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 sulpfuric 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

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* Corresponding Author.
E-mail address: nano.d@rediffmail.com (G.N. Chaudhari)
Tel: +91- 0721- 2660255, Fax: +91- 0721- 2660855

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-substituted benzene [4-10,11,12]. However, some of these catalysts were suffered with need of longer residence time, tedious workup procedures and above all, their expensiveness

MoO$_3$ based catalysts are well known and successfully tested for different applications like, trasesterification of dimethyl oxalate with phenol [13], thiophene hydrodesulfurization and 1-cyclohehene 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 TiO$_2$-ZiO$_2$ 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 TiO$_2$-ZrO$_2$ support as a catalyst in the nitration of o-xylene. In this respect, 12 wt % MoO$_3$ was deposited over TiO$_2$-ZrO$_2$ (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% HNO$_3$ 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 MoO$_3$ as a catalysts for nitration of o-xylene.

2. Materials and methods

2.1 Catalyst preparation

1:1 mole ratio of TiO$_2$-ZrO$_2$ mixed oxide support was prepared by homogeneous co-precipitation method using ammonia as a precipitating agent. Appropriate amount of cold TiCl$_4$ (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 ZrOCl$_2$.8H$_2$O (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 ^{o}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 AgNO$_3$ in the filtrate. The obtained sample was then oven dried at 120 ^{o}C for 16 h and finally calcinied at 500 ^{o}C for 6 h in an open air atmosphere.

Molybdena (12 wt %) was deposited on 1:1 mole ratio of TiO$_2$-ZrO$_2$ mixed oxide support by adopting wet impregnation method. To impregnate MoO$_3$, calculated amount of ammonium heptamolybdate was dissolved in doubly distilled water and few drops of dilute NH$_4$OH were added to make the solution clear and to keep pH constant. Finally, powdered calcinied 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 ^{o}C for 12 h; part of the obtained catalyst powder is again calcined at 500 ^{o}C, 600 ^{o}C, and 700 ^{o}C for 5h.

For the simplicity in discussion, catalyst with 12 wt% MoO$_3$ supported on TiO$_2$-ZrO$_2$ mixed oxide support, calcined at 500 ^{o}C, 600 ^{o}C, and 700 ^{o}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-kα (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/cm^2 self-

supporting wafers before measurements were conducted at room temperature in the range of 1500–400 cm^{-1}. Temperature programmed desorption of ammonia (NH$_3$-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 N$_2$ 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 ^{o}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% MoO$_3$/TiO$_2$-ZrO$_2$ catalyst calcined at various temperatures from 500 ^{o}C to 700 ^{o}C are shown in Figure 1. As can be noted from the this figure, diffactogram for sample MTZ-5 (catalyst calcined at 500 ^{o}C) exhibited few characteristics lines due to TiO$_2$-anatase (JCPDS file no. 21-1272) phase, ZrO$_2$ monoclinic phase (JCPDS file no. 13-307) and ZrTiO$_4$ compound (JCPDS file no. 7-290). ZrTiO$_4$ compound is resulted form the mutual interaction of TiO$_2$ and ZrO$_2$ counterparts of the support. Recently Fling and Wang [21] also reported the formation of the ZrTiO$_4$ compound coinciding with our observations. As no XRD lines were observed due to crystalline MoO$_3$ 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 ^{o}C the small increase in the intensity of the line due to ZrTiO$_4$ compound was noted whereas that of due to TiO$_2$ and ZrO$_2$ was found lowered. This clearly suggests the quantitative increase in the ZrTiO$_4$ compound at the expense of TiO$_2$ and ZrO$_2$ species. Upon further increase of the calcination temperature from 600 to 700 ^{o}C (MTZ-7) the formation of ZrMo$_2$O$_8$ was noted. Evidently, according to Ref. [22] heating of stoichiometric mixtures of zirconia and molybdena at 600-700 ^{o}C resulted in crystalline ZrMo$_2$O$_8$. Molybdenum oxide preferably reacts with ZrO$_2$ portion of ZrTiO$_4$ producing ZrMo$_2$O$_8$ compound and TiO$_2$ releases out in rutile form [23]. Formation of the ZrMo$_2$O$_8$ compound can be attributed to the resemblance in the sizes of ZrO$_2$ and Mo^{6+} as suggested in literature [24]. The general scheme for the formation of ZrMo$_2$O$_8$ compound is shown by the equation 1 and 2.
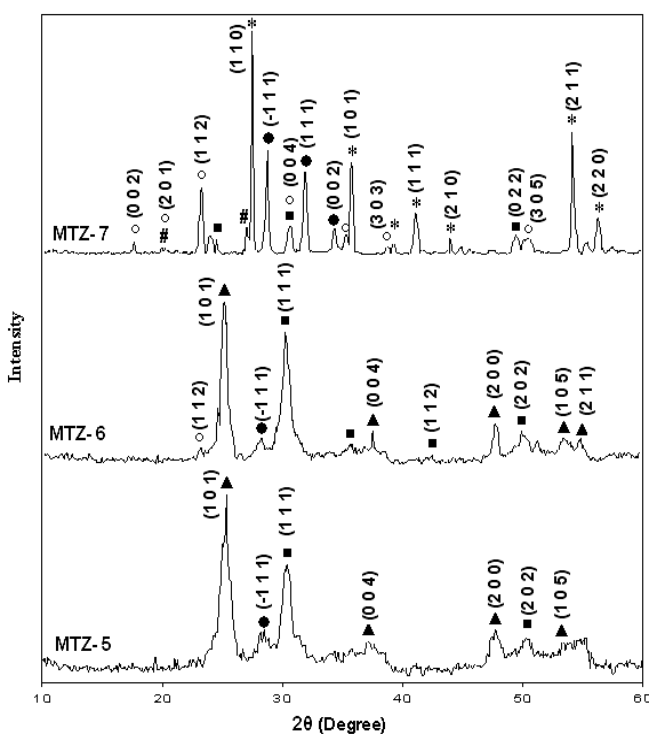

Figure 1. XRD pattern of calcined MoO$_3$/TiO$_2$-ZrO$_2$ catalyst: (▲) lines due to anatase phase; (■) ZrTiO$_4$; (•) ZrO$_2$; (○); ZrMo$_2$O$_8$; (∗) rutile phase of TiO$_2$;(#) container

$$TiO_2 + ZrO_2 \quad \rightarrow \quad ZrTiO_4 \qquad (1)$$
$$ZrTiO_4 + 2MoO_3 \rightarrow ZrMo_2O_8 + TiO_2 \text{ (rutile)} \quad (2)$$

In line to this, the diffraction pattern for MTZ-7 catalyst shows the evidence of formation of $ZrMo_2O_8$ compound and TiO_2 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 MoO_3 and calcination temperature of the catalyst. The dominant intensity of the lines due to TiO_2 (rutile) along with the appearance of new lines ascribed to ZrO_2 (monoclinic) phase also provides an indication of decomposition of $ZrTiO_4$ 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 MoO_3/TiO_2-ZrO_2 catalyst calcined at various temperatures are shown in Figure 2. Generally the IR spectrum of bulk MoO_3 shows absorption band at 1000 cm^{-1} due to M=O stretching vibration mode [27]. Frausen at al. [23] reported the formation of $ZrMo_2O_8$ by heating ZrO_2 with MoO_3 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 TiO_2-ZrO_2 calcined at 500 °C and above temperatures exhibits IR bands at 830 and 740 cm^{-1} ascribed to $ZrTiO_4$ species. In our case also, $ZrTiO_4$ and TiO_2 (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 $ZrTiO_4$ are masked which may be due to the interaction of molybdena phase with $ZrTiO_4$ 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 $ZrMo_2O_8$ and at 750 and 625 cm^{-1} for TiO_2 in rutile phase. Moreover, ZrO_2 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.
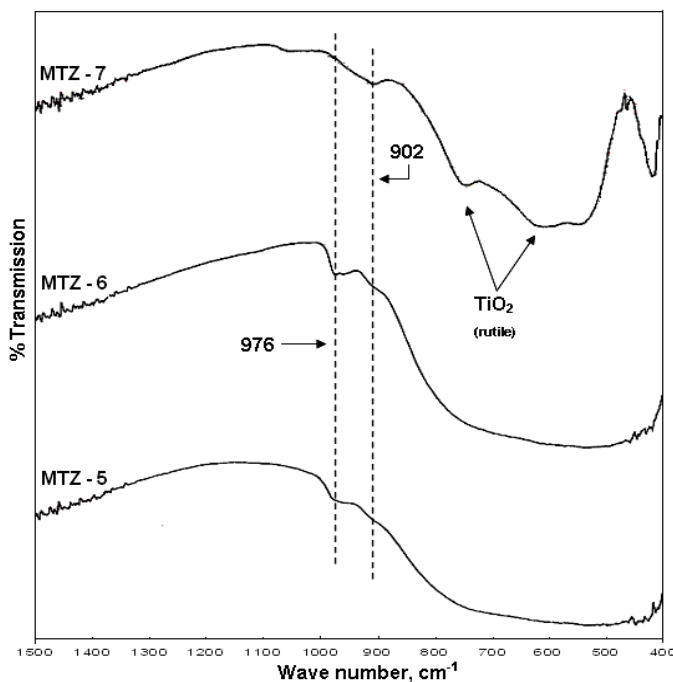

Figure 2. FT-IR spectra of MTZ series of catalyst samples

3.1.3. BET surface area and Pore size analysis

The surface area, pore volume and pore size analysis of 12 wt% MoO_3/TiO_2-ZrO_2 catalyst was carried out using N2 as a probe molecule and the corresponding results are presented in Table 1. Pure TiO_2-ZrO_2 support prepared in this investigation exhibited the surface area of 128 m^2/g. As can be noted form Table, after impregnating 12 wt % MoO_3 over TiO_2-ZrO_2 support and subsequently calcined at 500 °C (MTZ-5, SA = 96 m^2/g) the substantial decrease in the BET surface area was observed when compared to that of unpromoted TiO_2-ZrO_2 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 $ZrTiO_4$, $ZrMo_2O_8$ 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

Table 1. Surface area and acidity measurement of the catalysts

Catalyst	Surface area (m^2/g)	Average pore diameter (Å)	Average pore volume (cm^3/g)	Amount of NH_3 desorbed (mmol/g)
MTZ- **5**	96	69.66	0.1507	0.752
MTZ- **6**	82	62.74	0.1441	0.473
MTZ- **7**	21	23.62	0.0124	0.121

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 ^oC (MTZ-7). As the temperature changes from 500 ^oC to 700 ^oC, 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 (NH_3-TPD)

MoO_3/TiO_2-ZiO_2 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 NH_3 –TPD profile, peaks are generally distributed into two regions, high temperature (HT) region (T > 400 ^oC) and low temperature (LT)

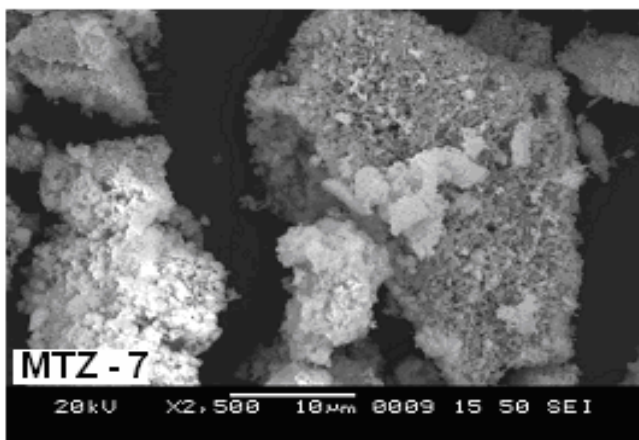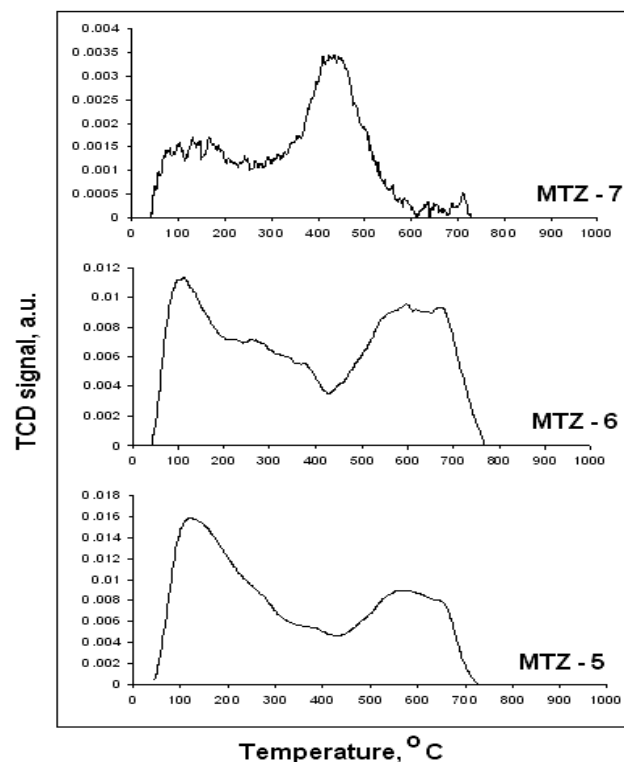**Figure 3**. Scanning Electron Micrographs of MTZ-7 catalyst

Figure 4. NH_3-TPD profiles for samples: MTZ-5, MTZ-6 and MTZ-7

region (T < 400 ^oC). Peaks in high temperature (HT) region are ascribed to desorption of ammonia from strong Brönsted and Lewis acid sites, while peaks in low temperature region are assigned to desorption of ammonia from weak acid sites [31, 32]. NH_3-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 ^oC (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 ^oC to 700 ^oC 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], MoO_3 at monolayer coverage on ZrO_2 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

temperature, Mo-O-Zr species transforms in to bulk $ZrMo_2O_8$ compound which eventually shows the lower acidity. Form XRD results of MTZ series of catalyst, it can be noted that MoO_3 was present in highly dispersed state till the calcination temperature of 600 °C but, catalyst when calcined at 700 °C, $ZrMo_2O_8$ crystallites along with TiO_2 (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 Brönsted acid sites, FT-IR analysis of pyridine adsorbed on catalyst surface was carried out and results are displayed in Fig. 5. Pyridine adsorbed on Brönsted 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 TiO_2-ZrO_2 can be represented as (i) and (ii). Both structures contain acidic and basic sites. When MoO_3 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 Brönsted 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 Zr^{4+}, Ti^{4+} and Mo^{6+} 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
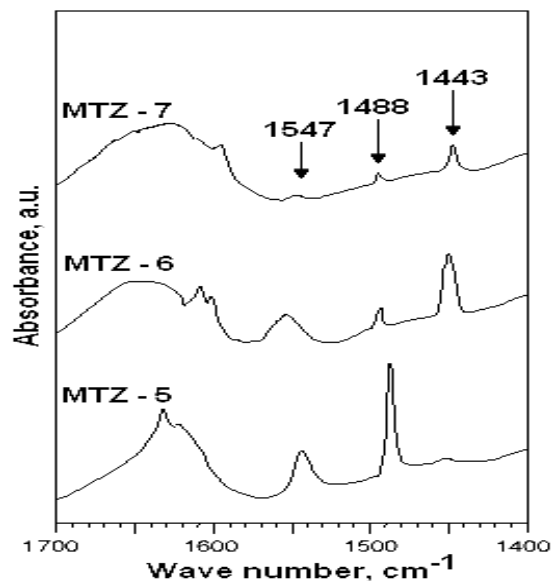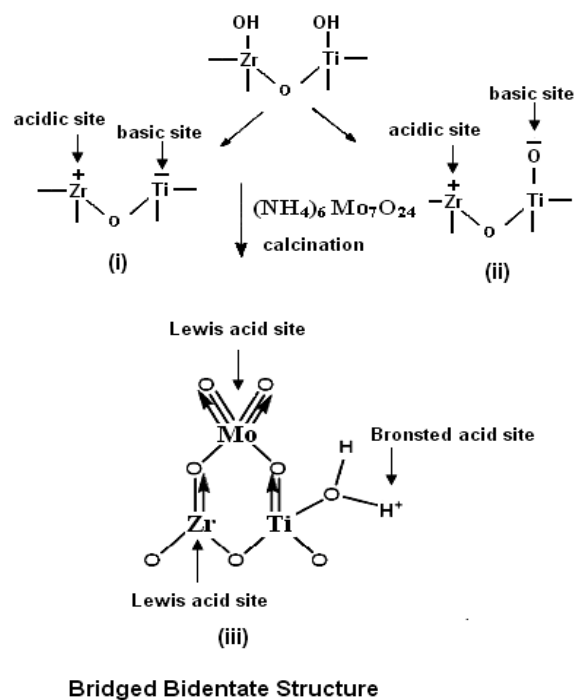

Figure 5. FT-IR spectra of pyridine adsorbed catalysts

Scheme 1: Schematic presentation of the structure of MoO_3 on titania-zirconia mixed oxide

presence of Brönsted as well as Lewis acid sites over its surface. Further for catalyst MTZ-6, it was observed that the intensities of bands associated with Brönsted acidity decreases as compared to that of Lewis acidity. Similar trend was also observed for MTZ-7 catalyst but the intensities of

Table 2. Liquid phase batch process nitration of *o*-xylene over MTZ series of catalysts [1]

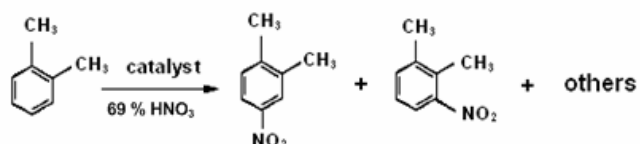| Catalyst	Reaction time, h	Conversion of *o*-xylene, %	Selectivity, %			4/3 NOX ratio
			3-NOX	4-NOX	Others	
H$_2$SO$_4$	1	19	57	42	1	0.73
MTZ-5	1	27	37	52	11	1.40
	3	34	26	38	36	1.42
MTZ-6	1	21	32	42	26	1.31
	3	25	19	25	57	1.33
MTZ-7	1	16	31	38	31	1.22
	3	17	19	23	58	1.21

[1] Reaction conditions: *o*-xylene /HNO$_3$=1; catalyst= 0.212 (20 wt% of *o*-xylene weight); HNO$_3$= 69 wt %; solvent = dichloroethane; temperature= 75 ºC. NOX= nitro-ortho-xylene. Others = tolualdehyde+ toluic acid+ methylphenyl nitromethane

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 MoO$_3$/TiO$_2$-ZrO$_2$ catalyst calcined at various temperatures. It shows that, among the various catalysts, MTZ-5 (calcined at 500 ºC) 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 ºC and 700 ºC 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% HNO$_3$ 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

Table 3. Nitration of different aromatic substrates: *Reaction conditions: o-xylene /HNO₃=1; catalyst= 0.212 (20 wt% of o-xylene weight); HNO₃= 69 wt %; solvent = dichloroethane; temperature= 75 °C. NOX= nitro-ortho-xylene. Others = tolualdehyde+ toluic acid+ methylphenyl nitromethane*

Aromatic substrate	Reaction conditions	Catalyst	Conversion (%)	Major products (Selectivity, %)
Benzene	a	MTZ-5	100	Nitrobenzene (100)
		MTZ-6	96	Nitrobenzene (100)
		MTZ-7	82	Nitrobenzene (94)
Toluene	b	MTZ-5	90	Ortho-nitro-toluene (57), Para-nitro-toluene (42)
		MTZ-6	83	Ortho-nitro-toluene (44), Para-nitro-toluene (45)
		MTZ-7	58	Ortho-nitro-toluene (43), Para-nitro-toluene (55)
Phenol	c	MTZ-5	97	Ortho-nitro-phenol (59), Para-nitro-phenol (40)
		MTZ-6	84	Ortho-nitro-phenol (46), Para-nitro-phenol (47)
		MTZ-7	71	Ortho-nitro-phenol (43), Para-nitro-phenol (52)

Table 4. Nitration of *o*-xylene with different solvents [2] 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.*

Entry	Solvent	Conversion of *o*-xylene, %	Selectivity, %			4/3 NOX ratio
			3-NOX	4-NOX	: Others	
1	DCM	19	31	40	29	1.29
2	n-Hexane	7	52	34	14	0.65
3	CCl₄	24	36	49	15	1.36
4	DCE	27	37	52	11	1.40

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
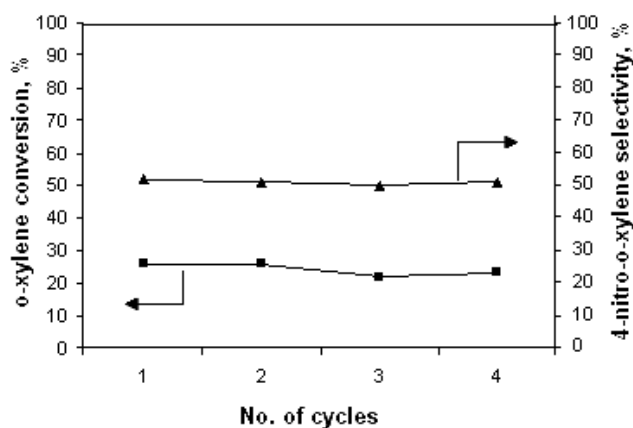
Figure 6: Consistency of the catalyst over the number of recycle

the other aromatic substrates interacts readily with the catalyst surface. That is why higher values of conversions are recorded as compared to that of for 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 entariner or otherway the best reaction medium, niration 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 CCl_4 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% HNO_3 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 HNO_3 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

[1] Olah, G.A.; Malhotra, R.; Narang, S.C. 1989. *Nitration: Method and Mechanisms*: VCH publisher Inc-New York 1989: 201-204.

[2] Booth, G., *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. A17: VCH-Weinheim.

[3] Coombes, R. G.; Crout D. G. H.; Hoggett, J. G.; Moodie, R. B.; and Schofield, K. 1970. Electrophilic aromatic substitution. Part VI. Kinetics and mechanism of nitration of halogenobenzenes. *Journal of Chemical Society* B: 347-357.

[4] Bernasconi, S.; Pringruber, G.; Kogelbauer, A.; Prins, R. 2003. Factors determining the suitability of zeolite BETA as para-selective nitration catalyst. *Journal of Catalysis* 219: 231-241.

[5] Smith, K.; Musson, A.; DeBoos, G.A. 1998. A Novel method for the nitration of simple aromatic compounds. *Journal of Organic Chemistry* 63: 8448-8454.

[6] Choudary, B.M.; Sateesh, M.; Kantam, M.L.; Rao, K.K.; Ramprasad, K.V.; Raghavan, K.V.; Sarma, J.A.R.P. 2000. Selective nitration of aromatic compounds by solid acid catalysts. *Chemical Communications*: 25-26.

[7] Yadav, G.D.; Nair, J.J. 1999. Sulfated zirconia and its modified versions as promising catalysts for industrial processes. *Microporous and Mesoporous Material* 33: 1-48.

[8] Kogelbauer, A.; Vassena, D.; Prins, R.; Armor, J.N. 2000. Solid acids as substitutes for sulfuric acid in the liquid phase nitration of toluene to nitrotoluene and dinitrotoluene. *Catalysis Today* 55: 151-160.

[9] Gigantee, B.; Prazeres, A.O.; Marcelo-Curto, M.J.; Cornelis, A.; Laszlo, P. 1995. Mild and selective nitration by claycop. *Journal of Organic Chemistry* 60: 3445-3447.

[10] Choudary, B.M.; Sarma, M.R.; Kumar, K.V. 1994. Fe3+-Montmorillonite catalyst for selective nitration of chlorobenzene. *Journal of Molecular Catalysis A: Chemical* 87: 33-38.

[11] Esakkidurai, T.; Pitchumani, K. 2000. Zeolite-mediated regioselective nitration of phenol in solid state. *Journal of Molecular Catalysis A: Chemical* 185: 305-309.

[12] Akolekar, D.B.; Lemay, G.; Sayari, A.; Kaliaguine, S. 1995. High-pressure nitration of toluene using nitrogen dioxide on zeolite catalysts. *Research on Chemical Intermediates* 21:7-16.

[13] Liu Y.; Ma X.; Wang S.; Gong J. 2007. The nature of surface acidity and reactivity of MoO_3/SiO_2 and MoO_3/TiO_2-SiO_2 for transesterification of dimethyl oxalate with phenol: A comparative investigation. *Applied Catalysis B: Environmental* 77:125-134.

[14] Rana, M.S.; Maity, S.K.; Ancheyta, J.; Murli Dhar, G.; Prasada Rao, T.S.R. 2003. TiO_2-SiO_2 supported hydrotreating catalysts: physico-chemical characterization and activities. *Applied Catalysis A: General* 253:165-176.

[15] Wang, I.; Huang, W.H.; Wu, J.C. 1985. Benzene hydrogenation over NI/TiO_2-ZrO_2 catalysts. *Applied Catalysis* 18: 273-283.

[16] Hu, H.; Waches, I.E. 1995.Catalytic Properties of Supported Molybdenum Oxide Catalysts: In Situ Raman and methanol Oxidation Studies. *Journal of physical chemistry* 99: 10911-10922

[17] Reddy, B.M.; Khan. A. 2005.Recent advances on TiO_2-ZrO_2 mixed oxides as catalysts and catalyst support. *Catalysis Reviews* 47: 257-296.

[18] Samantaray, S. K.; Parida, K. M. 2001. SO_4^{2-}/TiO_2-SiO_2 mixed oxide catalyst: 2. Effect of the fluoride ion and calcination temperature on esterification of acetic acid. *Applied Catalysis A:General* 211:175-187.

[19] Kobayashi, M.K.; Kuma, R.; Masaki, S.; Sugishima, N. 2005. TiO_2-SiO_2 and V_2O_5/TiO_2-SiO_2 catalyst: Physico-chemical characteristics and catalytic behavior in selective catalytic reduction of NO by NH3. *Applied Catalysis B: Environmental* 60:173-179.

[20] Patil, P.T.; Malshe, K.M.; Dagade, S.P.; Dongare, M.K. 2003. Regioselective nitration of o-xyleneto 4-nitro-o-xylene using nitric acid over solid acid catalysts. *Catalysis Communications* 4: 429-434.

[21] Fling, J.; Wang, I. 1991. Dehydrocyclization of C6-C8 n-paraffins to aromatics over TiO_2-ZrO_2 catalysts. *Journal of Catalysis* 130: 577-587.

[22] Said, A.A. 1994. Mutual influences between ammonium heptamolybdate and γ-alumina during their thermal treatments. *Thermochim. Acta* 236: 93-104.

[23] Delmon, B.; Jacobs, P. A.; Poncelet, G. eds. 1976. *Preparation of Catalysts*. Fransen, T.; Van-Berge, P.C.; Mars, P.: 405-420: Elsevier, Amstardam.

[24] Ono, T.; Kamisuki, H.; Hisashi, H.; Miyata, H. 1989. A comparison of oxidation activities andstructures of Mo oxides highly dispersed on group IV oxide supports. *Journal of Catalysis* 116: 303-307.

[25] Noguchi, T.; Mizuno, M. 1967. Phase Changes in Solids Measured in Solar Furnace, ZrO_2-TiO_2 System. *Solar Energy* 11: 56-61

[26] Wu, J.C.; Chung, C.S.; AY, C.L.; Wang, I. 1984. Nonoxidative dehydrogenation of ethylbenzene over TiO_2-ZrO_2 catalysts: II The effect of pretreatment on surface properties and catalytic activities. *Journal of Catalysis* 87: 98-107.

[27] Nyquist, R.A.; Putzig, C.L.; Leugers, M.A. eds. 1997. *Handbook of Infrared and Raman spectra of Inorganic Compounds and Organic Salts*, Academic Press, New York. pp. 295-350.

[28] Reddy, B.M.; Ganesh, I.; Reddy, E.P. 1997. Study of Dispersion and Thermal Stability of V_2O_5/TiO_2-SiO_2 Catalysts by XPS and Other Techniques. *Journal of Physical Chemistry B* 101: 1769-1774.

[29] Reddy, B.M.; Chowdhury, B. 1998.Dispersion and Thermal Stability of MoO_3 on TiO_2-ZrO_2 Mixed Oxide Support. *Journal of Catalysis* 179:413-419.

[30] Mao, D.; Lu, G.; Chen, Q. Influence of calcination temperature and preparation method of TiO_2-ZrO_2 on conversion of cyclohexanone oxime to Є-caprolactam over B_2O_3/TiO_2-ZrO_2 catalyst. *Applied Catalysis A: General* 263:83-89.

[31] Lonyl, F.; Valyon, J. 2001. On the interpretation of the NH_3-TPD patterns of H-ZSM-5 an H-mordenite. *Microporous Mesoporous Material* 47:293-301.

[32] Sawa, M.; Niwa, M.; Murakami, Y 1990. Relationship between acid amount and framework aluminum content in mordenite. *Zeolites* 10:532-538.

[33] Zhao, B.; Wang, H.; Ma, Y. Tang. 1996. Raman spectroscopy studies on the structure of MoO_3/ZrO_2 solid superacid. *Journal of Molecular Catalysis A: Chemical* 108:167-174.

[34] Yori, J.C.; Pieck, C.L.; Parera, J.M. 2000. Alkane isomerization on MoO_3/ZrO_2 catalysts. *Catalysis Letters* 64: 141-146.

[35] Rahman, A; Lemay, G.; Adnot, A.; Kaliaguine, S. 1988. Spectroscopic and catalytic study of P-modified ZSM-5. *Journal of Catalysis* 112: 453-463.

[36] Tanabe, K.; Sumiyoshi, T.; Shibata, K.; Kiyoura, T.; Kitagawa, J. 1974. A New Hypothesis Regarding the Surface Acidity of Binary Metal Oxides. *Bulletin of the Chemical Society of Japan* 47:1064-1066.

[37] Bosman, H.J.M.; Pijpers, A.P.; Jaspers A.W.M.A. 1996. An X-Ray Photoelectron Spectroscopy Study of the Acidity of SiO_2-ZrO_2 Mixed Oxides. *Journal of Catalysis* 161: 551-559.

[38] Kale, S.M.; Singh, A.P. 1999. A catalytic method for the selective chlorination of benzyl chloride to 4-chlorobenzyl chloride using zeolite catalysts. *Journal of Molecular Catalysis A: Chemical* 138: 263-272.