ELSEVIER

Catalysis Today 60 (2000) 275–287

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Potential routes for the nitration of toluene and nitrotoluene with solid acids

Diego Vassena, Andreas Kogelbauer[1], Roel Prins*

Laboratory of Technical Chemistry, Swiss Federal Institute of Technology, ETH-Zentrum, CAB, CH-8092 Zurich, Switzerland

Abstract

New synthesis routes have been investigated for the production of dinitrotoluenes (DNTs) from toluene or an equimolar mixture of 2-nitrotoluene (2-NT) and 4-nitrotoluene (4-NT) and nitric acid using solid acids as heterogeneous catalysts. The main objective was the replacement of liquid sulphuric acid. A secondary goal was the increase of 4-NT and 2,4-DNT in the product mixture, which are more valuable products. Particular consideration was given to the feasibility of future large-scale process implementation. Continuous flow vapour phase reaction, and liquid phase reaction with simultaneous distillation were investigated. DNT formation in the vapour phase reaction was negligible with all solid acids tested. Preshaped silica impregnated with sulphuric acid was the most active catalyst but a continuous loss of sulphuric acid with time-on-stream was observed. Zeolite beta provided a higher 4-NT to 2-NT ratio than ZSM-5, ZSM-12 and mordenite, but deactivated after 5–10 h on-stream. Regeneration of beta was possible by thermal treatment. The *para*-selectivity of mordenite could be improved by the creation of a mesoporous system. In the reaction with simultaneous distillation, supported liquid acids exhibited true catalytic behaviour for the conversion of NT to DNT, but a loss of the impregnated acid was observed. Zeolite beta was about half as active as supported liquid acids and gave an exceptionally high 2,4-DNT selectivity of up to 94%, compared to 74–79% obtained with all other solid acids. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Nitrotoluene; Dinitrotoluene; Vapour phase nitration; Reactive distillation; Zeolite beta; Solid acids

1. Introduction

Nitrotoluenes (NTs) and dinitrotoluenes (DNTs) find applications as intermediate products in the production of pharmaceutical compounds, dyes, perfumes, explosives, polymers, pesticides and fertilisers [1]. Thanks to a continued optimisation effort over the last decades, the mixed-acid process is still used to nitrate toluene [2]. In this process a mixture of nitric acid, sulphuric acid and water is used for the nitration. The main purpose of sulphuric acid is the formation of nitronium ions by protonation of the nitric acid. Sulphuric acid acts additionally as water binder and heat sink for the highly exothermic reaction [1]. The main drawback of the process by far is the production of huge amounts of spent acid which have to be regenerated because a simple neutralisation is inconceivable nowadays for environmental and economic reason [3].

An alternative could be the substitution of sulphuric acid with solid acids. The advantages would lie in the simpler regeneration of solid acids through a thermal treatment and a facilitated separation of the

---

* Corresponding author. Tel.: +41-1-632-5490;
fax: +41-1-632-1162.
E-mail address: prins@tech.chem.ethz.ch (R. Prins)

[1] Present address: Department of Chemical Engineering and Chemical Technology, Imperial College of Science, Technology and Medicine, London SW7 2BY, UK.

PII: S0920-5861(00)00344-8

catalysts from the products. In earlier work, we have demonstrated that the nitration of toluene to NT and DNT can be carried out in the liquid phase at ambient temperature using silica-supported sulphuric acid and 65 wt.% nitric acid [4]. A high concentration of acid sites was concluded to be required for sustaining catalytic activity rendering most natural solid acids such as zeolites impracticable. In order to maintain an active catalyst, the water must be continuously removed from the acid sites of any solid acid and from the acid sites of zeolites, in particular. Various nitration procedures have been described over the last years that make use of nitrating agents other than nitric acid like NO_2 (N_2O_4), N_2O_5, molten nitrate salts, alkyl and acylnitrates [5]. Although high *para*-selectivity was achieved in some of these approaches, the use of nitric acid, preferably of azeotropic composition, is mandated for large-scale nitration processes on the basis of price, handling, and safety considerations. One of the key issues pivots around the question how to remove the water from the reaction mixture. In principle, there are three options for achieving this goal.

The first one comprises raising the reaction temperature and thereby evaporating the water. Already in 1936, McKee and Wilhelm [6] studied the vapour phase nitration of benzene and toluene using nitrogen dioxide as the nitrating agent and silica gel as catalyst. The vapour phase nitration of benzene and toluene either with nitrogen dioxide or with nitric acid and different solid acid catalysts was a matter of further studies [7–21]. None of these studies has led to a commercial process yet although the commercial viability has been claimed for benzene nitration [20].

Another method for removing the water by chemical trapping with acetic anhydride was proposed by Smith et al. [22]. For large-scale production this route is problematic because of the costs involved for the reactant (acetic anhydride), the safety aspects (acetyl nitrate needs special care during handling), and the need to dispose or make other use of the reaction product acetic acid. However, this method proved to be very useful for studying the selective conversion of toluene into 4-NT and 2,4-DNT using zeolite beta under mild reaction conditions [23]. Binding the water could also be achieved using other agents. In Olin Corporation's nitration process based on nitric acid only [24], anhydrous nitrate salts such as zinc or magnesium nitrate are applied during the re-concentration of the diluted nitric acid.

The third method for removal of the water is distillation from the liquid reaction mixture in continuous or discontinuous operation. Othmer et al. first proposed to continuously nitrate benzene [25] and toluene [26] in a distillation column with nitric acid only as nitrating agent and removing the water as an azeotropic water–benzene or water–toluene mixture. A discontinuous procedure for the nitration of toluene with nitric acid and amberlite was proposed by Wright et al. [27]. Using Nafion-H, Olah et al. [28] reached turnover numbers higher than one during the azeotropic nitration of different aromatics with nitric acid. Considering the strong exothermicity of the nitration reaction, continuous distillation of the water may be even more attractive because it would make efficient use of the reaction enthalpy and would permit good control of the reaction temperature. An adiabatic liquid phase nitration process is already in use on an industrial-scale for the mononitration of benzene [29,30]. Du Pont has disclosed an azeotropic process for the mononitration of benzene in mixed acid [31] and described a method for removing water by passing an inert gas through the reaction mixture [32]. Bayer AG have recently disclosed a one-step process using classical mixed acid for the preparation of DNT from toluene under adiabatic conditions [33].

Literature concerning the synthesis of DNT using solid acids is very scarce. Waller et al. [34] recently proposed the use of lanthanide(III) triflates, water tolerant Lewis acids, as catalyst for the nitration of simple arenes with 69% nitric acid in 1,2-dichloroethane. No dinitrated products were obtained and the catalysts had to be recycled through evaporation of the water produced during the reaction. The use of hafnium(IV) and zirconium(IV) triflates was later reported for the nitration of 2-NT to DNT [35]. The nitration of 2-NT with dinitrogen pentoxide in dichloromethane at 0°C and zeolites as catalysts was proposed by Claridge et al. [36]. Because of the use of chlorinated solvents, dinitrogen pentoxide and triflates, it is doubtful that these two routes will find application at industrial stage in the present form, except perhaps for smaller quantities of fine chemicals.

In this paper, we present results regarding the vapour phase nitration of toluene with different solid acids, as well as the nitration combined with distillation (reactive distillation) of NT. In the reactive distillation, we concentrated on the difficult nitration step, namely the nitration of NT to DNT. These two methods, especially the reactive distillation, are regarded potential routes for substituting the mixed acid process in the nitration of aromatics.

2. Experimental

2.1. Catalyst

Zeolites (ZSM-5, ZSM-12, beta and mordenite) as well as non-zeolitic materials were used as catalysts. Zeolite ZSM-5 (PZ2/40), beta (PB5) and mordenite (PM22) were received from CU Chemie Uetikon. ZSM-12 was synthesised in our group [37]. The zeolites were first dried for 5 h at 120°C and then calcined at 500°C (mordenite) or 550°C (beta, ZSM-5, ZSM-12) for 8 h. The proton forms of the different zeolites were prepared by a threefold 1 h ion exchange of the parent Na-zeolites with a 1 M aqueous NH_4NO_3 solution (10 ml for 1 g zeolite) at reflux temperature. After washing with deionised water, the zeolites were dried and calcined in the same way as before the exchange. A modified dealuminated mordenite was prepared in the following way: the Na-form was ion exchanged first with 1 M HCl and then with 1 M NH_4NO_3. Subsequently it was calcined for 2 h at 750°C and then extracted with 6 N HNO_3 to remove the extraframework aluminium.

Non-microporous solid acids like Nafion (Fluka), Deloxan (a polysiloxane bearing alkylsulfonic acid groups of Degussa) and preshaped silicas impregnated with sulphuric acid were used. Preshaped silica spheres (Shell, 2 mm diameter) and tablets (Aerosil 300, Degussa 5 mm×5 mm) were first calcined in air at 400°C for 18 h and then cooled in a dessicator. An excess of H_2SO_4 of various concentrations was then added to the preshaped silica (1.8 g 70 wt.% H_2SO_4/g preshaped spheres; 1.04 g 8 wt.% H_2SO_4/g preshaped spheres; 1.6 g 80 wt.% H_2SO_4/g preshaped tablets). After one day, the resulting supported acids were decanted, dried at 120°C for 18 h and subsequently stored in a dessicator under vacuum.

2.2. Characterisation

The Si and Al contents of the zeolites were determined by atomic absorption spectrometry on a Varian SpectrAA instrument after dissolution of the zeolite in hydrofluoric acid. The structural integrity of the zeolites after each modification was checked by X-ray diffraction on a Siemens D5000 X-ray diffractometer using Cu Kα radiation. Nitrogen adsorption at -196°C was carried out on a Micromeritics ASAP 2000M volumetric analyser. The catalysts were degassed prior to analysis under vacuum at 400°C for at least 2 h. The specific surface area was evaluated using the BET method. The external surface area is given as the difference between the BET surface area and the micropore surface area, which was determined according to the *t*-plot method [38]. The average pore diameter of pores larger than 17 Å was estimated from the desorption branch of the isotherm using the BJH method [39]. TGA measurements were carried out on a Mettler Toledo TGA/SDTA851^e system. The samples were heated under 50 ml/min of flowing air at a rate of 10°C/min from ambient temperature to 800°C. The amount of sulphuric acid impregnated on the silica was determined by acid–base titration using 0.1 M NaOH after suspending and vigorously stirring the supported acid in distilled water. The corresponding weight of the silica carrier was determined after calcination at 400°C in static air.

Solid-state ^{27}Al and ^{1}H MAS NMR spectra were recorded on a Bruker AMX400 spectrometer at a magnetic field of 9.4 T. Chemical shifts are given relative to 1 M aqueous aluminium nitrate solution (^{27}Al) and tetramethylsilane (^{1}H). ^{27}Al MAS NMR spectra were recorded at a resonance frequency of 104.26 MHz, 2160 scans were acquired for each spectrum and rotors were spun at 10 kHz. ^{1}H MAS NMR spectra were recorded at a resonance frequency of 400.13 MHz and 256 scans were acquired for each spectrum. ^{1}H MAS NMR samples were dehydrated under vacuum (p=0.1 Pa) at 350°C for 6 h and sealed in zirconia rotors prior to data acquisition.

2.3. Catalytic tests

2.3.1. Vapour phase nitration

The catalytic tests were carried out in a fixed-bed downflow reactor system at atmospheric pressure between 130 and 160°C over a period of 26 h on stream. The long-term activity of sulphuric acid impregnated silica was tested in reaction experiments up to 120 h on-stream. The reactor consisted of a stainless steel tube of 17 mm inner diameter fitted with a thermocouple. The zeolite powder was pressed at 4 t/cm^2 and subsequently crushed and sieved to particles between 25 mesh (0.707 mm) and 45 mesh (0.354 mm) before being inserted in the reactor. An amount of 1.5 g of catalyst was placed between two plugs of glasswool. SiC of 5 cm^3 were put on top of the upper plug in order to facilitate mixing and preheating of the reagents before reaction, whereas 15 cm^3 were put beneath the lower plug in order to prevent the condensation of the products. Toluene was fed by means of a HPLC pump. Nitric acid (65 wt.%) was supplied in a liquid level gauge pressurised with nitrogen. The outlet of the level gauge was connected to a Brooks liquid mass-flow controller (Flomega 5881) exclusively equipped with teflon seals. The liquid reactants were each separately evaporated in a flowing stream of N_2 using heated SiC-packed vaporisers, and were combined shortly before the reactor to avoid reaction in the heated feed lines. This arrangement provided reliably a constant flow of both reactants to the reaction system. A HNO_3/toluene molar feed ratio between 1 and 2 and W/F between 4.7 and 7.4 g h mol^{-1} based on the total feed (reagents and inert) were applied. The catalysts were pre-treated in flowing N_2 at 158°C for at least 1 h and then saturated with nitric acid vapour for 0.5 h before starting the reaction. The reactor effluent was collected for a period of 0.5 h in a jacketed, cooled glass container (7–9°C) containing a mixture of water, dichloromethane and 1,3-dinitrobenzene as external integration standard. After separation from the aqueous solution, the organic layer was analysed off-line by gas chromatography using a HP 5890 gas chromatograph equipped with a HP-1 fused silica capillary column. The HNO_3 conversion was determined by back-titration of the aqueous layer.

2.3.2. *Reaction with simultaneous distillation*

The reaction was carried out in a three-neck glass flask to which a thermometer, a dropping funnel, a distillation bridge with Dean-Stark trap, and a reflux condenser were attached. The reaction vessel was stirred with a magnetic stirring bar, heated with an oil bath, and could be evacuated to about 70 mbar. The flask was charged with 3.10 g of catalyst, previously dried for at least 18 h at 130°C, and 0.23 mol of a 1:1 molar mixture of 2-NT and 4-NT. To prevent attrition from the mechanical friction of the magnetic stirrer, the silica spheres were suspended in a teflon basket equipped with small holes and completely immersed in the reaction mixture. The system was stirred and heated at 100°C under a reduced pressure of 70–80 mbar. An equimolar amount of 65 wt.% HNO_3 was then added through a dropping funnel over a period of 2 h at an overall rate of 1.92 mol/min. After the addition of nitric acid had started, the temperature in the reaction vessel rose to 130°C and was kept at 130°C (± 5°C) throughout the whole reaction. The evaporated water–nitric-acid mixture was condensed and collected in a Dean-Stark trap. After complete addition of the nitric acid the reaction mixture was allowed to react for another 20 min after which it was rapidly cooled to ambient temperature. The organic products were analysed in the same way as in the vapour phase nitration. Titration of the collected aqueous phase was carried out in order to determine the nitric acid mass balance.

3. Results and discussion

3.1. *Catalysts*

The characteristics of the zeolites are reported in Table 1. Compared to the other zeolites, H-beta is characterised by a very large external surface area.

Table 1
Characteristics of the zeolites

	Si/Al	BET surface area (m^2/g)	External surface area (m^2/g)	Pore volume (cm^3/g)	Average mesopore diameter (Å)	Micropore volume (cm^3/g)
H-beta	11.5	690	199	0.90	102	0.21
H-ZSM-5	16.9	433	64	0.51	98	0.16
H-ZSM-12	47	355	20	0.20	38	0.15
H-mor(4.6)	4.6	544	6	0.27	64	0.22
H-mor(74)	74	512	38	0.31	57	0.20

Table 2
Characteristics of the preshaped silica impregnated with H_2SO_4

Catalyst	Carrier	Shape	H_2SO_4 loading of the catalyst (%)
8% H_2SO_4/SHE	Preshaped silica (Shell)	Sphere, diam. 2 mm	6
70% H_2SO_4/SHE	Preshaped silica (Shell)	Sphere, diam. 2 mm	56
80% H_2SO_4/DEG	Preshaped silica (Degussa)	Tablet, 5 mm×5 mm	52

This is a sign of small crystallite size and/or the presence of mesopores. The proton-exchanged mordenite exhibited a small external surface of 6 m^2/g, whereas the dealuminated mordenite showed an external surface of 38 m^2/g. The increase in the pore volume and the shift of the maximum in the mesopore diameter distribution to smaller values suggests that the thermal treatment combined with the acid leaching created a secondary mesoporous system in H-mordenite. A description of the silica-supported sulphuric acid samples and their actual H_2SO_4 loadings are given in Table 2.

3.2. *Vapour phase nitration*

Table 3 shows typical results obtained using sulphuric acid impregnated silica and Deloxan after 4 h on-stream, at a constant 20 cm^3/min N_2 carrier flow, 3.84 or 7.68 g/h 65 wt.% HNO_3 and different reaction conditions. At 132°C using an equimolar reactant feed ratio, the NT yield was around 50% with both catalysts whereas only traces of DNT were detected. The selectivity to 4-NT was only slightly higher than that (36.5%) obtained with the mixed acid process [1]. Using a twofold molar flow of nitric acid in case of 70% H_2SO_4/SHE, the NT yield improved to about 65% without a corresponding increase in the DNT yield. Raising the reaction temperature to 158°C, an activity increase was observed and initially a minor quantity of DNT was formed. The DNT yield exceeded 5% when 70% H_2SO_4/SHE was used as catalyst at a HNO_3/toluene reactant ratio of 2. At the same reaction conditions, Deloxan showed a similar NT yield but a clearly lower activity to DNT (1.2% DNT yield). In all experiments, the 3-NT selectivity was around 5% of the total amount of NT, slightly higher than the 4% obtained in the classical mixed acid process [1]. We attribute the somewhat enhanced formation of 3-NT to nitration following a radical mechanism rather than to secondary isomerisation of the products on the outer surface of zeolites as suggested by Malysheva et al. [40].

An NT yield of ca. 20% (Fig. 1) but no formation of DNT (Table 4) was already reached in vapour phase nitration reactions without solid acid at 158°C, 3.84 g/h 65 wt.% HNO_3, HNO_3/toluene=1, 60.5 ml/min flowing nitrogen and W/F=5 g h mol^{-1}. The HNO_3 conversion was 32–34%, whereas the toluene conversion was slightly higher than the NT yield. Phenylnitromethane (<1.0 mol%), benzaldehyde (<0.5 mol%), and traces of benzylalcohol, 2- and 4-nitrobenzaldehyde were found as by-products. The

Table 3
Vapour phase nitration of toluene with non-microporous solid acids[a] (yield after 4 h on-stream)

Catalyst	Temperature (°C)	HNO_3/toluene[b]	NT yield (mol%)	4-NT/$\sum$NT	3-NT/$\sum$NT	DNT yield[c] (mol%)
Deloxan	132	1	50.9	0.41	0.046	Traces
Deloxan	158	1	56.1	0.42	0.049	Traces
Deloxan	158	2	75.2	0.41	0.050	1.2
70% H_2SO_4/SHE	132	1	47.4	0.40	0.051	Traces
70% H_2SO_4/SHE	132	2	64.6	0.40	0.051	Traces
70% H_2SO_4/SHE	158	1	60.3	0.41	0.052	1.4
70% H_2SO_4/SHE	158	2	76.7	0.40	0.052	5.8

[a] By-products: traces of benzaldehyde, benzylalcohol, 2-nitrobenzaldehyde, 4-nitrobenzaldehyde, phenylnitromethane.
[b] W/F=7.4 g h mol^{-1} in case of HNO_3/toluene=1, W/F=4.7 g h mol^{-1} in case of HNO_3/toluene=2.
[c] 2,4-DNT and 2,6-DNT. 2,4-DNT/$\sum$DNT=0.78–0.8.

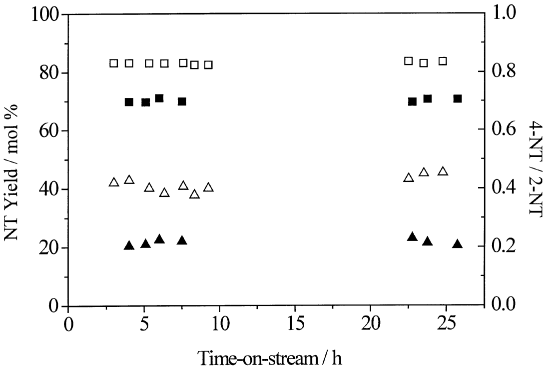

Fig. 1. Vapour phase nitration of toluene: blank experiment and nitration with Deloxan. Reaction conditions: 158°C, HNO_3/toluene=1, W/F=5 g h mol^{-1}. NT yield (mol%, left scale): (▲) without solid acid; (△) with Deloxan, 4-NT to 2-NT ratio (right scale): (■) without solid acid; (□) with Deloxan.

higher conversion of nitric acid compared to toluene is due to the disproportionation of part of the HNO_3 into NO_2. A yellow-brown gas, the typical colour of NO_2, was actually present in the sample collectors. Under the same reaction conditions Deloxan was stable, showed a twofold NT yield and did not lose its activity over a period of 24 h. The *para*-to-*ortho* ratio of the NT product was only slightly higher than in the blank experiment. The HNO_3 conversion was 69–73% and the same by-products but in somewhat higher amounts compared to the blank experiment (phenylnitromethane <1.5 mol%, benzaldehyde <1.0 mol%) were detected, indicating a higher activity also towards side reactions and disproportionation of nitric acid. Although the catalysts did not deactivate substantially for 24 h on-stream, significant sintering of the catalyst beads was observed after the recovery of the spent catalyst.

Table 4
Vapour phase nitration of toluene: DNT yield and 3-NT selectivity

Catalyst	DNT yield (mol%)			3-NT/$\sum$NT	
	4 h	24 h	48 h	4 h	24 h
Blank	0.0	0.0		0.049	0.049
Deloxan	0.2	0.2		0.049	0.049
70% H_2SO_4/SHE	1.4	0.3	0.0	0.050	0.050
80% H_2SO_4/DEG	1.2	0.5	0.1	0.049	0.047
H-mor(4.6)	0.02	0.0		0.050	0.050
H-mor(74)	1.9	0.1		0.048	0.048
H-beta	0.3	0.0		0.045	0.048
H-ZSM-5	0.0	0.0		0.050	0.050
H-ZSM-12	0.0	0.0		0.050	0.050

Long-term experiments at 158°C (Fig. 2) with impregnated silica using two different silica carriers (Degussa silica tablets and Shell preformed silica beads) gave comparable results regarding activity and selectivity (the bigger tablets were only slightly more selective to 4-NT than the smaller beads) but differences in the time-on-stream behaviour were observed. NT yields of >50% in the first two days on-stream were reached, whereas a clearly higher HNO_3 conversion (78–81% in case of 80% H_2SO_4/DEG and 72–75% in case of 70% H_2SO_4/SHE) points towards disproportionation of part of the HNO_3 into NO_2. After 50 h on-stream the activity of 70% H_2SO_4/SHE began to drop substantially, whereas the 80% H_2SO_4/DEG catalyst retained a constant activity until 100 h on-stream when the NT yield began to decrease only slightly. The faster deactivation of 70% H_2SO_4/SHE can be attributed to the longer contact time as well as to the smaller particle size. The 70% H_2SO_4/SHE catalyst exhibited a similar activity after 96 h on-stream as the 8% H_2SO_4/SHE catalyst, a preshaped silica with a significantly smaller initial H_2SO_4 loading (Fig. 2).

The results of the analysis of the acid content of the impregnated silicas before and after reaction are given in Table 5. It is evident that all supported solid acids lose sulphuric acid with time-on-stream except for the

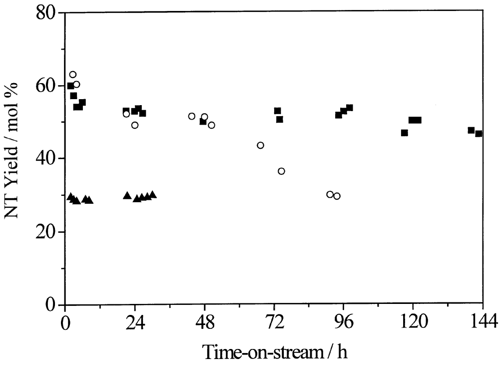

Fig. 2. Long-term experiment over preshaped silica impregnated with H_2SO_4. Reaction conditions: 158°C, HNO_3/toluene=1, W/F=7.4 g h mol^{-1} in case of 70% H_2SO_4/SHE, W/F=5 g h mol^{-1} in case of 80% H_2SO_4/DEG and 8% H_2SO_4/SHE. NT yield (mol%): (■) 80% H_2SO_4/DEG; (○) 70% H_2SO_4/SHE; (▲) 8% H_2SO_4/SHE.

Table 5
Sulphuric acid content of preshaped silica before and after nitration

Catalyst	Temperature (°C)	HNO_3 /toluene	Reaction time (h)	H_2SO_4 loading (%)	
				Before reaction	After reaction
70% H_2SO_4/SHE	125	[a]	18	56	51
70% H_2SO_4/SHE	132	1	26	56	37
70% H_2SO_4/SHE	132	2	26	56	34
70% H_2SO_4/SHE	158	1	96	56	8
70% H_2SO_4/SHE	158	2	26	56	32
80% H_2SO_4/DEG	158	1	145	52	18
8% H_2SO_4/SHE	158	1	32	6	6

[a] Catalyst was treated in 20 ml/min flowing N_2 only.

8% H_2SO_4/SHE catalyst after 32 h on-stream. A slight decrease in the H_2SO_4 loading is found even after prolonged heating of the supported sulphuric acid at a temperature as low as 125°C in flowing N_2 only. The activity loss in the long-term experiment presented in Fig. 2 is clearly related to this loss in acidity. Sato et al. [20] also showed a sudden loss of activity after extended hours on-stream in the vapour phase nitration of benzene over supported sulphuric acid on silica. They attributed this deactivation behaviour to the complete effusion of the sulphuric acid from the carrier. The H_2SO_4 loading of 70% H_2SO_4/SHE after 96 h was similar to that of 8% H_2SO_4/SHE. The NT yield was also comparable. It seems that after reaching a H_2SO_4 loading of 7–8% the deactivation stops or at least slows down substantially. No deactivation was actually observed with 8% H_2SO_4/SHE for 32 h on-stream.

Fig. 3 shows the results obtained with zeolites H-beta, H-ZSM-5 and H-ZSM-12. The activities of the zeolites (studied at 158°C only) were lower than those of the other solid acids and practically no formation of DNT was observed (Table 4). Only slightly higher NT yields compared with the blank experiment (Fig. 1) were observed, whereas nitric acid conversions were similar to that in the blank experiment. H-beta showed an enhanced *para*-selectivity during the initial reaction periods. A 4-NT to 2-NT ratio of >1 could be reached in the first hours on-stream. Both activity and selectivity decreased over a period of about 5–10 h on-stream. We attributed this decrease to the formation of strongly bound (by)products blocking the micropore system of H-beta [21] and we also showed that the deactivation was reversible. A Soxhlet extraction of the zeolite with $CHCl_3$ recovered only NT. Also, no DNT was found when the zeolite was destroyed using aqueous HF and subsequently extracted with CH_2Cl_2. A detailed analysis of the zeolite recovered after the nitration reaction suggested that oxidative by-products were the major reason for the deactivation in vapour phase flow nitration [21].

H-ZSM-5 showed only a slight increase in the 4-NT to 2-NT ratio (Fig. 3) compared with the blank experiment. The ZSM-5 structure consists of a three-dimensional channel system with relatively large channel intersections and pore openings limited by 10-membered rings. The dimension of the channels (5.3 Å×5.6 Å and 5.1 Å×5.5 Å) should be ideal for the *para*-selective nitration of toluene to NT (kinetic diameter of 2-NT: 6.7 Å; 4-NT: 5.2 Å [41]). We have

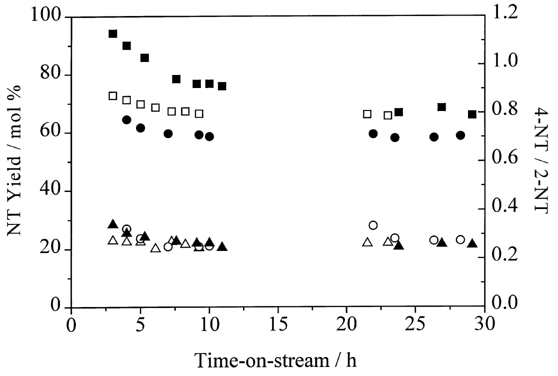

Fig. 3. Vapour phase nitration of toluene with H-beta, H-ZSM-12 and H-ZSM-5. Reaction conditions: 158°C, HNO_3/toluene=1, W/F=5 g h mol^{-1}. NT yield (mol%, left scale): (▲) H-beta; (△) H-ZSM-5; (○) H-ZSM-12, 4-NT to 2-NT ratio (right scale): (■) H-beta; (□) H-ZSM-5; (●) H-ZSM-12.

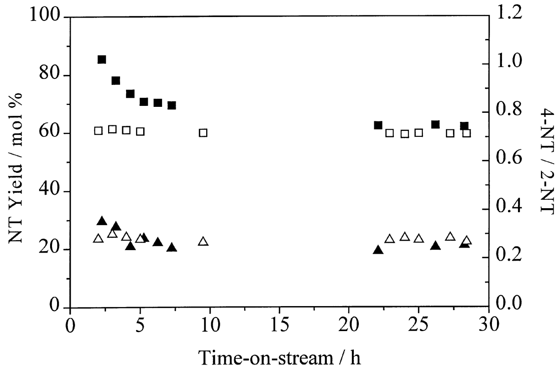

Fig. 4. Vapour phase nitration of toluene with mordenite. Reaction conditions: 158°C, HNO_3/toluene=1, W/F=5 g h mol^{-1}. NT yield (mol%, left scale): (▲) H-mor(74); (△) H-mor(4.6), 4-NT to 2-NT ratio (right scale): (■) H-mor(74); (□) H-mor(4.6).

shown through in situ IR adsorption experiments that 4-NT can diffuse into the pore system of H-ZSM-5, but diffusion of 2-NT is severely restricted [42]. The rapid deactivation of H-ZSM-5 might therefore be related to the formation of 2-NT in the channel intersections. 2-NT would be too bulky to leave the pore system of H-ZSM-5 thereby completely blocking the latter.

The enhanced selectivity to 4-NT of H-beta is probably linked to steric hindrance induced by adsorption rather than to shape selectivity in the classical sense [23] because both 2-NT and 4-NT can easily diffuse in the pore system of H-beta [42]. The H-beta used in the present work is characterised by a large external surface and small crystallites. Experiments with acetyl nitrate as nitrating agent under mild reaction conditions had shown that the selectivity patterns of H-beta were strongly dependent upon the crystallite size and the external surface area [43]. This trend was also observed in mordenite (Fig. 4) where the proton-exchanged sample with an external surface area of 6 m^2/g shows practically no enhanced *para*-selectivity. An improvement of the 4-NT to 2-NT ratio was observed when the H-exchanged mordenite was exposed to a thermal treatment combined with acid leaching that increases the external surface to 38 m^2/g by the formation of a mesoporous system. Also, in this case the catalyst deactivates after 5–10 h on-stream. H-mor(74) and H-beta were the only zeolites tested that gave a small DNT yield (Table 4). H-ZSM-12 with a mono-dimensional channel system with pore dimensions of 5.5 Å × 5.9 Å showed an even lower *para*-selectivity than H-ZSM-5 (Fig. 3). This zeolite should have been highly selective for 4-NT if transition-state selectivity was responsible for the selectivity enhancement. An attempt to introduce mesoporosity into ZSM-12 by subjecting it to the same treatment as mordenite failed because even a thermal treatment at 1000°C (after which the crystallinity of the zeolite was still intact) was insufficient.

The structural integrity of the zeolites after nitration was confirmed by XRD measurements (not shown). A small decrease in surface area and pore volume (Table 6) after calcination at 550°C (heating rate 1°C/min) of the zeolites used for the nitration was observed. This might be due to the incomplete removal of the (by)products in the pore system of the zeolite or a slight degradation of the zeolite structure during the combustion of the (by)products. ^{27}Al MAS NMR of H-beta before and after nitration with subsequent regeneration at 550°C showed no additional formation of extraframework aluminium (Fig. 5). The bulk Si/Al ratio after nitration was determined to be 12.0, practically the same as before the nitration considering the experimental error of AAS. ^{1}H MAS NMR

Table 6
Characteristics of the zeolites after nitration in the vapour phase and regeneration at 550°C for 5 h (heating rate 1°C/min)

	BET surface area (m^2/g)	External surface area (m^2/g)	Pore volume (cm^3/g)	Average mesopore diameter (Å)	Micropore volume (cm^3/g)
H-beta	645	198	0.87	102	0.19
H-ZSM-5	423	68	0.50	93	0.15
H-ZSM-12	341	14	0.19	37	0.14
H-mor(4.6)	491	7	0.25	64	0.20
H-mor(74)	498	36	0.32	64	0.19
H-beta[a]	665	222	0.93	105	0.20

[a] After threefold nitration with simultaneous distillation.

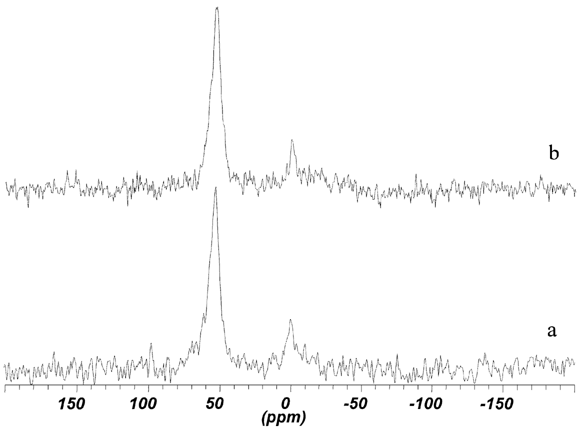

Fig. 5. ^{27}Al MAS NMR spectra of H-beta: (a) before nitration and (b) after nitration in the vapour phase and regeneration at 550°C for 5 h.

Table 7
Relative wt.% of the catalyst at ambient temperature (100=dried catalyst at 800°C) determined by TGA in flowing air at 10°C/min, before and after nitration in the vapour phase

Catalyst	Before nitration	After nitration[a]	Colour of the catalyst after nitration
H-beta	114.4	161.2	Brown
H-ZSM-5	108.1	124.0	Light brown
H-ZSM-12	105.0	112.6	Off-white
H-mor(4.6)	116.2	119.6	Off-white
H-mor(74)	104.0	125.4	Light brown
Deloxan	127.3	259.2	Brown

[a] Reaction conditions: 158°C, HNO_3/toluene=1, W/F=5 g h mol^{-1}.

before and after nitration showed very similar spectra (Fig. 6). A small decrease of the peak at 2.6 ppm, which is attributed to hydroxyl groups of extraframework aluminium, indicates that some extraframework aluminium was removed from the pores of the zeolites during the continuous nitration. TGA in flowing air confirmed the accumulation of (by)products in the pores of the zeolites and also on Deloxan after the nitration (Table 7). In the case of H-beta, discoloured brown materials were obtained and an accumulation of about 61% based on the weight of the fresh catalyst was observed. H-mor(4.6) was off-white and its weight had increased by only 19.6%. H-mor(74) was light brown and its weight had increased by 25.4%, a value higher than that of the mordenite without mesopores. H-ZSM-5 had a similar colour and almost the same amount of combustible residues (24.0%). The accumulation of (by)products on H-ZSM-12 was significantly smaller at 12.6% and the catalyst had an off-white colour. The accumulation of (by)products, the colour of the zeolite after the nitration, the pore volume and the external surface of the fresh zeolite (Table 1) are correlated with the 4-NT to 2-NT ratio obtained during the first hours on-stream of the vapour phase reaction. The higher the external surface area and pore volume, the higher the selectivity to 4-NT that can be attained. The accumulation of (by)products in the pore system of the zeolite paralleled the extent of discoloration. We conclude that a secondary mesopore system improves the diffusion of the reagents and the products in the zeolite crystallites. Similar findings were reported for the vapour phase nitration of benzene [14].

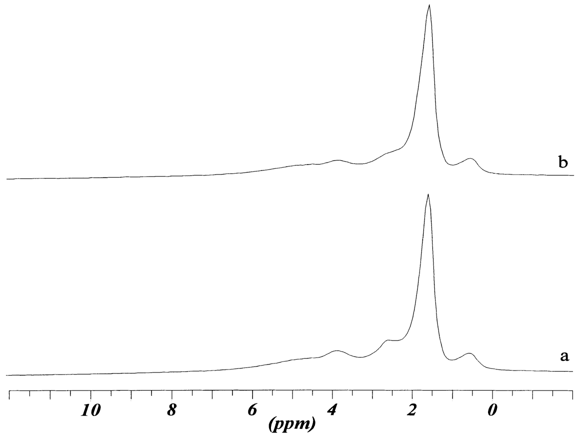

Fig. 6. ^{1}H MAS NMR spectra of H-beta: (a) before nitration and (b) after nitration in the vapour phase and regeneration at 550°C for 5 h.

3.3. *Reaction with simultaneous distillation*

In separate experiments using silica-supported sulphuric acid as catalyst it was found that quick removal of the water from the reaction mixture was crucial for sustaining catalyst activity. The combination of vacuum (70–80 mbar) and elevated temperature (130°C) was found to be optimal. Under these conditions, the NT reactants do not evaporate at a significant rate, the DNT products are liquid, and nitric acid and water are evaporating rapidly. As a matter of fact aqueous

Table 8
Nitration[a] with simultaneous distillation of a 1:1 mixture 2-NT/4-NT

Catalyst	HNO_3/NT	DNT yield (mol%)	2,4-DNT/(2,4-DNT+2,6-DNT)
Blank	1	0.0	–
70% H_2SO_4/SHE	1	46.1	0.79
Deloxan	1	0.9	0.77
Nafion	1	14.0	0.74
H-mor(4.6)	1	0.0	–
H-beta	1	20.1	0.94
H-beta reused[b]	1	11.6	0.94
H-beta regenerated[c]	1	19.3	0.93
H-beta	2	31.5	0.94
H-beta[d]	1	19.4	0.90

[a] Reaction conditions: 3.1 g catalyst, 0.23 mol 1:1 mixture 2-NT/4-NT, 130°C, 70–80 mbar, HNO_3 feed rate=1.92 mmol/min.
[b] After previous reaction H-beta was dried at 130°C for 18 h and then reused.
[c] After previous reaction H-beta was regenerated (3 h 120°C, 5 h 550°C, heating rate 1°C/min) and then reused.
[d] Only 2-NT as reagent.

nitric acid evaporates instantaneously under these reaction conditions upon introduction into the reactor. Therefore it has to be expected that some nitric acid will also distil over rather than react. In a true reaction–distillation column with catalyst packing this problem could be overcome by a counter-current flow of nitric acid and NT. Our feasibility approach therefore only simulates one plate in such a column without trying to attain optimum fluid–catalyst contact.

Table 8 shows the results for the nitration of NT using different solid acids. In these experiments, the reaction was stopped after the addition of one equivalent of nitric acid (65 wt.%) on a molar basis. No conversion to DNT was obtained when the reaction was carried out in the absence of solid acids (blank experiment) but the formation of NO_2 (yellow-brown gas) was observed. Preshaped silica impregnated with sulphuric acid turned out to be the most active catalyst. DNT yields as high as 46.1% with 99% DNT selectivity were reached. The selectivity to 2,4-DNT based on the total amount of DNT formed was 79%, similar to the value of 83% in the mixed acid process [1]. The sulphuric acid on silica catalyst, however, turned out to be unstable under these reaction conditions as can be seen from the lower amount of the acid loading after reaction (Table 9). This was related to the concomitant slow evaporation of sulphuric acid and was dependent on the nitric acid feed rate, the total reaction time, and the reaction temperature. Nafion was less active than the impregnated preshaped silica. Although the acid strength of the acid groups in Nafion is similar to 100% sulphuric acid [44], a large fraction of the active sites is not accessible to the reagents. Deloxan, characterised by a milder acidity than Nafion, showed almost no activity.

Zeolite H-beta performed best among the tested zeolites. It is furthermore remarkable that the 2,4-DNT selectivity was 94% as compared to 79% obtained with

Table 9
Nitration with simultaneous distillation using 70% H_2SO_4/SHE as catalyst[a] (influence of reaction parameters on the sulphuric acid content of preshaped silica before and after nitration)

Temperature (°C)	HNO_3/NT	HNO_3 feed rate (mmol/min)	DNT yield (mol%)	H_2SO_4 loading (%)	
				Before reaction	After reaction
130	1	1.84	45.2	56	39
130	1	3.07	36.8	56	30
120	2	4.19	23.0	56	47
120	3	1.75	58.3	56	32

[a] Reaction conditions: 3.1 g catalyst, 0.23 mol 1:1 mixture 2-NT/4-NT, 70–80 mbar.

the impregnated preshaped silica. This is not an effect of preferential adsorption and reaction of 4-NT because in a separate experiment using 2-NT as the only reactant we obtained a 2,4-DNT selectivity of 90% instead of the expected 67% with the same overall DNT yield. H-mordenite was totally inactive under those conditions. A 50% improvement in the DNT yield with H-beta was reached when two equivalents of nitric acid (65 wt.%) were added. When H-beta was recovered after the reaction, dried at 130°C for 18 h and reused under identical conditions, a decrease in the activity was observed. These last two experiments indicate a slow deactivation of H-beta during reaction, although the selectivity towards 2,4-DNT was still high. A subsequent regeneration of the sample already used twice, through a thermal treatment at 550°C for 5 h (heating rate: 1°C/min with previous drying at 120°C for 3 h) fully restored activity and selectivity, indicating that the deactivation was reversible. In all reactions, H-beta was brown after the nitration, while H-mordenite was only slightly yellow.

XRD measurements (not shown) confirmed the structural integrity of H-beta after the nitration. Surface area and pore volume (Table 6) after calcination at 550°C (heating rate 1°C/min) of the H-beta after three nitration reactions was similar to the parent zeolite. Both zeolites exhibited a similar weight loss during TGA (see Figs. 7 and 8) when analysed after nitration under the same reaction conditions. The residual weight after completed TGA up to 800°C is 82.8% in the case of H-beta and 79.4% in the case of H-mordenite. In contrast to H-mordenite, the colour of H-beta hints at the presence of nitro- and dinitro-compounds. The weight loss observed on H-mordenite after the reaction was mainly due to water and nitric acid present in the pore system. The mono-dimensional channel system of H-mordenite is therefore less suitable for the nitration and the aromatics probably do not manage to diffuse into the pores at a sufficiently high rate explaining the negligible activity of this catalyst. H-beta used with two equivalents of nitric acid and H-beta reused after one experiment showed an increased weight loss (residual weight: 73.4 and 72.9%) during TGA. That confirmed the deactivation of the catalyst with time, due to the formation of strongly bound (by)products blocking the micropore system. A significantly higher weight loss during TGA (residual weight: 52.4%) of H-beta after reaction with 2-NT as the only reagent was observed. Only 2,4-DNT is formed from 4-NT, whereas both 2,4-DNT and 2,6-DNT are formed from 2-NT. Probably, the diffusion of 2,6-DNT out of the zeolite pores is slower than that of 2,4-DNT. The concept that the *ortho* position is sterically hindered for electrophilic substitution in the pore system of H-beta was confirmed [23].

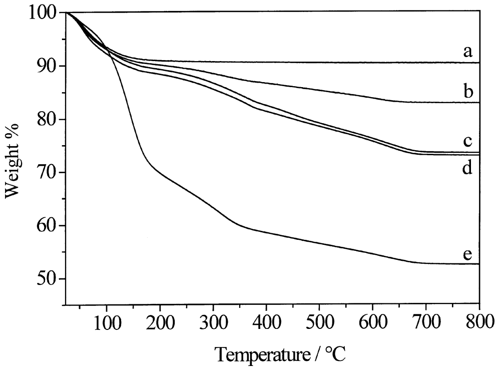

Fig. 7. TGA of H-beta (11.5): (a) before the reactive distillation, (b) after the reaction with 2-NT/4-NT and HNO_3/NT=1, (c) after the reaction with 2-NT/4-NT and HNO_3/NT=2, (d) after reuse of the catalyst in (b), (e) after the reaction only with 2-NT.

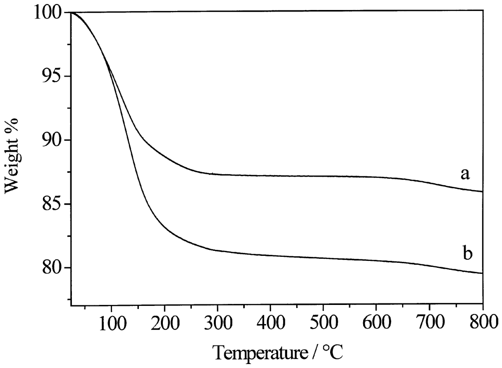

Fig. 8. TGA of H-mor(4.6): (a) before the reactive distillation, (b) after the reaction with 2-NT/4-NT and HNO_3/NT=1.

4. Conclusions

One of the key issues in the successful application of solid acids in the nitration of toluene and NT to DNT is the handling of the water in the reaction mixture. In liquid phase nitration at ambient temperature

DNT can only be produced by binding the water using solid acids with a substantially high acid site density such as silica impregnated with sulphuric acid. By carrying out the reaction in the vapour phase between 120 and 160°C, NT was observed as a reaction product. The formation of DNT was negligible, however, with all solid acids tested. Preshaped silica impregnated with sulphuric acid was the most active catalyst but a continuous loss of sulphuric acid with time-on-stream occurred. Deloxan, showing relatively good activity and stability, seems to be more promising although the loss of nitric acid through disproportionation to NO_2 was not negligible. H-beta was stable in the highly acidic reaction medium used and provided a higher *para*-to-*ortho* ratio than other zeolites such as ZSM-5, ZSM-12 and mordenite. The decrease in activity and *para*-selectivity with time-on-stream was reversible and was linked to the formation of strongly bound (by)products blocking the micropore system. The vapour phase nitration may become interesting for the production of NT if the high *para*-selectivity of H-beta is desired and if deactivation of the catalysts can be better controlled.

The reaction with simultaneous distillation was the only case where we observed true catalytic formation of DNT using classical natural solid acids and 65 wt.% nitric acid as only reactant. Supported liquid acids gave real catalytic behaviour for the conversion of NT to DNT. They were, however, not stable under those reaction conditions and a loss of the impregnated acid was observed. Zeolite beta turned out to be relatively stable under those conditions and about half as active as supported liquid acids. Regeneration of beta was possible by thermal treatment. An exceptionally high 2,4-DNT selectivity (up to 94%) was obtained with beta zeolite, compared to 74–79% obtained with all other solid acids. Regarding potential process implementations, significant advantages would arise from using a continuous mode reaction in a reaction–distillation column rather than the batch mode.

Acknowledgements

The authors thank Air Products & Chemicals for the financial support to this work and CU Chemie Uetikon, Degussa AG and Shell Research for providing us with free samples. We appreciate many helpful discussions with Dr. John N. Armor throughout the course of this work and the assistance in publishing this manuscript.

References

[1] K. Winnacker, L. Küchler, in: H. Harnisch, R. Steiner, K. Winnacker (Eds.), Chemische Technologie, Band 6, Org. Technologie II, 1982, p. 169.

[2] Ullmann's Encyclopedia of Industrial Chemistry, 5th Edition, VCH, Weinheim, 1991.

[3] C.M. Evans, in: L.F. Albright, R.V.C. Carr, R.J. Schmitt (Eds.), Nitration: Recent Laboratory and Industrial Developments, 1996, p. 250.

[4] A. Kogelbauer, D. Vassena, R. Prins, J.N. Armor, Catal. Today 55 (2000) 151.

[5] A. Kogelbauer, H.W. Kouwenhoven, in: R. Sheldon, H. van Bekkum (Eds.), Fine Chemicals through Heterogeneous Catalysis, Wiley/VCH, in press.

[6] R.H. McKee, R.H. Wilhelm, Ind. Eng. Chem. 28 (1936) 662.

[7] H. Schubert, F. Wunder, US Patent 4 112 006 (1978).

[8] I. Schumacher, K. Wang, US Patent 4 426 543 (1984).

[9] E. Suzuki, K. Tohmori, Y. Ono, Chem. Lett. (1986) 747.

[10] E. Suzuki, K. Tohmori, Y. Ono, Chem. Lett. (1987) 2273.

[11] L. Bertea, H.W. Kouwenhoven, R. Prins, Stud. Surf. Sci. Catal. 78 (1993) 607.

[12] L. Bertea, H.W. Kouwenhoven, R. Prins, Stud. Surf. Sci. Catal. 84 (1994) 1973.

[13] H.W. Kouwenhoven, L. Bertea, R. Prins, US Patent 5 324 872 (1994).

[14] L. Bertea, H.W. Kouwenhoven, R. Prins, Appl. Catal. A 129 (1995) 229.

[15] J.M. Smith, H. Liu, D.E. Resasco, Stud. Surf. Sci. Catal. 111 (1997) 199.

[16] T.G. Kuznetsova, K.G. Ione, L.V. Malysheva, React. Kinet. Catal. Lett. 63 (1998) 61.

[17] H. Sato, K. Hirose, Appl. Catal. A 174 (1998) 77.

[18] H. Sato, K. Hirose, K. Nagai, H. Yoshioka, Y. Nagaoka, Appl. Catal. A 175 (1998) 201.

[19] H. Sato, K. Nagai, H. Yoshioka, Y. Nagaoka, Appl. Catal. A 175 (1998) 209.

[20] H. Sato, K. Nagai, H. Yoshioka, Y. Nagaoka, Appl. Catal. A 180 (1999) 359.

[21] D. Vassena, D. Malossa, A. Kogelbauer, R. Prins, in: M.M.J. Treacy, B.K. Marcus, M.E. Bisher, J.B. Higgins (Eds.), Proceedings of the 12th International Zeolite Conference, Vol. 2, Materials Research Society, 1999, p. 1471.

[22] K. Smith, A. Musson, G.A. DeBoos, J. Org. Chem. 63 (1998) 8448.

[23] D. Vassena, A. Kogelbauer, R. Prins, Stud. Surf. Sci. Catal. 125 (1999) 501.

[24] A.B. Quakenbush, B.T. Pennington, in: L.F. Albright, R.V.C. Carr, R.J. Schmitt (Eds.), Nitration: Recent Laboratory and Industrial Developments, ACS Symposium Series 623, American Chemical Society, Washington DC, 1996, p. 214.

[25] D.F. Othmer, J.J. Jacobs, J.F. Levy, Ind. Eng. Chem. 34 (1942) 286.

[26] D.F. Othmer, H.L. Kleinhans, Ind. Eng. Chem. 36 (1944) 447.
[27] O.L. Wright, J. Teipel, D. Thoennes, J. Org. Chem. 30 (1965) 1301.
[28] G.A. Olah, R. Malhotra, S.C. Narang, J. Org. Chem. 43 (1978) 4628.
[29] V. Alexanderson, J.B. Trecek, C.N. Vanderwaart, US Patent 4 021 498 (1977).
[30] V. Alexanderson, J.B. Trecek, C.N. Vanderwaart, US Patent 4 091 042 (1978).
[31] M.W. Dassel, US Patent 3 928 475 (1975).
[32] R. McCall, US Patent 4 331 819 (1982).
[33] T. Schieb, G. Wiechers, R. Sundermann, U. Zarnack, Canada Patent 2 102 587 (1994).
[34] F.J. Waller, A.G.M. Barrett, D.C. Braddock, D. Ramprasad, J. Chem. Soc., Chem. Commun. (1997) 613.
[35] F.J. Waller, A.G.M. Barrett, D.C. Braddock, D. Ramprasad, Tetrahedron Lett. 39 (1998) 1641.
[36] R.P. Claridge, N.L. Lancaster, R.W. Millar, R.B. Moodie, J.P.B. Sandall, J. Chem. Soc., Perkin Trans. 2 (1999) 1815.
[37] S. Hitz, Diss. ETH Nr. 12 418, Zürich, 1997.
[38] B.C. Lippens, J.H. de Boer, J. Catal. 4 (1965) 319.
[39] E.P. Barret, L.G. Joyner, P.P. Halenda, J. Am. Chem. Soc. 73 (1951) 373.
[40] L.V. Malysheva, E.A. Paukshtis, K.G. Ione, Catal. Rev. Sci. Eng. 37 (1995) 179.
[41] T.J. Kwok, K. Jayasuriya, J. Org. Chem. 59 (1994) 4939.
[42] D. Vassena, A. Kogelbauer, R. Prins, Proceedings of the 12th International Congress on Catalysis, Stud. Surf. Sci. Catal., in press.
[43] D. Vassena, S. Bernasconi, A. Kogelbauer, R. Prins, in preparation.
[44] M.A. Harmer, W.E. Farneth, Q. Sun, J. Am. Chem. Soc. 118 (1996) 7708.