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Selective nitration of aromatic compounds catalyzed by H β zeolite using N₂O₅

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Abstract

A selective and efficient process for the electrophilic nitration is described using N_2O_5 as a green nitrating agent, H β zeolite as a solid acid catalyst and shape controlling agent under mild conditions.

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Nitration of aromatic substrates is one of the widely studied organic reactions as nitro aromatic compounds are industrially important intermediates during the synthesis of dyes, plastics and pharmaceuticals [1-4]. However, many commercial processes to produce such materials still rely on technology that was developed many years ago. The traditional method for nitration, involving a mixture of nitric acid and sulfuric acid, suffers from many disadvantages including the generation of large quantities of corrosive waste and in many cases the production of mixtures of isomers in which the most desirable one is not in high yield [5]. The obvious disadvantages of the commercial manufacturing process currently used have stimulated much research aimed at development of environmental friendly and reusable alternative procedures. Different solid acid catalysts tested so far included MoO₃/SiO₂ [6-8], SO₄²⁻/SiO₂ [9], WO₃-TiO₂/SiO₂ [10], WO₃-SO₄²⁻/SnO₂ [11], zeolite-based solid acid catalysts [12-15], melamine-(H₂SO₄)₃ [17] and polyvinylpyrrolidone– $(H_2SO_4)_n$ [18]; other sources of NO₂⁺ were involved, such as nitronium salts in organic media [19], $Zn(NO_3)_2 \cdot 6H_2O$ [20], guanidinium nitrate [21], N_2O_4 [22,23] and N_2O_5 [24–27]; organic nitrating agents of e.g. acetyl nitrates [13,16] and alkyl nitrates [21], other acids replacing sulfuric acid [28], etc., that generate less waste and provide product mixtures in which the most desirable isomer (often the para-isomer) is much more abundant. However, these processes are associated with the problems of leaching of acid from the support during reaction and calcination, requiring long reaction time and high reaction temperature, and giving poor selectivity towards some aromatic compounds.

The use of β zeolite in aromatic nitration is a subject of increasing interest, particularly with regard to unusual regioselectivity [13,29–31]. Smith has shown that the β zeolite plays an important role in the selective mononitration of toluene, where the *para*-selectivity of 67% by using benzoyl nitrate and the *ortho–para* isomer ratio of 0.23 by using

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R=H. F. Cl. Br. Me. Et. Pr. Bu.

Scheme 1. Nitration of simple aromatics using N_2O_5 catalyzed by H β zeolite.

acetyl nitrate have been achieved [13]. The method for aromatic nitration using NO₂/O₃ catalyzed by β zeolite gives excellent conversion of a wide variety of aromatic compounds under mild conditions (Kyodai nitration) [30,31]. However, use of ozone adds to the cost of the process. And the method where ozone is employed most likely involves dinitrogen pentoxide (N₂O₅), a highly active nitrating agent.

Previously, we reported two mild, efficient and eco-friendly nitration processes: (1) using MoO₃/SiO₂ [8] as catalyst and (2) using rare earth metal triflates [32] as catalyst, which gave the corresponding nitro products with high yield but low *para*-selectivity. Therefore, we have attempted to develop a selective process which uses N_2O_5 as the highly active nitrating agent and HB zeolite as a solid acid catalyst as well as shape controlling agent to improve the para-selectivity. Now, we report the substantial process in this letter.

In our study, the nitration of toluene using N_2O_5 in the presence of H β zeolite was examined (Scheme 1). The addition order of the agents had a remarkable effect on the para-selectivity of the process. As shown in Table 1, the best order (entry 5, 6) should be conducted by pre-mixing the HB zeolite with CH2Cl2 and then successively adding the nitrating agent (N_2O_5/CH_2Cl_2 solution) and toluene. In this cases, the best o/p ratio (para-selectivity) is 0.59 with the high conversion of 97%. The results showed that H β zeolite could promote the reaction and the isomer proportion moved to the orientation to favor the para-isomer, which indicated that the formation of electrophilic nitronium ions (NO_2^+) from N₂O₅ and the interaction of the reactants were conducted predominantly inside the H β zeolite channels. Although entry 4 in Table 1 shows good selectivity but with low conversion, that because of the heat released when N_2O_5/CH_2Cl_2 solution contacted with H β zeolite directly which caused the decomposition of N_2O_5 . Therefore, premixing the H β zeolite with CH₂Cl₂ is a necessary procedure. Although the higher conversion (98%) was obtained by adding the N₂O₅/CH₂Cl₂ solution added to a prepared mixture of H β zeolite and toluene (entry 2), the *para*-selectivity was very low (o/p ratio = 1.12). This was caused that N₂O₅ transferred into the zeolite channels incompletely, and the reaction was taken place mainly on the surface of catalyst showed low *para*-selectivity.

Fig. 1 shows the effect of the catalyst amount on the nitration selectivity. Even with as little as 0.05 g H β , the reaction showed remarkable *para*-selectivity with high conversion, and the best result has been obtained since 0.2 g Hβ zeolite was involved (conversion is 97%; o/p ratio is 0.59). Increasing the catalyst amount provides an increased pore volume and a greater number of catalytic sites. Consequently, a greater proportion of NO_2^+ can be generated inside the channels, leading to the increased *para*-selectivity. So $0.2 \text{ g H}\beta$ zeolite was used in subsequent experiments.

By means of the optimized reaction conditions, extended investigation on a variety of other aromatic compounds was studied (Scheme 1). The results were summarized in Table 2. As the results shown in Table 2, this new process is

Entry	Order of addition	Time (min)	Conversion (%) ^b	Product isomers (%) ^b			o/p ^b
				Ortho	Meta	Para	
1	А-В-С	10	86	51.4	2.5	46.1	1.11
2	A-B-C	30	98	51.3	2.8	45.9	1.12
3	A-C-B	10	46	34.1	1.8	64.1	0.53
4	A-C-B	30	51	36.0	1.9	62.1	0.58
5	A-D-C-B	10	85	35.0	1.8	63.2	0.55
6	A-D-C-B	30	97	36.3	1.8	61.9	0.59

Table 1 The effect of order of addition of reagents on the nitration of toluene.^a

^a Reaction conditons: A = H β (0.2 g), B = toluene (5 mmol, 0.46 g), C = N₂O₅/CH₂Cl₂ (5 mmol/5 mL), D = CH₂Cl₂ (2 mL), 20 °C.

^b Calculated from original GC data.



Fig. 1. The effect of catalyst amount (H β zeolite) on toluene nitration using N₂O₅. Reaction conditions: toluene (5.0 mmol), N₂O₅/CH₂Cl₂ (5.0 mmol/5.0 mL), H β (0.2 g) with 2 mL CH₂Cl₂, 30 min, 20 °C.

Table 2 Nitration of various aromatics using N_2O_5 catalyzed by H\beta zeolite. $^{\rm a}$

Entry	R	Conversion (%) ^b	Product isomers (%) ^b			o/p ^b	o/p ^c
			Ortho	Meta	Para		
1	F	100	21.3	_	78.7	0.27	0.48
2	Cl	99	29.6	_	70.4	0.42	0.78
3	Br	92	33.4	_	66.6	0.50	0.82
4	Н	100	_	_	_	_	_
5	Et	100	28.7	2.2	69.1	0.42	0.83
6	ⁱ Pr	98	16.8	3.6	79.6	0.21	0.35
7	^t Bu	100	11.2	2.9	85.9	0.13	0.16

^a Reaction conditions: substrate (5.0 mmol), N_2O_5/CH_2Cl_2 (5.0 mmol/5.0 mL), $H\beta$ (0.2 g), 30 min, 20 °C. All products are known and identified by comparison using GC with authentic samples.

^b Determined by original GC data.

^c Data from Ref. [32].

suitable for a range of moderate active aromatics, high conversions were obtained in all of the cases under mild reaction conditions, accompanied with a better *para*-selectivity compared with the data from Ref. [32].

In conclusion, we have developed a selective and efficient process for the nitration of simple aromatic compounds by using N_2O_5 and H β zeolite. This method can give high *para*-selectivity under mild conditions and is suitable for scale-up. The combination of H β zeolite and N_2O_5 seems to be a new direction for environmental chemistry in nitration.

1. Experimental

The H β zeolite (Si/Al ratio is 25) was purchased from Nankai University Catalyst Co. Ltd., and the rest chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd. and used without further purification; N₂O₅ was prepared according to the procedure of Ref. [25]. All products are known and identified by comparison using GC with authentic samples.

General procedure: To a cooled (0 °C) stirring mixture of the H β zeolite (0.2 g) and CH₂Cl₂ (2 mL), a solution of N₂O₅ (5 mmol) and CH₂Cl₂ (5 mL) was added slowly; then toluene (5 mmol) was introduced into the tube drop by drop. The reaction was carried out at 20 °C for 1 h, then the catalyst was filtered off and washed with some CH₂Cl₂,

which was added to the filtrate. The CH_2Cl_2 solution was washed with a few portions of saturated NaHCO₃ solution, then several times with water, dried with MgSO₄, and examined by GC.

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