Application of H-ZSM-5 Zeolite for Regioselective Mononitration of Toluene

Thomas J. Kwok* and Keerthi Jayasuriya*

GEO-Centers, Inc., at Energetic Materials Division, U.S. Army ARDEC, Bldg. 3028,
Picatinny Arsenal, New Jersey 07806-5000

Reddy Damavarapu and Bruce W. Brodman

Energetic Materials Division, U.S. Army ARDEC, Bldg. 3028, Picatinny Arsenal, New Jersey 07806-5000

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The nitration of toluene with *n*-propyl nitrate has been carried out in the presence of H-ZSM-5 as the catalyst. Several H-ZSM-5 catalysts with different Si/Al ratios were investigated to determine the influence of varying Si/Al ratios on the catalytic activity. It was found that high Si/Al ratios enhanced the regioselectivity for the *p*-nitrotoluene over the ortho isomer under comparable conditions. The best o:m:p product distribution (5:0:95) was achieved using H-ZSM-5 with a Si/Al ratio of 1000. The isolable yield is 54%. In contrast to conventional nitration methods, the product distribution reported in this study is remarkable.

Introduction

The nitration of aromatic compounds is an important process in both industrial and academic research.[1] In particular, the nitration of toluene is found to be useful for producing military explosives such as 2,4,6-trinitrotoluene (TNT) and pharmaceutical intermediates such as *p*-aminobenzoic acid (PABA). The conventional methods for nitration of aromatic compounds require corrosive nitric and sulfuric acids that afford a mixture of mono- and polynitroaromatics.[1c] Under these conditions, the nitration of alkyl-substituted aromatics such as toluene or xylenes often leads to oxidation of the alkyl side groups, and this could produce a mixture of byproducts. Developments in solid acid catalysts such as Nafion and other polysulfonic acid resins have reduced the corrosive nature and byproduct formation of the exisiting process.[2] However, the separation and removal of unwanted isomers from the product stream can be costly. Unfortunately, these sulfonic acid resin catalysts offer no significant contribution toward controlling regioselection in mononitration of alkyl aromatics such as toluene. The *p*-nitrotoluene isomer is highly desirable over the ortho and meta isomers because of its high commercial value.[3] Current trends in the nitration of aromatic compounds emphasize minimizing byproduct formation and improving regiocontrol of the desired isomer product using catalysts.

Recently Laszlo[3,4] and Smith[5] have independently reported novel methods for the nitration of aromatic compounds. Laszlo and co-workers have developed a reagent known as "claycop", which is $Cu(NO_3)_2$ supported on acidic monmorillonite clay, that selectively nitrates toluene, under Menke conditions (use of acetic anhydride as coreagent), affording a quantitative yield of mononitrotoluene with an ortho, meta, and para isomer distribution of 23:1:76, respectively. The conditions for achieving high conversion and regioselection for the para isomer require high dilution of toluene (1 mL) in CCl_4 (2 L) and 120 h reaction time. The authors suggest that the clay surface induces electronic stability favoring the para position. The disadvantages of this system are the requirement for high dilution, isolation of products, and reutilization of the catalyst. The excess acetic anhydride can be difficult to remove during the purification of products, and the stoichiometric use of copper nitrate makes regeneration of the system rather difficult in industrial applications. Smith and co-workers discovered that large port mordenite zeolite and benzoyl nitrate in toluene can afford 90% isolable yield of mononitrotoluene in a 42-h period and 60% selectivity for the para isomer.[5] Problems associated with benzoyl nitrate are difficulty in handling due to its sensitivity toward decomposition and the tendency toward detonation upon contact with rough surfaces.

Zeolites have well-defined pore structures and channels that are derived from the networking of SiO_2 and Al_2O_3 making them attractive candidates for shape selective catalysis.[6] In most cases zeolites are found to have both Lewis and Bronstead acidic sites throughout the inner and outer surfaces that can function as a solid acid.[7] This would be advantageous in large preparative scale reactions because of the ease in separation of catalyst from the product mixture and the minimal environmental impact. There have been many reports of zeolites that exhibit shape selective activity for such reactions as halogenation, alkylation, acylation, hydroxylation, and nitration.[5,6c,8] The nitration reaction of several aromatic compounds with benzoyl nitrate in the presence of

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amorphous aluminosilicate and zeolites, H-Y and H-ZSM-11, was reported by Nagy et al.[8b,c] The o:m:p product distribution reported for the nitration of toluene is 24:1:75, respectively. However, when H-ZSM-11 was treated with bulky tributylamine before the nitration to deactivate the outside active sites, the o:m:p product distribution changed to 2:<1:98, respectively. Unfortunately, the authors do not discuss the isolable yields, the formation of any byproducts, or the effect of the deactivation of outer active sites on the overall yield.

In this paper we report a method for catalytic mononitration of toluene using H-ZSM-5 zeolite and *n*-propyl nitrate that produces the para isomer with remarkable selectivity. Our approach is 2-fold. We performed computational analysis to determine the pore and channel sizes of various zeolites that affords the minimal size for the reactants to diffuse into the zeolite channels. On the basis of the analysis, we have selected H-ZSM-5 as an acid catalyst to attempt the nitration of toluene.

Results and Discussion

Computational Results. We have carried out ab-initio self-consistent field (SCF) molecular orbital calculations to determine the molecular dimensions of toluene and its three mononitro isomers. The shape selective characteristics of H-ZSM-5 can be determined by calculating the molecular dimensions of the reactants and products. The geometries of toluene, *n*-propyl nitrate, and three mononitrated isomers of toluene were optimized at 4-31G basis set level using Guassian 92 program.[9] In reactant shape selectivity, only the reactant molecules with the correct size can enter the zeolite channels.[6d] The size of the reactant molecule is important to determine the acceptable pore size of the zeolite. Reaction products of different sizes may be formed within the interior of the zeolite channels and only certain ones with the correct molecular dimensions can escape, and this selectivity is called product shape selectivity. For an example, the diffusion coefficient of *p*-xylene in H-ZSM-5 is approximately 10^3 times greater than that of either ortho or meta isomers.[10] In contrast, transition-state shape selectivity occurs when the space within the channels of H-ZSM-5 is not sufficient enough to allow the formation of several possible transition state intermediates, and this is a steric effect.[11]

The elliptical diameter of H-ZSM-5 is about 5.1−5.6 Å. Toluene, which is cylindrical in shape with a kinetic diameter of about 5.25 Å, fits rather closely inside the channels (Figure 1). It has been generally accepted that the active species for electrophilic nitration is usually the nitronium ion, NO_2^+, and that the reaction involves an intermediate σ complex.[12] In these σ complexes, the NO_2^+-bearing carbons are quasi-tetrahedral and their bond lengths to the neighboring carbon atoms are about 1.54 Å. The stabilization energies of these σ complexes decrease in the following order, para > ortho > meta.[13] Out of the three possible mononitrated isomers of toluene, the kinetic diameter of *p*-mononitrotoluene is about 5.25 Å and cylindrical in shape. Therefore, the product *p*-nitrotoluene can easily diffuse out.

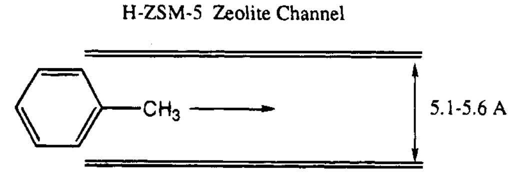


Figure 1. Toluene molecule entering H-ZSM-5 channel with pore opening of 5.1−5.6 Å.

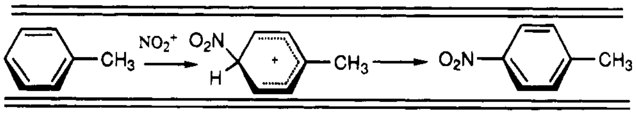
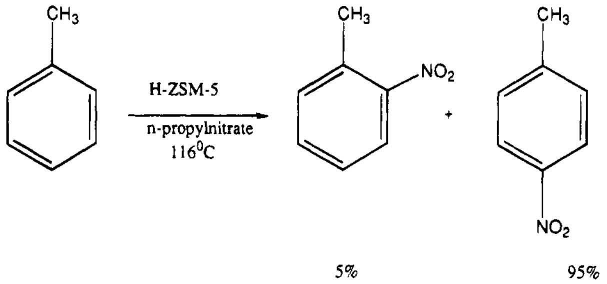


Figure 2. Formation of *p*-nitrotoluene inside H-ZSM-5 zeolite and diffusion of the product.

Scheme 1



Due to the spatial restrictions inside the zeolite channels, only the para position is available for an electrophilic attack by the nitronium ion, NO_2^+ (Figure 2). The other two isomers have a much larger kinetic diameter of about 6.7 Å, which is clearly much larger than the size of the pores of H-ZSM-5 catalyst. Therefore, the free movement of these two isomers is not permitted; hence, it is excluded by shape selective characteristics of the catalyst.

Nitration Experiments. The nitration reactions were performed as a slurry mixture where toluene and *n*-propyl nitrate were stirred over the catalyst. The *n*-propyl nitrate is an ideal nitrating agent because generation of NO_2^+ ion only occurs in the presence of acids.[2] Also, this reagent is safe to handle. A typical nitration reaction is shown in Scheme 1.

The nitration of toluene using H-ZSM-5 catalyst with Si/Al ratio of 30 gives a mixture of mononitrotoluenes with the isolable yield of 43%. Unlike in the conventional nitration process, the o:m:p product distribution under these conditions is 32:1:67, respectively (Table 1). The total yield of nitrotoluene was improved by increasing the amount of H-ZSM-5 catalyst used in the reaction while maintaining the product distribution. Increasing the temperature to a reflux temperature of toluene (116 °C) appeared to play a significant role on the total yield of the reaction. At room temperature, the reaction is very slow, requiring 7 days to achieve 20% conversion. It is

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Table 1. Nitration of Toluene with H-ZSM-5 and *n*-Propyl Nitrate[a]

entry	Si/Al ratio	H-ZSM-5/*n*-$PrONO_2$ (w/w)	isolable yield[b] (%)	product distribn[c] o:m:p	*T* (°C)
1	30	3:1	43	32:1:67	90
2	30	6:1	55	32:1:67	90
3	30	9:1	61	29:1:70	90
4	30	6:1	65	35:2:63	116
5[d]	30	6.7:1	20	20:1:79	20
6	80	6:1	61	29:1:70	90
7[e]	80	6:1	68	34:1:65	116
8[f]	80	6:1	50	32:1:67	116
9	1000	6:1	15	9:0:91	90
10	1000	6:1	18	9:0:91	116
11	1000	30:1	50	8:0:92	116
12	1000	40:1	51	6:0:94	116
13	1000	60:1	54	5:0:95	116
14[g]	1000	30:1	49	9:0:91	116
15	1000	40:1	67[h]	7:0:93	116

[a] Reactions were performed for 16 h unless otherwise noted. [b] Isolable yield was based on *n*-propyl nitrate. [c] The product distributions were determined by GC analysis and area responses calibrated externally with authentic samples. [d] Reaction stirred for 7 days. [e] This reaction was carried out on a large scale using 5 g of *n*-propyl nitrate. [f] Reaction stopped after 8 h. [g] Used recalcinated H-ZSM-5 catalyst. [h] Yield was determined by GC analysis using 2,4-dinitrotoluene as an internal standard.

clear from Table 1 that the isolable yields are consistently high, and selectivity favors the para isomer as the catalyst concentration and temperature increase. At higher catalyst concentrations with respect to the nitrating agent (>6:1), we have observed the formation of a mixture of normal and isopropyl methylbenzenes as byproducts with the major byproduct being 1-isopropyl-4-methylbenzene. It is possible that prolong heating may cause decomposition of the nitrating agent at reflux temperature. We did not observe any brown fumes in the nitrating reaction to suggest the formation of nitrogen oxides as a byproduct resulting from the decomposition of the nitrating agent.

There is a significant effect on the total yield and para selectivity of the reaction when we used a H-ZSM-5 catalyst with different Si/Al ratios. For example, H-ZSM-5 catalyst with a Si/Al ratio of 80 increases the total isolable yield to 61% at 90 °C, and the o:m:p product distribution is 29:1:70, respectively. A preparative scale reaction was performed using 5 g of *n*-propyl nitrate and 30 g of H-ZSM-5 catalyst at reflux temperature, and the isolable yield is 68% (see entry 7 in Table 1). An isolable yield of 50% was obtained after 8 h of the reaction without affecting the o:m:p product distribution. Under comparable conditions, the isolable yield increased when the reaction was carried out for 16 h. Prolong reaction time does not affect the product distribution. Using H-ZSM-5 catalyst with a Si/Al ratio of 1000, the selectivity of the para isomer improved significantly to over 90% of the product mixture but the isolable yield was 15%. At reflux temperature the isolable yield was 18% with the same selectivity favoring the para isomer. We were able to overcome this low yield by increasing the amount of catalyst used in the reaction, and under comparable reaction conditions the isolable yield increased to over 50%. The best o:m:p product distribution recorded was 5:0:95, respectively, and no byproducts were observed. For comparison, the o:m:p product distribution in the conventional nitration process is 56:5:39, respectively.[12] The yield determined by GC using 2,4-dinitrotoluene as an internal standard gives 67% under comparable reaction conditions (Si/Al = 1000, reflux temperature) with an o:m:p distribution of 7:0:93, respectively (see entry 15 in Table 1). No side alkylated products were detectable by GC. The fact that the yield obtained by GC is higher than the isolable yield suggests that we may be removing some products inadvertently in the process of stripping the solvent during the workup of the reaction.

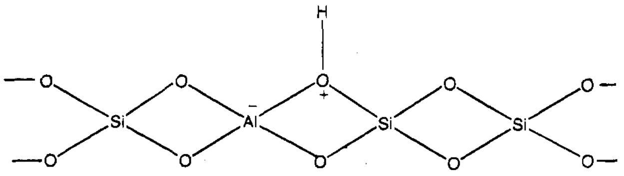

Figure 3. Bronstead acidic sites in H-ZSM-5.

On the basis of the several nitration reactions carried out using H-ZSM-5 with different Si/Al ratios the following observations are noteworthy:

(1) When we used a large amount of H-ZSM-5 with high Al content (Si/Al = 30), methylpropylbenzene was found as a byproduct with 1-isopropyl-4-methylbenzene as the major component in the mixture by GC/MS.

(2) We have made an attempt to investigate the possibility that nitrotoluene, particularly ortho and meta isomers, remains trapped within the pores of the zeolite. It is known that the H-ZSM-5 framework has low stability in base.[14] A sample of H-ZSM-5 (Si/Al = 1000) collected after the reaction was treated with saturated NaOH solution in an attempt to destroy the rigid structure of the zeolite and release the trapped compounds. The liquid mixture was separated from the slurry and extracted with hexanes and analyzed for nitrotoluene using GC method. Only a small amount *p*-nitrotoluene isomer was found in the GC analysis.

(3) It is possible that coking of the zeolite is limiting its reactivity, thus reducing the yield of nitration products. For example, addition of an extra quantity of *n*-propyl nitrate after 16 h of reaction time did not increase the yield of the reaction.

(4) The spent catalyst has been regenerated by recalcination under atmospheric conditions at 550 °C for about 16 h. The reactivity profile of a regenerated catalyst was tested under comparable conditions, and the isolable yield was 49% with the o:m:p product distribution 9:0:91, respectively (see entry 14 in Table 1). The regenerated catalyst has regained the activity completely.

(5) Due to the instability of *n*-propyl nitrate in the GC injection port, we were unable to quantify the amount of unreacted *n*-propyl nitrate in the reaction mixture.

There are numerous reports that suggest bridging oxygen atoms between silicon and aluminum atoms form active sites in the zeolite framework (see Figure 3).[7,14,15] The aluminum content throughout the entire zeolite framework directly correlates with the actual number of acid sites. It has been reported that only 5−10% of the total Bronstead acid sites in the H-ZSM-5 framework are located outside the channels.[16] Since the aluminum content directly correlates with the active sites in H-ZSM-

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5, catalyst with high Si/Al ratio (low aluminum content) have relatively few number of active sites outside the channels available for the formation of NO_2^+. The high regioselectivity for the para isomer can be attributed to the relatively large number of active sites found in the interior regions of the channels, where shape selective characteristics of the zeolite framework determines the product selectivity and diffusion of products depends on the diameter of the zeolite channels. These features explain the remarkably high regioselectivity for the para isomer found in H-ZSM-5 with high Si/Al ratio (o:m:p of 5:0:95). Nagy et al. reported an o:m:p distribution of 24:1:75, respectively, for the nitration of toluene using H-ZSM-11 and benzoyl nitrate.[8b] However, it is noteworthy to mention that by chemically modifying the catalyst, Nagy improved the o:m:p product distribution to 2:<1:98, respectively. No attempt was made to chemically modify the catalyst to deactivate the outer surface. However, the reactivity of the outer surface was controlled by selecting a catalyst with fewer active sites outside the channels. Steric factors inhibit the formation and diffusion of large ortho and meta isomers inside the channels. Therefore, it is assumed that the nitration of toluene takes place outside the channels indiscriminately and this is the source for ortho and meta isomers.

It has been established by researchers at Mobil that the highly selective *p*-xylene synthesis from methanol and toluene catalyzed by H-ZSM-5 is due to the enrichment of the para isomer via isomerization of ortho and meta isomers inside the channels.[10a] We have also investigated the possibility of isomerization among the three isomers of mononitrotoluene. A pure sample of each mononitrotoluene isomer was dissolved in toluene and refluxed over H-ZSM-5 (Si/Al = 80) for 16 h, and under these conditions no isomerization was observed. This is not surprising since no isomerization was observed in the conventional nitration process. We have also investigated the effect of other solvents on the nitration of toluene. It is surprising that the nitration of toluene is sluggish or inactive in many solvents other than toluene. For example, there was minimal activity in refluxing CCl_4 (isolable yield <10%, o:m:p distribution of 24:1:75, Si/Al = 80) No nitration was observed in THF, nitromethane, hexanes, and methyl alcohol. Contrary to what we have observed in our solid catalyst system, it has been reported that nitration reactions are efficient in CCl_4 with other solid catalysts.[2,3,4b,5] We are unaware of any other groups achieving the high regioselectivity for the para isomer (>91%) and elimination of the meta isomer in the mononitration of toluene using a chemically unmodified zeolite.

Conclusion

The results presented in this investigation show the reactivity pattern expected from conventional nitration process can be completely reversed by using a suitable catalyst. This has been achieved by the shape selective characteristics of H-ZSM-5 during the catalytic nitration of toluene. In addition, we believe that controlling the relative number of active sites outside the channels can regulate the product distribution. Case in point is that over 90% regioselectivity for the para isomer can be achieved by using a catalyst that contains a proportionately large number of active sites in the interior regions of the channels. Surprisingly, few researchers in this area have addressed this point as a possible explanation for zeolite catalyzed reactions where only modest regioselectivity is achieved. Nagy et al. have addressed this by chemically modifying the zeolite to deactivate the outer active sites.[8b] We believe external modification of zeolites would be an important consideration for future design of more sophisticated shape selective catalysts. Finally, we plan on investigating other aromatic substrates and electrophilic type reactions catalyzed by H-ZSM-5, in search of similar regioselectivity.

Experimental Section

General Methods. All solvents were obtained from either Fisher Scientific or Aldrich Chemical Co. Solvents were dried and distilled prior to use. The pure standard *o*-, *m*-, and *p*-nitrotoluenes were obtained from Chem Service. The *n*-propyl nitrate, obtained from Eastman Chemical Co., was dried over 4-Å molecular sieves prior to use. The H-ZSM-5 zeolites having a Si/Al ratio of 30 and 80 were obtained from the PQ corporation. The H-ZSM-5 zeolite with a Si/Al ratio of 1000 was a gift from the Degussa Corp. All zeolites were calcined in air at 550 °C for at least 16 h prior to use. The product mixtures were evaluated by GC analysis using Hewlett-Packard Model 5890 gas chromatograph fitted with capillary column (10 M × 0.533 mm) and FID detector.

A Typical Nitration Reaction Procedure. A single-neck 1000-mL round-bottom flask was charged with 200 mL of dry toluene, *n*-propyl nitrate (1.0 g, 0.0095 mol), and H-ZSM-5 (Si/Al ratio of 1000, 30.0 g). The charged flask was fitted with a water condenser and stopcock. The reaction mixture was purged and maintained under a stream of N_2. The mixture was heated to reflux temperature (116 °C) and stirred for 16 h. At the end of the reaction, the mixture was cooled to room temperature and filtered. The filtrate was distilled under reduced pressure removing all volatile components, and amber crystals were recovered. The crystals were dissolved in acetone and evaluated by GC analysis. The crystals were found to contain only *p*- and *o*-nitrotoluenes with a ratio of 92:8, respectively. The isolated yield was 50% (.67g).

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