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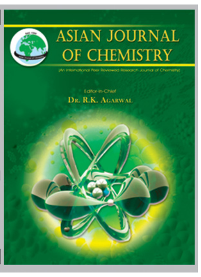

Zeolite-Assisted Regioselective Synthesis of Dinitronaphthalene

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Efficient methods of nitration of naphthalene or 1-nitronaphthalane with fuming nitric acid (wt. 95 %) in organic solvent over zeolite were investigated, where the regioselection of nitration can be improved and in certain cases the isomer ratio of nitration products can be reversed. The recovered zeolite was reused three times without appreciable loss of catalytic activity.

Key Words: Nitration, Regioselection, Synthesis, Dinitronaphthalene, Zeolite.

INTRODUCTION

Nitration of aromatic compounds is one of the most important chemical reactions and widely used in chemical industry. Classical nitration based on nitric acid and sulfuric acid is quite notorious, for the environmental pollution, potential danger of explosion, low regioselection, oxidative degradation byproducts and inefficient atomic economy. These disadvantages have encouraged extensive efforts to develop alternative methodologies to replace conventional nitration.

Given the ease of separation, recyclability and good regioselection, zeolite-based solid acid catalysts such as ZSM-5[1], Y[2], X[3] and beta[4] have been widely researched for nitration of various compounds. A variety of other solid acids such as sulfuric acid supported on silica[5], clay-supported metal nitrates[6], metal-exchanged clays[7], metal-modified montmorillonite KSF[8] and CMS-kaolinite[9] have also been broadly used for nitration of aromatic compounds. Our attention was drawn to zeolite catalysts.

The nitration of naphthalene has been widely studied[10]. We have recently reported that toluene[11], chlorobenzene[11] and 1-nitronaphthalane[12] can be nitrated with nitrogen dioxide in the presence of modified zeolite catalyst. In the present paper, we wish to report the nitration of naphthalene or 1-nitronaphthalane with fuming nitric acid (wt. 95 %) in organic solvent over zeolite, where the regioselection of nitration can be improved and in certain cases the isomer ratio of nitration products can be reversed.

EXPERIMENTAL

All reagents and solvents were commercially purchased. Hexane, dichloromethane, 1,2-dichloroethane, acetonitrile were dried over anhydrous Na_2SO_4, distilled and stored over molecular sieves. Catalysts FeBEA-25, CuBEA-25, CoBEA-25, CdBEA-25, LaBEA-25 were modified from HBEA-25 according to the reported procedures[12].

Nitration of naphthalene with fuming nitric acid in the presence of zeolite: Naphthalene (0.128 g, 1 mmol), fuming nitric acid (0.30 mL, 6 mmol, wt. 95 %), zeolite (0.260 g) and CH_2Cl_2 (5 mL) were placed in a three-neck flask. The mixture was stirred for 12 h at refluxing temperature. When the reaction was over, the zeolite was removed by filtration and the filter liquor was washed with $NaHCO_3$ (10 mL × 3) and water (10 mL × 3). The organic layer was separated, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give a yellow solid residue. The composition of which was analyzed by HPLC. The recovered zeolite was reused by washing and calcination.

Nitration of 1-naphthalene with fuming nitric acid in presence of zeolite: 1-Nitronaphthalene (0.173 g, 1 mmol), fuming nitric acid (0.20 mL, 4 mmol wt. 95 %), zeolite (0.173 g) and CH_2Cl_2 (5 mL) were placed in a three-neck flask. The mixture was stirred for 10 h at refluxing temperature. When the reaction was over, the zeolite was removed by filtration and the filter liquor was washed with $NaHCO_3$ (10 mL × 3) and water (10 mL × 3). The organic layer was separated, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give a yellow solid residue. The composition of which was analyzed by HPLC. The recovered zeolite was reused by washing and calcination.

Separation of dinitronaphthalene: Crude mixtures of dinitronaphthalene (5 g, from Table-3 run 8) was placed together with 50 mL acetone in a 100 mL flask, stirred and heated to reflux. The suspension was refluxing for 2 h and then cooled to 30 ºC by stirred and filtered quickly. The precipitate was recrystallized by acetone and 1,5-dinitronaphthalene as light yellow crystals (1.725 g) was got. Then the filter liquor was concentrated to one-thirds of original volume, filtered, the precipitate was recrystallized by toluene and 1,8-dinitronaphthalene as light yellow crystals (1.987 g) was got.

1, 5-Dinitronaphthalene: m.p. 215-216 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (t, 2H), 8.33 (d, 2H), 8.81 (d, 2H).

1, 8-Dinitronaphthalene: m.p. 172-173 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (t, 2H), 8.51 (dd, 4H).

RESULTS AND DISCUSSION

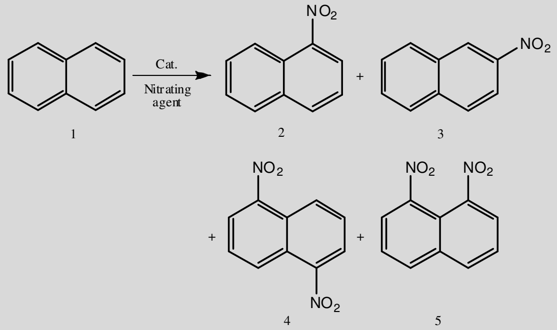
The nitration of naphthalene or 1-nitronaphthalane with fuming nitric acid (wt. 95 %) in organic solvent over zeolite was investigated. As shown in Table-1, with the traditional methodology involving a mixture of nitric acid and sulfuric acid and nitric acid (wt. 87 %) alone to prepare the dinitronaphthalene, the 1,5- : 1,8-dinitro isomer ratio was in the range of 0.4-0.7.

As shown (Table-2), when HBEA-25 was used as catalyst and CH_2Cl_2 as solvent, with the amount of catalyst increasing, better yield of **4** and **5** were got and 1,5- : 1,8-dinitro isomer ratio reached as high as 1.92. While more catalyst was used, a negative effect was got (runs 1, 4, 5 and 6). The amount of fuming nitric acid effected the result too (runs 2-4). The effect of different solvent in this reaction was evaluated. As revealed in Table-3, polar solvent systems appeared to play a negative role in attaining a higher 1,5-dinitronaphthalene and the yield

TABLE-1
NITRATION OF NAPHTHALENE WITH NITRIC ACID ALONE OR MIXED ACID

Entry	Nitrating agent	Reaction conditions	Yield (%)	Isomer proportion (%)		4:5 Ratio
1	HNO_3 (d = 1.42)-H_2SO_4 (d = 1.84)	No solvent, 0 ºC	91.0	33.1	66.9	0.49
2	HNO_3 (d = 1.42)-H_2SO_4 (d = 1.84)	$(CH_2Cl_2)_2$, 45 ºC	85.0	39.0	61.0	0.64
3	87 %-HNO_3	No solvent, 45 ºC	89.9	39.8	60.2	0.64
4	HNO_3 (d = 1.42)-H_2SO_4 (d = 1.84)	$(CH_3CO_2)O$, -10 ºC	91.3	31.2	68.8	0.45

TABLE-2
NITRATION OF NAPHTHALENE WITH FUMING NITRIC ACID (wt. 95 %) IN THE PRESENCE OF ZEOLITE[a]



Entry	Solvent	Catalyst[b]	Reaction time (h)	Conversion[c] (%)	Yield (%)[d]	Isomer proportion (%)[f]		Yield (%)[e]	Isomer proportion (%)[f]		4:5 Ratio
						2	3		4	5	
1	CH_2Cl_2	–	12.0	>99	70.4	89.4	10.6	25.0	35.2	64.8	0.54
2[g]	CH_2Cl_2	HBEA-25	12.0	>99	80.7	92.4	7.6	11.4	35.0	65.0	0.54
3[h]	CH_2Cl_2	HBEA-25	12.0	>99	48.4	88.8	11.2	40.2	58.1	41.9	1.38
4	CH_2Cl_2	HBEA-25[i]	12.0	>99	18.2	91.8	8.2	69.1	42.2	57.8	0.73
5	CH_2Cl_2	HBEA-25	12.0	>99	21.2	91.1	8.9	56.2	65.8	34.2	1.92
6	CH_2Cl_2	HBEA-25[j]	12.0	>99	38.8	91.6	8.4	50.1	42.7	57.3	0.75
7	CH_3CN	HBEA-25	12.0	>99	72.5	85.4	14.6	1.9	43.8	56.2	0.78
8	Hexane	HBEA-25	3.0	>99	3.5	78.2	21.8	75.5	44.4	55.6	0.80
9	EDC	HBEA-25	12.0	>99	72.4	88.5	11.5	9.6	39.4	60.6	0.65
10	CH_2Cl_2	HZSM-5	11.0	>99	2.7	>99	Trace	77.1	42.2	57.8	0.73
11	Hexane	HZSM-5	2.3	>99	2.6	94.2	5.8	84.1	44.9	55.1	0.81
12	CH_2Cl_2	HBEA-280	9.0	>99	59.3	88.9	11.1	31.9	33.9	66.1	0.51
13	CH_2Cl_2	HBEA-500	9.0	>99	5.0	91.8	8.2	82.0	42.2	57.8	0.73
14	CH_2Cl_2	FeBEA-25	6.3	>99	8.1	74.4	25.6	85.4	41.5	58.5	0.71
15	CH_2Cl_2	CuBEA-25	10.5	>99	60.3	89.0	11.0	24.9	48.7	51.3	0.95
16	CH_2Cl_2	CoBEA-25	6.2	>99	3.5	>99	trace	79.6	45.7	54.3	0.84
17	CH_2Cl_2	CdBEA-25	12.0	>99	45.1	88.8	11.2	37.8	46.0	54.0	0.85
18	CH_2Cl_2	LaBEA-25	12.0	>99	7.9	95.6	4.4	81.7	44.8	55.2	0.81

[a]All reactions were carried out in organic solvent (5.0 mL) using substrate **1** (1.0 mmol), fuming nitric acid (0.30 mL) and catalyst (0.260 g). When the organic solvent was CH_2Cl_2, the reaction was under refluxing; when the organic solvent was CH_3CN, EDC and hexane, the reaction temperature was controlled at 40 ºC. [b]Zeolites were calcined at 550 ºC for 2 h in air prior to use. [c]Determined by HPLC. [d]Combined yield of **2** and **3** based on consumed **1**. [e]Combined yield of **4** and **5** based on consumed **1**. [f]Calculated form HPLC peak areas, excluding other isomers and byproducts. [g]Fuming nitric acid (0.20 mL) and catalyst (0.173 g) were used. [h]Fuming nitric acid (0.25 mL) and catalyst (0.173 g) were used. [i]Catalyst (0.173 g) was used. [j]Catalyst (0.346 g) was used.

of **4** and **5** was low (run 5 and 7). When 1,2-dichloroethane (EDC) was used as solvent, the 1,5- : 1,8-dinitro isomer ratio and the yield of **4** and **5** were also inferior (run 5 and 9). The reaction was faster in hexane and the yield of **4** and **5** reached 75.5 % after a reaction of 3 h (run 8). The 1,5- : 1,8-dinitro isomer ratio was slightly higher than EDC and CH_3CN as solvent, but obviously lower than CH_2Cl_2. Thus CH_2Cl_2 was identified as the best solvent. Some other zeolites were investigated. HZSM-5 showed similarly results with HBEA-500, that, the yield was high, but the 1,5-site selectivity was relatively poor (runs 10 and 13). Both 1,5-site selectivity and yield of **4** and **5** were unsatisfactory with HBEA-280 (run 12). This may own to that the regioselection were affected by not only the size and shape of the pores in the zeolites but also surface of the zeolites. The metal-exchanged zeolites leaded to poor regioselection compared with HBEA-25. FeBEA-25 showed high yield of **4** and **5** but poor regioselection (run 14). On the contrary, CuBEA-25 and CdBEA-25 showed low yield of **4** and **5** but relatively high regioselection (runs 15 and 17). CoBEA-25 played similarly effects on the reaction with LaBEA-25 (runs 16 and 18).

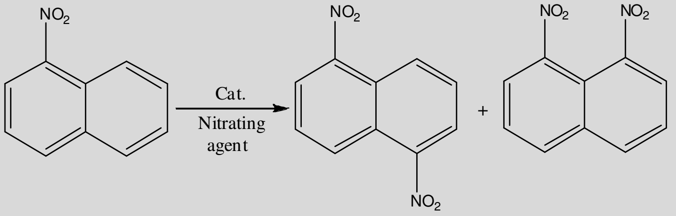
To compare with naphthalene, 1-nitronaphthalene as substrate was studied. As shown in Table-3, when HBEA-25 was used as catalyst and CH_2Cl_2 as solvent, both the increasing of the amount of catalyst and fuming nitric acid leaded to higher regioselection and conversion (runs 1-6). When the amount of catalyst was 1 g, the conversion reached 93.2 % and the 1,5- : 1,8-dinitro isomer ratio was 0.99. Noticeably, when 0.10 mL fuming nitric acid and 0.050 g HBEA-25 were used, the reaction showed the best 1,8-site selectivity (run 2). Then the effects of solvent for this reaction were evaluated. CH_3CN as solvent showed slightly high regioselection but low conversion (run 7). Both selectivity and conversion were satisfactory with hexane as solvent (run 8). When hexane was replaced by CH_2Cl_2, the 1,5- : 1,8-dinitro isomer ratio was nearly doubled (run 6, 8, 10 and 11). When 1,2-dichloroethane was used as solvent, the selectivity and conversion were both poor. (run 9). Some other zeolites were also investigated. When HZSM-5 and HBEA-500 were used as catalysts, the yield was high, but the 1,5-site selectivity was relatively poor (runs 10 and 13). HBEA-280 showed a slightly better 1,5-site selectivity, however the conversion was low (run 12). In five metal-exchanged zeolites, only CdBEA-25 played a positive role in attaining a higher 1,5- : 1,8-dinitro isomer ratio (run 17). FeBEA-25, CuBEA-25, CoBEA-25 and LaBEA-25 showed a higher conversion but poor regioselection.

Conclusion

In this work, the nitration of naphthalene or 1-nitronaphthalane with fuming nitric acid (wt. 95 %) in organic solvent over zeolite was reported. Compared with conventional nitration, the 1,5-site selectivity was remarkable improved and

TABLE-3

NITRATION OF 1-NAPHTHALENE WITH FUMING NITRIC ACID (wt. 95 %) IN THE PRESENCE OF ZEOLITE[a]



2 4 5

Entry	Solvent	Catalyst[b]	Reaction time (h)	Conversion[c] (%)	Yield[d] (%)	Isomer proportion (%)[e]		4:5 Ratio
						4	5	
1	CH_2Cl_2	–	10.0	40.8	32.6	30.0	70.0	0.43
2[f]	CH_2Cl_2	HBEA-25	9.0	15.2	8.1	19.0	81.0	0.23
3[g]	CH_2Cl_2	HBEA-25	5.5	93.2	51.0	49.8	50.2	0.99
4[h]	CH_2Cl_2	HBEA-25	10.0	52.8	37.7	30.6	69.4	0.44
5[i]	CH_2Cl_2	HBEA-25	10.0	78.7	57.8	33.3	66.7	0.50
6	CH_2Cl_2	HBEA-25	10.0	91.1	68.6	32.2	67.8	0.47
7	CH_3CN	HBEA-25	10.0	10.8	6.4	41.2	58.8	0.70
8	Hexane	HBEA-25	2.5	97.4	82.7	45.9	54.1	0.85
9	EDC	HBEA-25	10.0	17.6	12.4	31.6	68.4	0.46
10	CH_2Cl_2	HZSM-5	8.0	97.3	76.6	32.2	67.8	0.47
11	Hexane	HZSM-5	2.4	98.8	83.0	48.6	51.4	0.95
12	CH_2Cl_2	HBEA-280	11.0	46.8	35.6	40.7	59.3	0.69
13	CH_2Cl_2	HBEA-500	7.8	96.3	82.1	36.5	63.5	0.57
14	CH_2Cl_2	FeBEA-25	10.0	94.8	83.4	38.9	61.1	0.64
15	CH_2Cl_2	CuBEA-25	12.0	85.5	59.7	30.7	69.3	0.44
16	CH_2Cl_2	CoBEA-25	10.0	86.7	78.0	30.2	69.8	0.43
17	CH_2Cl_2	CdBEA-25	10.0	78.2	62.0	45.0	55.0	0.82
18	CH_2Cl_2	LaBEA-25	7.3	96.0	91.3	37.8	62.2	0.61

[a] All reactions were carried out in organic solvent (5.0 mL) using substrate **2** (1.0 mmol), fuming nitric acid (0.2 mL) and catalyst (0.173 g). When the organic solvent was CH_2Cl_2, the reaction was under refluxing; when the organic solvent was CH_3CN, EDC and hexane, the reaction temperature was controlled at 40 °C. [b] Zeolites were calcined at 550 °C for 2 h in air prior to use. [c] Determined by HPLC. [d] Combined yield of **4** and **5** based on consumed **2**. [e] Calculated form HPLC peak areas, excluding other isomers and byproducts. [f] Fuming nitric acid (0.10 mL) and catalyst (0.050 g) were used. [g] Catalyst (1.000 g) was used. [h] Catalyst (0.086 g) was used. [i] Fuming nitric acid (0.30 mL) and catalyst (0.086 g) were used.

in certain cases the isomer ratio of nitration products can be reversed. In addition, it is found that the regioselection was affected by not only the size and shape of the pores of the zeolites but also surface of the zeolites.

REFERENCES

1. (a) M.A. Bigdeli, M.M. Heravi and F. Nemati, *Synth. Commun.*, **37**, 2225 (2007); (b) B.M. Choudary, M. Sateesh, M. Lakshmi Kantam, K.K. Rao, K. V. Ram Prasad, K.V. Raghavan and J.A.R.P. Sarma, *Chem. Commun.*, 25 (2000).
2. (a) T. Essakkiduria and K.J. Pitchumani, *Mol. Catal. A.*, **185**, 305 (2002); (b) S. Samajdar and B.K. Banik, *Tetrahedron Lett.*, **41**, 8017 (2000); (c) A.M.M. Tanseem, K.C. Rajanna and P.K. Saiparakash, *Synth. Commun.*, **31**, 1123 (2001).
3. K. Smith, A. Musson and G. A. Doboos, *J. Org. Chem.*, **63**, 8448 (1998).
4. (a) K. Smith, T. Gibbins, R.W. Millar and R.P. Claridge, *J. Chem. Soc., Perkin Trans. I*, 2753 (2000); (b) S.K. Maurya, M.K. Gurjar, K.M. Malshe, P.T. Patil, M.K. Dongare and E. Kemnitz, *Green Chem.*, **5**, 720 (2003).
5. M.A. Zolfigol, E. Madrakian and E. Ghaemi, *Molecules*, **7**, 734 (2002).
6. (a) P. Laselo and P. Pennetreau, *J. Org. Chem.*, **52**, 2407 (1987); (b) A. Cornelis, P. Laszlo and P. Pennetreau, *J. Org. Chem.*, **48**, 4771 (1983); (c) B. Giganta, A.O. Prazeres, M.J. Marcelo-Curto, A. Cornelis and P. Laszlo, *J. Org. Chem.*, **60**, 3445 (1995); (d) S.M. Kemdeo, V.S. Sapkal and G.N. Chaudhari, *J. Mol. Catal. A: Chem.*, **323**, 70 (2010).
7. B.M. Choudary, M.R. Sarma and K.V. Kumara, *J. Mol. Catal. A*, **87**, 33 (1994).
8. W. Yin and M. Shi, *Tetrahedron*, **61**, 10861 (2005).
9. G.D. Yadav, P.M. Bisht and S.V. Lande, *Catal. Today*, **141**, 56 (2009).
10. (a) G.A. Olah, S.C. Narang and J.A. Olah, *Proc. Nat. Acad. Sci. USA*, **78**, 3298 (1981); (b) D.S. Ross, K.D. Moran and R. Malhotra, *J. Org. Chem.*, **48**, 2120 (1983); (c) A. Boughriet, C. Bremard and M. Wartel, *J. Electroanal. Chem.*, **225**, 125 (1987); (d) L. Eberson and F. Radner, *Acta Chem. Scand. B*, **34**, 739 (1980); (e) W.A. Pryor, G.J. Gleicher, J.P. Cosgeove and D.F. Church, *J. Org. Chem.*, **49**, 5189 (1984); (f) L. Eberson and F. Radner, *Acta Chem. Scand. B*, **39**, 343 (1985).
11. X. Peng, N. Fukui, M. Mizuta and H. Suzuki, *Org. Biomol. Chem.*, **1**, 2326 (2003).
12. X. Peng, H. Suzuki and C. Lu, *Tetrahedron Lett.*, **42**, 4357 (2001).