Res Chem Intermed
DOI 10.1007/s11164-012-0827-z

Zeolite-assisted regioselective mononitration of naphthalene with nitrogen dioxide/molecular oxygen

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Received: 29 May 2012 / Accepted: 20 September 2012

Abstract The nitration process using nitrogen dioxide and oxygen instead of the classical nitric acid–sulfuric acid system appears to be attractive and promising in the selective preparation of nitro compounds. The ratio of 1-nitronaphthalene isomer to 2-nitronaphthalene can reach 11 in a moderate yield of 60 % when the reaction is carried out in acetonitrile with 5.0 mmol naphthalene, 10 mmol nitrogen dioxide, and 0.13 g HZSM-5 under molecular oxygen atmosphere at −15 °C. The isomeric distribution of the product nitro-naphthalene was found to be superior to traditional methods. The zeolite could be easily regenerated and recycled and reused by simple work-up to give results similar to those obtained with the fresh catalyst.

Keywords Naphthalene · 1-Nitronaphthalene · Nitration · Nitrogen dioxide · Zeolite

Introduction

Nitration of aromatics is an important organic reaction in the preparation of intermediates of many compounds including pharmaceuticals, dyestuffs, explosives, pesticides, and so on [1–4]. However, the preparation of nitro compounds in industry still employs classical processes involving large quantities of nitric and sulfuric acid, which have many disadvantages [5–7], such as poor selectivity, over-nitration, oxidized byproducts, and waste acids. Therefore, it is urgent to develop an environmentally economic method for the preparation of nitro compounds.

In recent years, various clean nitration approaches have been explored which employ nitrogen oxides as nitrating agents, such as nitrogen dioxide [8, 9], dinitrogen tetroxide [10], dinitrogen pentoxide [11], etc., in the presence of some solid catalysts

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and supports [12–15]. A significant improvement of the isomer product ratios in the zeolite-assisted double Kyodai-nitration of toluene and chlorobenzene has been observed [16]. Especially, zeolite was a very attractive catalyst to make positive contributions to the positional selectivity in the novel nitration process. In this paper, we report the catalytic performance of zeolite for the mononitration of naphthalene with nitrogen dioxide as a nitration agent. Furthermore, the nitrogen dioxide/molecular oxygen system is a promising nitration process, while nitrogen dioxide and dioxygen are very cheap and easy for clean manufacture in industry.

Experimental

Regents and apparatus

^{1}H NMR spectra were determined in $CDCl_3$ on a Bruker 400 MHz spectrometer. TLC was performed with silica gel GF254 percolated on class plates, and spots were visualized with UV. HPLC (Shimadzu LC-10Avp Plus) was utilized to determine product isomer compositions. IR measurements were made on a Hitachi IR meter 260-10 for KBr pellets and only characteristic peaks were recorded. Melting points were determined on a WRS-2 apparatus and uncorrected. Zeolites were purchased from New Materials Research Center of Tianjin in China. All other chemicals were analytical grade without any further purification.

General procedure

Typical experimental procedure for zeolite cation-exchange

The standard procedure for cation-exchange involved stirring a supplied commercial zeolite (5.0 g) in a refluxing aqueous solution of the corresponding metal chloride (0.2 mol L^{-1}, 100 mL) for 24 h. The solid was filtrated, washed with deionized water until halide-free, and dried at 110 °C for 3 h, then calcined in air at 550 °C for 6 h.

Nitrate progress with nitrogen dioxide/molecular oxygen

Quantitative naphthalene, nitrogen dioxide, zeolite, and acetonitrile were placed in a flask. Oxygen was passed into the system to replace air, and a balloon filled with oxygen was connected. The mixture was stirred at a certain temperature and progress of the reaction was monitored by TLC. When the reaction was complete, excess nitrogen dioxide was removed by blowing air into the solution, and collected in a cold trap for reuse. The zeolite was removed by filtration and the filter liquor was washed with water, a 5 % aqueous solution of sodium bicarbonate followed by water. The organic phase thus separated was dried with anhydrous sodium sulfate, and concentrated under reduced pressure to give a yellow solid residue. The product was analyzed by HPLC. The yellow solid with further purification was analyzed by ^{1}H NMR. The used zeolite was recovered by washing and calcination.

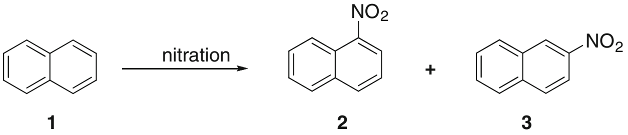
1-Nitronaphthalene ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.56$ (d, 1H), 8.23 (d, 1H), 8.12 (d, 1H), 7.96 (d, 1H), 7.72 (t, 1H), 7.62 (t, 1H), 7.54 (t, 1H); IR (KBr): 1,600, 1,569, 1,519, 1,339, 1,261, 872, 804, 789, 764 cm^{-1}.

2-Nitronaphthalene ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.75$ (s, 1H), 8.23 (d, 1H), 8.06–7.86 (m, 3H), 7.74–7.55 (m, 2H); IR (KBr): 1,630, 1,604, 1,531, 1,502, 1,442, 1,347, 1,081, 800, 769 cm^{-1}.

Results and discussion

1-Nitronaphthalene **2** is an important fine chemical with a constantly increasing world market owing to its usefulness as synthetic intermediates. The traditional method, using nitric acid and nitro-sulfuric acids, gave a mixture of 1-nitronaphthalene **2** and 2-nitronaphthalene **3** in the isomer ratio of around 4.3 and 5.0, respectively (entries 1 and 2 in Table 1). However, when substrate naphthalene **1** was subjected to the combined action of nitrogen dioxide and molecular oxygen, the formation of **2** was highly favored up to a ratio of 7.0–9.0 in **2–3** (entries 3–8 in Table 1), and an increase of the amount of nitrogen dioxide lowered the **2**:**3** mononitro isomer ratio. Moreover, a principal formation of dinitronaphthalenes of

Table 1 Nitration of naphthalene with nitrogen dioxide/molecular oxygen



Entry	Nitrating agent[a]	Reaction condition	Yield[b] (%)	Isomer proportion[c] (%)		2:3 ratio
				2	3	
1	HNO_3^d	CH_2Cl_2, reflux	76	81	19	4.3
2	HNO_3–$H_2SO_4^e$	CH_2Cl_2, 0 °C	93	82	18	5.0
3	NO_2–O_2 (1:2)	CH_3CN, reflux	72	89	11	8.3
4	NO_2–O_2 (1:4)	CH_3CN, reflux	87	88	12	7.0
5	NO_2–O_2 (1:6)	CH_3CN, reflux	71	84	16	7.3
6	NO_2–O_2 (1:2)	CH_3CN, 5 °C	73	90	10	9.1
7	NO_2–O_2 (1:4)	CH_3CN, 5 °C	82	89	11	8.4
8	NO_2–O_2 (1:6)	CH_3CN, 5 °C	70	85	15	8.1

[a] The ratio data in parentheses equal a molar amount in nitrogen dioxide to naphthalene. The reaction was carried out in acetonitrile (5.0 mL). The mixture was stirred at a certain temperature and the progress of the reaction was monitored by TLC

[b] Combined yield of **2** and **3** based on consumed **1**

[c] Proportion of products was determined by HPLC with nitrobenzene as internal standard

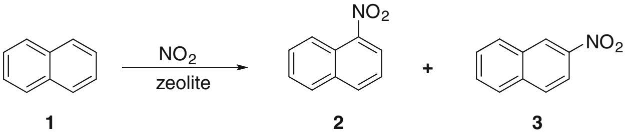
[d] The reaction was carried out in dichloromethane (5.0 mL) using **1** (5.0 mmol), 95 % nitric acid (10 mmol)

[e] The reaction was conducted in dichloromethane (5.0 mL) using **1** (5.0 mmol), 95 % nitric acid (10 mmol) and 98 % sulfuric acid (10 mmol)

1,5- and 1,8-dinitro isomers was produced. It was found that catalysts play important roles in the improvement of the regioselectivity. Some typical results are shown in Table 2.

Current trends in the nitration of aromatic compounds emphasize minimizing byproduct formation and improving regioselective of the desired isomer product by using a zeolite catalyst. Smith et al. [17] have reported that halobenzenes could be nitrated with nitrogen dioxide and molecular oxygen in the presence of zeolite HBEA catalyst to give products of nitration, in which the *para*-nitro isomer predominated over the *ortho*-isomer, while Suzuki and co-workers [8] reported that ZSM-5 appeared to have better catalytic selective characteristics. In the hope of improving the selectivity of 1-nitronaphthalene in the NO_2–O_2–zeolite system, hydrogen and its metal ion-exchanged BEA and ZSM-5 zeolites were employed.

Table 2 The effect of zeolite type on the nitration of naphthalene with nitrogen dioxide/molecular oxygen



Entry	Zeolite[a]	Temp. (°C)	Yield[b](%)	Isomer proportion[c](%)		2:3 ratio
				2	3	
1	HBEA-25	5 °C	74	83	17	4.9
2	HBEA-500	5 °C	73	85	15	5.7
3	HBEA-25	reflux	58	84	16	6.1
4	HBEA-150	reflux	72	85	15	5.7
5	HBEA-280	reflux	67	85	15	5.7
6	HBEA-500	reflux	64	86	14	6.1
7	CdBEA-25	reflux	56	86	14	6.1
8	CuBEA-25	reflux	77	86	14	6.1
9	FeBEA-25	reflux	77	85	15	5.7
10	LaBEA-25	reflux	80	84	16	6.1
11	CoBEA-25	reflux	68	84	16	6.1
12	HZSM-5	5 °C	70	91	9.0	10
13	CoZSM-5	5 °C	52	90	10	9.0
14	MgZSM-5	5 °C	54	90	10	9.0
15	CuZSM-5	5 °C	58	90	10	9.0
16	CdZSM-5	5 °C	74	90	10	9.0

All reactions were carried out in acetonitrile (5.0 mL) using substrate **1** (0.64 g, 5.0 mmol), liquid NO_2 (0.31 mL, 10 mmol) and catalyst (0.13 g). Oxygen was passed into the system to replace air, and a balloon filled with oxygen was connected. Acetonitrile was dried over 0.4 nm molecular sieves

[a] Zeolites were calcined at 550 °C for 2 h in air prior to use

[b] A combined yield of **2** and **3** based on consumed **1** is given

[c] Proportion of products was determined by HPLC with nitrobenzene as internal standard

Zeolite BEA was used as catalyst because preliminary screening suggested that it was quite active. And ZSM-5, a medium-pore zeolite, was included for comparison. Additionally, variation of the cation-exchanged zeolites was undertaken, with Co^{2+}, Cd^{2+}, Cu^{2+}, Fe^{3+}, and La^{3+} being used in the case of zeolite BEA-25, and Mg^{2+}, Co^{2+}, Cd^{2+}, and Cu^{2+} in the case of zeolite ZSM-5. Thus, the effects of pore size, channel structure, acidity, and cation size could be assessed. The results are shown in Table 2.

With the Si/Al ratio increasing of HBEA, a high ratio of formation of 1-nitronaphthalene was favored (entries 1–6 in Table 2). It may be due to the dealuminiation modifying the distribution of the size and shape of pores in the zeolites. However, with an increasing Si/Al ratio, the yield was lowered, probably because of the lower density of the effective catalytic sites.

Several metal ion-exchanged BEA-25s were tested in an attempt to find an even more selective catalyst. Among all the metal ion-exchanged zeolites, LaBEA-25 was observed to give a maximum yield of 80 % with 6.1 1-nitronaphthalene selectivity (entry 10 in Table 2). It may be that rare earth cation-exchanged zeolite would display both Lewis and Brφnsted types of acidity due to a high charge density which generated acidic hydroxyl groups inside the zeolite cavities. Otherwise, HZSM-5 displayed better 1-nitronaphthalene selectivity than zeolite BEA, while their difference was slight in total product yield (entry 12 in Table 2). It may be that HZSM-5 zeolite is a strong acid catalyst. Interestingly, the nature of the cation present appeared to have a negligible effect on the selectivity, the Co, Mg, Cu, and Cd forms of the ZSM-5 zeolites giving the same results for each reaction.

The effect of temperature on the reaction was investigated and the results are reported in Table 3. The results showed that the selectivity of 1-nitronaphthalene decreased with increasing temperature. Lower temperatures were preferable since the activation energy to generate 2-nitronaphthalene is higher than for 1-nitronaphthalene.

HZSM-5 was easily recovered to reuse from the reaction mixture by simple filtration (Table 4). Even after three times usage there was only a slight observed change in nitration selectivity and yield with little loss of original activity.

Table 3 Effect of reaction temperature in the nitration of naphthalene

Entry	Temp. (°C)	Yield[a] (%)	Isomer proportion[b] (%)		2:3 ratio
			2	3	
1	−15	60	92	8.0	11
2	5	54	91	9.0	10
3	25	49	89	11	8.5
4	45	78	87	13	6.5
5	65	61	84	16	5.3

All reactions were carried out in acetonitrile (5.0 mL) using substrate **1** (0.64 g, 5.0 mmol), NO_2 (0.31 mL, 10 mmol) and HZSM-5 (0.13 g). Acetonitrile was dried over 0.4 nm molecular sieves

[a] A combined yield of **2** and **3** based on consumed **1** is given

[b] Proportion of products was determined by HPLC with nitrobenzene as internal standard

Table 4 Efficiency of recycled HZSM-5 in the nitration of naphthalene

Entry	Yield[a] (%)	Isomer proportion[b] (%)		2:3 ratio
		2	3	
Fresh	69	92	8.0	11
1	67	91	9.0	10
2	65	90	10	9.0
3	64	90	10	9.0

Besides the 0.4 g catalyst employed, other conditions were the same as those given in Table 2. Acetonitrile was dried over 0.4 nm molecular sieves

[a] A combined yield of **2** and **3** based on consumed **1** is given

[b] Proportion of products was determined by HPLC with nitrobenzene as internal standard

Conclusion

Nitration of naphthalene in the presence of zeolites with a nitrogen dioxide/molecular oxygen system can show higher 1-nitronaphthalene selectivity in moderate yield. Furthermore, this system was atom economic to elemental reactions for organic intermediates by means of clean, cheap and readily available molecular oxygen. The solid catalysts can be recovered and reused with the avoidance of the toxic waste generated by traditional mineral acid catalysts. Moreover, the present reaction could provide a promising methodology for the clean synthesis of nitro compounds.

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