*Aust. J. Chem.* http://dx.doi.org/10.1071/CH14551

# **Regioselective Nitration of** *m***-Xylene Catalyzed by Zeolite Catalyst**

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Nitration with nitric acid and acetic anhydride via acetyl nitrate as nitrating species is efficient with the substrate *m*-xylene as solvent. Zeolite H $\beta$  with an SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 500 was found to be the most active of the catalysts tried both in yield and regioselectivity in the nitration of *m*-xylene. The molecular volume of the reactants was calculated with the *Gaussian* 09 program at the B3LYP/6–311+G(2d, p) level and compared with the size of the zeolite H $\beta$  channels. A range of other substrates were subjected to the nitrating system under the same conditions as those optimized for *m*-xylene and excellent selectivity was obtained.

Manuscript received: 9 September 2014. Manuscript accepted: 1 December 2014. Published online: 3 February 2015.

## Introduction

Nitro derivatives of *m*-xylene are important starting materials for a variety of fine chemical products including pharmaceuticals and agrochemical drugs. Typical nitration requires a mixture of concentrated nitric acid with sulfuric acid, leading to excessive acid waste streams, which leads to serious environmental issues. In order to address these problems, many efforts have been made and some progress has been achieved. Earlier studies of the nitration of *m*-xylene catalyzed by boron trifluoride with silver nitrate in acetonitrile solution were reported by Olah et al.<sup>[1]</sup> Lanthanide(III) triflates<sup>[2]</sup> and lanthanide(III) nosylates<sup>[3]</sup> were used as new nitration catalysts for the nitration of *m*-xylene. Kantam et al.<sup>[4]</sup> reported the nitration of *m*-xylene catalyzed by β-zeolite with nitric acid and acetic anhydride. Bharadwaj nitrated *m*-xylene catalyzed by  $Al(H_2PO_4)_3^{[5]}$  and acid phosphate-impregnated titania.<sup>[6]</sup> Recently, Wang and coworkers<sup>[7]</sup> reported the regioselective nitration of m-xylene under phase-transfer catalysis. The results are listed in Table 1 for comparison.

In our previous work,  $[^{8-11}]$  a series of aromatic compounds were nitrated with good regioselectivity catalyzed by zeolites and hydroxyl-aluminium cross-linked bentonites. To further improve the conversion of *m*-xylene and the ratio of 2,4dimethylnitrobenzene to 2,6-dimethylnitrobenzene, the nitration of *m*-xylene was investigated and excellent conversion and yield were obtained. The detailed results are reported in this paper.

# Experimental

## Materials

Solid catalysts were purchased and calcinated at 550°C for 2 h before use. Gas chromatographic analysis was carried out with a Shimadzu 2014-C (Wondacap-1; film thickness  $Df = 1.5 \ \mu m \times 0.53 \ mm$  inner diameter  $\times 30 \ m$ ) and a flame ionization detector

was utilized to determine product isomer compositions. The temperature program used was as follows: heating from 80 to  $120^{\circ}$ C at a rate of  $10^{\circ}$ C min<sup>-1</sup>; hold 1 min, then heating at  $20^{\circ}$ C min<sup>-1</sup> to  $170^{\circ}$ C. Product identities were proved by direct comparison with authentic samples. All other chemicals were of analytical grade and were used without any further purification.

## General Procedure

A typical nitration of *m*-xylene over zeolite with nitric acid and acetic anhydride was carried out as follows. Zeolite (0.1 g, calcinated at 550°C for 2 h before use), m-xylene (5 mL), and acetic anhydride (0.613 g, 6 mmol) were mixed under stirring at 0°C. Then nitric acid (0.199 g, 95 %, 3 mmol) was added dropwise. The mixture was stirred for 30 min and then allowed to warm to room temperature and allowed to stand for 24 h. The catalyst was removed by filtration and washed with dichloromethane (10 mL). The organic layers were washed with water  $(10 \text{ mL} \times 2)$ , NaHCO<sub>3</sub> solution (10%, 10 mL), and water  $(10 \text{ mL} \times 2)$ , and dried with MgSO<sub>4</sub>. A known amount of *p*-nitrotoluene was added as internal standard. Then the solution was analysed by gas chromatography to get the total yield and ratio of 2,4-dimethylnitrobenzene to 2,6-dimethylnitrobenzene. The products were characterized by <sup>1</sup>H NMR.: 2,4-dimethylnitrobenzene:  $\delta_{\rm H}$  (600 MHz, CDCl<sub>3</sub>) 2.39 (s, 3H), 2.58 (s, 3H), 7.12 (d, J 8.0, 2H), 7.91 (d, J 8.2, 1H); 2,6-dimethylnitrobenzene: δ<sub>H</sub> (600 MHz, CDCl<sub>3</sub>) 2.31 (s, 6H), 7.12 (d, J7.6, 2H), 7.26 (t, J 7.6, 1H).

### **Results and Discussion**

To improve the conversion of *m*-xylene and the regioselective formation of 2,4-dimethylnitrobenzene, different conditions were investigated. The detailed results are listed in Table 2.

#### Table 1. Nitration of *m*-xylene with different catalysts in the literature



2,4-dimethylnitrobenzene

*m*-xylene

2,6-dimethylnitrobenzene

3,5-dimethylnitrobenzene

Entry	Catalyst	Conversion	Yield [%]	Proportion [%]		2,4-dimethylnitrobenzene/
		[%]		2,4- dimethylnitrobenzene	2,6- dimethylnitrobenzene	2,6-dimethylnitrobenzene
1	Boron trifluoride <sup>[1]</sup>	_	_	87	13	6.69
2	Lanthanide(III) triflates <sup>[2]</sup>	>95	_	85	15	5.67
3	Lanthanide(III) nosylates <sup>[3]</sup>	>98	_	86	14	6.14
4	$\beta$ zeolite <sup>[4]</sup>	69	_	86	14	6.14
5	$Al(H_2PO_4)_3^{[5]}$	99	90	90	_	_
6	Acid phosphate-impregnated titania <sup>[6]</sup>	-	90	90	-	_
7	Sodium dodecyl sulfonate <sup>[7]</sup>	97.8	-	90.4	9.2	9.83

#### Table 2. Nitration of *m*-xylene under different conditions

Entry	Solvent	Acetic Catalyst	Catalyst	Conversion Y	Yield Proporti		ion [%]	2,4-dimethylnitrobenzene/
		anhydride		[%]	[%]	2,4- dimethylnitrobenzene	2,6- dimethylnitrobenzene	2,6-dimethylnitrobenzene
1 <sup>A</sup>	Dichloromethane	None	None	18.5	12.4	83.7	16.3	5.13
2 <sup>A</sup>	Dichloromethane	None	$H\beta^{B}$	48.5	24.8	88.4	11.6	7.58
3 <sup>A</sup>	Dichloromethane	6 mmol	None	98.3	98.1	84.3	15.7	5.36
$4^{\mathrm{A}}$	Dichloromethane	6 mmol	$H\beta^{B}$	100.0	98.9	89.8	10.2	8.78
$5^{\rm C}$	Acetic anhydride	5 mL	Hβ <sup>B</sup>	100.0	100	90.2	9.8	9.25
6	<i>m</i> -xylene	6 mmol	$H\beta^{B}$	-	100	93.5	6.5	14.4

<sup>A</sup>Dichloromethane was used as solvent and *m*-xylene (0.319 g, 3 mmol) was added.

<sup>B</sup>Ratio of SiO<sub>2</sub> to Al<sub>2</sub>O<sub>3</sub> was 500.

<sup>C</sup>Acetic anhydride was used as solvent and *m*-xylene (0.319 g, 3 mmol) was added.

Under catalysis with H $\beta$ , the conversion, yield, and regioselectivity were all improved (Table 2, entry 2) owing to the participation of Brønsted acid centres and the three-dimensional networks of the catalyst.

The conversion and yield were all greatly increased (Table 2, entry 3) when acetic anhydride was added because it can convert all the nitric acid into acetyl nitrate and all the water into acetic acid. Higher conversion with acetic anhydride is attributed to the in situ formation of acetyl nitrate as the active nitrating species in the presence of nitric acid.<sup>[12–16]</sup>

As expected, the conversion, yield, and regioselectivity were all greatly improved with the combination of H $\beta$  and acetic anhydride (Table 2, entry 4). Acetic anhydride and *m*-xylene as solvents were also investigated. The best ratio of 2,4- to 2,6-reached up to 14.4 when *m*-xylene was used as solvent. Therefore, the substrate *m*-xylene used as solvent was selected for more detailed study. Unreacted substrate can be recovered by distillation. The isomer 3,5-dimethylnitrobenzene was not found under the reaction conditions selected.

We then carried out reactions in which various zeolites were used as catalysts in an attempt to determine which zeolite would be the most effective for *m*-xylene nitration. The effects of pore size, channel structure, acidity, and SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio were all assessed. Representative results are summarized in Table 3.

Zeolites are potentially attractive catalysts in the nitration reaction because of their acidity and shape selectivity and as they are crystalline aluminosilicates with uniform pore dimensions. Compared with other solid acids, there are both Lewis and Brønsted acidic sites throughout the inner and outer surfaces of zeolites. As shown in Table 3, in the presence of all of the zeolites, the reactions gave higher yields than in the absence of any catalyst. The selectivity with zeolite HZSM-5 was as low as the reaction with no catalyst, for the ZSM-5 structure consists of a three-dimensional channel system with medium channel intersections that are not large enough to accommodate the reacting species and little of the reaction occurred inside the pores as it was occurring at the external surface.

As can be seen from Table 3, zeolite H $\beta$  has outstanding catalytic capacity in the regioselective nitration of *m*-xylene. Zeolite H $\beta$  has three-dimensional channels and large pore sizes that assist shape selectivity in the nitration of *m*-xylene. Zeolite H $\beta$  has been also used to catalyze the nitration of phenol,<sup>[17]</sup> benzonitrile,<sup>[13]</sup> *o*-xylene,<sup>[4,6,18]</sup> halogenobenzenes,<sup>[19–22]</sup> and toluene<sup>[22,23]</sup> with enhanced selectivity.

Entry	Catalyst (SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> )	Yield [%]	Proport	2,4-dimethylnitrobenzene/	
			2,4-dimethylnitrobenzene	2,6-dimethylnitrobenzene	2,6-dimethylnitrobenzene
1	None	88.5	84.9	15.1	5.62
2	HZSM-5 (25)	90.3	84.9	15.1	5.62
3	HZSM-5 (40)	97.4	85.3	14.7	5.80
4	HZSM-5 (200)	99.1	85.5	14.5	5.90
5	HZSM-5 (360)	99.8	85.3	14.7	5.80
6	Ηβ (25)	101.0	92.0	8.0	11.5
7	Нβ (150)	101.2	91.8	8.2	11.2
8	Ηβ (280)	98.8	93.5	6.5	14.4
9	Нβ (500)	100.0	93.5	6.5	14.4
10	HY	101.5	85.3	14.7	5.80





Fig. 1. The reactant molecule entering a zeolite H $\beta$  channel with an opening of 0.64–0.76 nm. The reactant molecules are *m*-xylene, 2,4-dimethylnitrobenzene, and 3,5-dimethylnitrobenzene, respectively.

Table 4. Comparison of surface areas and pore volumes for HZSM-5 and  ${\rm H}\beta$ 

Entry	Catalyst	Surface area (BET) $[m^2 g^{-1}]$	Total pore volume $[cm^3 g^{-1}]$
1	HZSM-5	386	0.20
2	Ηβ	528	0.32

In order to find out the reason of the shape selectivity of zeolite H $\beta$ , the molecular volume of the reactants was calculated with the *Gaussian 09* program<sup>[24]</sup> at the B3LYP/  $6-311+G(2d, p)^{[25,26]}$  level, and the results are listed in Fig. 1.

The pore size of zeolite H $\beta$  is 0.64–0.76 nm. The distance between 7H and 9H in *m*-xylene is 0.493 nm. Considering the diameter of the H atom, the minimum diameter of *m*-xylene is 0.599 nm. With the same calculation process, considering the volume of the H atom and O atom, the minimum diameter of 2,4-dimethylnitrobenzene, 2,6-dimethylnitrobenzene, and 3,5-dimethylnitrobenzene is 0.653, 0.672, and 0.724 nm respectively.

The minimum diameter of 2,6-dimethylnitrobenzene at 0.672 nm is longer than 2,4-dimethylnitrobenzene at 0.653 nm. This means 2,6-dimethylnitrobenzene is more restricted than 2,4-dimethylnitrobenzene in zeolite H $\beta$ , and hence a higher ratio of 2,4-/2,6- was reached. The largest molecule, 3,5-dimethylnitrobenzene, cannot be formed in the channel owing to the dimensions of the channels of zeolite H $\beta$ .

The SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of the zeolite used influenced the selectivity of the reactions. The zeolite with the highest SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio gave a higher 2,4-selectivity than that with a lower ratio. This is in accord with the results observed by Smith et al. in the nitration of halogenobenzenes.<sup>[20]</sup> This may be due to dealumination, which would modify the distribution of the size and shape of the pores in the zeolite.

Zeolite Y, which has the largest cavities, allowed a rapid reaction, with limited improvement in 2,4-selectivity.

The structure affects the Brunauer-Emmett-Teller (BET) surface area and pore volume of the zeolite, as indicated in Table 4. Table 4 shows that H $\beta$  had a higher surface area and total pore volume than HZSM-5, which favoured the nitration process.

None of the zeolites tried gave better regioselectivity than the one originally studied and further studies therefore concentrated on the use of zeolite H $\beta$  (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 500).

Entry	Quantities of catalyst [g]	Quantities of Yield [%] catalyst [g]	Proport	2,4-dimethylnitrobenzene/	
			2,4-dimethylnitrobenzene	2,6-dimethylnitrobenzene	2,6-dimethylnitrobenzene
1	None	93.8	85.6	14.4	5.94
2	0.01	98.6	89.0	11.0	8.09
3	0.03	99.0	91.2	8.8	10.4
4	0.05	97.0	91.9	8.1	11.3
5	0.07	90.9	92.7	7.3	12.7
6	0.10	100.0	93.5	6.5	14.4
7	0.12	99.3	93.7	6.3	14.9
8	0.15	100.1	93.9	6.1	15.4
9	0.20	97.2	94.1	5.9	15.9
10	0.30	98.4	94.1	5.9	15.9
11	0.40	95.9	94.3	5.7	16.5
12	0.50	97.0	94.2	5.8	16.2
13	1.00	95.9	94.5	5.5	17.2
14	1.50	74.5	95.0	5.0	19.0

Table 5. Nitration of *m*-xylene over various quantities of zeolite Hβ

 Table 6.
 Nitration of m-xylene over various quantities of acetic anhydride

Entry	Quantity of acetic anhydride [mL]	Yield [%]	Propor	2,4-dimethylnitrobenzene/	
			2,4-dimethylnitrobenzene	2,6-dimethylnitrobenzene	2,6-dimethylnitrobenzene
1	None	24.3	90.1	9.9	9.11
2	0.09 (1 mmol)	22.3	91.5	8.5	10.7
3	0.19 (2 mmol)	41.5	91.8	8.2	11.2
4	0.28 (3 mmol)	61.3	91.5	8.5	10.8
5	0.43 (4.5 mmol)	95.7	93.4	6.6	14.2
6	0.57 (6 mmol)	100.0	93.5	6.5	14.4
7	0.85 (9 mmol)	99.9	93.4	6.6	14.2
8	1.13 (12 mmol)	95.3	93.3	6.7	13.9
9	1.42 (15 mmol)	92.8	92.3	7.7	12.0
10	1.70 (18 mmol)	93.1	92.2	7.8	11.8
11	1.99 (21 mmol)	92.3	91.7	8.3	11.0
12	2.27 (24 mmol)	88.7	92.1	7.9	11.7

 Table 7.
 Nitration of *m*-xylene for various reaction times

Entry	Reaction time [h]	action time [h] Yield [%]	Proport	2,4-dimethylnitrobenzene/	
			2,4-dimethylnitrobenzene	2,6-dimethylnitrobenzene	2,6-dimethylnitrobenzene
1	1	71.1	92.5	7.5	12.3
2	2	84.8	93.1	6.9	13.6
3	3	87.0	92.6	7.4	12.5
4	4	83.9	93.2	6.8	13.7
5	6	99.3	93.5	6.5	14.4
6	8	99.7	93.4	6.6	14.2
7	10	100.9	93.5	6.5	14.4
8	12	99.6	93.4	6.6	14.2
9	16	100.9	93.5	6.5	14.4
10	20	100.2	93.5	6.5	14.4
11	24	100.0	93.5	6.5	14.4

# Table 8. Recycling of zeolite Hβ catalyst in nitration of *m*-xylene

Cycle	Yield [%]	Propor	Proportion [%]		
		2,4-dimethylnitrobenzene	2,6-dimethylnitrobenzene	2,6-dimethylnitrobenzene	
Fresh	99.3	93.5	6.5	14.4	
First	96.9	93.2	6.8	13.7	
Second	94.4	93.1	6.9	13.5	

In order to test the effect of the amount of zeolite H $\beta$ , reactions were carried out with several different quantities of zeolite H $\beta$ . The results are recorded in Table 5.

It is clear from the results in Table 5 that 2,4-selectivity increased with the quantity of catalyst. This is consistent with



Fig. 2. Powder X-ray diffraction (XRD) patterns of  $H\beta$ : (a) fresh; (b) after three uses.

the toluene nitration reaction.<sup>[14]</sup> With the amount of catalyst increasing, the reactant molecules have more chance to diffuse into the pores of zeolite H $\beta$ , on account of the higher interior surface area and also the more accessible number of Brønsted acid sites of the catalyst. Meanwhile, a greater proportion of the acetyl nitrate can be located inside the pores. When the amount of catalyst increased from 0.10 to 1.50 g, 2,4-selectivity increased only from 93.5 to 95.0%, and the total yield of dimethylnitrobenzene decreased from 100.0 to 74.5%. From the point of view of optimal reaction conditions, 0.10 g zeolite H $\beta$  was used in subsequent experiments.

Acetic anhydride reacts with HNO<sub>3</sub> to form the acetyl nitrate (AcONO<sub>2</sub>) intermediate as nitrating species as follows:

$$(CH_3CO)_2O + HNO_3 \rightarrow CH_3COONO_2 + CH_3COOH$$

The water released in the nitration reaction will affect the acidity of the zeolite. It is necessary to scavenge the water formed during the reaction out of the reaction zone to facilitate regeneration of active acid sites on the catalyst.<sup>[22]</sup> With acetic anhydride present, water molecules released during the reaction react with acetic anhydride to give acetic acid and thereby the acidity of the zeolite is retained. The reaction is shown as follows:

$$(CH_3CO)_2O + H_2O \rightarrow 2CH_3COOH$$

To convert all the nitric acid into acetyl nitrate and all the water into acetic acid, 6 mmol acetic anhydride was used. To test whether this is the optimum quantity of acetic anhydride,

Entry Substrate Yield [%] Proportion of products [%]  $NO_2$ 87.7 1 100 CH<sub>3</sub> CH CH<sub>3</sub> ĊH3 102 72.6 2 90.7 2.6 24.8 NO NO<sub>2</sub> CH<sub>3</sub> CH₃ CH<sub>3</sub> CH<sub>3</sub> CH<sub>3</sub> CH3 73.4 97.3 3 26.6 NO<sub>2</sub> NO<sub>2</sub> CH₃ ĊH₃  $NO_2$ 100 86.2 4 ĊH<sub>3</sub> ĊH<sub>3</sub>

Table 9. Nitration of various substrates under the optimized conditions

Table 10. NBO charge of all C atoms in benzene ring



a series of reactions were conducted in which the ratio of the anhydride to nitric acid was varied. The results are listed in Table 6.

As the results in Table 6 show, with 6 mmol acetic anhydride, the yield and 2,4-selectivity were excellent. Below that amount, the mechanism presumably switches to that of a nitric acid nitration, consequently leading to a slower reaction and a lower degree of 2,4-selectivity.<sup>[14]</sup> With a greater increase in the amount of acetic anhydride, the yield and 2,4-selectivity were both decreased.

Thus far, all experiments were allowed to react for 24 h. It was of interest to know if such an amount of time was actually necessary. To optimize the reaction time for maximum yield and 2,4-selectivity, we further investigated the effect of reaction time in the presence of 0.10 g catalyst. The results are showed in Table 7.

The results (Table 7) show that the yield and 2,4-selectivity increased with time. The best yield, near 100 %, and the ratio of 2,4-/2,6- of 14.4 were obtained at 6 h. With time increasing, the yield and regioselectivity did not change, which suggested that no reaction occurred after 6 h. Therefore, the total time for the nitration reaction was optimized to 6 h.

The used zeolite H $\beta$  was easily recovered by simple filtration and regenerated by calcination with little loss of activity (Table 8).

X-ray diffraction (XRD) patterns (Fig. 2) show that there is no obvious difference between the fresh H $\beta$  and that used for the third time.

A range of other substrates were subjected to the nitrating system under the same conditions as those optimized for *m*-xylene. The results are summarized in Table 9.

Using the *Gaussian 09* program, the natural bond orbital (NBO) net charge of each C atom on the benzene ring of the selected substrates was calculated at the B3LYP/6–311+G(2d, p) level and the values are listed in Table 10.

As the nitration reaction is an electrophilic substitution process, the reagent preferentially attacks the low-chargedensity position. In addition, steric effects can also affect the reaction selectivity.

As can be seen from Tables 9 and 10, this method offers high yield and outstanding regioselectivities for the selected substrates owing to the combined effects of steric effect, charge distribution, and shape selectivity of zeolite H $\beta$ .

For the nitration of toluene, *m*-xylene, and *o*-xylene, the effects of the three factors are consistent, which leads to excellent selectivity in the formation of 4-nitrotoluene (72.6 %), 2,4-dimethylnitrobenzene (93.5 %), and 3,4-dimethylnitrobenzene (73.4 %) respectively.

## Conclusion

Zeolite H $\beta$  is an effective catalyst for the nitration of *m*-xylene in a nitric acid/acid anhydride system. The catalyzed reaction produces only 2,4-dimethylnitrobenzene and 2,6-dimethylnitrobenzene in quantitative yield, with no 3,5-dimethylnitrobenzene produced under the conditions tested. Zeolite H $\beta$ with an SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 500 is the most selective of the catalysts tried and gives a high proportion of 2,4-dimethylnitrobenzene. Acetic anhydride can convert all the nitric acid into acetyl nitrate and all the water into acetic acid.

A range of other substrates were subjected to the nitrating system under the same conditions as those optimized for *m*-xylene and excellent selectivity was obtained.

This method has several practical advantages that should make it highly attractive for commercial application. The excess substrates can be recovered by distillation and the catalyst can be easily recovered and regenerated.

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