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Zeolite-assisted nitration of biphenyl using nitric acid

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Abstract The nitration process using 95 % nitric acid instead of the classical nitric acid–sulfuric acid system appears to be attractive and promising in the preparation of nitro compounds. The ratio of 2-nitrobiphenyl (**2a**) isomer to 4-nitrobiphenyl (**2b**) can reach 0.69 in a good yield of 78.42 %. The isomeric distribution of the product mononitrobiphenyl was found to be superior to traditional methods. Raising the ratio of 95 % nitric acid and biphenyl to 4:1, the yield of dinitration products can reach more than 78.08 %, as a mixture of 2,2′-dinitrobiphenyl (**3a**), 2,4′-dinitrobiphenyl (**3b**), and 4,4′-dinitrobiphenyl (**3c**).

Keywords Biphenyl · Mononitrobiphenyl · Dinitrobiphenyl · Nitration · Nitric acid · Zeolite

Introduction

Nitration of aromatics is one of the broadly studied organic reactions as nitro aromatic compounds are industrially important intermediates during the synthesis of dyes, explosives, and pharmaceuticals [1, 2]. The nitro derivatives of biphenyl isomers are used as intermediates for the preparation of fragrance, dyes, and plastics. Nitration of biphenyl by using nitric acid and sulfuric acid or acetic anhydride as the nitrating mixture gives a mixture of 4-nitrobiphenyl 30–56 % and 2-nitrobiphenyl 43–69 % [3, 4]. Except for the low yield of 4-nitrobiphenyl, generation of dilute acid waste poses costly and environmental problems. Recently, many new methods [5–8] for the nitration of biphenyl have been reported with the yield of 4-nitrobiphenyl about 70 %. Yuan et al. [9] have carried out the nitration of

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biphenyl and other aromatic compounds using 65 % nitric acid at reflux temperature over MCM-41-supported metal bis[(perfluoroalkyl)sulfonyl]imides with 98.8 % yield of mononitration production. The yield of 4-nitrobiphenyl only 34–43 % was achieved by using liquid $Ag_{0.51}$ $K_{0.42}Na_{0.07}$ NO_3 [10] and by using nitric acid over $H_3PO_4/TiO_2–ZrO_2$ [11]. However, none of them mentioned the dinitration of biphenyl.

In pursuit of our previous efforts on the nitration of toluene, chlorobenzene and naphthalene [12–14] using solid acid catalysts, we have studied the nitration of biphenyl over modified ZSM-5 catalysts by using 95 % HNO_3. The outcomes are reported in this paper.

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. GC 2014-C (WONDACAP-1 df = 1.5 μm 0.53 mm I.D × 30 m) was utilized to determine product isomer compositions. Melting points were determined on a WRS-2 apparatus and uncorrected. Zeolites were purchased from New Materials Research Center of Tianjin, 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 (2.50 g) in a refluxing aqueous solution of the corresponding metal chloride (0.2 mol/L, 50 mL) for 24 h. The solid was filtrated, washed with deionized water until halide-free and dried at 110 °C for 6 h, and then calcined in air at 550 °C for 6 h.

Nitrate progress with 95 % nitric

Quantitative biphenyl, nitric acid, zeolite, and dichloromethane were placed in a flask. The mixture was stirred at reflux temperature and progress of the reaction was monitored by TLC. When the reaction was complete, the zeolite was removed by filtration and the filter liquor was washed with water, 5 % aqueous solution of sodium bicarbonate followed by water. The organic phase separated was dried with anhydrous sodium sulfate, and filtrated to give a straw yellow liquid residue. The product was analyzed by GC. The straw yellow liquid with further purification by column chromatography was analyzed by ^{1}H NMR. The used zeolite was recovered by washing and calcination.

2-Nitrobiphenyl yellow oil ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.8$ (d, 1H), 7.6 (d, 1H), 7.5 (m, 1H), 7.4 (m, 4H), 7.3 (m, 2H).

4-Nitrobiphenyl white solid ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.3$ (m, 2H), 7.7 (m, 2H), 7.6 (d, 2H), 7.5(d, 2H), 7.4 (d, 1H).

2,4′-Dinitrobiphenyl yellow solid ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.2$ (d, 2H), 8.0 (d, 1H), 7.7 (t, 1H), 7.6 (t, 1H), 7.5 (d, 2H), 7.4 (d, 1H).

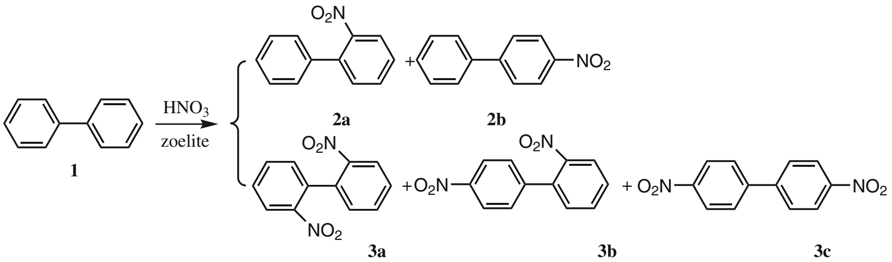
2,2′-Dinitrobiphenyl yellow solid ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.3$ (d, 2H), 7.7 (t, 2H), 7.6 (t, 2H), 7.3 (d, 2H);

4,4′-Dinitrobiphenyl yellow solid ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.4$ (d, 4H), 7.7 (d, 4H).

Results and discussion

The nitration of biphenyl with 95 % nitric acid alone gives a mixture of 2-nitrobiphenyl (**2a**), 4-nitrobiphenyl (**2b**), 2,2′-dinitrobiphenyl (**3a**), 2,4′-dinitrobiphenyl (**3b**), and 4,4′-dinitrobiphenyl (**3c**) (Scheme 1). Nitrobiphenyl are important fine chemicals with a constantly increasing world market owing to its usefulness as synthetic intermediates. When the reaction was carried out in nitric acid zeolite catalysts system, the yield was higher than nitric acid system alone. The result was shown in Tables 1 and 2.

The method simply using nitric acid gave a mixture of 2-nitrobiphenyl (**2a**) and 4-nitrobiphenyl (**2b**) in the isomer ratio of 0.91 (Table 1, entry 1). However, when substrate biphenyl **1** was subjected to the combined action of nitric acid and zeolites, the formation of **2b** was slightly favored up to a ratio of 0.62–0.83 (Table 1, entries 2–11). Furthermore, the reaction time becomes shorter and the yield is promoted in the existence of the zeolites. From these results, it is evident that, among the catalysts used, Fe^{3+}–ZSM zeolite was more active in the reaction. The activity of the zeolites may be due to the existence of stronger acid sites and metal cations, which can easily prompt the production of hydrogen ions (Scheme 2).



Scheme 1 .

Table 1 The effect of zeolites type on the nitration of biphenyl with 95 %HNO_3

Entry	Zeolites	Yield of 2 (%)	**2a**:**2b** ratio	Yield of **3** (%)	**3a**:**3b**:**3c** ratio
1	None	70.48	0.91	13.00	33:48:18
2	H^+-ZSM	67.86	0.78	14.82	38:8:54
3	Mg^{2+}-ZSM	75.66	0.69	15.81	34:46:19
4	Fe^{3+}-ZSM	78.42	0.69	9.06	32:51:16
5	La^{3+}-ZSM	74.11	0.88	7.28	31:50:19
6	Cd^{2+}-ZSM	75.11	0.83	12.54	37:49:13
7	Co^{2+}-ZSM	64.43	0.76	15.71	40:44:16

All reactions were carried out in dichloromethane (5.0 mL) using substrate **1** (4.0 mmol), 95 % HNO_3 (8 mmol) and catalyst (0.13 g). Zeolites were calcined at 550 °C for 2 h in air prior to use. The proportion of products was determined by GC with 4-nitrotoluene as internal standard

Table 2 Dinitration of biphenyl with 95 %HNO_3

Entry	Zeolites	Time (h)	Yield of **2** (%)	Yield of **3** (%)	**3a**:**3b**:**3c** ratio
1	None	90	9.64	55.48	25:43:30
2	H^+-ZSM	50	4.29	75.04	27:46:27
3	Mg^{2+}-ZSM	40	2.89	70.91	22:44:33
4	Fe^{3+}-ZSM	40	Trace	78.08	22:45:32
5	La^{3+}-ZSM	47	Trace	70.09	24:48:28
6	Cd^{2+}-ZSM	40	1.99	69.37	26:54:19
7	Co^{2+}-ZSM	90	5.05	75.78	23:48:29

All reactions were carried out in dichloromethane (5.0 mL) with substrate **1** (0.62 g, 4.0 mmol), 95 % HNO_3 (0.72 mL, 16 mmol) and catalyst (0.13 g). Zeolites were calcined at 550 °C for 2 h in air prior to use. The proportion of products was determined by GC with 4-nitrotoluene as internal standard

$$\text{ZSM-5-M}^+ + HNO_3 \longrightarrow \text{ZSM-5-M}^+NO_3^- + H^+$$

$$HNO_3 + H^+ \longrightarrow NO_2^+ + H_2O$$

$$NO_2^+ + \text{ArH} \longrightarrow \text{ArH-}NO_2 + H^+$$

Scheme 2 .

A few dinitration products were observed when the molar ratio of 95 % nitric acid to substrate was 2:1. Raising the ratio to 4:1, the dinitration of biphenyl was promoted. As shown in Table 2, the yield of dinitration products can reach 78.08 %, as a mixture of 2,2-(**3a**), 2,4-(**3b**), and 4,4-(**3c**) dinitro products and a negligible amount of mononitration products. However, the presence of zeolites did not improve the regioselectivity towards the dinitration isomer, although it markedly affects the overall reaction rate and the product yield.

There are two feasible explanations for the insufficiency of zeolite catalysis. The one is the pores of zeolite are too small for the dinitrated products to be formed in

Table 3 Effect of reaction temperature in the nitration of biphenyl

Entry	Temp. (°C)	Time (h)	Conversion	Yield of **2** (%)	**2a**:**2b** ratio	Yield of **3** (%)
1	−20	100	75.4	70.21	0.69	0.31
2	0	100	89.9	81.84	0.70	0.72
3	20	80	99.1	83.39	0.70	1.27
4	Reflux	20	>99	78.42	0.69	9.06

All reactions were carried out in dichloromethane (5.0 mL) with substrate **1** (0.62 g, 4.0 mmol), 95 % HNO_3 (0.36 mL, 8 mmol) and catalyst (0.13 g). Zeolites were calcined at 550 °C for 2 h in air prior to use. The proportion of products was determined by GC with 4-nitrotoluene as internal standard

Table 4 Efficiency of recycled Fe^{3+}ZSM-5 in the nitration of naphthalene

Entry	Yield of **2** (%)	**2a**:**2b** ratio	Yield of **3** (%)	**3a**:**3b**:**3c** ratio
Fresh	78.42	0.69	9.06	32:51:16
1	78.11	0.73	8.97	33:47:19
2	77.06	0.73	7.63	32:49:18
3	76.88	0.69	8.05	34:48:17
4	74.51	0.71	7.45	33:48:18

All reactions were carried out in dichloromethane (5.0 mL) with substrate **1** (0.62 g, 4.0 mmol), 95 % HNO_3 (0.36 mL, 8 mmol) and catalyst (0.13 g). Zeolites were calcined at 550 °C for 2 h in air prior to use. The proportion of products was determined by GC with 4-nitrotoluene as internal standard

them. The other is the concentration of 95 % nitric acid is so high that the solution reaction occurs very fast; therefore, the reactants do not have time to diffuse into the pore and so the reaction occurs mainly in free solution or at the external surface of the zeolites.

The effect of temperature on the reaction was also studied and the results are reported in Table 3. At reflux temperature, a slight decrease in yield was observed but with no effect on selectivity. This can be explained by loss from the system of NO_2 which was seen to evolve from the reaction system. Therefore, a decrease in the concentration of 95 % HNO_3 is obtained and so the side reaction of oxidation is increased. However, if the temperature is low, then a long reaction time is observed; hence, the optimal temperature was found to be reflux.

During the recycling investigation, the catalyst Fe^{3+}ZSM-5 was recycled five times and the yield of **2** decreased from 78.42 to 74.51 % without any appreciable change in product selectivity, which shows the stability of the catalyst in the reaction environment. The results of the recycling investigation are shown in Table 4.

Conclusion

Zeolites are effective catalysts for nitrating biphenyl. Nitration of biphenyl over zeolites with 95 % nitric acid can show higher 4-nitronaphthalene selectivity in good yield. Furthermore, when the amount of nitric acid is increased, the product of dinitrobiphenyl is achieved. The solid catalysts can be recovered and reused, with the avoidance of poisonous waste generated by traditional strong Lewis acid catalysts. Moreover, the present reaction could provide a benign method for the clean preparation of other aromatic nitro compounds.

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