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Research Article

# $MoO_3/SiO_2$-$ZrO_2$ Catalyst: Effect of Calcination Temperature on Physico-chemical Properties and Activities in Nitration of Toluene

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## Abstract

The 12 wt % molybdena was deposited over 1:1 silica zirconia mixed oxide support and the resultant catalyst was calcined between the 500 to 700 $^oC$ ranges of temperature. The samples were characterized by XRD, FT-IR, BET, SEM, $NH_3$-TPD and pyridine adsorbed FT-IR techniques. Nitration of toluene was studied as a model reaction over the prepared catalysts and parameters like effect of reaction temperature, effect of various solvents, catalyst reusability are studied. It was found that conversion of toluene varies with the presence of Brönsted acid sites over the catalyst surface and para-nitrotoluene selectivity is associated with pore size of the catalyst. Over the same catalysts, nitration was extended for some other aromatics. Avoid of sulfuric acid in the present process is an interesting concern in view of green chemistry.


***Keywords***: $MoO_3/SiO_2$-$ZrO_2$; $SO_2$-$ZrO_2$; $NH_3$-TPD; Nitration; ortho-nitro toluene

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## 1. Introduction

Nitration of aromatic substrates is extensively studied reaction of great industrial importance as many nitro-aromatics are widely utilized and act as chemical feedstock for useful materials such as pharmaceuticals, dyes, perfumes, and plastics, etc. [1]. In particular, nitro-toluene is found to be useful for producing military explosive such as 2, 4, 6-nitrotoulene (TNT). Till today, industry largely relies upon early technology for synthesis of nitro-aromatic compound involving mixture nitric acids and sulfuric acids, which is commonly known as 'Mixed acid' process. This classical mixed acid nitration system has many disadvantages like corrosion of processing equipments, over nitration and aqueous washing stage which results in to large inorganic waste which is costly to treat and environmentally unfriendly. Beside this, though the *para*-nitro-toluene has high demand in the market, the conventional mixed acid process fails towards its selective formation and gives the typical product distribution of *ortho*-, *meta*- and *para*- in order of about 58:4:38 [2]. To overcome these drawbacks nitration of aromatics using solid acids are gaining high importance. This might be due to the fact that solid acids are associated with the advantages like high selectivity, non corrosiveness and their easy separation abilities.

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In this respect nitration of toluene was reported by many authors over different solid acid catalysts. McKee and Wilhelm [3] studied the nitration of benzene and toluene over silica gel as a solid acid. Also, solid acids like sulfonated polyorganosiloxanes [4,5], acidic resins [6], modified clays [7], zeolites [8–10], sulfated zirconia [11], supported sulfuric acids [12], supported sulfonic acid [13], Lanthanide (III) complexes of aromatic sulfonic acids [14] and $CuFe_{0.8}Al_{1.2}O_4$ [15] has been tried for the nitration of toluene.

Para–isomer of nitrotoluene has great industrial significance as compared to ortho- and meta- isomer. As a matter of fact, being important pharmaceutical intermediate, it is sold at three times the cost of ortho- isomer [16]. Greater selectivity of this highly desirable para- isomer was successfully demonstrated over acidic zeolite catalysts such as H-mordenite, H-beta, H-ZSM-5 and H-Y, among which Zeolite H-beta has shown most favorable results [17-21]. But more or less, there is always a possibility of formation of higher nitration products along with unwanted by-products generated from oxidation of the methyl group [4-21], which decreases the yield of desired isomers.

There are various ways by which activity of catalyst can be improved such as change in the active metal concentration, impregnation of the supports with different kinds of active metals or the application of various supports. Among that variation of support is one of the most promising approaches. Inline to this, significant results have been obtained with mixed oxide supported catalysts [22-25]. It is well known that chemical mixing of two oxides often results into the formation of mixed oxide with high surface area and increased thermal stability. Accordingly, $SiO_2$-$ZrO_2$ mixed oxides have gained increasing attention in recent years because of their interesting characteristics and many applications which includes alkali durable glasses [26] catalyst support [27, 28] and as an advanced ceramic material [29]. Moreover, it is found that when mixed oxide like $TiO_2$-$ZrO_2$ is promoted with molybdate, tungstate or sulfate, the acidity of the resultant catalysts increases considerably [30]. Therefore, appreciating the advantages with mixed oxide supports the goal of present investigation was set to prepare $MoO_3/SiO_2$-$ZrO_2$ catalyst and access its performance in nitration of toluene.

In this direction, 1:1 mole ratio of $SiO_2$-$ZrO_2$ support was prepared by homogeneous co-precipitation method and impregnated with 12 wt % $MoO_3$ using ammonium heptamolybdate as a precursor. Further, resultant catalyst powder was calcined at 500, 600 and 700 $^oC$ and surface study of these catalytic systems were done using XRD, FT-IR, BET surface area, SEM, $NH_3$-TPD and pyridine adsorbed FT-IR techniques. Finally, all of these catalytic systems were very firstly employed in nitration of toluene and corresponding results are discussed in this paper.

## 2. Materials and Methods

### 2.1. Catalyst preparation

The 1:1 mole ratio of $SiO_2$-$ZiO_2$ mixed oxide support was prepared by homogeneous co-precipitation method using ammonia as a precipitating agent. Appropriate amount of $Na_2SiO_3$ (Loba Chemi, AR grade) was initially dissolved in distilled water. To this aqueous solution the required quantity of $ZrOCl_{2.8}H_2O$ (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=8 and heated to 115 $^oC$ with vigorous stirring. Instantly a white precipitate formed in the solution. The precipitate was allowed to stand at room temperature for 24 hours to facilate 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 $^oC$ for 16 h and finally calcined at 500 $^oC$ for 6 h in an open air atmosphere.

Molybdena (12 wt %) was deposited on SiO2-$ZrO_2$ mixed oxide support by adopting incipient wetness method. To impregnate $MoO_3$, calculated amount of ammonium heptamolybdate was dissolved in doubly distilled water and few drops of dilute $NH_4OH$ were added to make the solution clear and to keep pH constant (pH=8). 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 is then dried at 110 $^oC$ for 12 h, part of the obtained catalyst powder is again calcined at 500 $^oC$, 600 $^oC$, and 700 $^oC$ for 5 h.

For the simplicity in discussion, catalyst with 12 wt%$MoO_3$ supported on $SiO_2$-$ZrO_2$ mixed oxide support, calcined at 500 $^oC$, 600 $^oC$, and 700 $^oC$ are coded as MSZ-5, MSZ-6, and MSZ-7 respectively and commonly referred as MSZ.

### 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$^o$ 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 Toluene

Liquid phase batch process nitration of toluene was carried independently over MSZ-5, MSZ-6 and MSZ-7 catalysts at atmospheric pressure. In the particular experiment, to a stirring mixture of 0.200 ml of 69 wt% nitric acid and 1 g of catalyst powder was added a solution of 0.240 ml of toluene in 4 ml of 1,2-dichloroethane. This stirring reaction mixture was heated at reflux and continuous water removal is done through Dean and Stark condenser. After specific intervals of time small portion of reaction mixture was taken off and diluted with aqueous $NaHCO_3$. The settled, yellow organic phase was collected and dried over $MgSO_4$, evaporated and analyzed offline by GC. The reaction products were confirmed by comparing their GC retention times with that of corresponding authentic samples.

## 3. Results and Discussion

### 3.1. Surface study

#### 3.1.1. XRD

The XRD patterns of 12 wt. % $MoO_3$ supported on silica zirconia mixed oxide calcined at different temperatures are shown in Figure 1. Sample MSZ-5 (catalyst calcined at 500 $^oC$) was amorphous in nature, showing only a broad hump overlapping with the features of pure $ZrO_2$. There is absence of any phase corresponds to $MoO_3$ indicates that molybdena is present in highly dispersed state in to the support matrix at this calcination temperature. It can also be ascertain that the nominal 12 wt % loading of $MoO_3$ did not cover the whole surface of $SiO_2$-$ZrO_2$ support and so is less than its theoretical monolayer capacity. When catalyst is calcined further at 600 $^oC$ temperature, along with tiny amount of tetragonal zirconia (JCPDS file no. 17-923), a definite $ZrSiO_4$ compound (JCPDS file no. 6-266) was noticed. $ZrSiO_4$ compound results from the interaction of $SiO_2$ and $ZrO_2$ parts of the support material. The intensity of lines due to $ZrSiO_4$ increases with the increase in calcination temperature from 600 $^oC$ to 700 $^oC$. On this occasion, crystallite size calculated from the reflection of $ZrSiO_4$ phase at 2θ of 26.97 (using Scherer's equation) for sample MSZ-7 reaches to 11 nm.

In literature, similar kind of phenomenon has been proposed for $TiO_2$-$ZrO_2$ support where $TiO_2$ and $ZrO_2$ get combined to give $ZrTiO_4$ compound and $MoO_3$ when impregnated over this support, molybdenum preferentially reacts with $ZrO_2$ portion of $ZrTiO_4$ compound to produce $ZrMo_2O_8$ compound and release out some TiO2 species [31]. But in the present study, we did not observe the formation of $ZrMo_2O_8$ compound even at the calcination temperature of 700 $^oC$ which implies that the reaction between $MoO_3$ and $ZrSiO_4$ compound was in dormant state. This happening can be justified by high thermal stability of resulted $ZrSiO_4$ phase or low reactivity of $MoO_3$ towards $ZrSiO_4$ species at the respective temperature. Moreover, separate phases ascribed to crystalline $MoO_3$ were also absent suggesting its high dispersion or the crystallites formed may be of

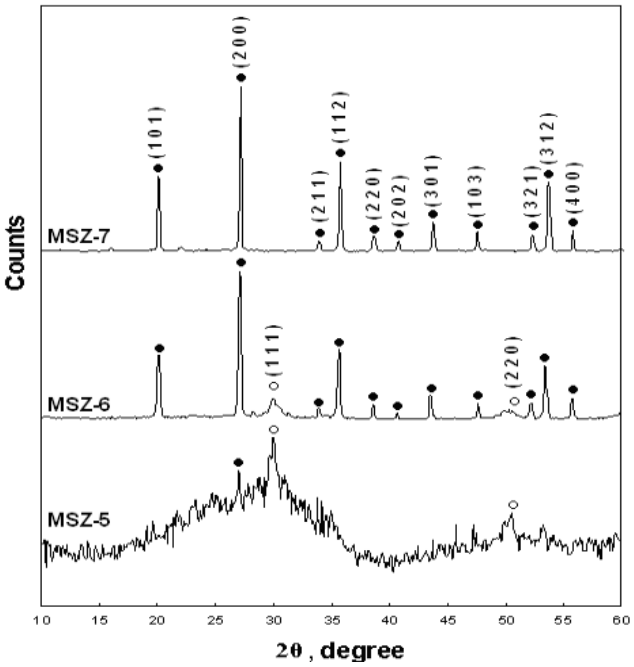



**Figure 1**: XRD pattern of calcined samples: (○) lines due to $ZrO_2$ phase; (●) lines corresponds to $ZrSiO_4$ phase

the size less than 4 nm, which is beyond the detection capacity of XRD technique.

From the XRD results it is assumed that the interaction of $SiO_2$ and $MoO_3$ with $ZrO_2$ hinders the transformation of $ZrO_2$ from its tetragonal to monoclinic phase that generally occurs beyond 400 $^oC$ in impurity free sample [32] and high thermal stability of a specific $ZrSiO_4$ compound restricts the formation of $ZrMo_2O_8$ compound.

### 3.1.2. FT-IR

FT-IR results of calcined samples are shown in Figure 2 for the mid-IR spectral range from 400 to 1500 $cm^{-1}$. For bulk $MoO_3$, the IR band at 1000 cm-1 is assigned to the M=O stretching mode [33]. $ZrSiO_4$ is made up of isolated $SiO_4$ groups characterized by four terminal Si–O bonds [34]. and its IR spectrum includes a band of modes at 885 $cm^{-1}$ and 989 $cm^{-1}$ generated by Si-O stretching mode and at 608 $cm^{-1}$ and 430 $cm^{-1}$ due to O-Si-O bending mode [35,36]. Whereas, $SiO_2$ can be identified from Si-O-Si stretch at 1097 $cm^{-1}$ [37] and pure $ZrO_2$ exhibits the IR band around 545 $cm^{-1}$ [38].

FT-IR spectra of the sample calcined at 500 $^oC$ (MSZ-5) do not show band corresponds to bulk $MoO_3$ phase which confirm its high dispersion in to $SiO_2$-$ZrO_2$ mixed oxide. The IR spectrum of the sample shows a broad shoulder peak centered at about 1072 $cm^{-1}$ attributed to Si-O-Si linear stretch in $SiO_2$ portion of the support that exists in amorphous state, on the other hand, $ZrO_2$ reflection was not clearly seen at this stage. When calcination temperature of the catalyst was increased from 500 to 600 $^oC$, considerable fall in the intensity of 1072 $cm^{-1}$ is noted and simultaneous upraise of new features around 895 $cm^{-1}$ and 619 $cm^{-1}$ were recorded. These new bands are associated with a terminal $Si\text{-}O_1$- bond which is a product of $SiO_2$ network disruption that occurs upon forming alloy with $ZrO_2$ [39,40]. The feature at 895 $cm^{-1}$ can be associated with a terminal oxygen atom covalently bonded to network of Si and making an ionic bond with $Zr^{4+}$ ion. These observations clearly indicate that $SiO_2$ species of the support gets consumed and produce a definite $ZrSiO_4$ compound as was confirmed by XRD technique previously. IR bands arise in low frequency region is a manifestation of bond breaking and the creation of terminal Si-O (isolated $SiO_4$) groups due to structural reordering of the solid in course of thermal treatment.

### 3.1.3. BET surface area measurement

The surface area, pore volume and pore size analysis of 12 wt% $MoO_3/SiO_2$-$ZrO_2$ catalyst calcined at different temperatures were carried out using $N_2$ as a probe molecule and the results are presented in Table 1. $SiO_2$-$ZrO_2$ mixed oxide support prepared by ammonia hydrolysis method in present investigation exhibited surface area of 178 $m^2/g$. Therefore, the calculated amount of molybdenum oxide (12 wt %) was impregnated over this support and subsequently calcined at 500 $^oC$. It was observed that, specific surface area of the support decreases considerably due to accumulation of the support by impregnated metal oxide. In this regard, sample MSZ-5 shows 72 $m^2/g$ of surface area and 0.1019 $cm^3/g$ of pore volume and calcination temperature when raised thereafter associates with rapid fall in surface area and pore volume. XRD measurement showed that high calcination temperature promotes crystallization in catalyst sample as a result of which $ZrSiO_4$ phases are produced in the respective samples. Therefore, amorphous species that exists in sample at low calcination temperature readily converts in to non porous crystalline phases having low surface areas. This phenomenon becomes more severe at high calcination temperature (700 $^oC$) and hence sample MSZ-7 exhibits surface area about 12 $m^2/g$ only.

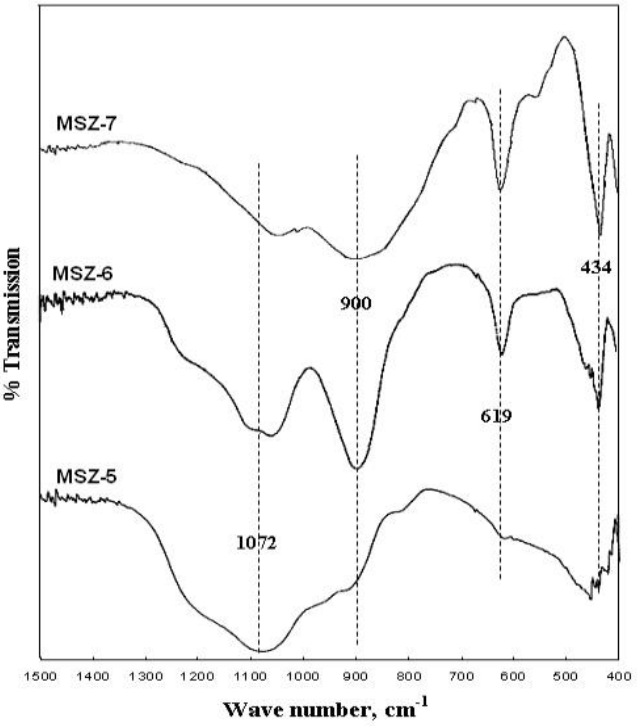



**Figure 2**: FT-IR spectra of MSZ series of catalyst samples

### 3.1.4. SEM

Scanning electron micrograms (SEM) of

calcined samples were recorded to know the particle size and morphology of the catalysts and displayed in Figure 3. From the photographs it can be clearly observed that progress of calcination temperature brings out the agglomeration of small particles, therefore average particle size of catalyst MSZ-5 was found shifted from 5-10 µm to > 70 µm for MSZ-7. Beside this, the surface of MSZ-7 catalyst appears to be sintered and volatilized indicating the effect of high calcination temperature (700 °C) on morphology of the catalyst. The agglomerate formed in MSZ-7 material looks dense, rough and faceted.

**Table 1**: Surface area and acidity measurement of the catalysts

| Catalyst | Surface area ($m^2/g$) ($cm^3/g$) | Average pore diameter (mmol/g) | Average pore volume | Amount of $NH_3$ desorbed (Å) |
|---|---|---|---|---|
| MSZ-5 | 72 | 55.86 | 0.1019 | 5.75 |
| MSZ-6 | 42 | 49.21 | 0.0519 | 1.97 |
| MSZ-7 | 12 | 14.96 | 0.0010 | 1.00 |

### 3.1.5. Ammonia desorption ($NH_3$-TPD)

$MoO_3$/ $SiO_2$-$ZrO_2$ catalysts calcined at various temperatures were subjected to temperature programmed desorption of ammonia ($NH_3$-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 °C) and low temperature (LT) region (T < 400 °C). Peaks in high temperature (HT) region are ascribed to desorption of ammonia from strong acid sites, while peaks in low temperature region are assigned to desorption of ammonia from weak acid sites [41,42]. $NH_3$-TPD profiles for the samples are shown in Figure 4 and an amount of ammonia desorbed is given in Table 1. Catalyst MSZ-5 (5.75 mmol/g) has highest acidity among all the samples and desorption profile of corresponding sample (MSZ-5) provides an indication that weak acid sites are present in excess as the maxima of ammonia desorption peak is centered at LT region. Hence weak acid sites are major contributor in total acidity of MSZ-5 sample. Generally, such weak acid sites are associated with surface hydroxyl groups of the support [43]. It is well established fact in literature that neutral, weakly acidic or basic hydroxyl groups are present over the surface of metal oxides that has been widely used as a support material [43, 44]. When molybdena is impregnated over these supports, Mo cation selectively interacts with hydroxyl groups of basic nature and suitable strength, leading to the formation of monolayer patches of $MoO_3$ on support surface [45, 46]. So it is obvious that all the surface hydroxyl groups cannot participate in Mo fixation process and remains unoccupied. These unoccupied hydroxyls groups of the support can be considered as the sources of weak acidity. With increase in calcination temperature form 500 °C to 700 °C, surface hydroxyl groups are removed in the form of water because of which acid amount of respective

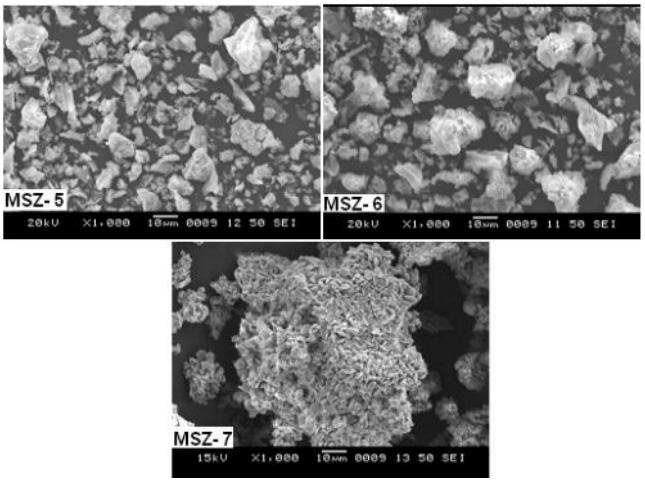



**Figure 3**: Scanning Electron Micrographs of MSZ series of catalysts

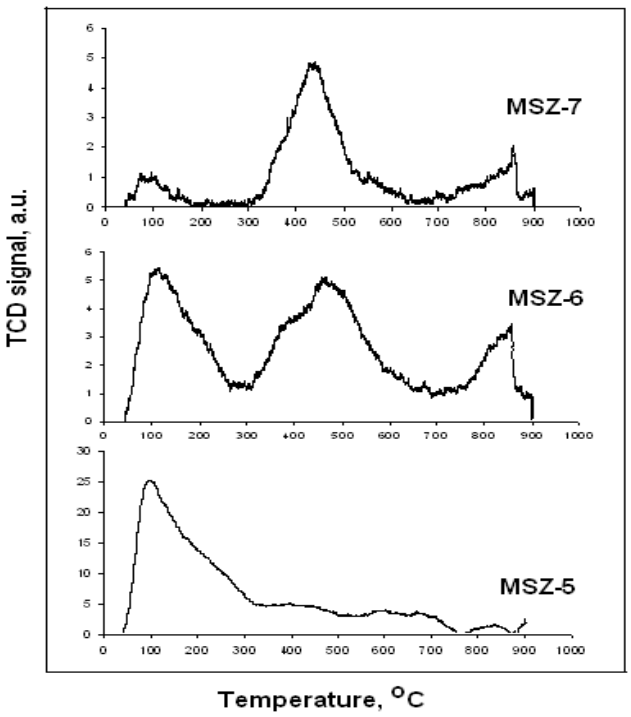



**Figure 4**: $NH_3$-TPD profiles for calcined catalyst

samples (MSZ-6, MSZ-7) decreases sharply. Beside this, it is well known that Mo-O-Zr species are formed between $ZrO_2$ and $MoO_3$ at low calcination temperature which are supposed to be the cause of super acidity of $MoO_3/ZrO_2$ catalyst as suggested by Zaho et al. [47]. They also proposed that at high calcination temperature Mo-O-Zr species readily converts in to bulk $ZrMo_2O_8$ and the acidity of the catalyst were found decreased likewise. Inline to this, we assumed that well dispersed $MoO_3$ into $ZrO_2$-$SiO_2$ mixed oxide support contains Mo-O-Zr species even at 700 °C and are responsible for acidity of the catalysts independent of very low surface area (MTZ-7= 12 $m^2/g$). From Figure 4, it can be observed that area under the peak in HT region (around 860 °C) of MSZ-7 is significantly lower as compared to that of in MSZ-6, suggesting the effect of calcination temperature on acid strength.

### 3.1.6. Pyridine adsorbed FT-IR

FT-IR spectra of pyridine adsorbed on catalyst surface were taken to determine the nature of acid sites present on its surface. Generally, pyridine adsorbed on Brönsted acid site produce characteristic IR bands at 1540 and 1638 $cm^{-1}$ due to vibrational modes of adsorbed pyridine and bands at 1450 and 1480 $cm^{-1}$ are assigned to pyridine coordinated with Lewis acid sites [48]. As could be seen in Figure 5, spectra of MSZ-5 sample shows the bands of varying intensities around 1545 and 1457 $cm^{-1}$ that confirms the presence of Brönsted as well as Lewis acid sites over the catalyst surface whereas sample MSZ-7 indicates the rapid fall in Brönsted acid sites from its surface.

When molybdenum is doped in to silica zirconia mixed oxide, the generation of Brönsted and Lewis acid sites can be interpreted with the help of model proposed by Vard and Ko [49]. We can assume large formation of Si-O-Zr-O-Zr-Si structures when $ZrO_2$ is mixed with $SiO_2$ [50]. When $MoO_3$ is deposited in to this mixed oxide support, it coordinates with immediately situated zirconia forming bidentate species while, the hydroxyl groups of silica (Si-OH) remains unoccupied as they are neutral. Thus, Brönsted acid sites results from the weakening such -OH group of neighboring silica by bidentately coordinated Mo species in order to satisfy the created coordinative unsaturation. Beside this, electronically deficient $Mo^{6+}$ and $Zr^{4+}$ act as Lewis acid centers. The general outline for this is presented in Scheme 1. At high calcination temperature surface of catalyst dehydroxylates excessively due to which demise of Brönsted acid sites is commonly expected.

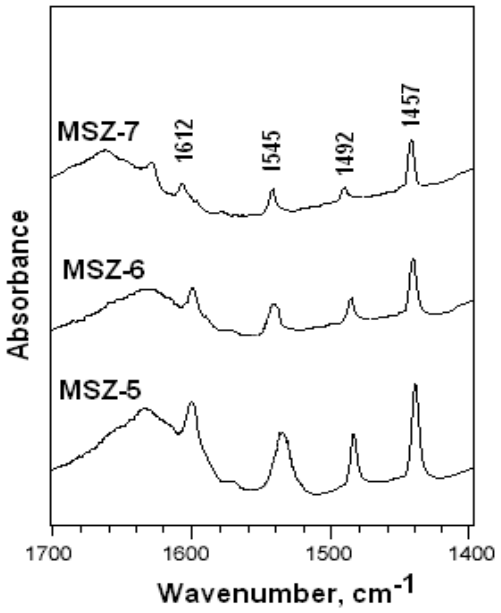
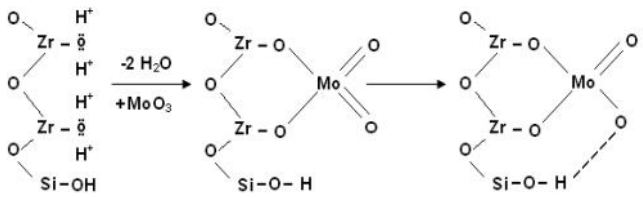



**Figure 5**: FT-IR spectra of pyridine adsorbed catalyst samples




**Scheme 1**: $MoO_3$ species proposed to exist over $SiO_2$-$ZrO_2$

### 3.2. Activity measurement

### 3.2.1. Nitration of toluene

A series of nitration reactions of toluene were carried out over $MoO_3/SiO_2$-$ZrO_2$ solid acid catalyst calcined at different temperatures and the results are listed in Table 2. As could be seen from the table, nitration of toluene is a somewhat self catalyzing reaction when nitric acid was used as nitrating reagent even if no catalyst existed. However, it seems that MSZ series of catalyst shows higher catalytic activity than the blank. When the reaction is carried out using MSZ-5 (catalyst calcined at 500 °C) sample, the conversion of toluene was highest (89 %) among all the members of series. The high conversion of toluene with MSZ-5 is attributed to the presence of large number of Brönsted acid sites over the catalyst surface which is responsible to produce number of nitronium ion from nitric acid that attacks the ring of toluene molecule at suitable position. At this stage (MSZ-5) the *para*-nitro-toluene selectivity is not much

**Table 2:** Liquid phase batch process nitration of toluene over MSZ series of catalysts

| Catalyst | Conversion of toluene % | Selectivity, % | | | | Total yield % | p/o ratio |
|---|---|---|---|---|---|---|---|
| | | ONT | MNT | PNT | Others | | |
| Blank | 6 | 53 | 5 | 42 | - | 6 | 0.79 |
| MSZ-5 | 89 | 55 | - | 46 | - | 90 | 0.83 |
| MSZ-6 | 83 | 43 | 2 | 51 | 4 | 78 | 1.19 |
| MSZ-7 | 42 | 38 | 1 | 60 | 1 | 42 | 1.58 |

**Operating conditions**: catalyst: 1 g; toluene/$HNO_3$: 1.0; $HNO_3$: 69%; solvent: 1,2-dichloroethane; temperature: reflux; time: ~60 minutes ONT: ortho-nitrotoulene; MNT: meta-nitrotoulene; PNT: para-nitrotoulene; others: oxidation products viz. benzaldehyde; benzoic acid; anthraquinone; 4-nitrobenzic acid; Total yield: ONT+PNT.

different from that of for blank reaction. The close values of *p*/*o* nitro-toluene ratio for uncatalyzed (blank) and MSZ-5 catalyzed nitration indicates that the reaction inside the larger pores of MSZ-5 catalyst takes place in the same fashion as that of in the bulk phase. Further, increase of catalyst calcination temperature (MSZ-6 and MSZ-7) show the decreasing trend for toluene conversion due to the loss of active acid sites and simultaneously promotes the yield of *para*- isomer because of modification in its pore structure. In this context, MSZ-7 shows 42 % of toluene conversion and 60 % *para*-isomer selectivity. It can be concluded therefore that the specific pore dimensions of MSZ-7 sample allow the toluene molecule to enter in such a way that *ortho*- and *meta*- sites are blocked and the nitration occurs selectively at *para*-position.

Nitration over MSZ-6 and MSZ-7 sample results into the formation of small amounts of byproducts due to presence of acid sites of higher strength as compared to MSZ-5 sample. These by products are generally associated with benzaldehyde, benzoic acid and other oxo-derivatives of toluene which are formed by side chain oxidation of toluene molecule by nitrous oxide (NO) species liberated due to the use of nitric acid of strength 69%. This observation in our case is similar to that of the conclusions made earlier [51, 52]. Other way, these by products might have been adsorbed on the catalyst surface that makes the catalyst surface non reactive and could be the cause of low conversion of toluene.

In all, it can be stated that the progress of calcination temperature induces the physico-chemical change in material which reduces the acid amount (Figure 4 - Y-axis) and pore size of catalyst (Table 1.) along with strength of acid sites (Figure 5) that intern have the negative impact on toluene conversion but favors formation of *para*-nitro-toluene.

### 3.2.2. Nitration of other aromatic substrates

Effect of calcination temperature of catalysts was also studied by extending the study to the nitration of some other aromatic substrates. Substrates like benzene phenol and o-xylene were subjected to the nitration over $MoO_3/SiO_2$-$ZrO_2$ catalyst under suitable reaction environment and the results are disclosed in Table 3. MSZ catalysts were found active towards the nitration of benzene. They show fairly good conversion leading almost full selectivity for nitrobenzene. The catalyst calcined at higher temperatures is associated with the formation of small amount of by products, mostly dinitrobenzene. Reaction proceeds very quickly even at room temperature suggesting the effect of catalyst.

In case of phenol nitration, highest conversion was noted with MSZ-5 (97%) with nearly equal *ortho*- to *para*- ratio of mononitophenol. Afterwards, gradual fall in phenol conversion is seen due to the acidity concern and value of which is recorded lowest in case of MSZ-7 (46%). But on the other hand, improvement in *ortho*- selectivity is observed that may be attributed to the rearrangement in pore structure of the catalyst in course of thermal treatment given. Thus in all it is observed that increase in calcination temperature directly affects the conversion and selectivity of the catalyst when tested in nitration of phenol. Importantly, the formation of by products can be minimized with the present method as the process is operated at room temperature.

As compared to the other, o-xylene is less favorable substrate for the nitration with MSZ catalysts. The low conversion of o-xylene is because of generation of large amount of side products that deactivates the catalysts for further reaction. Beside this, poorer selectivity is justified by weakly polar nature of alkyl group that restricts any

**Table 3:** Nitration of different aromatic substrates

| Aromatic substrate | Reaction conditions | Catalyst | Conversion (%) | Major products (Selectivity, %) |
|---|---|---|---|---|
| Benzene | a | MSZ-5 | 100 | NB (100) |
| | | MSZ-6 | 99 | NB (98) |
| | | MSZ-7 | 70 | NB (97) |
| Phenol | b | MSZ-5 | 97 | ONP (50), PNP (48) |
| | | MSZ-6 | 76 | ONP (55), PNP (40) |
| | | MSZ-7 | 46 | ONP (48), PNP (52) |
| O-xylene | c | MSZ-5 | 20 | 3-NOX (45), 4-NOX (50) |
| | | MSZ-6 | 17 | 3-NOX (30), 4-NOX (47) |
| | | MSZ-7 | 10 | 3-NOX (31), 4-NOX (32) |

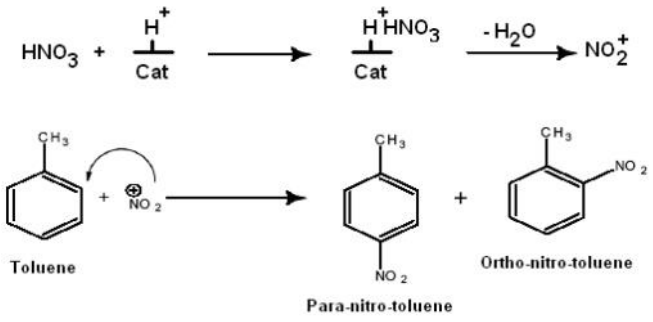
a: catalyst: 0.1 g; benzene: 0.20 moles; nitric acid: 1 equivalent; temperature:room temperature; time: ~15 minutes.
b: phenol/$HNO_3$=1; catalyst= 1 g; $HNO_3$= 30%; solvent=$CCl_4$; temperature: RT; reaction time: ~60 minutes
c: catalyst: 0.212 g (20% of o-xylene weight); o-xylene/$HNO_3$ mole ratio:1.0;$HNO_3$: 69 %; solvent: carbon tet rachloride; temperature: 75 $^oC$;, time: ~90 minutes
NB: nitrobenzene; ONP: ortho-nitrophenol; PNP: para-nitrophenol; 3-NOX: 3-nitro-o-xylene; 4-NOX: 4-nitro-o -xylene

interaction with the catalyst surface leading to the surface reaction mostly. But still MSZ-6 is best among the other members in view of conversion and selectivity aspect.

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

### 3.2.3. Mechanism for Nitration of toluene

It is well known that aromatic nitration is a classical electrophilic substitution using an attack by a nitronium ion ($NO^{2+}$), a nitrate species generally produced by the Brönsted acid sites of the catalyst (proton). Variety of evidences is available in literature regarding the generation of




**Scheme 2**: The plausible reaction mechanism of nitration of toluene over MSZ series of catalysts

$NO^{2+}$ species over Brönsted acid sites [52-54]. Therefore generation of nitronium ion shall be considered as the main objective of solid acid catalyst, when used instead of $H_2SO_4$ in combination with nitric acid. $HNO_3$ molecules are adsorbed on active sites of catalyst and dissociates into water, nitrate and nitronium ion.

Here we assumed that nitration of toluene involves the attack of nitronium ion at suitable position of ring of toluene molecule to produce mono-nitro-toluene isomers and releases one $H^+$ ion, which combines with the nitrate ions to form $HNO_3$ again. On the completion of this cycle, *ortho*- and *para*-nitrotoluene are formed as a main products whereas water generates as by product as shown in Scheme 2.

The *para*- selectivity trend provides an indication that in the solvent-filled pores the nitric acid is adsorbed on the pore wall surface and the nitrating agents are generated, and then adsorbed in the surface acid/solvent layer. Toluene molecules reach them from the organic phase to react with the nitrating agents and *para*- isomer is formed due the preferred orientation of the toluene molecule inside the narrow pores of catalyst.

Further, the effect of reaction temperature, effect of various solvent and reusability of the catalyst is studied for MSZ-7 system prior to its better regio-selectivity towards *para*- isomer of toluene and results are discussed in next sections.

### 3.2.4. Effect of Reaction temperature

The results of toluene nitration using nitric acid of strength 69% over MSZ-7 at different temperatures are given in Table 4. It can be observed form the Table that the conversion of toluene increases with the increase of the reaction temperature and attained the maximum value at 100 $^{o}$C (51.2 %). As the temperature of the reaction increases further the gradual fall in toluene conversion was noted and recorded lowest at 130 $^{o}$C (31.1 %). With increase of temperature from 80 $^{o}$C to 130 $^{o}$C, *p/o* nitrotoluene ratio linearly falls. This can be justified by the formation of excessive side products (oxidation products of toluene) at high temperatures that might have been blocked the pores of catalysts leads to non selective reaction.

### 3.2.5. Effect of various solvents

Performance of various solvent for the nitration of toluene over MSZ-7 catalyst has been studied to ensure the best entrainer and the results are displayed in Table 5. Results indicate that the chlorinated solvents are better as compared to the others. Among them 1,2 dichloroethane can be considered as a preferred medium for the corresponding reaction, as one can obtained the best value of toluene conversion and *para*-nitro-toluene selectivity with the use of same.

### 3.2.6. Reusability of the catalyst

Spent MSZ-7 catalyst is filtered off from the reaction mass, washed with acetone, dried in a hot air oven at 110 $^{o}$C for 2 h and reused in nitration of toluene. The above mentioned treatment was repeated for five such cycles and the observations are formatted in Table 6. As could be seen, the catalysts retain their activity for three cycles without sacrificing the toluene conversion and *para*-nitro toluene selectivity. Beyond this, the value for toluene conversion falls down to 27 % for the fifth run of catalyst due to the loss of active acid sites by pore blocking but *para*- selectivity

**Table 4:** Effect of temperature on catalyst activity

| Catalyst | Temperature $^{o}$C | Conversion of toluene % | Selectivity, % | | | | p/o ratio |
|---|---|---|---|---|---|---|---|
| | | | ONT | MNT | PNT | Others | |
| MSZ-7 | 80 | 42 | 38 | 1 | 60 | 1 | 1.58 |
| | 90 | 48 | 40 | 2 | 56 | 2 | 1.40 |
| | 100 | 51 | 41 | 2 | 55 | 2 | 1.34 |
| | 110 | 50 | 43 | 3 | 51 | 3 | 1.18 |
| | 120 | 43 | 40 | 2 | 54 | 4 | 1.35 |
| | 130 | 36 | 38 | 2 | 48 | 12 | 1.26 |

Operating conditions: catalyst: 1 g; toluene/$HNO_3$: 1.0; $HNO_3$: 69%; solvent: 1, 2-dichloroethane; time: ~60 minutes
ONT: ortho-nitrotoulene; MNT: meta-nitrotoulene; PNT: para-nitrotoulene; others: oxidation products viz. benzaldehyde; benzoic acid; anthraquinone; 4-nitrobenzic acid

**Table 5:** Effect of various solvents in nitration of toluene over MSZ-7 sample

| Catalyst | Solvent | Conversion of toluene % | Selectivity | | | | p/o ratio |
|---|---|---|---|---|---|---|---|
| | | | ONT | MNT | PNT | others | |
| MSZ-7 | $CCl_4$ | 41 | 40 | 3 | 55 | 2 | 1.37 |
| | Methanol | 31 | 32 | 8 | 42 | 18 | 1.31 |
| | Hexane | 36 | 31 | 5 | 50 | 14 | 1.61 |
| | 1, 2 DCE | 42 | 38 | 1 | 60 | 1 | 1.58 |

Operating conditions: catalyst: 1 g; toluene/$HNO_3$: 1.0; $HNO_3$: 69%; temperature: reflux; time: ~60 minutes
ONT: ortho-nitrotoulene; MNT: meta-nitrotoulene; PNT: para-nitrotoulene; others: oxidation products viz. benzaldehyde; benzoic acid; anthraquinone; 4-nitrobenzic acid

does not affected much which indicates the availability of few pores for the selective reaction.

### 3.2.7. Comparison with other solid acid catalysts

Catalysts tested in the present investigation and that of reported in literature for the nitration of toluene is compared and the data is presented in Table 7. From the table it is clear that MSZ series of catalyst is active in the nitration reaction as compared to the others. MSZ catalysts show the reasonable conversion for toluene and high *para*-nitro-toluene selectivity.

## 4. Conclusions

The conclusions that can be drawn from this study are summarized below.

1. All members of the MSZ series of catalyst are found active in nitration of toluene and various other aromatic substrates.
2. Highest catalytic activity for nitration of toluene with 69 % nitric acid was achieved with MSZ-5 sample (89 % toluene conversion) whereas MSZ-7 showed the highest selectivity (60 %) towards *para*-nitro-toluene.
3. The decrease of toluene conversion with increase of calcination temperature is related to the demise of Brönsted acid sites from the catalyst surface.
4. The pore structure of catalyst calcined at high temperature is suitable for the greater yields of *para*- isomer of nitro toluene.
5. Activities of the catalysts are more related to

**Table 6:** Influence of catalyst recycles on toluene conversion and *para*-selectivity

| Catalyst | Run | Conversion of toluene % | Selectivity | | | | p/o ratio |
|---|---|---|---|---|---|---|---|
| | | | ONT | MNT | PNT | others | |
| MSZ-7 | 1 | 42 | 38 | 1 | 59 | 2 | 1.55 |
| | 2 | 42 | 40 | 3 | 57 | - | 1.42 |
| | 3 | 40 | 34 | 5 | 52 | 6 | 1.52 |
| | 4 | 31 | 35 | 5 | 51 | 9 | 1.45 |
| | 5 | 27 | 31 | 8 | 49 | 12 | 1.58 |

Operating conditions: catalyst: 1 g; toluene/$HNO_3$: 1.0; $HNO_3$: 69%; solvent: 1, 2-dichloroethane; temperature: reflux; time: ~60 minutes ONT: ortho-nitrotoulene; MNT: meta-nitrotoulene; PNT: para-nitrotoulene; others: oxidation products viz. benzaldehyde; benzoic acid; anthraquinone; 4-nitrobenzic acid

**Table 7:** Comparison of activity and selectivity with different solid acids

| Catalyst | Temperature | Nitric acid strength | Conversion of toluene % | Selectivity | | | | p/o ratio | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| | | | | ONT | MNT | PNT | others | | |
| $Yb(Tos)_3$ | Reflux | 67 | 77 | 52 | 6 | 42 | - | 0.80 | [14] |
| $Yb(NSA)_3$ | Reflux | 67 | 98 | 52 | 6 | 42 | - | 0.80 | [14] |
| $Sc(OTf)_3$ | 60 | 70 | 79 | 54 | 4 | 43 | - | 0.79 | [55] |
| $Ln(OTf)_3$ | 60 | 70 | 24 | 56 | 3 | 41 | - | 0.73 | [55] |
| MSZ-5 | Reflux | 69 | 89 | 55 | - | 46 | - | 0.83 | This Work |
| MSZ-6 | Reflux | 69 | 83 | 43 | 2 | 51 | 4 | 1.19 | This Work |
| MSZ-7 | Reflux | 69 | 42 | 38 | 1 | 60 | 1 | 1.58 | This Work |

Operating conditions: catalyst: 1 g; toluene/$HNO_3$: 1.0; $HNO_3$: solvent: 1, 2-dichloroethane Time: ~60min; ONT: ortho-nitrotoulene; MNT: meta-nitrotoulene; PNT: para-nitrotoulene; others: oxidation products viz. benzaldehyde; benzoic acid; anthraquinone; 4-nitrobenzic acid

nature of acid sites rather than the surface area.

6. The catalyst is associated with the distinct advantages like simple filtration, non corrosive nature and better reusability. Zero emission of acidic effluents makes the process environmentally friendly.

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