Regioselective nitration of *o*-xylene to 4-nitro-*o*-xylene using nitric acid over solid acid catalysts

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Abstract

The regioselective nitration of *o*-xylene to 4-nitro-*o*-xylene (4-NOX) has been studied in the liquid and vapor phase over zeolites H-beta, H-ZSM-5 and silica supported molybdenum oxide (MoO$_3$/SiO$_2$) catalysts. Zeolite H-beta showed the maximum conversion of 28% and 63% selectivity for 4-NOX in liquid phase nitration at 70 °C with 70% HNO$_3$. The conversion increased to 65% when the reaction was carried out in vapor phase at 150 °C using dilute 30% HNO$_3$. The formation of α-methylphenyl nitromethane by alkyl nitration in liquid phase was decreased in vapor phase reaction. The formation of oxidation products was also decreased in vapor phase reaction with minor amounts of dinitro and ipso-products. The influence of experimental parameters such as temperature, nitric acid concentration and WHSV on conversion and selectivity has been investigated. The use of dilute nitric acid and the selective formation of 4-NOX using dilute HNO$_3$ makes this process environmental friendly with a potential for commercialization.
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Abbreviations: NOX, nitro-*o*-xylene; OP, oxidation products; α-MPNM, α-methylphenyl nitromethane

Keywords: *o*-Xylene nitration; H-beta; Solid acids; 4-Nitro-*o*-xylene

1. Introduction

Nitration of aromatic substrates is a widely studied reaction because of its industrial importance. Many nitroaromatics are extensively used as intermediates for the manufacture of dyes, pharmaceuticals, perfumeries and pesticides.

Nitroxylenes are especially important because 4-amino-*o*-xylene (xylidine), reduction product of 4-nitro-*o*-xylene, is used as starting material for the production of riboflavin [1]. Nitration of *o*-xylene by the conventional method, by using a mixture of nitric acid and sulfuric acid as the nitrating mixture gives a mixture of 4-NOX (4-nitro-*o*-xylene) 31–55% and 3-NOX (3-nitro-*o*-xylene) 45–69%. Apart from the low selectivity for 4-NOX, generation of dilute sulfuric acid waste poses environmental problems. Recently, Tomaz and Jaroslav [2] reported the liquid phase

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nitration of *o*-xylene using 100% nitric acid over silica supported solid catalysts with high yields (up to 90%) but poor selectivity for 4-NOX (41–57%) and *o*-nitrotoluene as side product. Landau and Kogan [3] have reported the nitration of *o*-xylene in vapor phase using nitrogen dioxide as a nitrating agent over different zeolites. Zeolite beta was found to be the most active catalyst for the selective production of 4-NOX and phthalic anhydride was the major by-product. Choudhari et al. [4] have carried out the nitration of *o*-xylene and other aromatic hydrocarbons in liquid phase using fuming nitric acid at reflux temperature and by azeotropic removal of water with a Dean–Stark apparatus over modified clay catalysts. Low yield and poor 4-NOX selectivity (52%) was reported in nitration of *o*-xylene.

In continuation of our earlier efforts on nitration of aromatics [5,6] using solid acid catalysts, we have studied the nitration of *o*-xylene in liquid as well as vapor phase over solid acid catalysts by using dilute HNO_3 which is an industrially preferred nitrating agent. The results are reported in this paper.

2. Experimental

2.1. Catalysts preparation and characterization

Commercially available zeolite H-beta (Si/Al = 30) and H-ZSM-5 (Si/Al = 40) were procured from United Catalyst India Ltd. MoO_3/SiO_2 (MoO_3: 20 wt%) was prepared by dissolving 35.28 g of ammonium molybdate in 150 ml hot distilled water and adding it dropwise to a solution of 120 g ethyl silicate-40 (CAS Registry No. 18954-71-7) as a silica source in 50 ml isopropyl alcohol under constant stirring. The resulting greenish gel was air dried, ground and calcined at 500 °C in air in a muffle furnace. The catalyst was characterized before and after the reaction for its physical and chemical properties using various techniques such as X-ray diffraction (XRD) (Rigaku, Miniflex), surface area measurement (Nova 1200) and the temperature programmed desorption (TPD) of ammonia (Micromeritics Autochem 2910). For the TPD of ammonia, the catalyst (0.4–0.5 mm diameter) was placed in a fused quartz tube and

activated in flowing helium (70 ml/min) from 30 to 500 °C followed by cooling the sample to 80 °C. A dose of 10% ammonia in helium was given for 30 min followed by heating in the flow of pure helium at 100 °C for 10 min to remove physisorbed ammonia. After cooling the sample to 80 °C, the sample was heated at the rate of 10 °C per minute up to 750 °C and the evolved NH_3 was recorded.

2.2. Catalytic reaction

All liquid phase catalytic nitration reactions were carried out in a batch reactor. In a typical run; 10 mmol *o*-xylene (1.06 g) in 10 ml carbon tetrachloride, 10 mmol nitric acid (0.9 g, 70 wt%) and 0.212 g freshly activated catalyst (20 wt%, based on *o*-xylene) were taken in a 50 ml two neck round bottom flask and the mixture was continuously stirred at 75 °C under nitrogen atmosphere. The temperature of the reaction was maintained by using an oil bath. The samples were periodically collected, neutralized using sodium hydrogen carbonate and analyzed by gas chromatography (Perkin–Elmer Autosystem XL, equipped with capillary column PE-1, 30 m, 0.25 mm ID, 1 μm film thickness and flame ionization detector). Products were confirmed by GC/MS (Shimadzu, DB-I column) and GC/IR (Perkin–Elmer Spectrum 2001, DB-1, 25 m, 0.32 mm ID).

Vapor phase nitration experiments were performed in a fixed-bed continuous down-flow glass reactor at the atmospheric pressure. 10 g zeolite beta catalyst in extrudates of 1.5 mm was loaded in a tubular glass reactor of 15 mm diameter and 25 mm length. The upper part of the reactor was packed with inert ceramic beads as the preheating zone. Before the reaction, the catalyst was preheated at 450 °C for 12 h in a 10 ml/min flow of air. The reactions were carried out by passing dilute nitric acid and *o*-xylene using syringe pumps (Sage feed pump), in the temperature range of 120–180 °C with nitrogen as carrier gas at the rate of 10 cm^3/min. The weight hourly space velocity (WHSV) was varied from 0.085 to 0.34 h^{-1}. The reaction products were collected in a receiver maintained at 5 °C. The mixture of products was extracted with diethyl ether and neutralized by sodium bicarbonate, and was analyzed by GC as indicated above.

3. Results and discussion

3.1. Catalyst characterization

The X-ray diffraction (XRD) patterns of the samples were recorded to ascertain their phase purity. The XRD patterns of zeolites H-beta and H-ZSM-5 matched well with the reported patterns of the standard materials. The XRD pattern of MoO_3/SiO_2 calcined at 500 °C showed the presence of crystalline MoO_3 without any crystalline silica reflections. The surface areas of the zeolite samples were 665 and 375 m^2/g, respectively, and that of MoO_3/SiO_2 was 145 m^2/g. The total pore volume of 0.288 m^2/g and the average pore diameter was 79 Å in case of MoO_3/SiO_2.

The TPD results of the catalysts (Fig. 1) show the following order of total acidity for the catalysts as: MoO_3/SiO_2 > H-beta > H-ZSM-5. MoO_3/SiO_2 showed a larger number of weaker acid sites than H-beta, whereas H-beta showed a larger number of stronger acid sites than MoO_3/SiO_2.

3.2. Liquid phase nitration of o-xylene

The results of the liquid phase nitration *of o-xylene* are given in Table 1. From these results it is evident that, among the catalysts used, H-beta
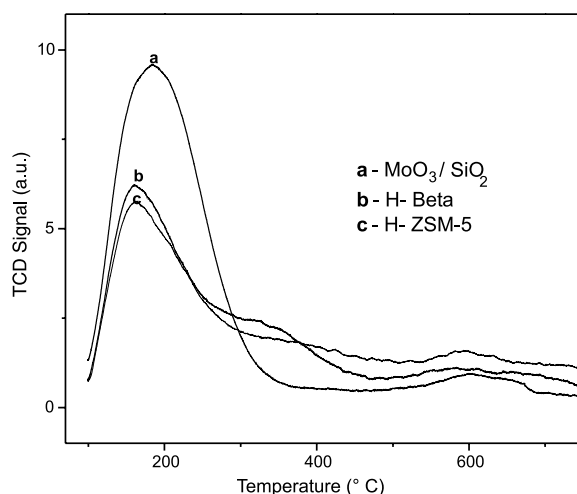

Fig. 1. TPD profiles of the catalysts: (a) Mo/SiO$_2$, (b) H-beta and (c) H-ZSM-5.

zeolite was more active (activity = 13.3 mmol/g/h) in the initial hour of reaction time. As the reaction progressed, after 4 h the conversion marginally increased in case of H-beta (28–33.3%), whereas a substantial increase was noticed in case of MoO_3/SiO_2 (20–37%). The higher activity of H-beta zeolite in the first hour of reaction may be due to stronger acid sites which are easily accessible due to the open framework structure of this zeolite. However, these active sites are sufficiently strong to catalyze side products also, which poison the active sites thereby restricting the rise in conversion. Whereas in the case of MoO_3/SiO_2, the number of weaker acid sites are higher than for the zeolite, hence lower reaction rate in the first hour of reaction time. Because of the weaker nature of the active sites, the formation of side products is also less and the activity continues to increase faster with time on stream. Accordingly, the selectivity for 4-NOX is higher (65%) in the initial hour in case of H-beta and is lowered after 4 h of reaction time because of the formation of oxidation products like tolualdehyde, toluic acid and α-MPNM by side chain nitration (Scheme 1). The 4-NOX to 3-NOX ratio was marginally higher (1.8) over H-beta zeolite as compared to H-ZSM-5 and MoO_3/SiO_2 (1.7) which may be due to the larger pores (pore size = 7.6 × 6.4 Å) of beta zeolite and its open framework structure leading to the faster diffusion of 4-NOX than 3-NOX because of the difference in kinetic diameter. It is interesting to note that the formation of α-MPNM was comparatively higher in case of H-ZSM-5 (30.7–44%) may be because of the smaller pores (pore size = 5.6 × 5.4 Å) compared to beta leading to surface reaction. This indicates that the side chain nitration of *o*-xylene is comparatively slower than the ring nitration taking place on the surface of ZSM-5 catalyst. The MoO_3/SiO_2 catalyst prepared by the sol–gel technique has mesopores and beta zeolite being large pore zeolite, the acid sites in these pores can readily catalyze ring nitration rather than side chain nitration.

The liquid phase nitration of *o*-xylene over H-beta was tested in absence of solvent also. With 70% nitric acid this reaction leads to oxidation rather than nitration. Even though the conversion was high (71.3%) the selectivity for 4-NOX was low

Table 1
Nitration of *o*-xylene in liquid phase over different solid acid catalysts[a]

Catalysts	React. time (h)	*o*-Xylene conv. (wt%)	Product selectivities (wt%)				4-/3-ratio	Activity[e] (mmol/g/h)
			4-NOX[b]	3-NOX	OP[c]	α-MPNM[d]		
H-beta	1	28.1	63.3	35.1	–	1.6	1.8	13.3
	4	33.3	46.6	25.8	7.3	20.3	1.8	
H-ZSM-5	1	20.9	38.7	22.8	8.7	30.7	1.7	9.8
	4	26.3	29.5	17.4	9.1	44.0	1.7	
Mo/SiO₂	1	20.2	57.6	33.8	–	8.6	1.7	9.5
	4	37.0	49.9	29.7	8.1	12.3	1.7	
H-beta[f]	1	71.3	26	15.3	31	27.7	1.7	33.7

[a] Reaction conditions: *o*-xylene/HNO₃ mole ratio, 1.0; *o*-xylene (mole), 0.01; HNO₃ (wt%), 70%; catalyst (g), 0.212 (20% of *o*-xylene weight); temp (°C), 75; solvent, carbon tetrachloride.
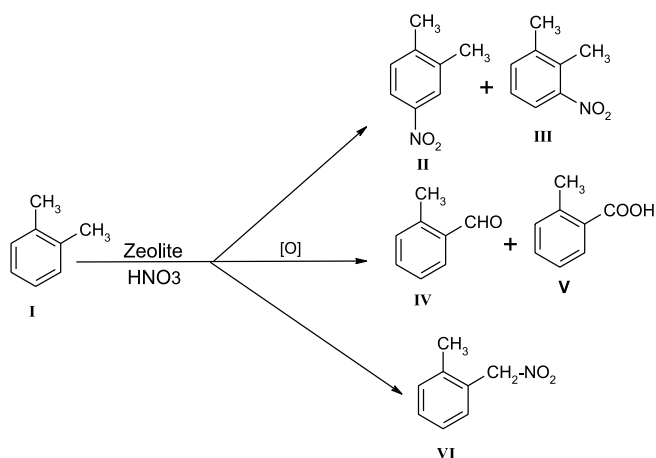[b] NOX, nitro-*o*-xylene.
[c] OP, oxidation products (tolualdehyde + toluic acid).
[d] α-MPNM, α-methylphenyl nitromethane.
[e] mmol of *o*-xylene converted at 1 h/g of catalyst.
[f] Reaction without solvent.

Scheme 1.

(36%) due to the formation of oxidation products. The use of dilute nitric acid (30%) for liquid phase nitration showed a very low conversion.

Because of the eventually slightly more activity and selectivity of H-beta zeolite in the first hour, the vapor phase nitration of *o*-xylene was carried out over H-beta zeolite.

3.3. Vapor phase nitration of o-xylene

When the vapor phase nitration was carried out over beta zeolite at higher temperature compared to the liquid phase reaction with 70% nitric acid, the oxidation products were formed in higher yield leading to a fast deactivation of the catalyst, as was observed earlier in case of toluene nitration [5]. Therefore, further studies were carried out using 30% nitric acid.

3.3.1. Influence of temperature

Fig. 2 shows the influence of temperature on the vapor phase nitration with *o*-xylene/HNO₃ ratio of 1.5 using 30% nitric acid. Initially the reaction was carried out at 120 °C where the
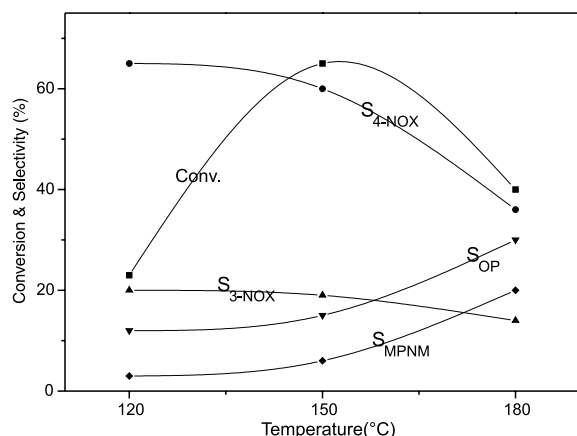
Fig. 2. Influence of temperature on conversion and selectivity of *o*-xylene. Reaction conditions: catalyst, H-beta; catalyst (g), 10; *o*-xylene/HNO$_3$ mole ratio, 1.5; *o*-xylene feed rate (ml/h), 2; HNO$_3$, 30%; WHSV, 0.17 h^{-1}; TOS (h), 5.

conversion was low (23%) compared to the liquid phase (33%) due to the lower residence time whereas the selectivity for 4-NOX was almost the same (~64%). When the temperature was increased from 120 to 150 °C the conversion also increased up to 65% with marginal decrease in selectivity for 4-NOX. The formation of oxidation products was higher as in the liquid phase reaction, whereas the side chain nitro product formation was low because of a lower residence time compared to the liquid phase. The formation of 3-NOX is almost constant whereas the ratio of 4-NOX/3-NOX was higher (3), this may be due to a faster diffusion of 4-NOX at the higher temperature than in the liquid phase nitration. As the temperature is increased to 180 °C the conversion decreased (40%) due to decomposition of nitric acid at higher temperature but the selectivity for NOX also decreased (50%) because of the formation of oxidation and side chain nitration products.

The nitration of *o*-xylene being an exothermic reaction, the use of dilute nitric acid provides water vapor, which dissipates the heat of reaction minimizing the formation of oxidation products. Dilute nitric acid is safer to handle compared to concentrated nitric acid, which is an added advantage for commercialization of the process.

3.3.2. Influence of WHSV

The influence of the weight hourly space velocity (WHSV) on the conversion and selectivity was studied in the range 0.085–0.34 h^{-1} at 150 °C under otherwise identical conditions (see Fig. 3). At the lower WHSV of 0.085, the conversion was higher (80%) with the formation of oxidation and side chain nitro products. As the WHSV was increased to 0.17 h^{-1}, the conversion decreased to 60% and the formation of oxidation and side chain nitro products was low indicating the influence of WHSV on product distribution due to lower residence time. A minor deactivation of the catalyst is observed after 78 h, indicating the high stability of the catalyst. The deactivated H-beta catalyst was washed with acetone and the washing was analyzed by gas chromatography. It showed the presence of 4-NOX, *o*-toluic acid, *o*-tolualdehyde and α-MPNM indicating the deactivation of the catalyst due to surface fouling. The deactivated catalyst was heated up to 550 °C in air and the XRD patterns of this sample was similar to the fresh catalyst showing that heat treatment and reaction does not result in the loss of crystallinity showing the structural stability of the catalyst in the acid environment of the reaction.
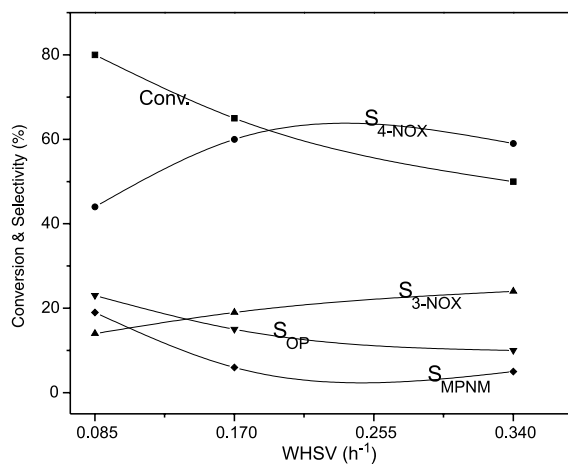

Fig. 3. Influence of WHSV on conversion and selectivity of *o*-xylene. Reaction conditions: catalyst, H-beta; catalyst (g), 10; *o*-xylene/HNO$_3$ mole ratio, 1.5; *o*-xylene feed rate (ml/h), 2; HNO$_3$, 30%; WHSV, 0.17 h^{-1}; TOS (h), 5. Temp, 150 °C.

4. Conclusions

4-NOX is regioselectively formed in a continuous process by vapor phase nitration of *o*-xylene using dilute nitric acid over H-beta zeolite at 150 °C with high yield. Low conversion, formation of alkyl nitro product, use of chlorinated solvents and concentrated nitric acid are the major drawbacks in liquid phase nitration which have been overcome significantly in the vapor phase nitration. A maximum conversion of 65% with 60% selectivity for 4-NOX and a 4-/3-isomer ratio of 3 have been obtained in vapor phase nitration without any formation of dinitro and ipso-substituted products. α-Methylphenyl nitromethane (α-MPNM), formed by alkyl nitration, *o*-tolualdehyde and *o*-toluic acid, formed by oxidation of methyl group, are the major by-products in this reaction. The use of dilute nitric acid and selective formation of 4-NOX are the main advantages of this process making it an environmentally benign process.

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