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Characterization of mixed oxide supported MoO_3 catalysts and their activity measurement for nitration of benzene

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TiO_2-ZrO_2 mixed oxide support was impregnated with 12 wt% MoO_3 taking ammonium heptamolybdate as a source of MoO_3. Resultant catalyst powder was calcined at different temperatures. Further these catalysts were investigated by XRD, FT-IR, BET, SEM, and NH_3-TPD methods. XRD studies reveled high dispersion of MoO_3 in TiO_2-ZrO_2 support. All these catalytic systems were when employed in nitration of benzene showed no significant effect of calcination temperature on either benzene conversion or nitrobenzene selectivity. Comparatively they showed beneficial results over other catalysts. Study suggests environment friendly method for nitration reaction using solid acids instead of corrosive and hazardous sulfuric acid.

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1. Introduction

Mononitrobenzene is widely used in the manufacture of important chemical intermediate for drugs, pesticides, explosives, rubber chemicals and itself used in shoe and metal polishes [1, 2, and 3]. Earlier, sulfuric acid and nitric acid mixture, commonly known as ‘Mixed acid’, was used as a nitrating agent for carrying out the nitration reactions. But, for sulfuric acid, risk involved in handling, corrosiveness, and problem associated with spent acid disposal were the major drawbacks.

This gave birth to researches in solid acid catalysts, which substituted sulfuric acid in nitration reactions. In this context, nitration of benzene has been tried by Suzuki et al. but, process suffered with low yield of nitrobenzene [4]. Kuznetsova et al. studied the nitration of benzene over H-ZSM-5 at 140 °C-170 °C, here the process encountered with rapid deactivation of the catalyst [5]. Moreover variety of mixed oxides comprises of TiO_2-ZnO_2, TiO_2-WO_3, ZrO_2-WO_3, TiO_2-MoO_3 has also been tested for nitration reaction of benzene but, they were also required temperature around 150 °C–170 °C, to reach up to maximum conversion of benzene [6].

Among all such difficulties and limitations with these solid acids, a need of higher temperature is unsafe because, flash point of nitrobenzene is nearly half (88 °C) that of processing temperature. Also, it reacts explosively, when heated with conc. alkalis, nitric acid, sulfuric acid, aluminum chloride, phenol, aniline or oxidants [3].

In respect of this, a fine breakthrough is found, when MoO_3 supported on binary oxide was employed as a catalyst in the nitration of benzene which showed high activity at room temperature.

Mixed oxide supported MoO_3 catalysts were widely tested trans-esterification of di-methyl oxalate with phenol [7] and for hydro processing applications [8]. In present investigation, 1:1 mole ratio of TiO_2-ZrO_2 mixed oxide support was prepared and impregnated with 12 wt% MoO_3, calcined at 500 °C, 600 °C and 700 °C, the prepared samples were then investigated by XRD, SEM, FT-IR, BET, and NH_3-TPD techniques to know surface properties. Finally all the catalytic systems were employed in nitration of benzene and results are reveled in this paper.

2. Experimental

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 $ZrOCl_2.8H_2O$ (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 °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 °C for 16 h and finally calcinied at 500 °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_4OH 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 °C for 12 h; part of the obtained catalyst powder is again calcined at 500 °C, 600 °C, and 700 °C.

For the simplicity in discussion, catalyst with 12 wt% MoO_3 supported on TiO_2-ZrO_2 mixed oxide support, calcined at 500 °C, 600 °C, and 700 °C are coded as MTZ-5, MTZ-6, and MTZ-7 respectively. Generally referred as MTZ

2.2. Catalyst characterization

XRD analysis was carried out with Phillips Holland, XRD system, PW1710 using Cu-kα (1.5405 Å) radiation, the diffractograms were recorded in 10°- 60° range of 2θ, The XRD phases present in the samples were identified with the help JCPDS card files. Fourier Transform Infrared (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 a Micromeritics Autochem 2920 instrument.

Scanning Electron Micrograms (SEM) were obtained using Instrument, JEOL JSM-6380. BET surface area was estimated by, Quantachrome Autosorb Automated Gas Sorption System, using N_2 as a probe molecule, taking, 16.2 $Å^2$ as area of cross-section. Gas chromatogarmas were recorded on Perkin-Elmer Autosystem XL, with PE-1 column.

2.3. Activity measurement

Batch process nitration of benzene was carried out in liquid phase at atmospheric pressure, over 12 wt% MoO_3 supported on TiO_2-ZrO_2 catalyst calcined at 500 °C, 600 °C and 700 °C. In the particular experiment, a mixture containing 1 equivalent of HNO_3 (69 wt %) and 1 g of catalyst pre-dried at 110 °C was stirred for 10 minutes at room temperature. In this stirring mixture, 15.62 g (0.20 mole) of benzene was added drop wise and stirred continuously. Reaction performance was continuously monitored by TLC, after the completion of reaction catalyst was filtered off and products were analyzed offline by gas chromatography and identified by their GC-retention times [9].

3. Results and discussion

3.1. Catalyst surface study

An amount of MoO_3 required to cover the support surface as single layer can be estimated from literature [10]. But Kim et al. [11], reported the actual value of MoO_3 loading on TiO_2 for monolayer coverage is 70 % that of theoretical value. Therefore, 1:1 mole ratio of TiO_2-ZrO_2 mixed oxide support prepared in the present investigation having surface area, 128 m^2/g, was impregnated with 12 wt % MoO_3. Further, catalyst powder obtained was calcined at 500 °C, 600 °C, and 700 °C and subjected to X-ray diffraction analysis. XRD patterns of these calcined samples are displayed in Fig. 1. For all the samples, no peak due to MoO_3 was noticed. This indicates high dispersion of MoO_3 in TiO_2-ZrO_2 support. TiO_2 and ZrO_2 interact to form $ZrTiO_4$ compound, progressively, MoO_3 reacts with ZrO_2 portion of this compound and produce $ZrMo_2O_8$ species along with TiO_2 in rutile form. Formation of $ZrMo_2O_8$ compound can be attributed to resemblance in sizes of Mo^{6+} and ZrO_2. Such observations are made by many authors in literature [12, 13]. In our case also, lines corresponding to $ZrTiO_4$ and $ZrMo_2O_8$ of varying intensities depending upon calcination temperature can be seen for sample MTZ-5 and MTZ-6. Diffraction pattern for MTZ-7 (Fig.1 (c)) shows, intense peaks at 2θ = 27.39, 54.2, and 31.56 due to rutile phase of TiO_2. At this temperature (700 °C), intensities of the peaks corresponds to $ZrTiO_4$ and $ZrMo_2O_8$ were found decreased suggesting the effect of calcination temperature. Amount of rutile phases of TiO_2 formed depends on preparation methods, amount of loading of MoO_3 and calcination temperature [14]. General scheme for phase formation in MoO_3 supported on TiO_2-ZrO_2 catalytic system is shown in Eq. (1) and Eq. (2).

$$TiO_2 + ZrO_2 \xrightarrow{\qquad\qquad} ZrTiO_4 \quad (1)$$

$$ZrTiO_4 + 2\,MoO_3 \xrightarrow{\qquad\qquad} ZrMo_2O_8 + TiO_2\ (\text{rutile}) \quad (2)$$

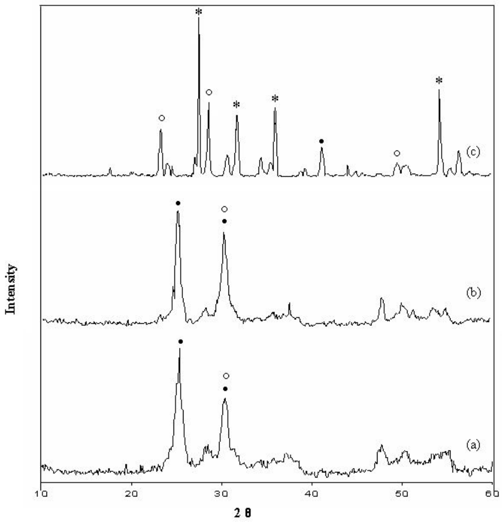


Fig. 1. XRD pattern of calcined samples: (a) MTZ-5 (b) MTZ-6 (c) MTZ-7, (•) lines due to $ZrTiO_4$; (○) lines due to $ZrMo_2O_8$; (*) lines due to TiO_2 rutile phase.

FT-IR spectroscopy is an important tool to study the structural properties through modes of vibration offered by catalyst surface species. Formation of $ZrMo_2O_8$ compound was reported by Frausen et al. when MoO_3 was incorporated in to ZrO_2 [15], which showed characteristic IR bands at 980, 920, 800 cm^{-1}. Where as, crystalline MoO_3 showed the IR band at 1000 cm^{-1}. FT-IR spectra of all samples are shown in Fig. 2. From the figure it is notable that, there is absence of band at 1000 cm^{-1} in all of the samples, indicating high dispersion of MoO_3 in to TiO_2-ZrO_2 matrix. For sample MTZ-5, the bands at 920 cm^{-1} and 980 cm^{-1} are ascribed to formation of $ZrMo_2O_8$ and $ZrTiO_4$ compounds respectively. For sample MTZ-6, we can see both of these bands with higher intensity, suggesting the effect of calcination temperature. FT-IR spectra of sample MTZ-7 show some new bands along with the bands for $ZrMo_2O_8$ and $ZrTiO_4$. New IR band at 740 cm^{-1} for sample MTZ-7 corresponds to rutile phase of TiO_2 [13]. Liberation of TiO_2 simultaneously reduces the intensities of band due to $ZrTiO_4$. Decreased intensity of this band can be justified by formation of $ZrMo_2O_8$ at the expense of $ZrTiO_4$. Domination of the catalyst surface by TiO_2 species could be the cause for reduced intensity of IR band ascribed to $ZrMo_2O_8$. All these observations are in line with XRD measurements.

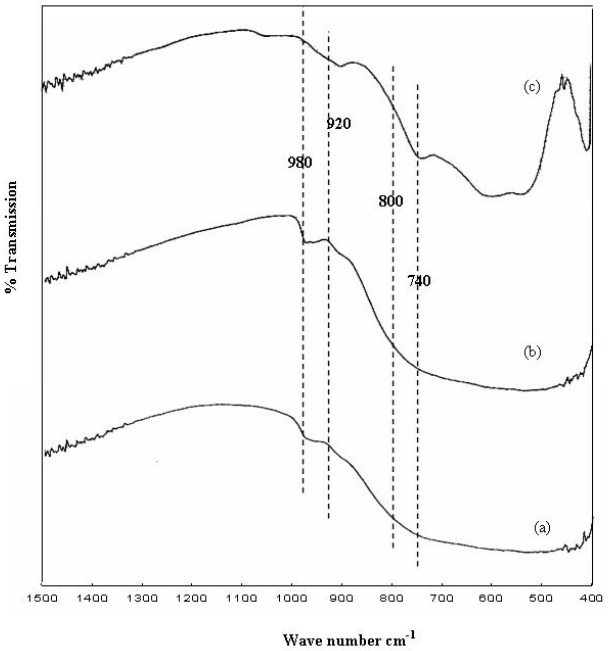


Fig. 2. FT-IR spectra of catalyst samples: (a) MTZ-5 (b) MTZ-6 (c) MTZ-7

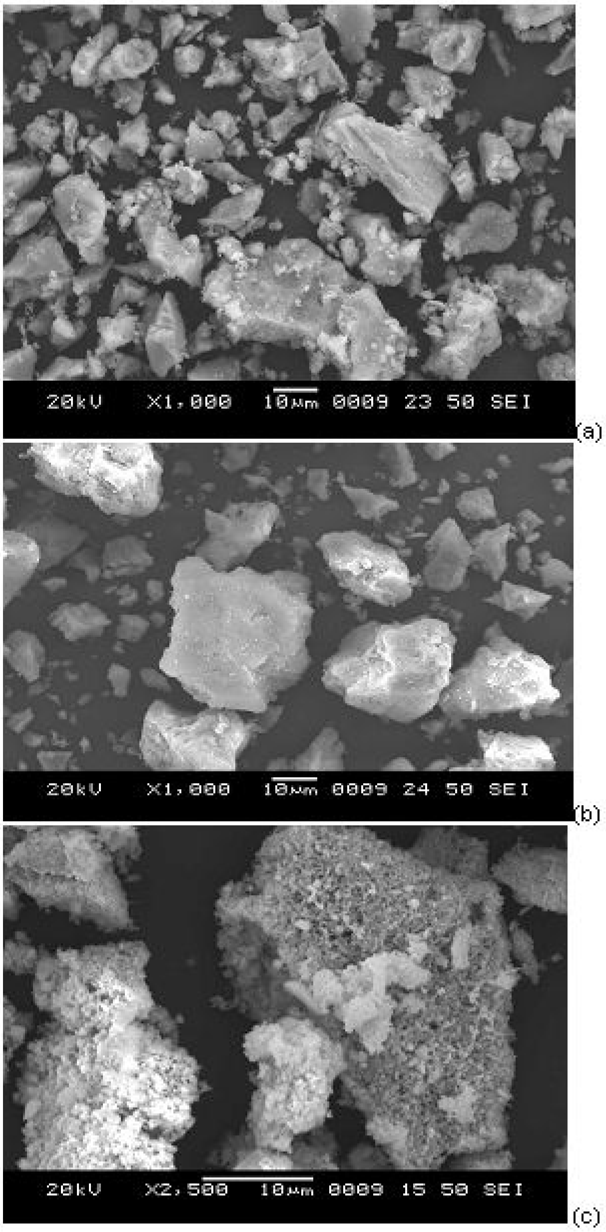


Fig. 3. Scanning Electron Micrographs of sample: (a) MTZ-5 (b) MTZ-6 (c) MTZ-7

Scanning Electron Micrographs were recorded to demonstrate the morphology of all the catalytic systems. As shown in Fig. 3, with the progress of calcination temperature from 500 °C (MTZ-5) to 600 °C (MTZ-6), crystallite size was found increased. This is mainly due to agglomeration of small crystallite at higher calcinations temperature. SEM of MTZ-7 sample showed modified morphology, suggesting the sintering of catalyst at higher calcination temperature. At this temperature, formations of some new species are also indicative.

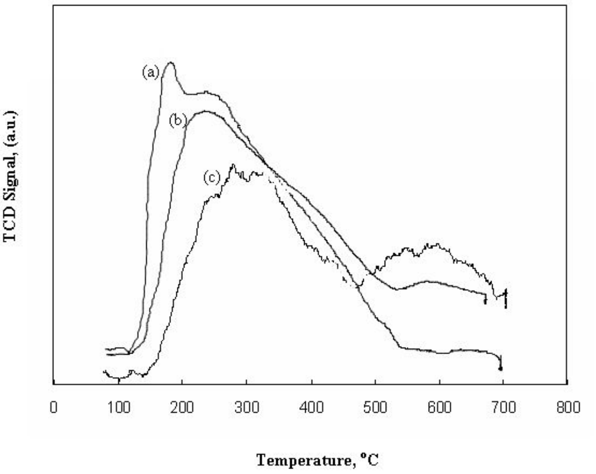


Fig. 4. NH_3-TPD profiles for samples: (a) MTZ-5 (b) MTZ-6 (c) MTZ-7

BET surface areas of catalyst samples are evaluated using N_2 as an adsorbate molecule having cross sectional area of 16.2Å^2 and results are presented in Table 1. (TiO_2-ZrO_2 = 128 m^2/g, not shown in table) MTZ-5 exhibit, 82 m^2/g of surface area which reduces to 18 m^2/g for MTZ-7. High surface area is attributed to amorphous or poorly crystalline nature of the catalyst. The down trend in surface area values for MTZ system with the progress of calcination temperature is related to, pore blockage of the TiO_2-ZrO_2 oxide support by impregnated MoO_3. With increase in calcination temperature, small crystallites of non porous $ZrMo_2O_8$ and other species are formed and combined to give bigger crystallite which showed reduced surface area. Sintering is general phenomenon for catalysts at higher calcination temperature.

Table 1. Surface area and acidity measurement of the catalysts.

Catalyst	Surface area m^2/gm	Amount of NH_3 desorbed mmol/gm
MTZ-5	82	0.509
MTZ-6	31	0.180
MTZ-7	18	0.20

In respect of acidity measurement, catalysts were subjected to temperature programmed desorption (TPD) of ammonia. 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 Brönsted and Lewis acid sites, while peaks in low temperature region are assigned to desorption of ammonia from weak acid sites [16, 17]. NH_3-TPD profiles for the samples are shown in Fig. 4. An amount of ammonia desorbed is given in Table 1. Total amount of ammonia desorbed in case of MTZ-5 (0.509 mmol/gm) is highest among all the catalytic systems, indicating higher acidity. Weak acid sites are major contributor in total acidity, as peak for sample MTZ-5 lays in LT region. The greater acidity is expected due to plenty available amorphous Mo-O-Zr species [18] and hydroxyl group present on TiO_2-ZrO_2 support. Increased calcination temperature (sample MTZ-6) reduces the acid amount due to transformation of Mo-O-Zr species in to $ZrMo_2O_8$ crystallite which exhibit lower acidity. This observation is in accordance with Zhao et al. [19].MTZ-7 shows, negligible increase in acid amount as compare to MTZ-6. Extended shoulder of NH_3-TPD curve in to HT region for sample MTZ-7 can be well justified by strong acidity imparted by TiO_2 rutile phase itself.

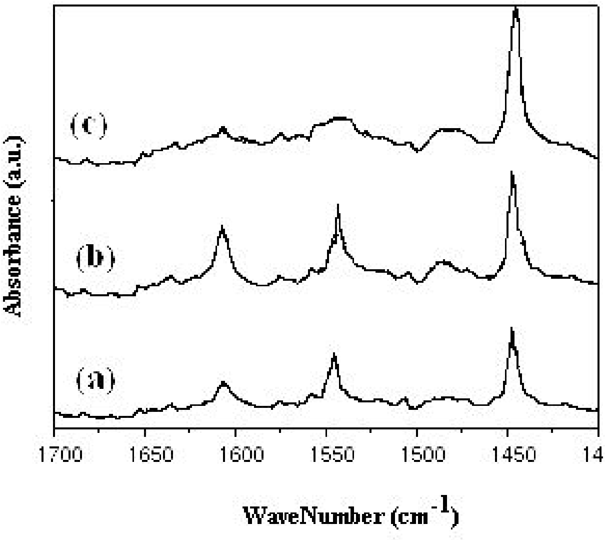
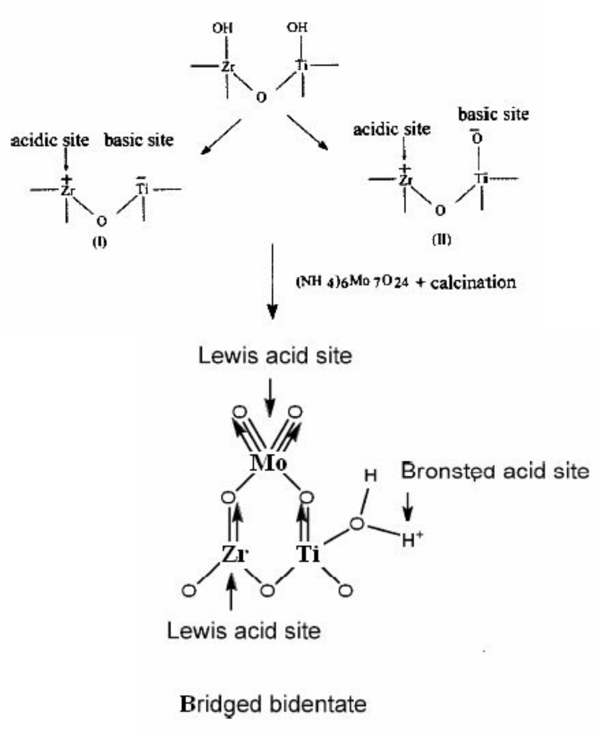


Fig. 5. FT-IR spectra of pyridine adsorbed catalyst samples: (a) MTZ-5 (b) MTZ-6 (c) MTZ-7

For determination of nature of acidity, the catalysts were evacuated (1 Pa) at 420 °C for 1.5 h, then exposed to 30 °C during 2 h. Following this, catalysts were exposed to 30 Torr of pyridine for 30 min, finally evacuated for additional 1 h at 200 °C, and analyzed by FT-IR spectroscopy. Generally the IR bands at 1450 cm^{-1} and 1490 cm^{-1} are assigned to pyridine adsorbed on Lewis acid sites and that of 1545 cm^{-1} and 1638 cm^{-1} are associated with pyridine adsorbed on Brönsted acid sites [20]. Results of FT-IR analyses of pyridine adsorbed catalysts are presented in Fig. 5. Samples calcined at 500 °C and 600 °C exhibit bands at 1450 cm^{-1} and 1540 cm^{-1} indicates the presence of Brönsted as well as Lewis acid sites whereas sample MTZ-7 shows strong band for Lewis acidity. As, Zr is more electronegative than Ti (Pauling value Zr-1.4 and Ti-1.5) Lewis acidity is expected in TiO_2-ZrO_2 matrix due to created charge imbalance. When MoO_3 was incorporated in to this matrix, Lewis acidity of the support was found decreased, as MoO_3 saturate the positive charge on Zr cation. With the progress of calcination temperature hydroxyl groups of titania rich domain of the support are attached to Mo^{+6} centres to satisfy the co-ordinative unsaturation [21]. Due to this, newly formed Mo^{+6}-OH cluster, act as a center for Brönsted acidity. Therefore, Mo^{+6}-OH species dominantly impart Brönsted acidity till the calcination temperature of 600 °C (MTZ-6). Further increase in calcination temperature (700 °C) brings out structural changes for catalyst due to complete dehydroxylation of the surface which include release of TiO_2 rutile phase, possess Lewis acidity, as observed from band at 1450 cm^{-1}. Scheme 1 represents acid sites generation in MTZ system.



Scheme 1

3.2. Nitration of benzene

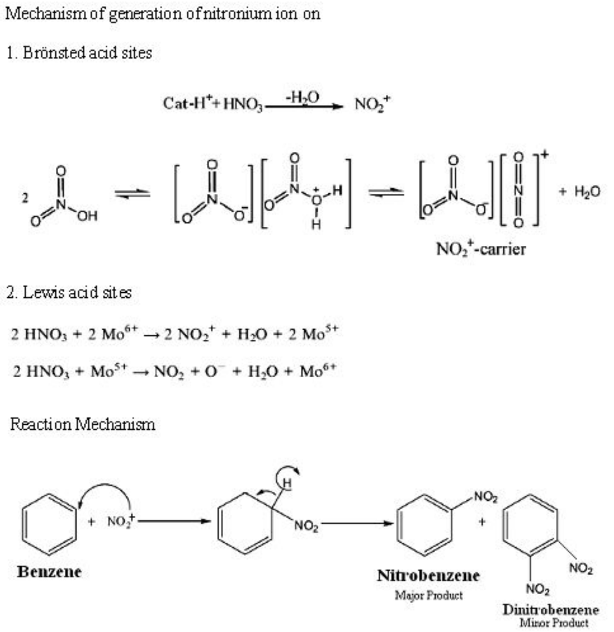
Results displayed in Table 2 revels, nitrobenzene as the major product for nitration of benzene over MoO_3 supported on TiO_2-ZrO_2 mixed oxide catalyst calcined at various temperature. 100% conversion of benzene over MTZ-7 catalyst was observed. For all the catalyst, reported conversion of benzene was achieved in less than 15 min. Presence of Lewis acid sites on MTZ-7 has stronger affinity with HNO_3 produces greater number of nitronium ions. Nitronium ion thus formed reacts with benzene to give nitrobenzene. So, strength rather than number of acid sites might be the reason for higher conversion of benzene in MTZ-7 system. Comparatively, MTZ-5 showed a little less conversion of benzene indicating effect of acid strength. Conversions of benzene were not significantly affected by acid amount of the catalyst, proves, strong as well as weak acid sites present on catalyst surface are capable of converting benzene in to the product. Nitrobenzene selectivity was highest in case of MTZ-5 and lower down to some extent for MTZ-6 and MTZ-7, suggesting, weak acid sites, produces less side products. No considerable impact of surface area on either benzene conversion or nitrobenzene selectivity was observed. Hence, activity of the catalyst can be corelated with acidity rather than catalyst surface area.

Table 2. Liquid phase batch process nitration of benzene over MTZ series of catalysts.

Catalyst	Calcination Temperature °C	Benzene Conversion %	Nitrobenzene Seletivity %
MTZ-5	500	99.99	99.81
MTZ-6	600	99.96	99.62
MTZ-7	700	100	99.62

Operating conditions: catalyst: 1gm; benzene: 0.20 moles; nitric acid: 1 equivalent; temperature: room temperature; pressure: 1 atm.; time: ~15 minutes.

Generation of nitronium ion shall be considered as the main objective of catalyst, when it is used in combination with nitric acid. HNO_3 molecules are adsorbed on active sites of catalyst and dissociates into water, nitrate and nitronium ion. This nitronium ion attacks benzene ring to produce nitro-benzene and releases out one H^+ ion, which combines with the nitrate ions to form HNO_3 again. Finally, the reaction product is nitrobenzene and water is generated as a byproduct. Such type of mechanism was proposed by S.B. Umbarkar et al., during the evaluation of the performance of MoO_3/SiO_2 catalyst for nitration of benzene [22]. For MoO_3 supported on TiO_2-ZrO_2 mixed oxide catalyst, possessing, Brönsted and Lewis acidity, similar mechanism is expected, as presented in Scheme 2.



Scheme 2

3.3. Effect of calcination temperature

No significant effect of calcination temperature on benzene conversion and nitrobenzene selectivity was found. Generally, increased calcination temperature increases crystalline nature of the catalyst and reduces the surface area and acidic species. Thus catalyst calcined at higher temperature have less number of total active sites available for reaction, but all MTZ catalytic systems calcinied at different temperature showed good enough benzene conversion and nitrobenzene selectivity, suggesting all the crystalline phases formed are active in nitration reaction. Nitrobenzene selectivity was slightly decreased with the progress of catalyst calcination temperature, recommends that, weak acid sites produce no side products whereas strong acid sites generate side product, mostly dinitrobenzene.

3.4. Comparison

Comparison of various catalysts employed in nitration of benzene, based on essential parameters such as, conversion of benzene, temperature of the reaction and nitrobenzene selectivity has taken in to account, independent of reaction phases. Corresponding results are displayed in, Table 3. From the table, it is clear that, $CuFe_{0.8}Al_{1.2}O_4$ was unable to initiate the reaction at room temperature. At 70 ^{o}C, the same catalyst gives only 55% benzene conversion .Further, reaction was not continued at temperature greater than 80 ^{o}C because of safety reasons, as stated [10]. It is to be noted from the table, vapor phase reaction needs, temperature around 150 ^{o}C, which is risky in the production of nitrobenzene as it has flash point about 88 ^{o}C. Catalyst employed in vapor phase reaction also suffers with low conversion of benzene. Catalysts other than MTZ series was a little advantageous for nitrobenzene selectivity only but, not at the sacrifice of benzene conversion and most importantly reaction temperature. Moreover, time required to achieve complete conversion of benzene on this catalytic systems was less than 15 minutes. Among all of the catalytic system listed, MTZ-5 was found best.

Table 3. Comparison of various catalysts for nitration of benzene.

Serial. no.	Catalyst	Phase Of Reaction	Temperature ^{o}C	Conversion of Benzene %	Nitrobenzene Seletivity %	Ref.
1	20 mol% MoO_3/SiO_2	Vapor	150	61.7	100	22
2	$CuFe_{0.8}Al_{1.2}O_4$	Liquid	70	55	100	10
3	$CuFe_{0.8}Al_{1.2}O_4$	Liquid	RT	----------- No reaction--------		10
4	MTZ-5	Liquid	RT	99.99	99.81^{a}	This work
5	MTZ-6	Liquid	RT	99.96	99.62^{a}	This work
6	MTZ-7	Liquid	RT	100	99.62^{a}	This work

Reaction conditions varies for sr.no.1-3, fixed for Sr. no 4-6;
RT: room temperature; a: rest of the product is dinitrobenzene
Ref: reference number.

4. Conclusion

Batch process, liquid phase nitration of benzene using dilute nitric acid over 12 wt% MoO_3 supported on TiO_2-ZrO_2 mixed oxide calcinied at various temperatures showed nearly 100% conversion of benzene in just 15 minutes with maximum 99.81% selectivity for mono nitrobenzene importantly, at room temperature, indicating acceptability of the process. Since the sulfuric acid is not used in process, corrosion of the processing equipment can be avoided successfully. Along with the advantage of easy separation of catalysts, process is proposed as environmental friendly. Further studies are under active progress to access the activity of the same catalysts in the nitration of some other aromatics.

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