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Zeolite-assisted nitration of neat toluene and chlorobenzene with a nitrogen dioxide/molecular oxygen system. Remarkable enhancement of *para*-selectivity

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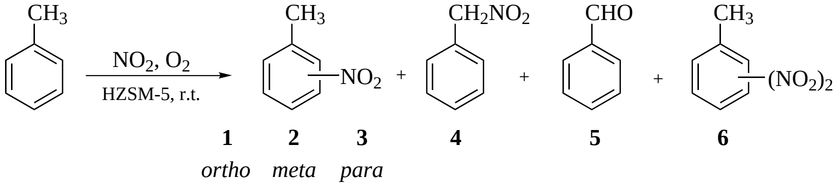
Abstract—In the presence of molecular oxygen and HZSM-5, neat toluene reacted with liquid nitrogen dioxide in a regioselective manner at room temperature to yield mononitrotoluenes as the main product, where the *para* isomer predominated up to 90% and the *ortho–para* isomer ratio improved to 0.08. Chlorobenzene behaved similarly, giving a *para*-predominant nitration product. © 2001 Elsevier Science Ltd. All rights reserved.

Classical methodology for the preparative nitration of toluene involves mixtures of nitric and sulfuric acids. The reaction is not selective and gives rise to a mixture of ca. 60% *o*-nitrotoluene, ca. 37% *p*-nitrotoluene and less than 3% *m*-nitrotoluene, along with some oxidation and/or polynitration products.[1] Since *p*-nitrotoluene has more market demand than the *o*-isomer, large amounts of the unwanted products in general pose a problem in industrial manufacture. Moreover, the disposal of waste products and spent acids is environmentally unfriendly and can be costly.

The Kyodai nitration using a NO_2/O_3 system has demonstrated excellent conversion of a variety of aromatic compounds into the corresponding nitro derivatives.[2] The reaction bears the general appearance of being an electrophilic process and is characterized by some unique feature as operating under neutral conditions. Further efforts to find an alternative means to activate nitrogen dioxide has led to the Fe(III)-catalyzed nitration of aromatic compounds with a NO_2/O_2 system.[3] Rather unfortunately, the product composition differs little from those of the Kyodai nitration and conventional aromatic nitration.

Over the past few decades there has been a considerable interest in improving the *para*-selectivity of toluene nitration and many attempts have been made using the catalysts supported on porous inorganic solids. Laszlo has developed Claycop ($Cu(NO_3)_2$/montmorillonite-K10) that selectively nitrates toluene in acetic anhydride/CCl_4 with an isomer distribution of *ortho* 23, *meta* 1 and *para* 76%.[4] Smith has shown that mordenite and zeolite β can play an important role in the selective mononitration of toluene, where the *para*-selectivity of 67% by using benzoyl nitrate[5] and the *ortho–para* isomer ratio of 0.23 by using acetyl nitrate[6] have been achieved. Toluene also has been nitrated with isopropyl



Scheme 1.

Keywords: nitration; regioselection; nitrogen oxides; arenes; nitro compounds; zeolites.

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nitrate in the presence of HZSM-5, producing a product of isomeric composition *ortho* 5, *meta* 0 and *para* 95%.[7] Zeolite catalysts are attractive for being inexpensive and reusable, and direct use of NO_2 as the source of nitro group has considerable potential in industrial application. Thus, in search for the *para*-selective methodology of aromatic nitration under neutral conditions, we have investigated the reaction of neat toluene and chlorobenzene with liquid NO_2 in the presence of a variety of zeolites by using each substrate as its own solvent. We now report the activation of nitrogen dioxide on the zeolite surface that results in the *para*-selective nitration of these aromatic substrates.

Weakly activated toluene was quite reluctant to react with NO_2 alone, but passage of O_2 into the reaction mixture resulted in a certain degree of conversion into nitrated compounds. Unfortunately, the reaction was quite slow and unselective, giving a mixture of nitrotoluenes (*ortho*- **1**, *meta*- **2** and *para*- **3**), phenylnitromethane **4**, benzaldehyde **5** and dinitrotoluenes **6** (Scheme 1). Trace amounts of a nitrophenol was also detected. In the presence of oxygen and HZSM-5, however, the reaction was promoted and the *para*-selectivity was found to increase considerably. Thus, in the hope of improving the *para*-selectivity further, the NO_2–O_2–zeolite system has been investigated systematically and the representative results are summarized in Table 1. Wider pore zeolite β and various types of modified zeolites were also examined and some selected results were included for comparison.

All zeolites were found to promote the reaction and the isomer proportion always moved to the direction to favor the *para*-isomer. HZSM-5 exhibited better *para*-selectivity than zeolite β, but their difference was slight as to the total product yield. Zeolites modified with metal ion or heteropoly acid were not so effective to accelerate the reaction and brought about complicated variation in the product distribution. In contrast, zeolites treated with methanesulfonic acid considerably facilitated nuclear nitration and the isomer proportion approached those of conventional nitration. Increasing the amount of NO_2 led to higher conversion, but was indifferent to the *ortho*–*para* isomer ratio, while increasing the amount of zeolites worked favorably for the nuclear nitration as well as *para*-substitution. The rise of reaction temperature from −10 to 10 to 50°C improved both product yield and extent of *para*-substitution considerably, the *ortho*–*para* isomer ratio turning for the better from 0.33 to 0.15 to 0.07.[8] The positive effect of elevated temperature would probably be due to the enhanced transport and interaction of the reactants inside the zeolite channels.

Table 1. Regioselectivity of nitration of toluene with NO_2–O_2 over various zeolite catalysts[a]

Catalyst	Yield[b] (mmol)	Product distribution (mol%)						*ortho*–*para*	*R*/*S*[d]
		1	**2**	**3**	**4**	**5**	**6**		
–[e]	0.47 (1)	7	7	5	34	35	12	1.48	0.45
–	1.15 (5)	34	7	23	6	12	18	1.47	4.6
HZSM-5[f]	2.12 (11)	17	4	57	10	7	5	0.30	4.9
HZSM-5[f,g]	4.62 (24)	6	2	74	10	7	1	0.08	4.9
HZSM-5/$MeSO_3H$	7.30 (46)	51	3	44	Trace	Trace	2	1.15	>99
BiHZSM-5[h]	2.45 (14)	24	6	58	4	3	5	0.41	13
CuHZSM-5[h]	1.00 (6)	26	4	69	Trace	Trace	1	0.38	>99
FeHZSM-5[h]	1.47 (8)	15	5	66	4	4	6	0.22	12
ZnHZSM-5[h]	2.08 (11)	30	7	47	7	5	4	0.64	7.3
P_2O_5HZSM-5[i]	1.62 (8)	21	6	51	9	8	5	0.41	4.9
$Mo_2O_3P_2O_5$HZSM-5[i]	2.63 (14)	17	7	60	5	5	6	0.29	9.0
Hβ-25[j]	4.16 (22)	30	8	46	7	4	5	0.64	8.1
Hβ-150[j]	2.13 (13)	36	5	52	2	3	2	0.70	19
FeHβ-150[h]	1.10 (6)	37	6	49	2	4	2	0.75	16
NaMFI-90[j]	2.63 (14)	25	6	51	6	4	8	0.49	9.0

[a] All reactions were carried out by stirring a mixture of toluene (5.0 ml), liquid NO_2 (0.5 ml), catalyst (2.0 g), 3 Å molecular sieves (0.5 g), and cyclododecane (internal standard) at room temperature for 22 h under oxygen, unless otherwise noted. Toluene was dried over 4 Å molecular sieves.

[b] Sum of products **1**–**6**, estimated by GC. Numeral in parenthesis refers to total yield of nitrotoluenes based on NO_2.

[c] Calculated from GC data.

[d] Ratio of ring and side-chain reaction products.

[e] Under exclusion of oxygen.

[f] HZSM-5 is a commercial product (Acros) of Si/Al ratio 1000. All catalysts except HZSM-5/$MeSO_3H$ were calcined in air at 500°C for 8 h prior to use.

[g] Double amount of catalyst.

[h] Prepared as follows; a suspension of zeolite (5 g) in 0.2 M solution of a given salt in water (100 ml) was stirred for 24 h under reflux. The solid was washed, dried at 110°C for 3 h, and calcined in air at 500°C for 8 h.

[i] Prepared by stirring HZSM-5 with aqueous phosphomolybdic acid ($H_3PMo_{12}O_{40}\cdot nH_2O$) or 85% phosphoric acid for 48–68 h at room temperature. Without washing, the solid was dried at 110°C for 5 h and calcined in air at 500°C for 8 h.

[j] A gift from the Catalytic Society of Japan.

Our results contrast to those reported by Smith, where HZSM-5 was less effective than zeolite β and the *ortho* and *para* isomers were obtained in comparable amount.[6,9] This difference may well be attributed to the absence of intervention by chlorinated solvent molecules, as well as the higher Si/Al ratio of our zeolite samples (Si/Al 1000). Mixing of toluene with a large excess of NO_2 over HZSM-5 at room temperature led to complete consumption of the substrate, leading to the distribution of products **1**–**6** of 41:6:47:3:1:2 and an *ortho*–*para* ratio of 0.87.

To our knowledge, no substantiated mechanisms have been proposed to date for the nitration of arenes on the surface of solid catalyst. High *ortho*–*para* preference along with insignificant formation of *m*-isomer reflects the general characteristic of electrophilic substitution involving the nitronium ion. However, concurrent formation of a slight amount of side-chain nitration and oxidation products suggests a minor involvement of a radical process.

In the presence of a radical scavenger such as *m*-dinitrobenzene, no obvious change was observed as to the relative ratio of ring and side-chain substitution products as well as the *ortho*–*para* isomer ratio. The Brønsted active sites resulting from the hydroxylic oxygen atoms bridging between the silicon and aluminum atoms in the zeolite framework are located over 90% of total amounts in the interior of channels.[7,10] They would play a role similar to mineral acids inside the channel system of HZSM-5, leading to the *para*-selective nitration.

The side-chain reaction products **4** and **5** were probably formed through the capture of the benzyl radical, partly derived from toluene via the direct abstraction of hydrogen by NO_2 and partly via the electron transfer between zeolite followed by proton release from alkyl side-chain, by nitrogen dioxide and oxygen, respectively. Nitrogen dioxide has been known to trap the benzyl radical more efficiently than molecular oxygen,[11] thus favoring phenylnitromethane **4** over benzaldehyde **5**. Small amounts of dinitrotoluenes **6** were simultaneously formed in spite of the presence of a large excess of toluene. Since none of the isomeric mononitrotoluenes reacted further to form dinitro derivatives under the conditions employed, these dinitro compounds are most likely to form directly from toluene via the addition–elimination sequence, as suggested previously.[12]

Under similar conditions, chlorobenzene also reacted in a *para*-selective manner. Thus, on stirring a mixture of chlorobenzene (5.0 ml), liquid NO_2 (0.5 ml), HZSM-5 (2.0 g) and 3 Å molecular sieves (0.5 g) at room temperature for 22 h under oxygen, chloronitrobenzenes (3.74 mmol) were obtained in the isomer ratio of *ortho* 8, *meta* 2 and *para* 90. The *ortho*–*para* ratio 0.09 was better than those (0.25–0.40) previously reported by Smith.[9] In the absence of HZSM-5, the reaction was quite sluggish and unselective, affording the nitrated product in the ratio *ortho*:*meta*:*para* = 32:15:53.

In conclusion, the present work has revealed that the *ortho*-rich composition ordinarily expected from conventional nitration of toluene can be reversed to the *para*-dominant one by using a NO_2–O_2 system in the presence of HZSM-5, the *ortho*–*para* ratio being improved to 0.08 and the *para*-selectivity up to 90%. The solvent-free nitration of toluene with NO_2 is most likely to occur in the interior of zeolite channels via the electrophilic process involving the nitronium ion, partly accompanied by an ordinary radical process that leads to side-chain reaction products.

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