Improved Regioselective Di-nitration of Biphenyl over Reusable HBEA-500 Zeolite

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Nitration of aromatics is one of the most broadly studied and famous non-selective organic reaction which provides key organic intermediates or energetic materials.[1-4] However, the industrial syntheses of nitro compounds suffer many disadvantages: employing large quantities of sulfuric acids as catalysis, which may generate acid waste that is expensive to dispose off, over nitration, low selectivity, oxidation by-products and safety problems. Major efforts have therefore been made to dispense the use of sulfuric acid for the aromatic nitration and develop environmentally benign and clean processes to replace conventional nitration.[5-8]

The nitro derivatives of biphenyl are used as intermediates for the preparation of fragrance, dyes, plasticizer and polymer. The earlier attempts of nitration of biphenyl derivatives have been made by using nitric acid and sulfuric acid or acetic anhydride as the nitrating mixture gives a mixture of 4-nitrobiphenyl and 2-nitrobiphenyl.[9,10] Recently, many new methods of the nitration of biphenyl were reported.[11-17] However, few of them mentioned about the di-nitration of biphenyl. Thus, it is necessary to develop a clean and commercial process for the selective di-nitration of biphenyl in high conversion and yield.

In pursuit of our former efforts on nitration of toluene, chlorobenzene, naphthalene and biphenyl[18-21] using zeolite catalysts, we hope to improve the selectivity and yield in the di-nitration of biphenyl by the use of zeolite.

Catalysts always play an important role in the kinetics of chemical reactions, thereby influencing the selectivity of a desired isomer directly. Zeolites have well-defined pore structures and channels that are derived from the networking of SiO_2 and Al_2O_3 making them attractive candidates for shape selective catalysis.[22]

To optimize the reaction time for maximum di-nitration yield, samples were analyzed at varied time ranging from 1 to 24 h. The main data (Table 1) showed that the highest di-nitration yield was obtained at 24 h with HBEA-500 (0.3 g) zeolite as a catalyst.

Zeolites facilitated the reaction and gave a high di-nitration yield as compared with no catalyst (Entry 1 Table 1). With the Si/Al ratio increasing of HBEA zeolite catalyst, a high ratio of formation of 4,4'-dinitrobiphenyl **3c** was favored (Entries 3-8, from Table 1). HBEA zeolite catalyst with a low Si/Al ratio showed a worse selectivity for **3c** than that of high Si/Al ratio possibly because of the dealuminiation, which would modify the distribution of the size and shape of the pores in zeolites. The average particle sizes of the HBEA zeolites decrease with Si/Al ratio which was detected from the SEM images. High alumina containing zeolites show a very-hydrophilic character, whereas, high

Table 1. Nitration of biphenyl with nitric over catalyst

Entry	Catalyst	Time (h)	Yield of **2** (%)[a]	Yield of **3** (%)[a]	Isomer proportion **3a** : **3b** : **3c** (%)[b]
1	none	24	66.70	20.55	29 : 61 : 10
2	HZSM-5	24	66.66	25.12	19 : 60 : 21
3	HBEA-25	1	46.38	44.99	6 : 37 : 57
4	HBEA-25	24	17.73	73.56	6 : 51 : 43
5	HEBA-280	1	14.98	76.00	4 : 43 : 52
6	HEBA-280	24	2.09	89.19	3 : 53 : 44
7	HEBA-500	1	12.88	79.80	3 : 46 : 50
8	HEBA-500	24	1.40	90.89	3 : 52 : 45
9[c]	H_2SO_4	4	trace	92.02	13 : 44 : 42

[a]Combined yield of products based on consumed substrate. [b]Proportion of products was determined by GC with 4-nitrotoluene as internal standard. [c]Reaction was carried out in dichloromethane (5.0 mL) using biphenyl (4.0 mmol), and a mixture of 65% HNO_3 (16 mmol) and 98% H_2SO_4 (16 mmol) was added dropwise with stirring in an ice bath, then reflux for 4 h.
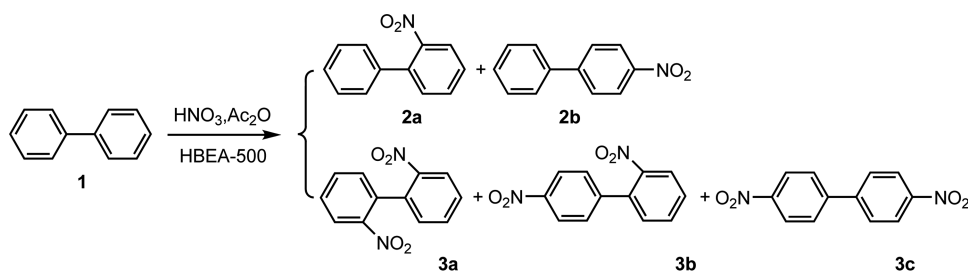
Scheme 1
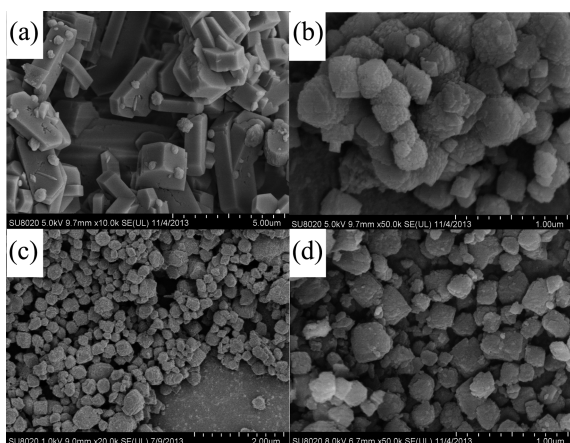
Figure 1. SEM images: (a) HZSM-5, (b) HBEA-25, (C) HBEA-500, (d) HBEA-500 used 4 cycles.

silica containing zeolites tend to be more hydrophobic.[23] In addition, the dimensionality of the zeolite channels needs to be considered. HZSM-5, a medium-pore zeolite, was included for comparison. Both selectivity and di-nitration yield were unsatisfactory with zeolite HZSM-5 (Entry 2, from Table 1). This may be attributed to the medium pore size structure, which would place more restriction on the transport of the substrate through the pores and the dinitrated products can not be formed within them. Among all the zeolite catalyst, HBEA-500 displayed the best **3c** isomeric proportion of 45% and di-nitration yield 90.89% (Entry 8, from Table 1).

The effect of HBEA-500 catalyst quantity on the selectivity was investigated (Table 2). Increasing the amount of the catalyst improved the regioselectivity of **3c** and the yield of di-nitration. These could be due to the higher internal/external surface area, in which the accessible amount of the acid sites of the catalyst increased. However, the use of a large amount of catalyst would cause the absorption of substrate and products, resulting in a bit decrease in the yield of di-nitration.

The effect of temperature on the reaction was also studied and the results were shown in Table 3. At 10 °C, a lower yield of di-nitration but higher selectivity of **3c** were

**Table 2.** Effect of amount of HBEA-500

Entry	HEBA-500 (g)	Yield of **2** (%)[a]	Yield of **3** (%)[a]	Isomer proportion **3a** : **3b** : **3c** (%)[b]
1	0.12	6.27	86.21	4 : 57 : 39
2	0.24	1.65	89.52	3 : 53 : 44
3	0.36	0.54	91.31	3 : 47 : 51
4	0.48	0.47	92.12	2 : 44 : 54
5	0.60	trace	92.49	2 : 42 : 56
6	0.72	trace	92.37	2 : 38 : 60
7	0.84	trace	92.15	2 : 37 : 61

[a]Combined yield of products based on consumed substrate. [b]Proportion of products was determined by GC with 4-nitrotoluene as internal standard.

Table 3. Effect of reaction temperature in the nitration of biphenyl

Entry	Temp. (°C)	Yield of **2** (%)[a]	Yield of **3** (%)[a]	Isomer proportion **3a** : **3b** : **3c** (%)[b]
1	-15	5.21	88.31	4 : 57 : 39
2	-5	1.40	90.89	3 : 52 : 45
3	10	1.25	83.85	3 : 50 : 47
4	35	0.98	82.92	3 : 49 : 48

[a]Combined yield of products based on consumed substrate. [b]Proportion of products was determined by GC with 4-nitrotoluene as internal standard.
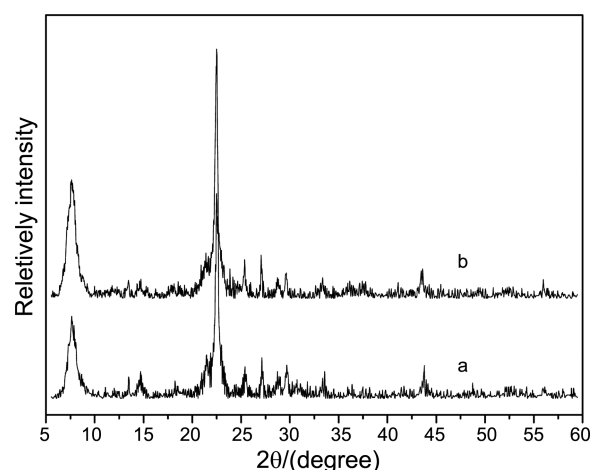
Figure 2. XRD patterns: (a) fresh HBEA-500, (b) HEBA-500 used 4 cycles.

observed. The lower yield can be explained by formation of side-product which was detected as orange color in the reaction at 10 °C. So, lower temperature was preferable for good yield. However, if the temperature was too low, then a decrease in di-nitration yield was observed. This could be ascribed to by low reaction rate. Hence, the optimal temperature was −5 °C.

HBEA-500 was easily recovered from the reaction mixture by simple decantation or filtration and could be reused. The XRD spectrum of fresh and used 4 cycles catalyst showed the reflections at 2θ 7.6 and 22.5, exhibit presence of similar structure of BEA zeolite. SEM showed the same results. Therefore, it was observed that with increase in the

Table 4. Efficiency of recycled HBEA-500 in the nitration of biphenyl

Entry	Yield of **2** (%)[a]	Yield of **3** (%)[a]	Isomer proportion **3a** : **3b** : **3c** (%)[b]
fresh	trace	92.51	2 : 37 : 61
1	trace	92.52	2 : 37 : 61
2	trace	92.43	2 : 37 : 61
3	trace	91.05	2 : 38 : 60
4	trace	91.45	2 : 38 : 60

[a]Combined yield of products based on consumed substrate. [b]Proportion of products was determined by GC with 4-nitrotoluene as internal standard.

Notes

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number of usage times of the catalyst, its catalytic activity was slight decreased after four usage times. The yield of di-nitration product was only decreased from 92.15% to 91.45%, and the yield of **3c** was also slightly decreased.

In conclusion, a clean and higher para-selective process for the di-nitration of biphenyl was described in this paper, compared to the incumbent process using nitric and sulfuric acid. Therefore, the present process will provide a general and practical method for the synthesis of nitro compounds. The catalyst was readily recyclable and we believe this to be a major step forward in the area of clean technology for aromatic nitration.

Experimental

General Procedure of Nitration. All reactions were carried out in a 50 mL one-necked round bottomed flask equipped with a water condenser and a magnetic stirrer. In a typical experiment, a mixture of zeolite HBEA-500 (0.30 g) which was calcined at 550 °C for 2 h in air prior to use, biphenyl (0.61 g, 4 mmol), nitric acid (95%, 0.35 mL, 8 mmol) was stirred in acetic anhydride (5.0 mL) at −5 °C for 24 h. When the reaction was over, 10 mL of dichloro-methane was added, then the zeolites was removed by filtration and the filtrate was washed with water (3 × 10 mL) and 5% aqueous solution of $NaHCO_3$ (10 mL) and water (3 × 10 mL). The organic phase separated was dried with anhydrous sodium sulfate, and filtrated to give a straw yellow liquid. The isomer distribution and yields of products were estimated from the peak areas based on the internal standard technique using gas chromatography. The straw yellow products with further purification by column chromato-graphy, and were identified by comparison of their analytical data with those of authentic samples.

Catalyst Regeneration. The used zeolite was recovered from the reaction mixture by filtration and washed with dichloromethane. The catalyst was dried at 110 °C for 4 h in the oven and ground into powder, then, calcined at 550 °C for 6 h.

^{1}H-NMR of Nitrated Products: 2-Nitrobiphenyl yellow oil ^{1}H NMR (400 MHz, CDCl$_3$) δ 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$_3$) δ 8.3 (m, 2H), 7.7 (m, 2H), 7.6 (d, 2H), 7.5 (d, 2H), 7.4 (d, 1H).

2,2'-Dinitrobiphenyl Yellow Solid: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.3 (d, 2H), 7.7 (t, 2H), 7.6 (t, 2H), 7.3 (d, 2H).

2,4'-Dinitrobiphenyl Yellow Solid: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.2 (d, 2H), 8.0 (d, 1H), 7.7 (t, 1H), 7.6 (t, 1H), 7.5 (d, 2H), 7.4 (d, 1H).

4,4'-Dinitrobiphenyl Yellow Solid: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.4 (d, 4H), 7.7 (d, 4H).

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