

Improved regioselective mononitration of toluene over ZSM-5 zeolite catalysts

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Received 13 June 2007; revised 19 August 2007; accepted 3 November 2007

Available online 11 December 2007

Abstract

We show for the first time that the NH_4^+ exchanged form of ZSM-5 zeolite is as effective as the H^+ form of the catalyst for the regioselective conversion of toluene to mononitrotoluene (MNT) using 90% nitric acid as the sole nitrating agent. The auto-ionization of the acid in the absence of protons on the zeolite surface is sufficient for the formation of reactive nitronium ions. We also find that the regioselectivity for the formation of *p*-MNT is substantially increased over both forms of the zeolite catalyst by first intercalating the acid in the zeolite micropores prior to the introduction of toluene. For instance, the *p/o* isomer ratio is increased from values in the range 1.3–2.3 under conventional batch reaction conditions to values of 1.8–8.9 when the acid is sequestered in the zeolite. The sequestration of nitric acid in both ion exchanged forms of the zeolite confines more of the nitration reaction to the regioselective environment of the micropores and reduces the extent of reaction in homogeneous toluene solution. However, the ammonium form of the zeolite is preferred over the protonated form when the Si/Al ratio of the zeolite allows for the presence of at least one ammonium ion per unit cell ($\text{Si/Al} \leq 40$), because under these conditions far less benzaldehyde and other undesired reaction products are formed in comparison to the protonated form of the zeolite at the same Si/Al ratios. The ability of NH_4^+ -ZSM-5 derivatives to limit the formation of unwanted toluene oxidation products is not well understood, but the observed selectivity may be related to the replacement of ammonium ions by protons, the formation of ammonium nitrate, and the buffering of nitric acid within the micropores of the zeolite.

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Keywords: Toluene; Nitration; ZSM-5 zeolite; Regioselectivity

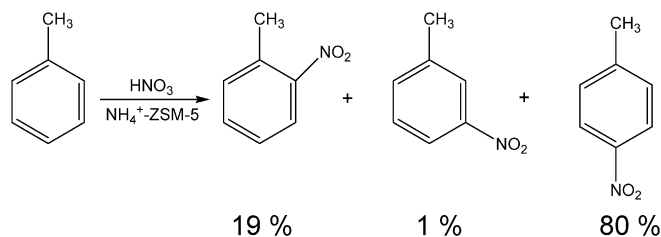
1. Introduction

Mononitrotoluene (MNT), particularly the *para*-substituted isomer, is a highly desired intermediate for the production of many important aromatic compounds [1,2]. Mixtures of nitric acid and sulfuric acid typically yield of the *ortho* isomer in excess of the *para* isomer. Although the *meta* MNT isomer is produced in minor yield, it is undesirable, particularly if the MNT is to be used as a precursor to further substitution reactions. Still further, the nitration and further oxidation of the methyl group leads to additional unwanted by-products.

In efforts to overcome these limitations, various solid acids have been investigated as possible regioselective catalysts for the mononitration of toluene [3–9]. While Nafion-H and other polysulfonic acid resin catalysts reduce the corrosive nature of nitration reaction mixtures, they do not substantially improve the regioselectivity for the *para* isomer [10]. However, acetic anhydride- CCl_4 suspensions of $\text{Cu}(\text{NO}_3)_2$ supported on K-10 montmorillonite clay (Claycop), selectively catalyze the HNO_3 conversion of toluene to MNT with an *o:m:p* isomer distribution of 23:1:76 [11,12]. Analogous improvements in MNT regioselectivity have been achieved using amorphous aluminosilicates and crystalline zeolite catalysts, including H-Y and H-ZSM-11 zeolites [13,14] and, especially, H-ZSM-5 zeolite with a very high Si/Al ratio of 1000 [7,15,16], particularly when *n*-propyl nitrate is the nitrating agent. The regioselectiv-

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Scheme 1. MNT regioselectivity achievable with NH_4^+ -ZSM-5 as catalyst.

ity provided by H-ZSM-5 zeolite is retained using NO_2/O_3 or NO_2/O_2 as the nitrating agent [18,19]. Improved *para* isomer selectivity also has been achieved with zeolite Beta as the catalyst [5,17], particularly when nitric acid is used in combination with acetic anhydride [20]. Independent of the MNT isomer distribution achieved in each of these nitration systems, unwanted oxidation by-products such as benzaldehyde invariably reduce overall yields, especially when nitric acid is the nitrating agent.

We report here a new approach to improving the regioselectivity and overall yields of MNT obtained in the ZSM-5-catalyzed nitration of toluene with nitric acid as the nitrating agent. The new process is based in the first instance on the sequestration of the nitric acid in the micropores of the catalyst prior to the addition of the substrate. This strategy confines the nitration reaction to the intracrystal pores of the catalyst and minimizes the nonselective extra-zeolitic transformation of the substrate. Furthermore, we show for the first time that the ammonium-exchanged form of the zeolite can be even more effective than the protonated zeolite in providing improved regioselective conversions and in minimizing unwanted benzaldehyde and related alkyl group oxidation products. Under optimal catalytic conditions the MNT regioselectivity show in Scheme 1 can be achieved at nitric acid conversion of 95%, while maintaining the fraction of undesired oxidation products to <5%.

2. Experimental

2.1. Materials

Toluene and nitric acid (90 wt%), were purchased from Aldrich Chemical Co. Benzaldehyde and *o*-, *m*-, and *p*-nitrotoluene also were obtained from Aldrich and used as references for GC calibration. Four NH_4^+ -exchanged forms of ZSM-5 zeolite having Si/Al ratios of 12, 25, 40, and 140 were purchased from Zeolyst International.

2.2. NH_4^+ -ZSM-5 and H^+ -ZSM-5 catalysts

As-received NH_4^+ -exchanged forms of ZSM-5 zeolite were denoted NH_4^+ -ZSM-5 (x), where the value of x indicates the Si/Al ratio of the framework. The ammonium forms of the zeolite were converted to the protonated derivatives by calcination at 500 °C for 5 h and were denoted H^+ -ZSM-5 (x).

The dealumination of the external surfaces of NH_4^+ -ZSM-5 catalysts with differing Si/Al ratios was accomplished by reaction with oxalic acid, citric acid, and ethylenediamine tetraacetic acid (H_4EDTA) as complexing agents for aluminum [21–23]. In a typical reaction with oxalic and citric acids as the

dealumination reagent, 30 g of as-received NH_4^+ -exchanged zeolite was added to 450 ml of 44 mM organic acid at 100 °C. For dealumination with EDTA, 20 g of zeolite was allowed to react with 300 ml of 14 mM acid. After a reaction time of 1 h, the hot suspension was filtered, washed with hot water three times and oven-dried at 160 °C overnight.

2.3. Catalyst characterization

The structural integrity of ZSM-5 catalysts was monitored by X-ray diffraction using $\text{CuK}\alpha$ radiation ($\lambda = 1.542 \text{ \AA}$) and a Rigaku Rotaflex diffractometer equipped with a rotating anode operated at 45 kV and 100 mA. N_2 adsorption and desorption isotherms were obtained at $-196 \text{ }^\circ\text{C}$ on a Micromeritics Tristar sorptometer in static adsorption mode. Samples were outgassed under vacuum ($1.3 \times 10^{-4} \text{ Pa}$) at 200 °C for a minimum of 12 h prior to analysis. BET surface areas were calculated from the linear portion of the BET plot according to IUPAC recommendations.

2.4. Catalytic reactions

The catalytic nitration of toluene under conventional batch reaction conditions is representative of the general methodology used in previous studies of the nitration of toluene over ZSM-5 catalysts [16]. In a typical reaction a 5.0-g quantity of the desired catalyst was added to a round-bottom flask at room temperature, and 10 ml of toluene was slowly added into the flask. The mixture was blended with a spatula and kept at 90 °C for 30 min. Then, 0.34 g of 90% nitric acid was added dropwise to the heated mixture. The catalytic reaction was run for 4 h while maintaining the reaction mixture at a temperature between 90 and 100 °C. The reaction mixture was cooled to room temperature and acetone was added to the reaction mixture to dissolve the reaction products. The acetone solution was filtered off and the product distribution in the filtrate was determined by gas chromatography on a HP 5890 instrument equipped with a FID detector. A 15-meter SPB-1 capillary column was used for the analysis of reactant and products. X-ray powder diffraction patterns for the spent catalysts indicated the retention of crystallinity under reaction conditions.

Toluene nitration reactions with remarkably improved regioselectivity were carried out in the presence of zeolite-sequestered nitric acid. In this procedure 0.34 g of 90% nitric acid solution was added into a round flask at room temperature containing 5.0 g of the desired ZSM-5 catalyst. The mixture was blended with a spatula and equilibrated at room temperature overnight to allow sequestration of the nitric acid in the micropores of the catalyst. A 10-ml quantity of toluene was slowly added into the flask and the blended mixture was heated in an oil bath to a reaction temperature between 90 and 100 °C for four hours. The cooled reaction mixture was extracted with acetone, and the product distribution was determined by gas chromatography. The fraction of toluene converted to products was determined by GC, and the overall conversion was based the corresponding amount of nitric consumed as the limiting reagent.

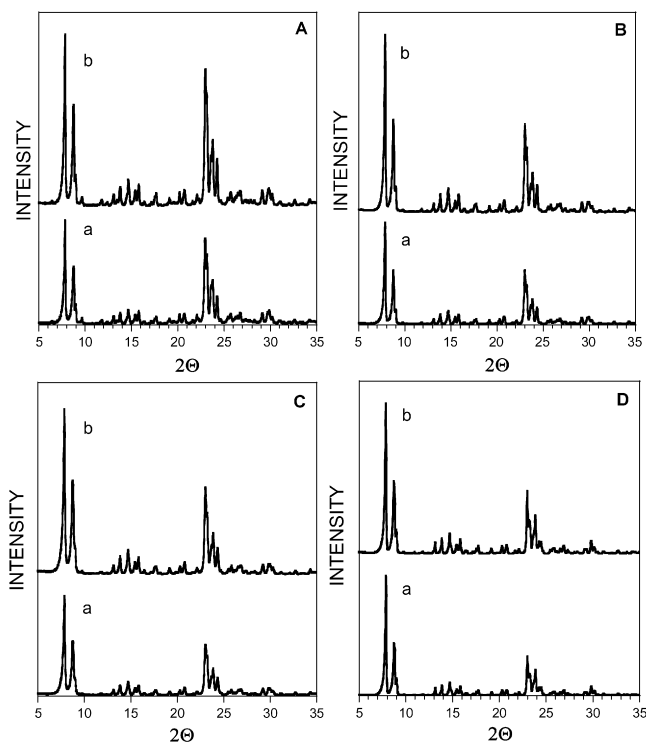


Fig. 1. Powder XRD patterns of ZSM-5 (x) catalysts with initial Si/Al values (x) equal to (A) 12, (B) 25, (C) 40, and (D) 140. The patterns labeled (a) are for as-received NH_4^+ -exchanged zeolites and those labeled (b) were dealuminated (b) reaction with oxalic acid.

3. Results

3.1. ZSM-5 catalysts

The as-received NH_4^+ -ZSM-5 (x) compositions, where x represents the Si/Al ratio of the framework, were modified in two ways. The first modification was achieved through calcination at 500 °C to obtain the zeolite in protonated form, denoted H^+ -ZSM-5 (x). The second modification was accomplished by reaction with H_4EDTA , oxalic acid and citric acid as complexants to selectively remove acidic aluminum sites from the external surfaces of the zeolite crystals without removing aluminum from the internal micropores [21–23]. The objective of the dealumination reactions was to minimize the less regioselective nitration reactions that may occur at the external surfaces of the zeolite crystals.

The modification of NH_4^+ -ZSM-5 (x) compositions through calcination to form the protonated derivative or through reaction with carboxylic acids to form surface-dealuminated derivatives did not compromise the crystallinity or the textural properties of the zeolite framework, as judged by powder X-ray diffraction and nitrogen adsorption studies. Fig. 1 provides the X-ray powder diffraction patterns for the as-received NH_4^+ -ZSM-5 (x) compositions with $x = 12, 25, 40, 140$, along with the dealuminated analogs obtained by reaction with oxalic acid. Equivalent powder patterns were obtained for dealuminated derivatives obtained using H_4EDTA and citric acid as dealumination reagents. The apparent increases in diffraction intensity for the dealuminated compositions may indicate that the dealu-

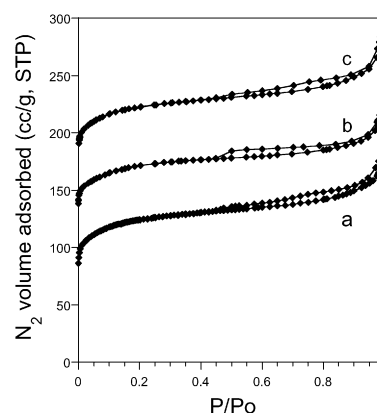


Fig. 2. Nitrogen adsorption–desorption isotherms for ZSM-5 (40) catalysts (a) as-received NH_4^+ -exchanged zeolite, (b) calcined H^+ -zeolite, and (c) NH_4^+ -exchanged zeolite dealuminated by reaction with oxalic acid. The isotherms are offset by 50 cc/g for clarity.

mination process removes amorphous debris from the external surfaces of the crystals or, alternatively, improves the packing of the zeolite crystals and increases in the bulk density of the compacted powder used to obtain the XRD patterns.

Representative nitrogen adsorption–desorption isotherms are provided in Fig. 2 for ZSM-5 (40) in NH_4^+ -exchanged and calcined H^+ forms, as well as for the dealuminated NH_4^+ form obtained through reaction with oxalic acid. BET surface areas and pore volumes for as-received NH_4^+ -ZSM-5 (x) compositions and the corresponding compositions after dealumination of the external surfaces are compared in Table 1. The surface areas for the as-received catalysts compare favorably with the values of 400–425 m^2/g provided by the supplier [24]. Similar surface areas values were obtained for H^+ -ZSM-5 (x) compositions obtained through calcination of the NH_4^+ -exchanged precursors. The dealumination of external surfaces by reaction with carboxylic acids hardly affects the BET surface area and pore volume of the zeolite, as indicated by the comparison of textural properties in Table 1.

3.2. Regioselective nitration reactions

The conventional method used for the ZSM-5-catalyzed mononitration of toluene combines the proton form of the zeolite, toluene, and 90% nitric acid in a batch reactor and equilibrating the mixture at elevated temperatures [16]. Using similar batch reactions conditions and H^+ -ZSM-5 (x) with different Si/Al ratios (x), we obtained the conversions and *o*-, *m*-, and *p*-MNT product distributions provided in Table 2. Included in the table is the fraction of non-MNT by-products (denoted *bp*) formed in the reaction, of which, benzaldehyde is the major component. We also include in Table 2 for comparison purposes the conversions and product distributions obtained using the ammonium form of the zeolite in place of the protonated analog. We note, rather surprisingly, that the as-received ammonium forms of the catalysts provide conversions and product distributions competitive with the protonated forms. Under equivalent reaction conditions in the absence of a ZSM-5 catalyst, a nitric acid conversion of 50% is achieved, but nearly

Table 1
Comparison of surface areas and pore volumes for as-received and dealuminated NH_4^+ -ZSM-5 (x) catalysts^a

Catalyst	Dealumination agent	Surface area (BET, m ² /g)	Micropore volume ^b (cc/g)	Total pore volume ^c (cc/g)
NH_4^+ -ZSM-5 (11.5)	None	386	0.18	0.20
NH_4^+ -ZSM-5 (25)	None	412	0.19	0.23
NH_4^+ -ZSM-5 (40)	None	429	0.20	0.25
NH_4^+ -ZSM-5 (140)	None	401	0.19	0.21
NH_4^+ -ZSM-5 (11.5)	Oxalic acid	369	0.17	0.18
NH_4^+ -ZSM-5 (25)	Oxalic acid	427	0.20	0.24
NH_4^+ -ZSM-5 (40)	Oxalic acid	433	0.20	0.25
NH_4^+ -ZSM-5 (140)	Oxalic acid	408	0.19	0.22

^a Samples were out-gassed at 200 °C for 20 h prior to the determination of textural properties by nitrogen adsorption.

^b The micropore volumes were obtained from the nitrogen uptake at $P/P_0 = 0.40$.

^c The total pore volumes were obtained from the nitrogen uptake at $P/P_0 = 0.98$.

Table 2
Product distributions for the ZSM-5-catalyzed nitration of toluene under conventional batch reaction conditions

Zeolite catalyst	Conversion ^a (%)	Product mole ratios $bp^b:o:m:p$	p/o ratio
H^+ -ZSM-5 (12) ^c	43	12:35:2:51	1.5
H^+ -ZSM-5 (25)	58	11:32:2:55	1.7
H^+ -ZSM-5 (40)	71	7:36:3:54	1.5
H^+ -ZSM-5 (140)	60	21:23:2:54	2.3
NH_4^+ -ZSM-5 (12)	33	3:41:4:52	1.3
NH_4^+ -ZSM-5 (25)	52	2:34:3:62	1.8
NH_4^+ -ZSM-5 (40)	57	8:39:3:51	1.3
NH_4^+ -ZSM-5 (140)	55	14:27:1:57	2.1

^a The conversion was based on nitric acid as the limiting reagent.

^b bp represents by-products other than mononitrotoluene (mainly benzaldehyde); o , m , and p represent the *ortho*-, *meta*-, and *para*-isomers of MNT.

^c The number in parenthesis indicates the Si/Al ratio.

one-third of the products are not MNT and include benzaldehyde, benzoic acid, dinitrotoluenes, among others.

As is shown by the data in Table 3, the regioselective nitration of the toluene ring is substantially altered by first sequestering the nitric acid in the zeolite prior to the addition of toluene. The improved regioselectivity toward the *para* isomer is realized for both the protonated and ammonium form of the zeolite. Also, the effects of nitric acid sequestration are evident over the entire range of Si/Al values from $x = 12$ to 140.

In an effort to evaluate the potential effects of catalytic nitration at the external surfaces of the zeolite, we sequestered the nitric acid in zeolite derivatives in which the external surfaces of the NH_4^+ -ZSM-5 (x) catalysts were dealuminated by reaction with oxalic acid, citric acid, and ethylenediamine tetraacetic acid (H_4EDTA). The results are presented in Table 4. Comparing the results for the dealuminated catalysts in Table 4 with those for NH_4^+ -ZSM-5 (x) compositions in Table 3 that were not dealuminated, we see that dealumination increases the con-

Table 3
Product distributions for the nitration of toluene with nitric acid sequestered in ZSM-5 catalysts

Zeolite catalyst	Heat treatment	Conversion (%)	Product mole ratios $bp:o:m:p$	p/o ratio
H^+ -ZSM-5 (12)	500 °C	45	16:11:3:70	6.4
H^+ -ZSM-5 (25)	500 °C	63	11:14:tr:75	5.4
H^+ -ZSM-5 (40)	500 °C	90	13:14:1:61	4.4
H^+ -ZSM-5 (140)	500 °C	76	19:8:2:71	8.9
NH_4^+ -ZSM-5 (12)	As-received	25	tr ^a :12:2:86	7.2
NH_4^+ -ZSM-5 (25)	As-received	65	4:22:1:72	3.3
NH_4^+ -ZSM-5 (40)	As-received	69	6:33:2:59	1.8
NH_4^+ -ZSM-5 (140)	As-received	62	17:9:1:73	8.1
NH_4^+ -ZSM-5 (12)	160 °C	58	1:12:2:85	7.1
NH_4^+ -ZSM-5 (25)	160 °C	53	tr:16:tr:84	5.3
NH_4^+ -ZSM-5 (40)	160 °C	67	3:32:tr:65	2.0
NH_4^+ -ZSM-5 (140)	160 °C	56	21:9:tr:69	7.7

^a tr indicates trace quantities (<0.5%).

Table 4
Product distributions for the nitration of toluene by reaction with nitric acid sequestered in dealuminated ZSM-5 catalysts

Dealuminated catalyst	Dealumination reagent	Conversion (%)	Product mole ratios $bp:o:m:p$	p/o ratio
NH_4^+ -ZSM-5 (12)	H_4EDTA	54	2:15:2:80	5.3
NH_4^+ -ZSM-5 (25)	H_4EDTA	79	3:24:1:72	3.0
NH_4^+ -ZSM-5 (40)	H_4EDTA	83	5:33:3:59	1.8
NH_4^+ -ZSM-5 (140)	H_4EDTA	65	15:13:1:70	5.4
NH_4^+ -ZSM-5 (12)	Oxalic acid	71	1:17:2:80	4.7
NH_4^+ -ZSM-5 (25)	Oxalic acid	90	5:10:1:70	4.2
NH_4^+ -ZSM-5 (40)	Oxalic acid	95	7:35:1:57	1.6
NH_4^+ -ZSM-5 (140)	Oxalic acid	80	18:11:1:71	6.5
NH_4^+ -ZSM-5 (12)	Citric acid	67	tr:12:2:86	7.2
NH_4^+ -ZSM-5 (25)	Citric acid	95	4:18:1:77	4.3
NH_4^+ -ZSM-5 (40)	Citric acid	95	7:35:2:56	1.6
NH_4^+ -ZSM-5 (140)	Citric acid	89	18:9:2:72	8.0

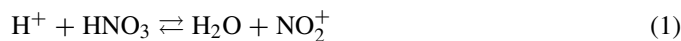
version of nitric acid with retention of selectivity toward the *para* isomer.

4. Discussion

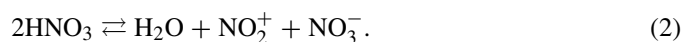
The reaction of toluene-nitric acid mixtures over H^+ -ZSM-5 and the related pentasil zeolite H^+ -Beta under liquid and vapor phase reaction conditions, respectively, has been shown previously to improve the regioselective conversion to MNT in comparison to the conversions achieved under homogeneous reaction conditions [16,17]. The results of the present work (cf., Table 2) verify the improvement in regioselectivity in the presence H^+ -ZSM-5 zeolites. Depending on the Si/Al ratio of the zeolite, nitric acid conversions of 40–60% are achieved, 7–21% of the products are unwanted oxidation derivatives, and the p/o ratio of MNT isomers is in the range 1.5–2.5. A conversion of 50% is observed under equivalent homogeneous reaction conditions, but almost one-third of the products benzaldehyde, ben-

zoic acid, dinitrotoluenes, and other non-MNT derivatives and the *p/o* MNT isomer ratio is well below 1.5. Clearly, a significant fraction of the nitration reaction occurs within the shape-selective micropores of the H⁺-ZSM-5 zeolite.

The selection of the protonated form of the zeolites in earlier studies presumably was motivated by the expectation that the strong Brønsted acidity in the micropores promotes formation of electrophilic nitronium ions through the equilibrium shown in Eq. (1). However, as shown by the data in Table 2 for reaction under conventional batch reaction conditions,



the HNO₃ conversions and *p/o*-MNT isomer ratios obtained using weakly acidic ammonium ion exchanged forms of ZSM-5 catalysts are comparable to those observed for the analogous protonated forms of the zeolites. Thus, the self-ionization of nitric acid in the micropores of NH₄⁺-ZSM-5 according to Eq. (2) is sufficient to provide conversions comparable to those observed for H⁺-ZSM-5.



One especially notable property of the H⁺-ZSM-5 (*x*) and NH₄⁺-ZSM-5 (*x*) zeolite families is the substantially lower fraction of undesired benzaldehyde and related oxidation products formed at Si/Al ratios below *x* = 140. For all framework Si/Al ratios investigated, the *o/p* MNT isomer ratio is in the range 1.3–2.3 and less than 5% of the product is in the form of *m*-MNT (cf., Table 2). Nevertheless, under conventional batch reaction conditions, homogeneous reaction in toluene solution plays an important role in limiting the product selectivity, as revealed below.

We further investigated the nitration of toluene over H⁺- and NH₄⁺-ZSM-5 (*x*) catalysts by first intercalating the nitric acid into the framework micropores of the zeolites prior to the addition of toluene. Our rationale for doing so was based on the expectation that the sequestration of the nitrating agent within the zeolite micropores would minimize the less-selective reactions occurring in homogeneous solution and thereby enhance the regioselective conversion of toluene to the *para*-MNT isomer. As shown by the product distributions in Table 3, the *p/o* MNT isomer ratios indeed are generally increased to values in the range 4.4–8.9 and 1.8–7.7 for the H⁺- and NH₄⁺-exchanged forms of the zeolite, respectively. To our knowledge these are the highest *p/o* ratios yet observed for the mononitration of toluene using nitric acid as the nitrating agent in the absence of a nitronium ion promoter.

Para/ortho MNT isomer ratios up to 19 at MNT yields of 15–50% have been reported for the nitration of toluene over H⁺-ZSM-5 using *n*-propyl nitrate as the nitrating agent [7]. Also, quantitative conversions of toluene to MNT with *p/o* ratios in the range 1.0–5.4 have been achieved using the protonated form of zeolite beta as the catalyst and acetyl nitrate formed in situ from nitric acid and acetic anhydride [5]. Although far more costly than nitric acid alone, *n*-propyl nitrate and acetyl nitrate offer certain advantages as nitrating agents. For these latter nitrating agents, reactive nitronium ions form only when the reagents encounter protons in the micropores of

the zeolites, thus ensuring that nitration is confined almost exclusively to the shape-selective environment of the catalyst.

The present work demonstrates that sequestration of nitric acid in ZSM-5 prior to the addition of toluene also is effective in promoting MNT formation within the intracrystal pores of the zeolites. The dramatic improvement in product selectivity that occurs when toluene is added to zeolite-intercalated nitric acid indicates that toluene addition helps to keep the nitric acid in the sequestered state and prevents the reaction system from rapidly re-equilibrating to a mixture of zeolite and a solution of nitric acid in toluene. That is, the binding of toluene limits diffusion of nitric acid out of the micropores and confines the reaction largely to the shape-selective pores of the zeolite framework.

Returning to the product distributions in Table 3, we see that for the H⁺-ZSM-5 catalysts the pre-intercalation of nitric acid in the zeolite framework does not substantially reduce the formation of undesired benzaldehyde in comparison to the fraction of such products generated under conventional batch reaction conditions (cf., Table 2). Nevertheless, nitric acid sequestration in H⁺-ZSM-5 (*x*) compositions greatly increases the regioselectivity for MNT formation, as indicated by the substantially improved *p/o* MNT ratios. Although pre-intercalation of nitric acid confines much of the nitrating agent to the micropores of the protonated zeolite and promotes intra-crystal formation of MNT, the protonated zeolite also permits the formation of the undesired oxidation products within the framework pores. However, the NH₄⁺-exchanged forms of the zeolite at Si/Al ratios ≤ 40 not only promote intracrystal formation of the *para* MNT isomer, but also greatly reduce the fraction of benzaldehyde and other undesired oxidation products formed in the reaction. Unlike the H⁺-ZSM-5 (*x*) compositions, NH₄⁺-ZSM-5 (*x*) catalysts with *x* ≤ 40 are effective in reducing benzaldehyde formation both under conventional batch reaction conditions (cf., Table 2) and under conditions where nitric acid is pre-intercalated in the zeolite framework (cf., Table 3). Pre-drying the zeolite at 160 °C further reduces the fraction of benzaldehyde formed under intercalated reaction conditions (cf., Table 3).

The role of NH₄⁺ exchange cations in reducing benzaldehyde formation is not clearly understood. It may be that the ammonium ion mediates the acid–base equilibria in the zeolite micropores. The need for the presence of an ammonium ion in each unit cell is indicated in part by the ineffective role of NH₄⁺-ZSM-5 (*x*) with a Si/Al ratio of *x* = 140 (cf., Tables 2 and 3). At this catalyst composition, half the unit cells in the zeolite crystal lack ammonium cations. For Si/Al ratios ≤ 40, however, there is on-average more than one ammonium ion per T₉₆O₁₉₂ unit cell (T = Si or Al). It is likely that some of the ammonium ions in NH₄⁺-ZSM-5 (*x*) catalysts are replaced by protons, or even nitronium ions, leading to the formation of ammonium nitrate in the micropores and a reduction in the fraction of free nitric acid in the pores in comparison to H⁺-ZSM-5 (*x*) catalysts. Indeed, the ratio of HNO₃/NH₄⁺ is > 1.0 under all reaction conditions except for NH₄⁺-ZSM-5 (*x*) with a Si/Al ratio of *x* = 12, where the HNO₃/NH₄⁺ ratio is ~0.80. But the product selectivity of the ammonium exchange form is always superior to the selectivity observed for the fully protonated zeolite, so long as the

nitric acid is sequestered in the micropores of a ZSM-5 framework with a Si/Al ratio ≤ 40 . This observation suggests that the ammonium ions may buffer the intercalated nitric acid by forming ammonium nitrate in the micropores and protons on the exchange sites of the zeolite framework.

As indicated by the data in Table 4, the dealumination of the external surfaces of NH_4^+ -ZSM-5 (x) zeolites by H_4EDTA , citric acid or oxalic acid did not appreciably affect the product distributions in comparison to the initial catalysts. This result suggests that potentially less-selective reactions on the external surfaces of the zeolite play little or no role in the observed product distributions. However, the dealumination typically improves the reactivity substantially, as indicated by the increases in conversion (cf., Tables 3 and 4). Also, the increases in catalytic activity parallel the increases in the intensities of the Bragg reflections in the X-ray powder diffraction pattern of the catalysts after dealumination. Thus, the role of the weak acids may indeed be to remove amorphous debris from the external surfaces of the zeolite crystals.

We note that the improved MNT regioselectivity and reduced yields of undesired oxidation products observed in this work were achieved under conditions where the volume of 90% nitric acid used for nitration represented approximately 30% of the framework pore volume of the zeolite catalyst (~ 0.19 cc/g, cf., Table 1). Increasing the amount of nitric acid beyond the pore volume of the zeolite compromised both the regioselectivity for MNT, as well as the yield of unwanted oxidation products. For instance, for the citric acid dealuminated NH_4^+ -ZSM-5 (12) catalyst in Table 4, the conversion is 67%, less than 0.5% of the product is benzaldehyde, and the p/o isomer ratio of MNT is 7.2 under conditions where the volume of nitric acid used in the nitration is 30% of the micropore volume. Increasing the volume of nitric acid to 120% of the micropore volume of the same catalyst results in approximately the same conversion (64%) but 6% of the product is benzaldehyde and the p/o isomer ratio is decreased to 1.8.

The limited volume of nitric acid that can be sequestered in NH_4^+ -ZSM-5 micropores restricts the amount of nitric acid and toluene that can be processed per unit weight of catalyst. For this reason it may not be practical to use batch reaction conditions for the large scale production of MNT over this zeolite. As in the case of most catalytic processes, creative process design will be needed to realize the full potential of NH_4^+ -ZSM-5 catalysts for the practical mononitration of toluene.

5. Conclusions

The pre-intercalation of nitric acid in the micropores of NH_4^+ and H^+ exchanged forms of ZSM-5 zeolite confines the

mononitration reaction to the shape-selective micropores of the zeolite and thereby substantially improves the regioselectivity toward the para isomer of mononitrotoluene (MNT). Although the MNT regioselectivity is similar for the two exchanged forms of the zeolite, the NH_4^+ form is preferred over the H^+ form because it dramatically reduces the amount of toluene that is oxidized to benzaldehyde and other unwanted oxidation products. At Si/Al ratios corresponding to the presence of more than one ammonium ion per unit cell (i.e., at Si/Al ratio ≤ 40), the para position of toluene is preferentially nitrated by the sequestered nitric acid with little or no oxidation of the methyl group. However, at Si/Al ratios corresponding to less than one ammonium ion per unit cell (e.g., Si/Al ratio = 140), the methyl position of toluene undergoes oxidation, leading to the formation of substantial fraction of benzaldehyde as an undesired reaction product.

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