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NOTE

Regioselective Catalyzed Nitration of Toluene by Zeolites

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The nitration of toluene with nitric acid and nitrogen dioxide as nitration agent was studied. The effect of zeolite catalysts was also discussed. By using zeolite as catalysis, the yield of nitro-toluene was improved with nitric acid as nitration agent. The conversion of toluene and yield of nitro-toluene were both greatly enhanced with nitrogen dioxide as nitration agent.

Keywords: Nitration, Toluene, Nitric acid, Nitrogen dioxide, Zeolite.

The nitration of aromatic compounds is an important process in both industrial and academic research for the widely uses of nitro-arene as pharmaceuticals, dyes, explosives and plastics[1]. Conventional nitration processes are carried out by employing a mixture of nitric acid and sulfuric acid, which have the major defects such as corrosion, over-nitration, oxidation and poor selectivity[2].

To overcome these problems, many researchers have reported their findings in nitration of arene. The gained significant progresses are mainly focused on the selection of nitrifying agents and catalysts. Liquid nitrogen dioxide[3] and nitric acid with anhydride[4] were used to nitrify a series of aromatic compounds and good yield was obtained. Better selectivity was obtained when the nitration was catalyzed with ionic liquids[5] and zeolites[6].

Nitration of toluene with nitric acid: Dichloromethane (5 mL), zeolite (0.1 g) and toluene (0.319 mL, 3 mmol) were added in a round-bottomed flask under stirring at 0 °C. Then nitric acid (95 %, 0.660 mL, 15 mmol) was added dropwise. The mixture was stirred for 12 h. The organic layers was washed with water (10 mL × 2), $NaHCO_3$ solution (10 %, 10 mL) and water (10 mL × 2), dried with $MgSO_4$. A certain amount of *p*-nitro-chlorobenzene was added as internal standard. Then the solution was analyzed by gas chromatography.

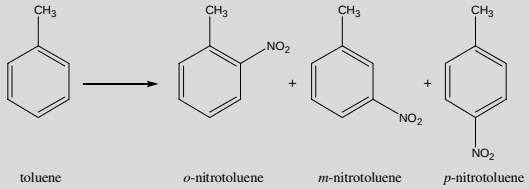
Nitration of toluene with nitrogen dioxide: Dichloromethane (5 mL), zeolite (0.1 g, calcined in air at 550 °C for 2 h) and toluene (0.319 mL, 3 mmol) were added in a round-bottomed flask under stirring at 0 °C. Then a certain amount of liquid nitrogen dioxide was added dropwise. The mixture was stirred for 12 h under an oxygen almosphere. The organic layers was washed with water (10 mL × 2), $NaHCO_3$ solution (10 %, 10 mL) and water (10 mL × 2), dried with $MgSO_4$. A certain amount of *p*-nitro-chlorobenzene was added as internal standard. Then the solution was analyzed by gas chromatography.

Generally, the nitration reaction occurs with an intermediate nitronium ion. The presence of sulfuric acid can greatly strengthen the nitric acid dissociation process to form nitronium ion. However, the strongly corrosive spent acid can pollute the environment. To avoid the use of sulfuric acid, we carried the nitration of toluene with 1 equivalent nitric acid. However, poor conversion and yield were obtained (Table-1, entry 1). To enhance the conversion and yield, we increased the amount of nitric acid. The results are listed in Table-1.

With the increasing amount of nitric acid, the conversion of toluene increased. When 15 mmol nitric acid was used, the maximum conversion 100 % and yield 80.4 % were obtained. For some consumption of toluene occurred double nitration and dinitro-toluene was produced, the yield of nitro-toluene was decreased to 72.1 % with the further increasing of nitric acid to 24 mmol. So the 15 mmol nitric acid was used in the sequence reaction.

Zeolites are attractive catalysts which were widely used in catalysis reaction. Some progresses in catalyzed nitration with zeolites have been reported[7,8]. To enhance the yield of nitro-toluene, a series of zeolites were used to catalyze nitration of toluene. The reaction without zeolite was carried for comparison. The results are listed in Table-2.

TABLE-1
NITRATION OF TOLUENE WITH DIFFERENT AMOUNT OF NITRIC ACID



Entry	Amount of nitric acid (ratio of toluene/nitric acid)	Conversion (%)	Yield (%)	Product distribution (%)		
				o-	*m-*	*p-*
1	0.20 mL(1:1)	36.3	16.4	55.2	2.5	42.3
2	0.26 mL(1:2)	49.3	37.2	55.1	2.7	42.2
3	0.40 mL(1:3)	87.2	69.8	54.6	2.9	42.5
4	0.52 mL(1:4)	93.6	72.9	56.0	3.4	40.6
5	0.66 mL(1:5)	100	80.4	56.5	3.2	40.3
6	0.80 mL(1:6)	100	78.1	53.4	3.2	43.4
7	0.92 mL(1:7)	100	75.8	53.4	3.3	43.3
8	1.04 mL(1:8)	100	72.1	53.0	3.4	43.6

TABLE-2
NITRATION OF TOLUENE WITH DIFFERENT ZEOLITE

Entry	Amount of nitric acid (ratio of toluene/nitric acid)	Catalyst	Conversion (%)	Yield (%)	Product distribution (%)		
					o-	*m-*	*p-*
1	0.66 mL (1:5)	None	100	80.4	53.3	3.1	43.6
2	0.66 mL (1:5)	HZSM-5 (40)	100	85.4	56.5	3.2	40.3
3	0.66 mL (1:5)	HZSM-5 (360)	100	86.5	55.6	3.9	40.5
4	0.66 mL (1:5)	Hβ (150)	100	89.4	53.1	3.3	43.6
5	0.66 mL (1:5)	Hβ (500)	100	87.5	51.3	2.5	46.2
6	0.66 mL (1:5)	3A	100	84.6	54.0	3.3	42.7
7	0.66 mL (1:5)	4A	100	87.3	53.6	3.0	43.4
8	0.66 mL (1:5)	5A	100	83.1	53.8	3.2	43.0
9	0.66 mL (1:5)	HY	100	81.2	53.5	3.1	43.4

From Table-2, all the zeolites can obviously improve the yield of nitro-toluene compared with the reaction absence of zeolite. When Hβ (150) was used, the maximum yield 89.4 % was got. Therefore, Hβ (150) was used in the following reaction.

To further optimize the reaction conditions, we used nitrogen dioxide instead of nitric acid as nitrating agent to nitrify toluene. The effects of Hβ(150) and amount of nitrogen dioxide were discussed. The results are shown in Fig. 1.

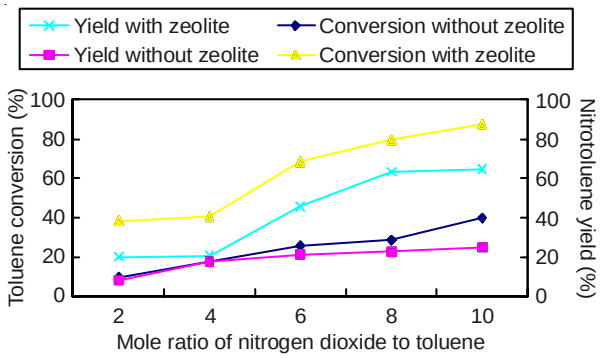


Fig. 1. Effects of Hβ (150) and amount of nitrogen dioxide

With the amount of nitrogen dioxide increasing, the conversion and yield were both enhance as the same as the nitration with nitric acid. Due to their dimensional microporous structure and Brønsted acidic sites of Hβ (150), conversion and yield were greatly augmented compared with the reaction absence of Hβ (150).

Conclusion

Under the catalysis of zeolite, the conversion and yield were both greatly improved with nitric acid and nitrogen dioxide as nitration agent. The zeolite can be easily recovered and reused by simple filtration. This process has great promising industrial applications.

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