Improved Regioselective Mononitration of *o*-Xylene over HBEA-500 Zeolite Catalyst

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Nitration of aromatic compounds is one of the most fundamental and important reaction in organic synthesis, which provides key organic intermediates or energetic materials.[1-3] The traditional method for nitration, involving use of a mixture of nitric and sulfuric acids, though still in widespread commercial use, suffers from many disadvantages of classical nitration method including strong acidic media, formation of environmentally unfriendly waste that is expensive to dispose off, over nitration, low selectivity and safety problems. These disadvantages have encouraged extensive efforts to develop alternative methods[4-7] to replace conventional nitration.

Current trends in the nitration of aromatics emphasized minimizing by product formation and improved region-control of the desired product through the use of catalysts. Smith and coworks have utilized zeolites to enhance the *para*-selectivity in chlorination,[8] acylation,[9] and methane-sulfonylation[10] of simple aromatic substrates. The present investigation was to develop a mild, easy to operate and efficient catalyst[11-14] without involving sulfuric acid and some progress has been achieved.

4- and 3-Nitro-*o*-xylenes are used as intermediates for the production of vitamins, fragrances, agrochemicals, dyes, *etc.* 4-Nitro-*o*-xylene is important as the precursor to high performance polyurethane resins and greater market demand than 3-nitro-*o*-xylene. The earlier attempts[15-17] toward selective nitration of xylene isomers have been made with either expensive or hazardous starting materials with lower selectivity. Thus, there still remains a need for an environmentally-friendly, commercially viable process for the selective nitration of aromatic compounds at high conversion. Our hope was that the use of a zeolite might enhance the yield or selectivities available in the nitration of *o*-xylene with acetic anhydride. In this paper, we have carried out the mononitration reaction of *o*-xylene under modest conditions with acetic anhydride over zeolites, where the regioselection of nitration can be improved.

In the case of nitration of monosubstituent *o*-xylene (Scheme 1), 4-nitro-*o*-xylene (4NOX) isomer the more commercially desirable isomer but a large excess of the less desirable 3-nitro-*o*-xylene (3NOX) isomer is formed (4NOX: 3NOX ratio of 45:55) when traditional mixed-acid nitration procedure is employed.[18] When the reaction was carried out
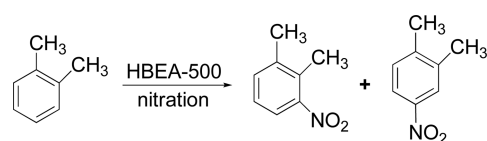
Scheme 1

in nitric acid-acetic anhydride system, the yield was improved. To optimize the reaction time for maximum conversion and selectivity of 4NOX, samples were analyzed immediately after the addition of nitric acid. The progress of reaction was monitored by running multiple reactions side-by-side and quenching the reactions at different times. The results were shown in Table 1.

As the results in Table 1 indicated, *o*-xylene had been completely consumed after 2 h and produced a reasonable yield of nitro-*o*-xylene (75.1%). However, the 4NOX was fairly low. With increasing of reaction time, 4NOX/3NOX ratio was also increased. The selectivity of 4NOX was highest when the reaction time up to 10 h, and the selectivity of 4NOX decreased after 10 h. 10 h was selected for further experimental studies due to its optimum performance.

Catalysts are always a determining factor in the kinetics of chemical reactions, thereby impacting the selectivity of a desired product directly. Zeolites have well-defined pore structures and channels that are derived from the networking

Table 1. Nitration of *o*-xylene over various reaction times

Entry	Reaction time (h)	Yield[b] (%)	Isomer proportion[c] (%)		4NOX:3NOX ratio
			4NOX	3NOX	
1	2	75.1	40	48	0.83
2	4	70.0	50	39	1.28
3	6	67.5	53	38	1.40
4	8	65.6	54	31	1.74
5	10	63.2	61	33	1.85
6	12	63.1	60	33	1.80
7	14	61.8	59	33	1.79

[a]Reaction conditions: *o*-xylene:nitric acid (65) = 1:2 (mole ratio, reaction temperature was room temperature, *o*-xylene:acetic anhydride = 0.6:5 (v/v). [b]Combined yield of 4NOX and 3NOX based on consumed *o*-xylene. 4-Nitrotoluene was used as an internal standard. [c]Proportion of products was determined by GC.

Table 2. Nitration of *o*-xylene with nitric and acetic anhydride over zeolite catalyst

Entry	Catalyst	Yield[b] (%)	Isomer proportion[c] (%)		4NOX:3NOX ratio
			4NOX	3NOX	
1	none	63.2	61	33	1.85
2	HY-5	70.8	57	38	1.50
3	HBEA-25	79.3	68	29	2.34
4	HBEA-280	95.4	69	23	3.01
5	HBEA-500	81.9	67	21	3.19
6	HZSM-5	69.6	56	40	1.40

[a]Reaction conditions: *o*-xylene:nitric acid (65) = 1:2 (mole ratio), reaction temperature was room temperature, *o*-xylene:acetic anhydride = 0.6:5 (v/v), reaction time = 10 h. Amount of catalyst was 0.53 g. [b]Combined yield of 4NOX and 3NOX based on consumed *o*-xylene. 4-nitrotoluene was used as an internal standard. [c]Proportion of products was determined by GC.

of SiO$_2$ and Al$_2$O$_3$ making them attractive candidates for shape selective catalysis.[19] It was found that catalysts played an important role in the improvement of the regioselectivity. Some typical results were shown in Table 2.

Zeolites facilitated the reaction and gave a high yield as compared with catalyst (Table 2). With Si/Al ratio increasing of HBEA zeolite catalyst, a high ratio of formation of 4NOX was favored (Entries 3-5, from Table 2). HBEA-500 zeolite catalyst with a high Si/Al ratio showed a better selectivity for 4NOX than low Si/Al ratio possibly due to the de-aluminiation, which would modify the distribution of the size and shape of the pores in zeolites. High alumina containing zeolites show a very-hydrophilic character, whereas, high silica containing zeolites tend to be more hydrophobic. In addition, one needs to consider the dimensionality of zeolites channels. HZSM-5 with a medium-pore zeolite was included for comparison. Both selectivity and yield were unsatisfactory with zeolites HZSM-5 (Entry 6, from Table 2). This may be attributed to the medium pore size structure, which would place more restriction on the transport of a

Table 3. Effect of amount of HBEA-500

Entry	Amount of catalyst (g)	Yield[b] (%)	Isomer proportion[c] (%)		4NOX:3NOX ratio
			4NOX	3NOX	
1	0.10	68.9	61	34	1.79
2	0.20	70.3	57	25	2.23
3	0.32	76.5	58	26	2.28
4	0.42	80.5	65	22	2.95
5	0.53	81.9	67	21	3.19
6	0.64	84.4	68	20	3.40
7	0.74	88.9	72	19	3.79
8	0.85	85.6	75	18	4.17
9	0.95	92.3	79	17	4.65
10	1.0	88.1	80	17	4.70

[a]Reaction conditions: *o*-xylene:nitric acid (65%) = 1:2 (mole ratio) reaction temperature was room temperature, *o*-xylene:acetic anhydride = 0.6:5 (v/v), reaction time = 10 h). [b]Combined yield of 4NOX and 3NOX based on consumed *o*-xylene. 4-Nitrotoluene was used as an internal standard. [c]Proportion of products was determined by GC.

Table 4. Efficiency of recycled HBEA-500 in the nitration of *o*-xylene

Entry	Yield[b] (%)	Isomer proportion[c] (%)		4NOX:3NOX ratio
		4NOX	3NOX	
fresh	92.3	79	17	4.65
1	86.6	78	18	4.33
2	87.9	79	19	4.16
3	85.4	78	20	3.90
4	84.1	78	21	3.71

[a]Reaction conditions: *o*-xylene:nitric acid (65%) = 1:2 (mole ratio) reaction temperature was room temperature, *o*-xylene:acetic anhydride = 0.6:5 (v/v), reaction time = 10 h. Amount of HBEA-500 was 0.95 g. [b]Combined yield of 4NOX and 3NOX based on consumed *o*-xylene. 4-nitrotoluene was used as an internal standard. [c]Proportion of products was determined by GC.

substrate through the pores. Among all the zeolites catalyst, HBEA-500 displayed the best isomeric ratio 3.19 (Entry 5, from Table 2). And the amount of HBEA-500 catalyst quantity was investigated (Table 3).

From Table 3, by increasing the amount of HBEA-500 catalyst the regioselectivity of 4NOX increased and the percentage of yield increased, probably because of the higher internal/external surface area, and effective catalytic sites. HBEA-500 was easily recovered from the reaction mixture by simple decantation or filtration and could be reused. It was observed that with increase in the number of usage times of the catalyst, its catalytic activity was decreased, the yields of mono-nitration product was decreased from quantitative to 84.1%, and the ratio of 4NOX/3NOX was also decreased.
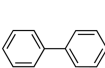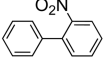
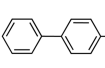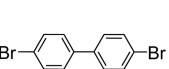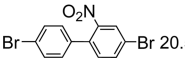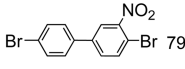A comparative analysis of the nitration aromatic compounds under similar conditions was also described. And the results were summarized in Table 5. The catalyst was very effective towards activated aromatic compounds (Entries 1-3, from Table 5) and the corresponding nitro products were readily obtained in good to excellent yields. It was notable that poly aromatic hydrocarbon biphenyl (Entry 4, from Table 5) and 4,4'-dibromobiphenyl (Entry 5, from Table 5) underwent regioselective nitration under the same reaction conditions. In the nitration of biphenyl (Entry 4, from Table 5) and 4,4'-dibromobiphenyl (Entry 5, from Table 5), low conversion was shown by this nitration system.

In conclusion, this paper described a better, more environmentally-friendly, sustainable, efficacious, and selective process for the nitration of *o*-xylene, compared to the incumbent process using nitric and sulfuric acid. Therefore, the present reaction will provide a general and practical method for the synthesis of nitro compounds. The catalyst was readily recyclable and we believed this to be a major step forward in the area of clean technology for aromatic nitration.

Experimental

Quantities are recorded in the footnotes to the appropriate tables. All reactions were carried out in a 50 mL two-necked round bottomed flask equipped with a water condenser and a

Table 5. Nitration of various substrates with nitric acid and zeolite HBEA-500 in acetic anhydride

Entry	Substrate	Conversion[b] (%)	Yield[c] (%)	Distribution[d] (%)
1[e]	(benzene/toluene)	99.5	79.6	o-NO₂ 8.7; m-NO₂ 2.6; p-NO₂ 88.6
2	(m-xylene)	99.7	87.3	38.9; 60.2
3	(p-xylene)	99.3	86.4	97.3
4	(biphenyl)	72.8	66.2	2-NO₂ 49.6; 4-NO₂ 50.4
5	(4,4'-dibromobiphenyl)	70.8	66.3	20.5; 79.5

[a]Reaction conditions: substrate:nitric acid (65%) = 1:2 (mole ratio) reaction temperature was room temperature, reaction time = 10 h. Amount of HBEA-500 was 0.95 g. [b]Determined by GC. [c]Combined yield of products based on consumed substrate. 4-Nitrotoluene was used as an internal standard. [d]Proportion of products was determined by GC with 4-nitrotoluene an internal standard. [e]Nitrobenzene was used as an internal standard.

magnetic stirrer. In a typical experiment, a mixture of zeolite HBEA-25 (Si/Al = 25, 0.11g), o-xylene (0.60 mL, 5 mmol), nitric acid (65%, 0.68 mL, 10 mmol) in acetic anhydride (5.0 mL) at room temperature for 10 h. When the reaction was over, the zeolite was removed by filtration and the filter liquor was washed with NaHCO₃ (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 residue. 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 chromatography, and were identified by comparison of their analytical data with those of authentic samples.

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