

# Influence of the properties of zeolite BEA on its performance in the nitration of toluene and nitrotoluene

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## Abstract

The nitration of toluene and 2-nitrotoluene was investigated using different batches of zeolite BEA. In the nitration of toluene, notable differences in the product composition were obtained depending on the batch of BEA used. In the nitration of 2-nitrotoluene, all the catalysts displayed a good selectivity, but different conversions. Steaming improved the performance of the catalysts, but strong dealumination with oxalic acid had a negative effect. The positive effect of steaming was attributed to the enhanced transport of the reaction products out of the pores. Lewis acidity did not seem to play a role in the nitration reaction. A high concentration of Brønsted sites was detrimental, because it slowed down the diffusion of the products, but a small concentration of Brønsted sites was required to catalyze the heterogeneous reaction. © 2004 Elsevier Inc. All rights reserved.

**Keywords:** Nitration; Acetyl nitrate; BEA; Toluene; Nitrotoluene; Dinitrotoluene; *para*-Selectivity; Activity; Brønsted sites; Diffusion

## 1. Introduction

The nitration of toluene is one of the most important ways to obtain substituted aromatics in the production of chemical intermediates [1]. Nitrotoluenes (NT) and dinitrotoluenes (DNT) are important intermediates in the production of various compounds, mainly after reduction of the nitro group, and the *para*-substituted products are strongly desired. In the conventional industrial nitration, however, the production of the *ortho*-isomer exceeds that of the *para*-isomer. To overcome this limitation, various nitration systems using solid acids as catalysts were investigated [2–8]. Of particular interest is the high *para*-selectivity achieved with zeolite BEA and the combination of nitric acid and acetic anhydride as a nitrating agent, as reported initially by Smith et al. [4,9] and later investigated in our laboratory [10,11]. Our previous work has shown that only with zeolite BEA does the heterogeneous-catalyzed reaction compete effectively with the homogeneous reaction in the liquid phase [12]. High *para*-selectivity is induced by the spatial constraints within the zeolite pores, where the reaction with a surface-bound acetyl nitrate complex directs the formation of the Wheland

intermediate. However, notable differences in the product composition and in the activity of the reaction were observed depending on the batch of BEA used.

In several liquid-phase reactions, diffusion has been proven to be rate limiting; the performance of the catalyst could be improved by an increased diffusivity of the reactants and the products within the zeolite crystals. To improve the diffusion inside the zeolite a hydrothermal treatment and/or an acid leaching is carried out. These methods are already used on a large scale for zeolite MOR [13] and FAU [14]. Several studies have also demonstrated the favorable effect of steaming and acid leaching on the performance of zeolite BEA [15–17].

Here we present the results of the nitration of toluene and 2-nitrotoluene (2-NT), performed with a wide variety of BEA zeolites with different Si/Al ratios and different sizes of crystallite. The goal of the study was to elucidate the reasons for the differences in activity and selectivity observed using various batches of zeolite BEA.

## 2. Experimental

### 2.1. Catalysts

A number of commercially available BEA zeolites was used. PB1, PB3, PB5, and PB13 are different batches ob-

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Table 1  
Nomenclature of the modified samples used

Zeolite/treatment	Sample name
H-PB3	
Steaming (6 h)	H-PB3-st
Steaming (6 h) + leaching (6 M HNO <sub>3</sub> )	H-PB3-lc
H-PB13	
Steaming (1 h)	H-PB13-1st
Steaming (2 h)	H-PB13-2st
Steaming (3 h)	H-PB13-3st
Steaming (6 h)	H-PB13-6st
Leaching (0.5 M oxalic acid)	H-PB13-0.5ox
Leaching (1 M oxalic acid)	H-PB13-1ox
Leaching (2 M oxalic acid)	H-PB13-2ox
H-MCBeta	
Steaming (6 h)	H-MCBeta-st
Steaming (6 h) + leaching (6 M HNO <sub>3</sub> )	H-MCBeta-lc

tained from Zeochem AG (formerly CU Chemie Uetikon AG). BEA-24 and BEA-150 were obtained from Süd-Chemie AG, and PQ-Beta from Zeolyst International. All the zeolites were used in the proton form, which was prepared by a threefold ion exchange of the parent zeolites with a 1 M aqueous NH<sub>4</sub>NO<sub>3</sub> solution (10 ml for 1 g zeolite) under reflux for 1 h. After washing with deionized water, the zeolites were dried at 393 K for 5 h and then calcined in air at 773 K for 8 h.

In addition to the commercial BEA samples, a macrocrystalline BEA was synthesized in our laboratory according to the procedure of Kunkeler et al. [18]. A mixture of 50.09 g 40% tetraethylammonium hydroxide (TEAOH, Fluka), 5.96 g NaCl, and 23.59 g NaOH was diluted in 199.63 g distilled water. SiO<sub>2</sub> (67.45 g, Cab-Osil, Fluka) was added while stirring vigorously. Sodium aluminate (1.61 g), dissolved in distilled water, was then added. The gel was heated in a Teflon-lined autoclave at 413 K for 3 days. The obtained zeolite, referred to as MCBeta, was washed until the pH of the filtrate was neutral. The template was removed by calcination at 813 K for 10 h. The heating rate was 0.2 K/min up to 643 K and 0.5 K/min up to 813 K. MCBeta was ion-exchanged in the same way as the commercial BEA zeolites.

After the ion exchange, other postsynthesis modifications of the macrocrystalline BEA and some of the commercial samples were carried out. H-MCBeta underwent a hydrothermal treatment at 773 K for 6 h in a stream of water of 0.25 ml H<sub>2</sub>O/min. Acid leaching with 6 M HNO<sub>3</sub> followed this treatment. H-PB3 and H-PB13 were modified in the same way. Moreover, H-PB13 underwent different hydrothermal treatments, the duration of which varied. Steaming lasted from 1 to 6 h. Furthermore, H-PB13 was dealuminated with oxalic acid [19]. The zeolite was treated with three different concentrations (0.5, 1, and 2 M) of acid at room temperature for 1 h. After modification of all the samples, they were calcined at 773 K for 5 h. Table 1 gives the nomenclature of the modified samples.

## 2.2. Characterization

The structural integrity of the zeolites after each modification was monitored by X-ray diffraction on a Siemens D5000 X-ray diffractometer using Cu-K<sub>α</sub> radiation. After dissolving the zeolites in HF, the Si and Al contents were determined by atomic absorption spectrometry on a Varian SpectrAA instrument. Nitrogen adsorption at 77 K was carried out on a Micromeritics ASAP 2000M volumetric analyzer. The catalysts were degassed under vacuum prior to analysis at 673 K for at least 2 h. The specific surface area was evaluated using the BET model. The external surface area, the micropore volume, and the total pore volume were determined by means of the *t*-plot method. SEM images of the samples coated with a 5-nm-thick platinum layer were taken on a Hitachi S-900 microscope. Solid-state MAS NMR spectra were recorded on a Bruker AMX400 spectrometer operating at a magnetic field of 9.4 T. <sup>27</sup>Al MAS NMR measurements were performed on fully hydrated zeolite samples at a resonance frequency of 104.26 MHz and a rotor spinning rate of 10 kHz. For each spectrum 9720 scans were acquired using a 1.1-μs pulse length (flip angle of 15°) and a relaxation delay of 2 s. Chemical shifts are given relative to a 1 M aqueous aluminum nitrate solution. <sup>1</sup>H MAS NMR spectra were recorded at a resonance frequency of 400.13 MHz, a spinning rate of 10 kHz, a pulse length of 2.25 μs, and a delay time of 10 s. All the zeolites had been previously dehydrated under vacuum under a residual pressure of 10<sup>-4</sup> Pa at 623 K for 6 h. For a quantitative comparison, all the samples were weighed, and the spectra were calibrated by measuring a known amount of 1,1,1,3,3,3-hexafluoro-2-propanol under identical conditions [19]. IR spectra were recorded at 473 K on a Bio-Rad Excalibur FTS 3000 IR spectrometer equipped with a MCT detector at a resolution of 4 cm<sup>-1</sup>. Prior to analysis, the samples were degassed at 673 K for 1 h at atmospheric pressure in a helium flow.

## 2.3. Catalytic tests and diffusion experiments

For a typical reaction experiment 35 mmol 90 wt% nitric acid and 1.0 g of dried catalyst (403 K, overnight) were mixed and stirred at 273 K. Acetic anhydride (53 mmol) was added to convert nitric acid into acetyl nitrate and the water present in nitric acid into acetic acid (AcOH). After 15 min the aromatic substrate (35 mmol toluene or 3.5 mmol 2-NT) was added drop by drop at room temperature and the mixture was stirred for 30 min. The reaction was stopped by filtering of the mixture and washing of the catalyst with methylene chloride. After filtering of the catalyst, the organic products were separated from the aqueous phase by extraction with methylene chloride and analyzed by means of gas chromatography using an HP-1 fused silica capillary column and 1,3-dinitrobenzene as the integration standard. Small samples were collected every 5 min during the reaction for the kinetic experiments.

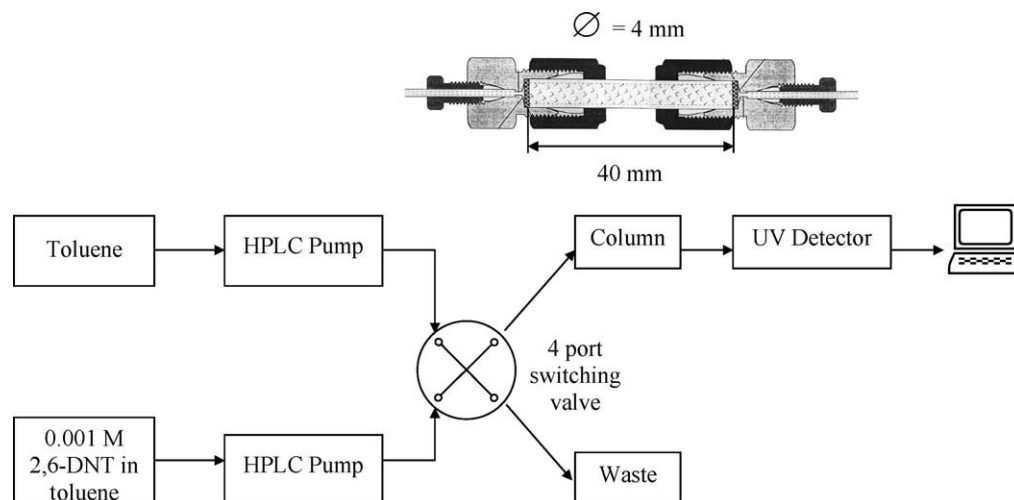


Fig. 1. Setup for the diffusion experiments.

The composition of the products inside the pores was analyzed by dissolving the filtered zeolites in 48 wt% HF. The products were extracted with methylene chloride and the organic phase was analyzed by gas chromatography.

The diffusion experiments in the liquid phase were carried out using the ZLC method for liquid phase described by Ruthven and co-workers [20,21]. Fig. 1 shows the setup for the diffusion experiments. Two HPLC pumps (Shimadzu LC-6A) were used to pump toluene and a 0.001 M solution of 2,6-DNT in toluene at a constant flow rate (2 ml/min). The dry zeolite ( $\sim 200$  mg) was loaded into a column, which had been constructed with Valco “zero dead volume” fittings. First, the catalyst was saturated with toluene and then, using a 4-port switching valve, 2,6-DNT was flown through the column for 30 min. Thereafter, toluene was pumped again into the column in order to desorb the 2,6-DNT. The adsorption and desorption of 2,6-DNT were monitored by a UV detector (Shimadzu SPD-6A).

Adsorption experiments in the gas phase were monitored by IR on a Mattson Galaxy 6020 IR spectrometer with a MCT detector at a resolution of  $4\text{ cm}^{-1}$ . After activating the samples (1 h, 773 K, in vacuum), 2-NT (Fluka) was adsorbed on the zeolite at 323 K and a pressure of 0.2 Pa for 5 h. The IR spectra were collected in-situ after different adsorption times. The normalized difference spectra were obtained by subtracting the spectrum of the zeolite prior to adsorption from the spectra of the zeolite impregnated with 2-NT. In these spectra the area of the peak corresponding to the symmetrical stretching of  $\text{NO}_2$  at  $1344\text{ cm}^{-1}$  was integrated and reported as a function of time.

### 3. Results

#### 3.1. Catalysts

Table 2 lists the characteristics of the different BEA zeolites used in this work. All the microcrystalline BEA zeolites

are composed of small crystallites ( $0.03\text{--}0.1\ \mu\text{m}$ ). The bulk Si/Al ratio of these zeolites varied from 9 to 15, except for H-BEA-150 with a bulk Si/Al ratio of 74. The synthesized BEA zeolite was composed of larger crystallites ( $1\text{--}10\ \mu\text{m}$ ). All the samples had a comparable BET surface area, except for the macrocrystalline BEA, which had a lower external surface area. The micropore volume of all the zeolites was similar.

The postsynthesis modifications hardly affected the external surface area and pore volume of the catalysts. XRD measurements confirmed that the crystallinity of the samples was still intact after the treatments. The bulk Si/Al ratio of the modified catalysts did not change significantly after hydrothermal dealumination, but it increased dramatically after acid leaching.  $^{27}\text{Al}$  solid-state MAS NMR (not shown) carried out on H-MCBeta revealed a decrease in both the tetrahedral and the octahedral aluminum after steaming and subsequent acid leaching. IR measurements on different BEA samples, conducted after each treatment, confirmed a gradual decrease in the peak corresponding to the Brønsted acid sites ( $3607\text{ cm}^{-1}$ ), especially after dealumination with oxalic acid, when the peak disappeared. Fig. 2 shows the IR spectra of H-MCBeta and the modified H-MCBeta-st and H-MCBeta-lc.

#### 3.2. Nitration with acetyl nitrate

##### 3.2.1. Nitration of toluene

Conversions between 80 and 95 mol% were achieved with all the BEA zeolites used (Table 3). The enhanced 4-NT selectivity induced by BEA and observed earlier by Smith et al. [4,9,22] was confirmed by the results of most of the BEA samples used in this study. However, depending on the BEA batch used, notable differences in the product selectivity were obtained. The selectivity observed with the nonmodified commercial BEAs varied from 61 to 74% (Table 3). It was not possible to achieve a good 4-NT selectivity with the synthesized macrocrystalline zeolite H-MCBeta.

Table 2  
Characteristics of the beta zeolites

	Bulk Si/Al <sup>a</sup>	BET surface area (m <sup>2</sup> /g)	External surface area (m <sup>2</sup> /g)	Total pore volume (cm <sup>3</sup> /g)	Micropore volume (cm <sup>3</sup> /g)
H-PB1	15	722	221	0.77	0.21
H-PB3	12	645	156	0.45	0.18
H-PB3-st	12	595	171	0.44	0.16
H-PB3-lc	41	643	179	0.47	0.17
H-PB5	12	690	199	0.90	0.21
H-PB13	9	670	233	0.75	0.18
H-PB13-1st	11	595	206	0.68	0.16
H-PB13-2st	12	575	197	0.68	0.16
H-PB13-3st	12	571	199	0.68	0.17
H-PB13-6st	12	596	215	0.64	0.18
H-PB13-0.5ox	70	616	250	0.65	0.19
H-PB13-1ox	77	616	249	0.63	0.19
H-PB13-2ox	91	614	250	0.65	0.19
H-BEA-24	12	696	170	0.65	0.22
H-BEA-150	74	722	139	0.63	0.25
H-PQ	13	634	182	1.06	0.19
H-RAMB	39	614	44	0.42	0.24
H-RAHB	142	582	94	0.63	0.21
H-MCBeta	12	632	8	0.30	0.28
H-MCBeta-st	16	590	10	0.33	0.27
H-MCBeta-lc	45	636	13	0.37	0.29

<sup>a</sup> From AAS.

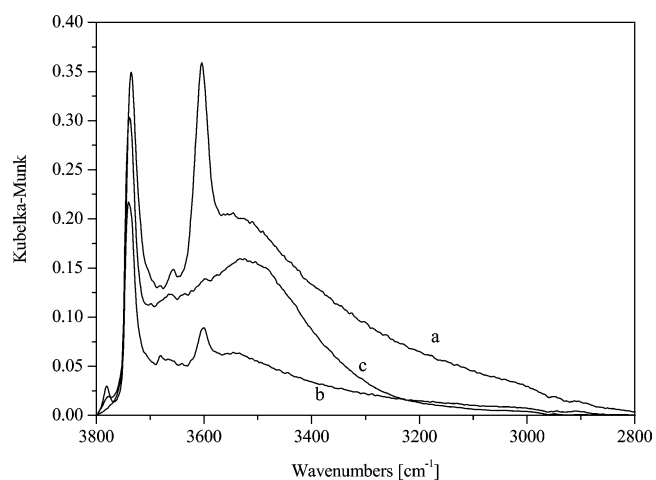


Fig. 2. FTIR of the macrocrystalline samples: (a) H-MCBeta, (b) H-MCBeta-st, and (c) H-MCBeta-lc.

However, after hydrothermal treatment of H-MCBeta, the *para*-selectivity was higher. The hydrothermal treatment, followed by acid leaching, was also very effective with the microcrystalline commercial BEA. The same trend as for the macrocrystalline BEA was found for H-PB3 and H-PB13. In both cases, the treated samples had a higher *para*-selectivity than the parent materials. However, dealumination with oxalic acid, carried out on the H-PB13, led to a decrease in the formation of the *para*-product.

### 3.2.2. Nitration of 2-nitrotoluene

The nitration of 2-NT was carried out under the same experimental conditions as for toluene. As reported previously [12], 2-NT reacted with a high selectivity to 2,4-DNT

Table 3  
Nitration of toluene using different beta samples (90 wt% HNO<sub>3</sub>, Ac<sub>2</sub>O, toluene/HNO<sub>3</sub> = 1, 30 min)

	Toluene conversion (mol%)	S <sub>2</sub> -NT (mol%)	S <sub>3</sub> -NT (mol%)	S <sub>4</sub> -NT (mol%)
Blank	81	59	3	38
H-PB1	84	36	3	61
H-PB3	90	37	2	61
H-PB3-st	91	21	3	76
H-PB3-lc	91	22	3	75
H-PB5	83	26	2	72
H-PB13	81	37	2	61
H-PB13-6st	80	23	3	74
H-PB13-1ox	86	45	2	53
H-BEA-24	81	31	3	66
H-BEA-150P	88	24	2	74
H-PQBeta	86	24	3	73
H-MCBeta	86	55	3	42
H-MCBeta-st	93	25	3	72
H-MCBeta-lc	95	28	3	69

on all the BEA zeolites. On the other hand, the conversion of 2-NT observed for the different BEA samples fluctuated considerably (Table 4). The macrocrystalline sample was the least active catalyst with a conversion of only 18 mol%. Upon hydrothermal dealumination the conversion increased to 86 mol%. The microcrystalline H-PB13 was dealuminated in steam for different reaction times and, it was observed that the activity increased with reaction time. After 6 h steaming a conversion of 94 mol% was obtained. In contrast, a strong dealumination method, such as acid leaching with oxalic acid, led to a drastic decrease in the activity. The sample treated with 2 M oxalic acid had the lowest conversion.

Table 4  
Nitration of 2-NT using different beta samples (90 wt% HNO<sub>3</sub>, Ac<sub>2</sub>O, 2-NT/HNO<sub>3</sub> = 0.1, 30 min)

	NT conversion (mol%)	S <sub>2,6</sub> -DNT (mol%)	S <sub>2,4</sub> -DNT (mol%)
Blank	9	— <sup>a</sup>	— <sup>a</sup>
H-PB1	41	7	93
H-PB1 <sup>b</sup>	45	7	93
H-PB3	53	6	94
H-PB3-lc	86	5	95
H-PB5	72	6	94
H-PB13	59	9	91
H-PB13-1st	77	5	95
H-PB13-2st	84	5	95
H-PB13-3st	86	5	95
H-PB13-6st	94	5	95
H-PB13-0.5ox	24	9	91
H-PB13-1ox	21	9	91
H-PB13-2ox	16	9	91
H-BEA-24	48	7	93
H-BEA-150P	82	5	95
H-PQBeta	81	6	94
H-MCBeta	18	7	93
H-MCBeta-st	86	5	95
H-MCBeta-lc	82	5	95

<sup>a</sup> Too low amounts for a reliable value.

<sup>b</sup> Excess of acetic acid (20 mmol) was used.

Table 5  
Ratio between reagent and products in the liquid phase and inside the pores, depending on the concentration of Brønsted acid sites

	(2,4-DNT + 2,6-DNT)/2-NT		
	Concentration of Brønsted acid sites (μmol/g) <sup>a</sup>	Liquid phase	Pores
H-PB5	144	1.35	2
H-PB3	285	0.65	2.94

<sup>a</sup> From <sup>1</sup>H MAS NMR.

In order to test whether the presence of acetic acid could influence the performance of the catalyst, the nitration of 2-NT was carried out using an excess of acetic acid (20 mmol). The acetic acid was added to the reaction mixture prior to addition of the aromatic substrate. The results (Table 4) showed that the presence of acetic acid has no influence on the catalyst.

Analysis of the products retained inside the pores was carried out by destroying the zeolite framework with 48 wt% HF. 2,4-DNT, 2,6-DNT, and some of the 2-NT reagent remained in the channel system of all the catalysts. The ratio between the reagent and the reaction products inside the pores depended on the amount of Brønsted acid sites (Table 5). In the zeolite with more Brønsted acid sites more products remained inside the pores. Moreover, the *o/p* ratio inside the pores was 0.12, whereas it was 0.06 in the reaction mixture. This indicates that the *para*-isomer diffuses out of the pores of the zeolite faster than the *ortho*-isomer. The results suggest that diffusion plays a major role in determining the performance of the BEA zeolites in the nitration reaction.

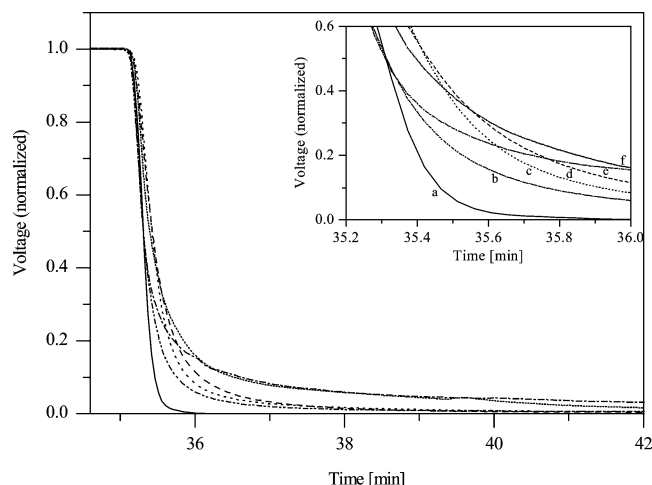


Fig. 3. Desorption of 2,6-DNT from the zeolite pores: (a) SiC (reference), (b) H-BEA-150P, (c) H-PQBeta, (d) H-PB5, (e) H-PB13, and (f) H-BEA-24.

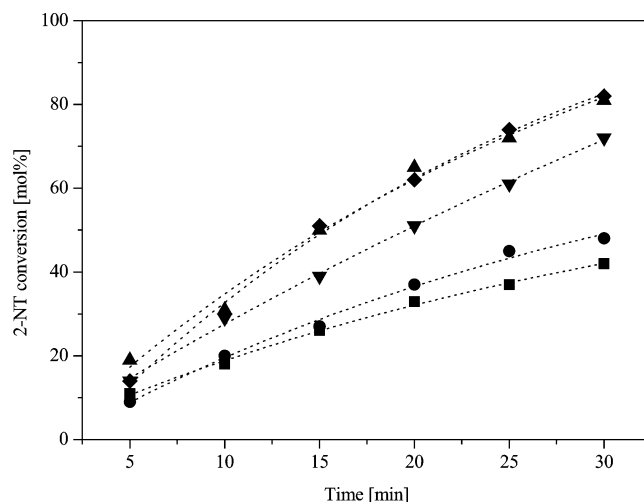


Fig. 4. 2-NT conversion for different zeolite samples as a function of time. (◆) H-BEA-150P, (▲) H-PQBeta, (▼) H-PB5, (●) H-BEA-24, (■) H-PB13.

### 3.3. Diffusion experiments

The adsorption and desorption of the bulkier 2,6-DNT were measured for different BEA samples. Fig. 3 shows the desorption curve. H-BEA-150P, H-PQBeta, and H-PB5 displayed rapid desorption, whereas in H-BEA-24 and H-PB13 the diffusion of the *ortho*-isomer out of the pores was slower. A comparison of the kinetic experiments (Fig. 4) and the diffusion measurements (Fig. 3) shows a clear correlation between the activity of the nitration reaction and the diffusion rate. The faster the products diffuse out of the pores, the higher the yield of the reaction.

The improvement of the catalysts upon hydrothermal dealumination, which was observed for the nitration of toluene and 2-NT, is also due to diffusion. The diffusion rate of 2,6-DNT increased significantly for the hydrothermally dealuminated samples H-PB3-st and H-PB13-6st compared to the parent material (Fig. 5). This indicates that the increase

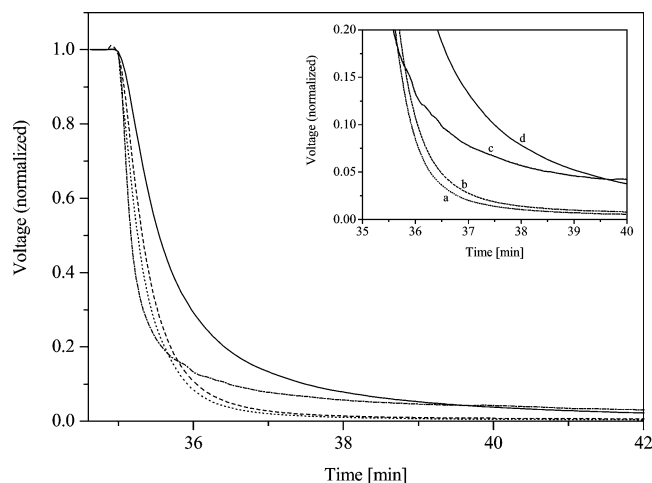


Fig. 5. Desorption of 2,6-DNT from the zeolite pores: (a) H-PB13-st, (b) H-PB3-st, (c) H-PB13, and (d) H-PB3.

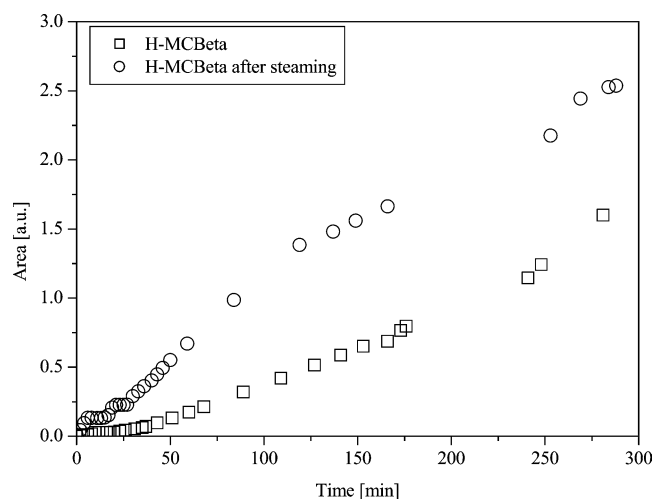


Fig. 6. Gas-phase adsorption of 2-NT on (□) H-MCBeta and (○) H-MCBeta-st.

in activity upon dealumination was caused by the higher rate of molar transport.

The diffusion measurements with H-MCBeta were carried out in the gas phase. In situ infrared measurements of the adsorption of 2-NT showed that 2-NT diffuses into the modified H-MCBeta-st faster than into H-MCBeta (Fig. 6).

#### 4. Discussion

Our previous work has shown that the enhanced *para*-selectivity during the nitration of toluene and 2-NT is a unique property of BEA and that it is due to the formation of an adsorbed complex inside the pores [12,23,24]. Almost all the BEA samples used in that study displayed a higher *para*-selectivity than the other types of zeolites. However, different batches of BEA led to differences in the selectivity of the reaction. Some commercial samples had a lower *para*-selectivity; with the macrocrystalline BEA more 2-NT

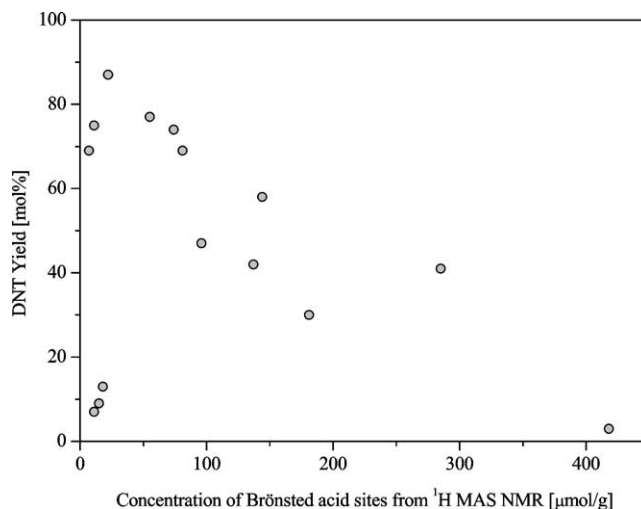


Fig. 7. Correlation between the concentration of Brønsted acid sites and the activity of the nitration of 2-NT.

than 4-NT formed. Hydrothermal treatment of the macrocrystalline sample improved the selectivity toward the *para*-product. The same trend was observed for the hydrothermally treated microcrystalline samples. IR characterization revealed that a high number of Brønsted acid sites is characteristic of the less selective catalysts. The macrocrystalline BEA had the highest number of Brønsted acid sites. Steaming of the sample, followed by acid leaching with mineral acid, led to a decrease in the number of Brønsted acid sites (Fig. 2) and, at the same time, to higher 4-NT selectivity. Moreover, our study on the dealumination of the macrocrystalline BEA [25] showed that, upon hydrothermal treatment, a secondary pore channel system formed in the (001) plane. This newly formed pore network enables a better diffusion inside the catalyst, as shown by the IR adsorption experiments (Fig. 6). Slow diffusion results in a less efficient competition between the heterogeneously and homogeneously catalyzed nitration, thereby inducing a greater contribution of the reaction in the homogeneous phase. In the case of the macrocrystalline sample this effect led to very low *para*-selectivity due to the fact that large crystals result in a long diffusion path. The positive effect of steaming is ascribed to the generation of mesopores, which facilitate transport. Moreover, the concentration of Brønsted acid sites is reduced, which is also favorable for the diffusion rate, as will be shown later. A stronger dealumination method, such as treatment with oxalic acid, which was carried out on a microcrystalline sample, almost completely removed the Brønsted acid sites and led to a decrease in the selectivity. An optimum number of Brønsted sites seems to be necessary to achieve the highest *para*-selectivity.

In the nitration of 2-NT to DNT the 2,4-DNT selectivity was exceptionally high for all the BEA samples. Nevertheless, the 2-NT conversions depended on the BEA batch used (Table 4). The macrocrystalline BEA displayed the lowest conversion. As for the nitration of toluene, the performance of the catalysts improved upon hydrothermal dealumina-

Table 6  
Differences in the ratio between the *ortho*- and the *para*-products for the nitration of 2-NT

	2,6-DNT/2,4-DNT ratio
Outside the pores	0.06
Inside the pores	0.12
Homogeneous reaction	0.72

tion. The effect was even stronger for the nitration of 2-NT than for the nitration of toluene. With the macrocrystalline BEA, the conversion increased from 18 to 86 mol% for the steamed sample and to 82 mol% for the leached sample. The same trend was observed for the modified microcrystalline commercial BEAs. H-PB13 was treated with steam, and there was a gradual increase in the activity with the time, with a maximum conversion of 94 mol% for the sample steamed for 6 h. A comparison of the results obtained with the different BEA samples (Table 3) shows a negative correlation of conversion with the concentration of Brønsted acid sites (Fig. 7). The H-PB13 sample was also dealuminated with different concentrations of oxalic acid. After these treatments, there was a drastic decrease in the conversion. The sample treated with 2 M oxalic acid for 1 h at room temperature displayed a conversion of only 16 mol% compared to 59 mol% for the parent material. This suggests that, although a high number of acid sites is unfavorable, a small but finite number of Brønsted acid sites is necessary to catalyze the nitration reaction (Fig. 7). The samples, which were only treated hydrothermally, and the samples, which were first steamed and then leached, had almost the same conversion and selectivity. Therefore, Lewis acidity does not play a large role in determining the performance of BEA in the nitration reaction.

The analysis of the products, which remained in the pores of the BEA after the nitration reaction, shows that the negative influence of a high concentration of Brønsted sites is also related to diffusion. Catalysts with a high concentration of Brønsted acid sites had more dinitroproducts inside the pores; i.e., their transport out of the pores was slower. Moreover, the higher *o/p* ratio inside the pores shows that the diffusion of 2,6-DNT is slower than that of 2,4-DNT (Table 6). Such a difference in the diffusion rate was not observed for 2-NT and 4-NT [12].

## 5. Conclusion

The nitration of toluene and 2-NT, carried out with different BEA samples, demonstrated that the number of Brønsted acid sites and diffusion play a major role in determining the performance of BEA. Diffusion of the products is supposed to be the rate-determining step. This suggests that the catalytic reaction takes place inside the BEA pores. The number of Brønsted acid sites influences the selectivity and activity.

A high number of Brønsted acid sites is unfavorable for the reaction, meaning a low *para*-selectivity for the nitration of toluene and a low activity in the nitration of 2-NT, because a high density of sites hinders the diffusion. On the other hand, acid sites are required to catalyze the heterogeneous nitration reaction, which has to compete with the fast nitration of toluene in the homogeneous phase. Lewis acidity does not seem to play a large role in the nitration reaction. Diffusion limitations play an important role, especially in the nitration of 2-NT. The high selectivity toward 2,4-DNT is induced by stereodirection of the surface-bound acetyl nitrate [12], but the reaction rate is determined by the transport of the dinitroproducts out of the zeolite pores.

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