Beta zeolite: an efficient and eco-friendly catalyst for the nitration of o-xylene with high regio-selectivity in liquid phase

Mannepalli L. Kantam*, Boyapati M. Choudary,
Nadakuditi S. Kumar, Kompella V. Ramprasad

Inorganic Chemistry Division, Indian Institute of Chemical Technology, Tarnaka 500007, Hyderabad, India

Abstract

o-Xylene is nitrated in liquid phase with high regio-selectivity using beta zeolite as a catalyst with stoichiometric quantity of nitric acid. The use of acetic anhydride is completely eliminated with almost zero emission of effluents. There is no formation of oxygenates or side chain nitration. The influence of experimental conditions like effect of solvent, rate of addition of nitric acid, effect of SiO_2/Al_2O_3 ratios, are also investigated. The process is eco-friendly and less expensive and represents a clean synthesis of nitro aromatic compounds with higher regio-selectivity.
© 2004 Elsevier B.V. All rights reserved.

Keywords: Nitration; Beta zeolite; o-Xylene; Regio-selectivity; 1,2-Dichloroethane
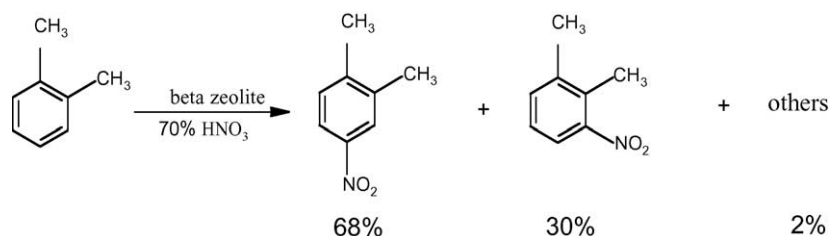
1. Introduction

Nitration of aromatic compounds is a widely used reaction to realise organic intermediates required in large tonnages for the fine chemical industry. The conventional eco-unfriendly nitration process, employing a nitrating mixture of nitric acid and sulfuric acid, for the last two centuries has remained unchallenged in the commercial arena owing to the uneconomical alternative options [1–2]. Research in dispensing the use of sulfuric acid in general in the nitration of aromatic compounds and selective synthesis of the desired isomer in the nitration of substituted benzenes in particular is of topical interest, since it reduces pollution caused by spent acid and unwanted isomers and more specifically to respond to market demand. Various novel options, meeting international environmental laws, and also avoiding the recovery of the spent acid in the conventional mixed acid process have been explored in the nitration of benzene and toluene [3–13]. However, these options fall short of expectations to commercial realisation in view of low space-time yields, high dilution,

and/or use of explosive and relatively expensive mixtures in the form of acetic anhydride-nitric acid or expensive acyl or alkyl nitrate. Nitration reactions performed with ionic liquids [14], albeit, at very low temperatures offers no isomeric selectivity. We recently reported an efficient methodology with high p-selectivity for the nitration of mono substituted aromatic compounds employing beta zeolite as catalyst with nitric acid as nitrating agent [15].

The mononitro derivatives of o-, m-and p-xylenes isomers are used as intermediates for the production of vitamins, agrochemicals, fragrances and dyes. Although 4- and 3-nitro-o-xylenes are useful starting materials for the production of riboflavin (Vitamin B2) and mefenamic acid, an agrochemical, respectively, the former is required in large tonnage. Selective nitration of o-xylene, thus, assumes higher importance. Nitration of o-xylene in the conventional method, using a mixture of nitric acid and sulfuric acid as the nitrating mixture gives a mixture of 4-nitro-o-xylene 31–55% and 3-nitro-o-xylene 45–69%. The earlier attempts [16–21] of nitration of xylene isomers have been made with either expensive or hazardous starting materials with lower selectivity. Nitration of o-xylene catalyzed by beta zeolite in vapour phase using the N_2O_4 as a nitrating agent [22] and in liquid phase using acetic

* Corresponding author. Tel.: +91 40 2719 3510; fax: +91 40 2716 0921.
E-mail address: mlakshmi@iict.res.in (M.L. Kantam).

Scheme 1.

anhydride, nitric acid mixture [11] and by silica supported solid catalysts with 100% nitric acid [23] offers lower selectivity towards 4-nitro-*o*-xylene with simultaneous production of large amounts of oxygenates, like tolualdehyde, toluic acid or side products, such as *o*-nitrotoluene, etc. We have a European patent granted in 2003 [24] for the nitration of *o*-xylene using beta zeolite with 40% conversion and 68% of 4-nitro-*o*-xylene and 30% of 3-nitro-*o*-xylene with a small amount of dinitro derivative in liquid phase. Very recently, Dongare and co-worker [25] reported the nitration of *o*-xylene using beta zeolite in liquid phase exhibits a conversion of 28% and selectivity of 63% of 4-nitro-*o*-xylene initially, which is fast decreasing, in vapour phase with a conversion of 65% and 60% of 4-nitro-*o*-xylene, 19% of 3-nitro, *o*-xylene and 21% of oxygenates and α–MPNM.

The excellent applications of nitroxylene isomers in general and the poor isomeric selectivity towards 4-nitro-*o*-xylene or large amounts of oxygenates expressed in the nitration of *o*-xylene in particular prompted us to undertake the present the nitration of xylenes using beta zeolite in an effort to evolve eco-friendly and high atom utilization process. We report in this paper the nitration of *o*-xylene with highest isomeric selectivity for 4-nitro-*o*-xylene using beta zeolite catalyst (Scheme 1) in liquid phase with reuse of the solid acid catalyst being possible by azeotropic removal of water formed in the reaction and present in nitric acid.

2. Experimental

2.1. General

Beta zeolite catalyst was procured from Zeolyst International. Dichloroethane, *o*-xylene and nitric acid were obtained from commercial sources and used as such without further purification. All the results are based on GC analysis. The products formed were confirmed by GC–MS. BET analysis was done on Quantachrome Autosorb Automated Gas Sorption System.

2.2. General procedure for nitration of o-xylene

In a typical experimental run, 10 mmol of *o*-xylene (1.06 g) and 0.1 g (10.0% by weight, based on xylene) of the catalyst were taken in a 50 ml two-necked round-bottomed flask along with 6 ml of dichloroethane as the solvent. The resulting mixture was heated to reflux temperature and when the steady state is acquired, 12 mmol of nitric acid (70%) was slowly added for 1 h. After addition of nitric acid, the temperature was maintained for 3 h. Water formed during the reaction was separated by a reverse Dean–Stark apparatus. On completion of the reaction, the reaction mixture was filtered and the filtrate was subjected to base wash to remove the excess acid. Under similar conditions the nitration of *m*- and *p*-xylenes were also performed.

3. Results and discussion

3.1. Influence of various catalysts

In an effort to evolve the best catalyst, different solid acid catalysts were screened under identical reaction conditions in the nitration of *o*-xylene (Table 1). ZSM-5 zeolite (entry-1) afforded a poor isomeric ratio of 4-nitro/3-nitro-*o*-xylenes, 0.62. This is because of the low diffusion of aqueous HNO_3 in the hydrophobic pores of ZSM-5 and the resulting density of acidic sites is too low to promote the generation of nitronium ions from nitric acid and hence the reaction takes place only on the surface of the zeolite. The use of Fe^{3+} and H^+-montmorillonites (entries 2 and 3) catalysts increased the isomeric ratio to 0.92. Among all the solid acid catalysts, beta zeolite-II displayed the best isomeric ratio 2.26 (entry 6).

3.2. Influence of Si/Al ratio

Among all the solid acid catalysts, beta zeolite-II displays the best isomeric ratio 2.26 as well as conversion (entry-6).

Table 1
Nitration of *o*-xylene with different catalysts[a]

Entry	Catalyst	Conversion (%)	Selectivity (%)		
			3-Nitro	4-Nitro	Others
1	ZSM-5	21.5	61.4	38.6	–
2	Fe^{3+}-Mont	51.0	46.5	43.5	10.0
3	H^+-Mont	10.0	52.0	48.0	–
4	NaY-zeolite	12.0	42.0	50.0	8.0
5	Beta zeolite-I[b]	20.0	35.0	54.0	21.0
6	Beta zeolite-II[b]	42.0	30.0	68.0	2.0

[a] One hundred milligram catalyst, 10 mmols *o*-xylene; 12 mmols of 70% HNO_3; 6 ml of 1,2-dichloroethane, reflux, 1 h addition and 3 h maintenance.
[b] SiO_2/Al_2O_3 ratio: beta zeolite-I: 27, beta zeolite-II: 22.

There is no formation of oxygenates and side chain nitration products. In the experiments with beta zeolites of SiO_2/Al_2O_3 ratios 22 and 27 (Table 1, entries 5 and 6), high SiO_2/Al_2O_3 provides a low selectivity towards 4-nitro-*o*-xylene.

The particle size of the beta zeolite catalysts is determined by TEM photographs. More agglomeration was observed in the catalyst with low SiO_2/Al_2O_3 ratio. Despite of the agglomeration of the particles, the acidity increases as the SiO_2/Al_2O_3 ratio decreases, which in turn yields higher activity. Thus, effect of particle size is masked and allows higher activity due to increased acidic sites. On the other hand, the higher selectivity obtained with the low SiO_2/Al_2O_3 ratio may be due to the agglomeration of particles.

3.3. Influence of rate of addition of nitric acid

The influence of rate of addition of nitric acid, nature of solvent used and reaction time on the conversion and regio-selectivities of the reaction in the nitration of *o*-xylene was studied. We performed the nitration by different rates of addition of the nitric acid (Fig. 1). It reveals that the decrease in the rate of addition of nitric acid increases the selectivity towards 4-nitro isomer. A maximum selectivity of 4-nitro isomer was achieved when the rate of addition of nitric acid was 1.0 ml/h. One possible reason for the better selectivity at slow addition of nitric acid is the immediate azeotropic removal of water formed during the reaction, which otherwise causes the deactivation of the catalyst.

3.4. Influence of solvent

In order to determine the best reaction medium, we tested different solvents on the conversion and 4-nitro selectivity of the reaction (Table 2). Among the solvents used, hydrocarbons provided lower yields. On the other hand, the chlorinated solvents, CCl_4 and dichloroethane (DCE) are proved to be the best entrainers for the effective removal of water azeotropi-
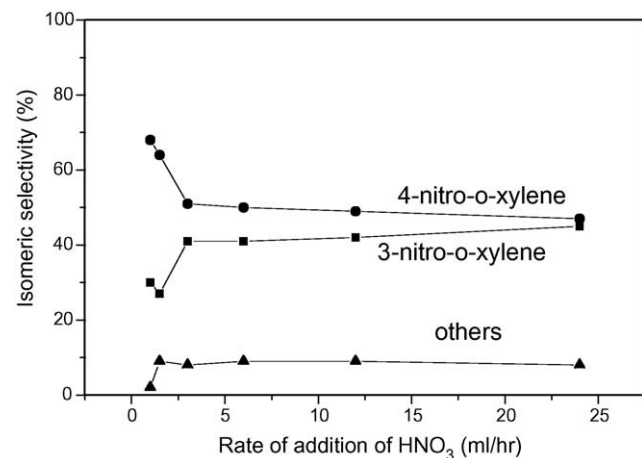
cally to provide higher conversions. Dichlormethane is not an effective entrainer, as it gives side products in large amounts. Dichloroethane was found to be the effective solvent providing high selectivity and conversions. This was also observed in the selective chlorination by Kale [26].

To observe the rate of change of conversion and selectivity with time, we followed the nitration reaction by GC at regular intervals of time during the reaction and the results were as shown in Fig. 2. The conversion gradually increases with increase of time, with consistent selectivity towards 4-nitro-*o*-xylene. Finally, *m*- and *p*-xylenes were also nitrated under similar conditions and the results were as shown in Table 3.

Table 2
Nitration of *o*-xylene with different solvents with beta zeolite[a]

Entry	Solvent	Conversion (%)	Selectivity (%)		
			3-Nitro	4-Nitro	Others
1	DCM	23.4	29.6	46.0	24.4
2	*n*-Hexane	<5	52.5	47.5	–
3	CCl_4	30.0	42.0	57.0	1.0
4	*n*-Heptane	10	43.0	57.0	–
5	DCE	42.0	30.0	68.0	2.0

[a] One hundred milligram catalyst, 10 mmols *o*-xylene; 12 mmols of 70% HNO_3; 6 ml of solvent, reflux; 1 h addition and 3 h temperature maintenance (beta zeolite with $SiO_2/Al_2O_3 = 22$).
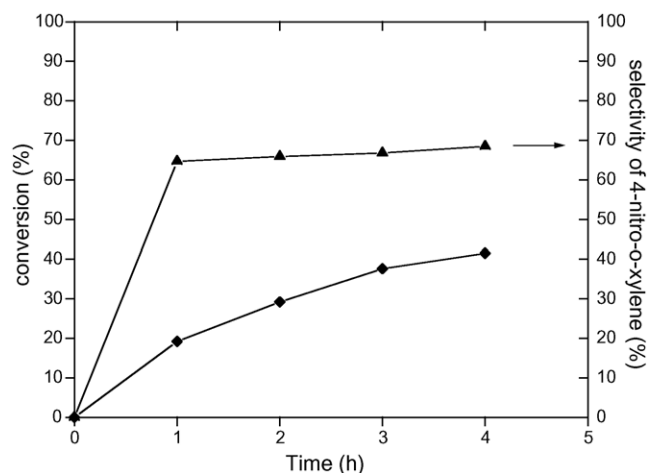

Fig. 2. Conversion and selectivity with time.

Table 3
Nitration of xylenes with beta zeolite catalyst

Entry	Substrate	Conversion (%)	Product distribution		
1	*o*-Xylene	42.0	30.0[a]	68.0[b]	2.0
2	*m*-Xylene	69.0	14.0[c]	86.0[d]	–
3	*p*-Xylene	55.0	–[e]		

[a] 3-Nitro-*o*-xylene.
[b] 4-Nitro-*o*-xylene.
[c] 2-Nitro-*m*-xylene.
[d] 4-Nitro-*m*-xylene.
[e] 2-Nitro-*p*-xylene (beta zeolite with $SiO_2/Al_2O_3 = 22$).

Fig. 1. Effect of rate of addition of nitric acid on isomeric selectivity in the nitration of *o*-xylene.
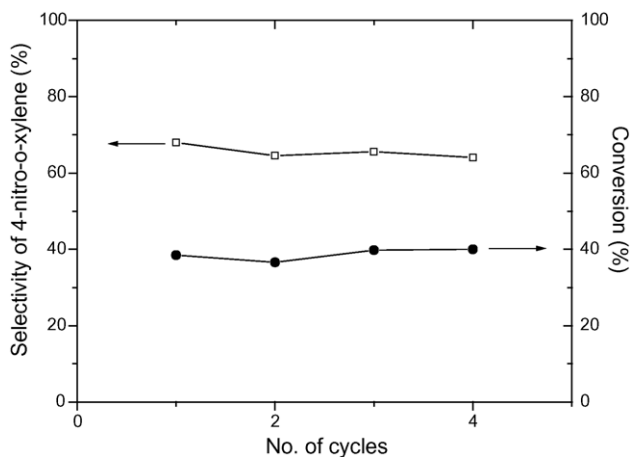
Fig. 3. Consistent activity of the catalyst.

3.5. Consistent activity of the catalyst

In order to test the activity of the catalyst, after the completion of the 4 h of the reaction, again 10 mmol of o-xylene and 12 mmol of 70% HNO_3 were added in the same manner as stated above and continued further for 4 h. Similarly, two more cycles were done and found that the activity and selectivity were retained (Fig. 3) for total four cycles. The XRD analysis of the used catalyst did not show any degradation in the framework of the zeolite. However, there is a considerable increase in the surface area and mesopore volume of the used catalyst as indicated by BET analysis.

4. Conclusion

In conclusion, a process for the nitration of o-xylene with enhanced regio-selectivity and activity was achieved by using beta zeolite catalyst having low SiO_2/Al_2O_3 ratio using nitric acid as nitrating agent and dichloroethane as the best entrainer. The higher regio-selectivity is attributed to the agglomeration of particles, while the higher activity is due to increased acidic sites prompted by high Al concentration.

This catalyst has the several advantages over conventional approach, viz., easy separation of catalyst by simple filtration, zero emission of effluents, higher regio-selectivities and more over its non-corrosive nature.

References

[1] G.A. Olah, R. Malhotra, S.C. Narang, Nitration Methods and Mechanism, VCH, New York, 1989, pp. 5–15.
[2] K. Schofield, Aromatic Nitration, Cambridge University Press, Cambridge, 1980.
[3] A. Cornelis, L. Delaude, A. Gerstmans, P. Laszlo, Tetrahedron Lett. 29 (1988) 5657.
[4] L. Delaude, P. Laszlo, K. Smith, Acc. Chem. Res. 26 (1993) 607.
[5] K. Smith, Bull. Soc. Chim. Fr. (1989) 272, and references therein.
[6] T.J. Kwok, K. Jayasuriya, R. Damavarapu, B.W. Brodman, J. Org. Chem. 59 (1994) 4939.
[7] G.A. Olah, R. Malhotra, S.C. Narang, J. Org. Chem. 43 (1978) 4628.
[8] B.M. Choudary, M. Ravichandra Sarma, K. Vijaya Kumar, J. Mol. Catal. 87 (1994) 33.
[9] H. Sato, K. Hirose, K. Nagai, H. Yoshika, Y. Nagaoka, Appl. Catal. A 175 (1998) 201.
[10] L. Bertea, H.W. Kouwenhoven, R. Prins, Appl. Catal. A 129 (1995) 229.
[11] K. Smith, A. Muson, G.A. DeBoos, J. Org. Chem. 63 (1998) 8448.
[12] F.J. Waller, A.G.M. Barrett, D.C. Braddock, D. Ramprasad, Chem. Commun. (1997) 613.
[13] M. Shi, S.C. Cui, J. Fluorine Chem. 113 (2002) 207.
[14] K.K. Laali, V.J. Gettwert, J. Org. Chem. 66 (2001) 35.
[15] B.M. Choudary, M. Sateesh, M.L. Kantam, K.K. Rao, K.V. Ramprasad, K.V. Raghavan, J. Chem. Soc. Chem. Commun. 1 (2000) 25.
[16] F.C. Rauch, G.M. Blanc, A.J. Fanelli, Appl. Catal. 9 (1984) 63.
[17] M.E. Kurz, L.A. Yang, E.P. Zahora, R.C. Adams, J. Org. Chem. 38 (1973) 2271.
[18] G.A. Olah, S.J. Kuhn, J. Am. Chem. Soc. 84 (1962) 3684.
[19] R.G. Coombes, L.W. Russel, J. Chem. Soc., Perkin Trans. 1 (1974) 1751.
[20] S. Uemura, A. Toshimitsu, M. Okano, J. Chem. Soc., Perkin Trans. 1 (1978) 1076.
[21] G.A. Olah, S.C. Narang, A.P. Fung, J. Org. Chem. 46 (1981) 2706.
[22] M.V. Landau, S.B. Kogan, D. Tavor, M. Herskowitz, J.E. Koresh, Catal. Today 36 (1997) 497.
[23] M. Tomaz, J. Jaroslav, Syn. Commun. 31 (2001) 173.
[24] M.L. Kantam, B.M. Choudary, N.S. Kumar, K.V.R. Prasad, K.V. Raghavan, EP 1,323,705 (2003).
[25] P.T. Patil, K.M. Malshe, S.P. Dagade, M.K. Dongare, Catal. Commun. 4 (2003) 429.
[26] S.M. Kale, A.P. Singh, J. Mol. Catal. 138 (1999) 263.