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Solid acids as substitutes for sulfuric acid in the liquid phase nitration of toluene to nitrotoluene and dinitrotoluene

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Abstract

Our results demonstrate that sulfuric acid supported on preshaped silica is a good catalyst for the nitration of toluene to dinitrotoluene using 65 wt.% nitric acid with respect to catalyst performance (activity, selectivity, regenerability) and catalyst handling (storage, stirring, separation). It is imperative to carefully control the water content of the catalyst prior to reaction in order to obtain high activity. The reusability of the catalyst without compromising performance has been demonstrated. Non-polar solvents seem to be required in order to prevent dissolution of the impregnated acid. Hence, the application of acetic anhydride as a solvent with potential water trapping ability was unsuccessful. Solvent-free operation is limited by the necessity to maintain a mixture that can be stirred. Hence, a maximum conversion of about 30% is achievable for the nitration of nitrotoluene to dinitrotoluene in one reaction cycle. ©2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The nitration of benzene and toluene is one of the most important routes to substituted aromatics in the production of chemical intermediates. Dinitrotoluene (DNT) is a key intermediate in the manufacture of polyurethanes through its subsequent conversion into toluene diamine and toluene diisocyanate. The industrial nitration of toluene is performed by means of mixed acid, a mixture of nitric acid, sulfuric acid, and water [1]. The main purpose of sulfuric acid is the protonation of nitric acid, thereby forming nitronium ions, which are the actual nitrating species [2]. Sulfuric acid additionally acts as water binder and heat sink for the highly exothermic reaction. Despite the high efficiency, the mixed-acid process has some drawbacks among which the huge amount of spent acid formed is by far the most crucial [1]. In large-scale production, typical for bulk chemicals such as nitrobenzene (NB) and nitrotoluenes (NT), neutralization and disposal are environmentally and economically unsound. The regeneration of spent acid requires expensive and energy intensive recovery, purification, and reconcentration steps which makes an alternative solution desirable [3].

Nitration using solid acids may be the answer to these problems. Due to the attachment of the acid function to a solid surface corrosion would be less a concern. Separation would be facilitated and continuous operation using packed beds becomes feasible. Regeneration of the solid acid would be achieved by a simple thermal treatment. In addition, the introduction of shape-selectivity in the case of zeolites would possibly permit to influence the product composition

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in favor of the more desired 4-nitrotoluene (4-NT). The goal for an economically competitive production of DNT based on solid acids combines the use of a solvent-free liquid-phase reaction and nitric acid of azeotropic composition as the cheapest and industrially favored nitrating agent.

A variety of combinations of solid acids and nitrating agents has been investigated for their suitability as nitration systems for aromatics. For the nitration of benzene and toluene, solid acids comprising zeolites [4], partially dealuminated [5] or cationic-exchanged zeolites [6], tributylamine modified zeolites [7], and some Fe, B, and Ti-substituted forms [8] have been investigated. Besides zeolites, other catalysts such as sulfonated ion-exchange resins (polystyrenesulfonic acid [9], perfluorinated resin sulfonic acid [10]), clay-supported metal nitrates ('claycop' [11,12], Fe^{3+} on K10 montmorillonite [13]), modified silica [6], modified silica–alumina, and supported acids [14–17] have been used. Various nitrating agents such as nitric acid, nitric acid–acetic anhydride, mixed acid, nitrogen dioxide (dinitrogen tetroxide), acyl nitrates (benzoyl nitrate, acetyl nitrate) and alkyl nitrates were tested [2]. The majority of these approaches tackled the problem of increased para-selectivity in the nitration of substituted aromatics. As a consequence, rather exotic nitrating agents and sometimes expensive catalysts were used, which are acceptable for the production of small quantities of fine chemicals but totally unsuitable for large scale manufacture of chemical intermediates. In other cases, where the nitrating agent poses a potential hazard and is difficult to handle, safety aspects limit large-scale applicability [18].

With respect to the production of DNT, only a very limited number of reports exist. Akolekar et al. reported on the high pressure nitration of toluene using NO_2 and zeolite catalysts [19]. Only limited DNT yields were obtained at relatively drastic conditions of ca. 120°C and pressures exceeding 160 bar and the product selectivity was characteristic of radical nitration with a high 3-NT fraction. A new industrial DNT production has been reported by Olin Corporation who developed a single acid DNT process [20]. This process avoids sulfuric acid by using concentrated (>95%) nitric acid for the nitration and nitrate salts during the nitric acid reconcentration steps to break the azeotrope of the nitric acid–water binary system. Another development was reported by Bayer AG who demonstrated that toluene can be nitrated adiabatically in a single step to DNT, however, using classical mixed acid [21].

We report on an investigation regarding the suitability of a solid acid system for the nitration of toluene to DNT. Due to the lack of previous work our approach was rather exploratory. Therefore, the scope of this work was the identification of solid acid catalysts that affect the nitration of toluene to DNT under the given boundary conditions and the identification and possible tuning of critical parameters in order to make a solid acid based process for the nitration of toluene to DNT feasible.

2. Experimental

2.1. Catalysts

H-mordenite was obtained from Chemie Uetikon in Na form and ion exchanged three times with aqueous 1 M HCl and calcined in static air at 650°C for 3 h. The resulting material was twice dealuminated with 6 M HCl under reflux for 16 h with intermediate calcination at 650°C for 3 h to give H-mordenite with a Si/Al ratio of 63.5 [5].

Silica-supported heteropolyacid was obtained following the procedure of Kozhevnikov et al. [22] by impregnating silica gel 60 (Merck) with 12-tungstophosphoric acid (HPAW) yielding catalysts with 20 wt.% loading of HPAW. The resulting material was dried at 120°C and calcined at 200°C in static air prior to reaction. XRD of the final catalyst confirmed that HPAW was dispersed.

Sulfated zirconia was prepared using a controlled impregnation technique of 1 M sulfuric acid onto freshly precipitated zirconium hydroxide [23]. The catalyst was dried in a muffle furnace by raising the temperature at the rate of 10°C/min to 150°C and maintaining it for 12 h. Subsequent calcination occurred at 580°C for 5 h.

WO_x/ZrO_2 catalysts were obtained from Air Products and used as received. Prior to reaction, they were calcined in flowing air (shallow bed in a muffle furnace) at 500°C for 1 h.

$NaHSO_4/SiO_2$ was prepared by incipient wetness impregnation of silica gel 60 with an aqueous solution of $NaHSO_4$ yielding a loading of 17 wt.% [24]. The resulting solid was dried in static air at 200°C for 24 h

Table 1
Compilation of silica-supported sulfuric acid

Catalyst	Carrier[a]	H_2SO_4 loading of the catalyst (%)[b]
50% H_2SO_4/SiO_2	Silica gel 60	37
70% H_2SO_4/SiO_2	Silica gel 60	48
50% H_2SO_4/SHE	Preshaped silica	47
70% H_2SO_4/SHE	Preshaped silica	56
80% H_2SO_4/SHE	Preshaped silica	56
96% H_2SO_4/SHE	Preshaped silica	60

[a] Preshaped silica was obtained from Shell Research as spheres of ca. 2 mm diameter.
[b] Expressed as pure H_2SO_4 based on the total catalyst weight.

and stored in a desiccator under vacuum. Prior to use, the catalyst was reactivated at 200°C for 12 h.

For the silica-supported sulfuric acid catalysts, silica gel 60 as well as commercially available preshaped silicas (Shell) were used. The silica supports were calcined in static air at 400°C for 18 h and cooled in a desiccator. The silica was then added to an excess of 50–96% H_2SO_4 based on the total pore volume of the silica (1.2–1.8 g H_2SO_4 solution/g silica). This mixture was vigorously shaken for 5 min and allowed to rest for 1–10 days in a closed glass flask without maintaining incipient wetness. The resulting catalyst was filtered using a glass fritt and dried at 120°C in static air for 18 h. Subsequently, the catalyst was stored in a desiccator under vacuum and recalcined at 120°C prior to reaction. A compilation of the silica-supported sulfuric acid catalysts is given in Table 1.

2.2. Characterization

Nitrogen adsorption at 77 K was carried out on a Micromeritics ASAP 2000M volumetric analyzer. The catalysts were degassed prior to analysis under vacuum at 400°C (120°C for H_2SO_4 impregnated catalysts). The specific surface area was evaluated using the BET method.

The amount of sulfuric 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 titration and calcination at 400°C in static air.

TGA/DSC measurements were carried out on selected catalysts before and after use with a Polymer Laboratories STA 1500H thermal analyzer. Typically, 10 mg of catalyst were heated under 50 cm^3 of flowing N_2 at a rate of 10°C/min from 20 to 700°C while monitoring the weight change and heat flux.

2.3. Reaction studies

Nitration reactions were carried out using toluene as well as NT as substrate. Since 4-NT is solid at ambient temperature and since the products obtained from the nitration of toluene contain a mixture of the three NTs anyhow, an equimolar mixture of 2-NT and 4-NT was chosen as substrate. This provided liquid reactants in a ratio representative to that obtained during mononitration. Initial attempts to carry out the reaction in a solvent-free medium failed since large amounts of solid acid catalyst were required which led to sludges or sometimes just barely moistened powders that could be neither stirred nor worked up for product sampling. Thus, CCl_4 and acetic anhydride (Ac_2O) were applied as solvent furtheron. Ac_2O as solvent has been claimed to efficiently trap the water formed during the reaction [25].

For the actual reaction experiments, the calculated amounts of substrate (toluene or a 2-NT/4-NT mixture) were exactly weighed in a three-neck pyrex flask. Then, the required amount of 65 wt.% nitric acid was added and subsequently 5 ml of solvent. To this mixture, the activated catalysts were quickly added wile they were not yet completely cooled. The reaction mixture was then stirred at ambient temperature for 24 h after which a sample was taken and analyzed. In some cases samples were also taken at much shorter times to follow the reaction progress with time. The liquid phase after reaction was checked for sulfate with an excess of 0.1 M $BaCl_2$ solution and qualitatively checked for $BaSO_4$ precipitate in order to assess whether sulfuric acid was washed out from the silica during reaction. The reaction experiments were carried out using a molar ratio of HNO_3/toluene of 2 and a molar ratio of HNO_3/NT between 0.05 and 3. The reaction temperature was typically ambient and raised up to 72°C in selected cases. As control experiments the nitration of toluene was also carried out without solid acids and with mixed acid (60 wt.% H_2SO_4, 20 wt.% HNO_3, and 20 wt.% H_2O matching compositions used in industrial nitration [1]).

Table 2
Nitration of toluene using H-mordenite[a]

	H-mordenite	None	H-mordenite	None	Mixed acid[b]
HNO_3 (wt.%)	65	65	100	100	
Temperature (°C)	72	72	52	52	52
Conversion (%)	58.0	57.9	90.7	93.5	99.9
NT Yield (%)	46.3	48.8	64.6	70.4	58.6
DNT Yield (%)	0.00	0.00	25.1	22.3	41.3
Other[c] (%)	10.5	9.0	0.9	0.5	0.0
4-NT/2-NT	0.67	0.68	0.76	0.78	0.88
2,4-DNT/2,6-DNT	–	–	4.41	4.35	3.38

[a] 1 g of freshly activated zeolite was used for 20 g toluene without solvent, HNO_3/toluene = 2, 24 h reaction time; the ratio of acid sites of the zeolite (expressed as lattice Al) to HNO_3 was about 5×10^{-4}.
[b] 20 wt.% HNO_3, 60 wt.% H_2SO_4, 20 wt.% H_2O.
[c] Mainly benzaldehyde and benzoic acid.

In order to test the reusability of catalysts, the reaction mixture was filtered through a glass fritt and the catalyst was thoroughly washed with CCl_4. The recovered catalyst was then reactivated in static air at 130°C and used again as described above. In situ activation of the catalyst was done by heating it in the reaction vessel under flowing N_2 for 18 h at 130°C under slow stirring (100 rpm).

For GC analysis a HP 5890 Series II GC equipped with a 30 m Rtx 200 capillary column and FID was used. The liquid samples that were taken from the reaction mixture were diluted with CH_2Cl_2 and unreacted HNO_3 was neutralized to pH 6–7 using a saturated aqueous $NaHCO_3$ solution prior to injection. This procedure ensured complete analysis of the interesting products which was checked by GC analysis of the acetone-extracted residue of the aqueous phase after complete evaporation of the water. After completion of the reaction, the catalyst was separated by filtration through a glass fritt, washed with CH_2Cl_2 and water, dried in an oven at 80°C, and subsequently stored in a vial for eventual later analysis (TGA, titration).

3. Results and discussion

3.1. Introductory studies

Typical results for the nitration of toluene with 65 wt.% nitric acid using H-mordenite at a reaction temperature of 72°C are shown in Fig. 1. After 5 h reaction time the reaction came essentially to an end at a toluene conversion of 57.9%. Only mononitrated products were observed in ratios typical for acid-catalyzed nitration besides some side chain nitration and oxidation products. The control experiment without catalyst (Table 2) showed comparable conversion (57.9%) after 5 h reaction suggesting only a minute effect of the catalyst if at all. A significantly higher conversion of 90.7% and an overall yield of 25.1% of DNT were obtained within 5 h reaction time at a lower reaction temperature of 52°C using 100% nitric acid (Table 2). Again, the control experiment without catalyst indicated no effect of the presence of H-mordenite in the reaction mixture. The fact that nitration occurred without a catalyst is due to the self protonation equilibrium of nitric acid which is also exploited in the Olin process. In accordance with this, nitric acid of higher concentration (higher acidity) is more efficient at lower temperatures and mixed acid

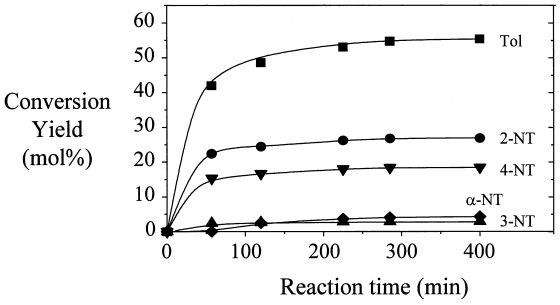

Fig. 1. Nitration of toluene using H-mordenite and 65 wt.% HNO_3 at 72°C (reaction conditions see Table 2).

Table 3
Nitration of 2-NT/4-NT using solid acids[a]

	$NaHSO_4/SiO_2$	WO_x/ZrO_2	ZrO_2/SO_4	H-mordenite	HPAW	None
Conversion (%)	0.4	1.4	0.2	1.8	2.1	0.2
DNT Yield (%)	0.4	1.4	0.0	0.5	2.1	0.1
Other[b] (%)	0.0	0.0	0.2	1.3	0.0	0.1

[a] Reaction conditions: catalyst weights between 1 and 5 g with a constant weight-to-65 wt.% HNO_3 ratio of 8.7 were used, HNO_3/NT = 1, 65 wt.% HNO_3, 25°C, 5 ml CCl_4 solvent, 24 h reaction time.
[b] Mainly benzaldehyde and benzoic acid.

Table 4
Nitration of 2-NT/4-NT using 50% H_2SO_4/SiO_2[a]

50% H_2SO_4/SiO_2	Cat H^+/HNO_3[b]	Conversion (%)	DNT Yield (%)	2,4-DNT/2,6-DNT
Fresh	1.2	59.0	58.9	4.5
Fresh	3.2	89.8	89.8	4.9
Fresh	6.3	95.0	94.3	4.8
Reused	6.3	83.5	83.5	4.6
Wet	6.3	30.0	30.0	3.9

[a] Reaction conditions: 3.2 g catalyst activated in static air at 120°C for 18 h, 65 wt.% HNO_3, HNO_3/NT = 1, T = 25°C, solvent 5 ml CCl_4, 24 h reaction time.
[b] Corresponds to the ratio of sulfuric acid to nitric acid on a molar basis at the beginning of the reaction.

is even more effective. H-mordenite, as any other natural solid acid, has too few acid sites and therefore does not significantly contribute to the overall activity (note that the concentration of protons in the mixed acid experiment in Table 2 was about 4 orders of magnitude higher than in the experiment using H-mordenite). In order to overcome this 'masking' effect by the homogeneously catalyzed reaction we studied the more demanding second nitration step in which NT, partially deactivated due to the nitro group for electrophilic substitution, is nitrated to DNT.

3.2. Nitration of NT to DNT

Table 3 shows the results for the nitration of an equimolar mixture of 2-NT and 4-NT using different solid acids. It is obvious that despite minute differences in activities all solid acids tested were essentially inactive for the nitration of NT to DNT. When 50% H_2SO_4/SiO_2 was used as catalyst, the DNT yield was up to 59% at 25°C with 100% selectivity to DNT and the 2,4-DNT/2,6-DNT ratio of about 4.5 (Table 4). The yield increased to 95% by increasing the amount of solid acid used. This result is in line with the earlier experiments showing that an increased amount of acidity leads to more complete conversion of NT to DNT. Table 4 also underlines the importance of proper reactivation of the catalyst prior to reaction. DNT yields dropped to 83.5% when the catalyst was reused after drying at 120°C but were only 30% under identical reaction conditions when a catalyst was used that had been stored in a desiccator for 1 week without repeating the drying at 120°C prior to reaction. This suggests that moisture plays a crucial role in determining the strength of the solid acid and thereby influences the activity. Initial concerns that the water in 65 wt.% HNO_3 and that formed during the reaction dissolves major parts of the sulfuric acid from the support could not be substantiated because no sulfate was found in the product mixture. TGA measurements of 50% H_2SO_4/SiO_2 before and after reaction (Fig. 2) showed that the weight loss associated with the desorption peak at 260°C which is assigned to sulfuric acid corresponds to 29.6% before and to 29.3% after reaction (37% based on the dry sample) which is identical considering the accuracy of the measurement. Therefore, loss of sulfuric acid did not occur as a consequence of the nitration reaction.

The results given in Fig. 3 prove that the amount of moisture was responsible for the reduction in activity. Repeated experiments with regeneration of the

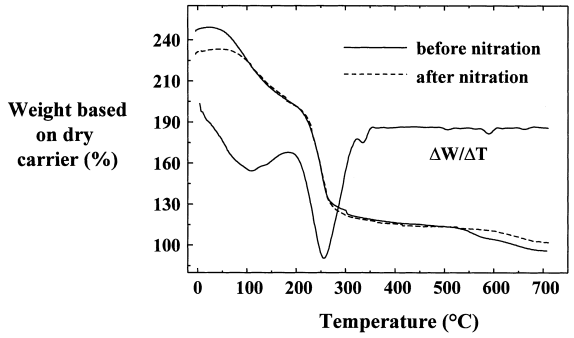

Fig. 2. TGA of 50% H_2SO_4/SiO_2 in flowing N_2 before and after nitration.

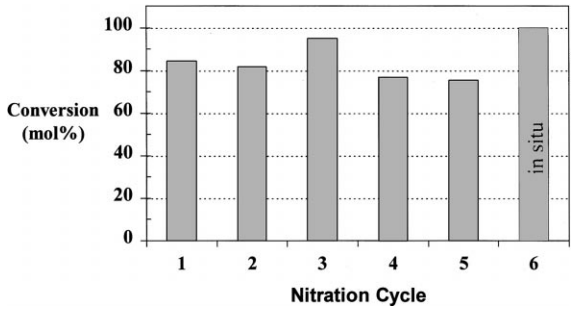

Fig. 3. Successive nitration of 2-NT/4-NT using 50% H_2SO_4/SHE; HNO_3/NT = 1, 65 wt.% HNO_3, 25°C, CCl_4 solvent, Cat H^+/HNO_3 = 8, 24 h reaction time.

catalyst in static air at 130°C gave conversions between 75 and 95%, whereas 100% conversion to DNT was reached by in situ regeneration in flowing nitrogen prior to the last run. In parallel, no loss of acidity of the recovered catalyst was determined by TGA and titration. This performance can be obtained repeatedly which is exemplified in Fig. 4 showing the results of subsequent nitration runs with in situ activation/regeneration. Note, that complete conversion was already obtained after 2 h of reaction.

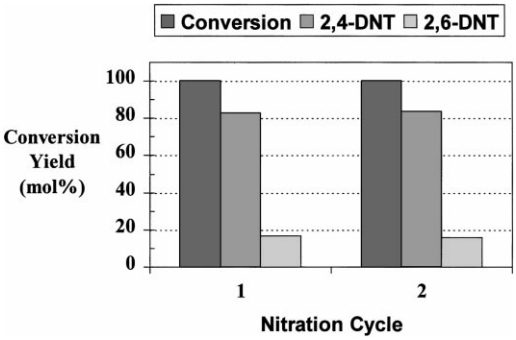

Fig. 4. Successive nitration of 2-NT/4-NT using 50% H_2SO_4/SHE applying in situ activation; HNO_3/NT = 1, 65 wt.% HNO_3, 25°C, CCl_4 solvent, Cat H^+/HNO_3 = 8, 2 h reaction time.

3.3. Nitration of toluene to DNT

The single-step nitration of toluene to DNT was also feasible using silica-supported sulfuric acid which is demonstrated in Table 5. The amount of solid acid in the reaction mixture is again the parameter governing reactivity patterns and temperature only plays a minor role. Through a three-fold increase in the amount of solid acid the product pattern can be shifted from mainly NT to the exclusive formation of DNT. Reusing the same catalyst after intermediate reactivation under identical conditions gave again complete conversion of toluene to DNT. These results led to the important conclusion that although toluene can be converted in a single-step process to DNT the reaction will not work with toluene in excess as its own solvent because toluene will always be more easily nitrated than NT and the water formed in this step is going to mediate

Table 5
Nitration of toluene using 50% H_2SO_4/SiO_2[a]

Cat H^+/HNO_3	Temperature (°C)	Conversion (%)	NT Yield (%)	4-NT/2-NT	DNT Yield (%)	2,4-DNT/2,6-DNT
3.2	25	100	99.0	0.69	1.0	–
3.2	50	100	96.7	0.70	3.3	3.1
9.5	25	100	0.0	–	100.0	4.0
9.5[b]	25	100	0.0	–	100.0	3.2

[a] Reaction conditions: 3.2–3.8 g catalyst activated in static air at 120°C for 18 h, 65 wt.% HNO_3, HNO_3/toluene = 2, solvent 10 ml CCl_4, 24 h reaction time.
[b] Regenerated and reused.

Table 6
Nitration of 2-NT/4-NT using 70% H_2SO_4/SiO_2[a]

Catalyst	Temperature (°C)	Conversion (%)	DNT Yield (%)	2,4-DNT/2,6-DNT
Fresh	25	32.5	32.2	4.4
Fresh	50	42.1	41.8	4.3
Reused	50	0.20	0.20	–

[a] Reaction conditions: 3.2 g catalyst activated in static air at 120°C for 18 h, 65 wt.% HNO_3, HNO_3/NT = 1, Cat H^+/HNO_3 = 1, solvent 5 ml CCl_4, 24 h reaction time.

Table 7
Characterisation of silica and silica-supported sulfuric acid

	BET area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (Å)	H_2SO_4 loading (wt.%)
SiO_2 (silica gel 60)	430	0.76	71	–
50% H_2SO_4/SiO_2	204	0.40	78	37
70% H_2SO_4/SiO_2	54	0.11	81	48
SHE (Shell preshaped silica)	254	0.83	131	–
50% H_2SO_4/SHE	113	0.37	133	47
SHE after extraction[a]	256	0.84	131	0

[a] The H_2SO_4 loaded SHE was washed until the water was neutral and then calcined at 400°C.

the acidity. Hence, only a two step process or a process with solvent would seem feasible.

3.4. Effect of the characteristics of supported liquid acids

A higher loading of sulfuric acid on the support did not improve the performance in the nitration. Only 32.5% conversion of aromatics at 25°C were obtained with 70% H_2SO_4/SiO_2 (Table 6) as compared to 59% conversion with 50% H_2SO_4/SiO_2 (Table 4). Although the employed ratio of sulfuric acid/HNO_3 was somewhat higher in the case of 50% H_2SO_4/SiO_2, the DNT yield based on the amount of sulfuric acid present in the reaction mixture was still lower when 70% H_2SO_4/SiO_2 was used as solid acid. Activities were even lower upon reuse of 70% H_2SO_4/SiO_2 due to the difficulties encountered during drying of these very hygroscopic materials. The characterization results of silica-supported sulfuric acid are compiled in Table 7. The loading of sulfuric acid onto silica gel led to a reduction in the BET surface area and a concomitant decrease of the pore volume. For 70% H_2SO_4/SiO_2 this decrease was substantially higher than for 50% H_2SO_4/SiO_2. This suggests that despite the higher acid loading fewer catalytically active sites may be accessible for reactants if the reaction occurs either on the liquid surface or by dissolution in the supported H_2SO_4 rather than by dissolved H_2SO_4. The observed increase in the average pore diameter furthermore suggests that smaller pores are preferentially filled and that an acid film is not formed on the carrier surface.

The characterization of the supported acids based on preshaped silicas shows that a higher surface area is retained after acid impregnation. Also, a higher acid loading was obtained when sulfuric acid of the same concentration was used for the impregnation. This was related to the higher average pore diameter of the preshaped silica supports. Upon further increase of the sulfuric acid concentration used for impregnation loadings of up to 60 wt.% acid could be achieved (compare Table 1), however, these materials were unsuitable for practical application because of the extreme difficulties involved in their handling due to their highly hygroscopic nature. The textural properties of the silica support itself were not altered by the acid impregnation which was confirmed by N_2 adsorption on the preshaped silica support after removal of the sulfuric acid by leaching in water (compare Table 7).

3.5. Removal of the water

Since it was shown that the presence of water impairs the activity of the solid acid attempts were made

Table 8
In situ water trapping during nitration[a] of 2-NT/4-NT

Catalyst	Solvent	Cat H^+/HNO_3	HNO_3/NT	Conversion (%)	DNT Yield (%)	Other (%)	2,4-DNT/2,6-DNT
50% H_2SO_4/SiO_2 + 3A[b]	CCl_4	1.2	1	9.3	9.3	0.0	4.2
50% H_2SO_4/SiO_2 + 3A	CCl_4	1.2	2	8.7	8.7	0.0	4.1
None	Ac_2O	–	1	1.1	0.4	0.7	–
50% H_2SO_4/SHE	Ac_2O	8	1	40.7	40.1	0.5	3.0
50% H_2SO_4/SHE[c]	Ac_2O	4	2	63.6	62.6	1.0	3.3
50% H_2SO_4/SHE reused	Ac_2O	8	1	13.9	7.9	6.0	2.4

[a] Reaction conditions: 3.2 g catalyst activated in static air at 120°C for 18 h, 65 wt.% HNO_3, 10 ml solvent, 24 h reaction time.
[b] 3.6 g molecular sieve 3A.
[c] HNO_3/NT = 2 was obtained by addition of 1 equivalent of HNO_3 to the previous reaction.

to remove the water during reaction by using molecular sieve 3A or Ac_2O. Yields of DNT, however, were down to ca. 9% compared with 59% under identical conditions without molecular sieve regardless of the amount of HNO_3 used (Table 8). Since 3A contains potassium this is most likely exchanged for protons from dissociated HNO_3 and subsequent dealumination and hence destruction of the high aluminum A zeolite is very likely. When Ac_2O was used as solvent for the nitration reaction, only modest conversion of 4-NT was observed at 25°C after 20 h without a solid acid. The low conversion of 4-NT is an indication that Ac_2O not only consumes the water present in 65% HNO_3 but also forms acetylnitrate ($AcONO_2$) which acts as nitrating agent. $AcONO_2$ is only weakly dissociated in organic solvents and requires the presence of acids to exhibit sufficient reactivity in nitration [2]. In accordance with this, the addition of one extra equivalent HNO_3 led to a slight increase in the conversion of 4-NT.

Using 50% H_2SO_4/SHE as catalyst for the conversion of an equimolar mixture of 2-NT and 4-NT in Ac_2O gave about 40% conversion within a relatively short reaction time of 1.6 h at ambient temperature. However, the reaction came to a stop after reaching 40.7% conversion. Addition of one extra equivalent of 65% HNO_3 increased the conversion to about 63% within short time and again no further increase was observed after an additional 18 h. Neither further addition of HNO_3 nor addition of Ac_2O affected any further change. A dramatic decrease in the activity was observed, however, when the recovered and reactivated catalyst was used under identical conditions. This was attributed to a significant loss of sulfuric acid from the catalyst apparently due to the polarity of the solvent and/or compound formation. TGA of the catalyst after the first use revealed that the major part of sulfuric acid was lost during the nitration reaction (Fig. 5). Concomitantly, sulfate was found as $BaSO_4$ precipitate in the filtrate after the first reaction. These results show that the use of Ac_2O and probably also other polar solvents is not advisable with supported liquid acid catalysts.

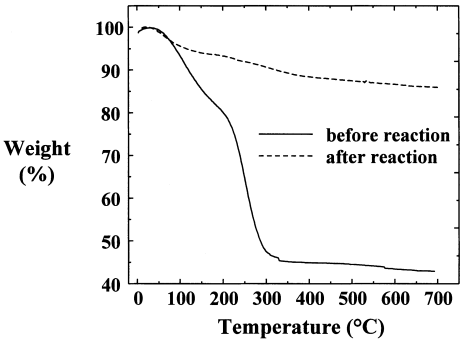

Fig. 5. TGA of 50% H_2SO_4/SiO_2 in flowing N_2 before and after nitration using Ac_2O as solvent.

The TGA analyses in Figs. 2 and 5 suggest that up to 200°C only water evaporated from silica-supported sulfuric acid yielding roughly a 20% weight loss. A comparison of the weight loss of silica-supported sulfuric acid determined by TGA after in situ pretreatment in flowing nitrogen at 120°C for 18 h with the amount of sulfuric acid determined by titration gave an estimation of the concentration of sulfuric acid on the silica support after activation. The concentration of sulfuric acid on the silica support after activation at 120°C was thereby estimated to be 88%, which is close to the value of the monohydrate. It was therefore

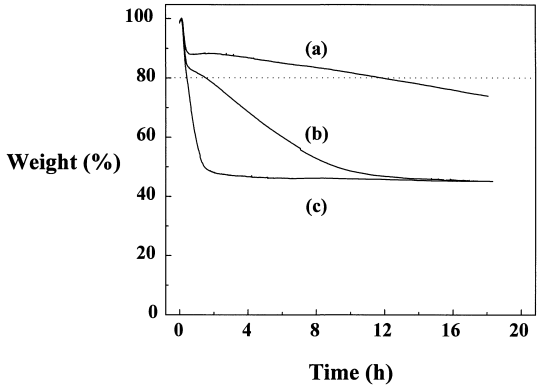

Fig. 6. Weight loss of 50% H_2SO_4/SiO_2 during drying in flowing N_2 at different temperatures. Freshly prepared samples were heated at a rate of 10°C/min to (a) 130°C, (b) 160°C, (c) 200°C and subsequently maintained at that temperature.

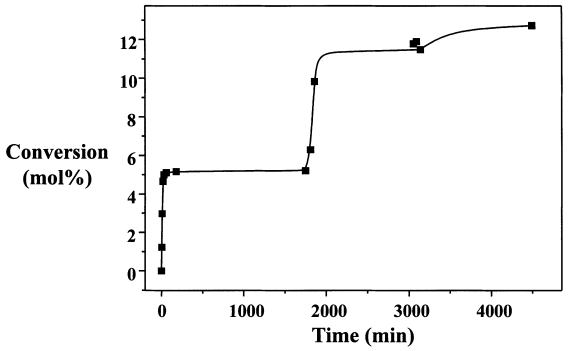

Fig. 7. Solvent-free nitration of 2-NT/4-NT using 50% H_2SO_4/SHE; HNO_3/NT = 0.05–0.15, 65 wt.% HNO_3, 25°C, no solvent.

of interest to explore the limits of thermal stability and regeneration of these materials. Fig. 6 shows the dependence of the weight of silica-supported sulfuric acid on the temperature and duration of drying. Aiming for 20% weight loss, which corresponds to the desorption of water during the typical 18 h pretreatment at 120°C, it can be deduced that regeneration of the supported liquid acid can be achieved within about 12 h at 130°C or within 2 h at 160°C. Regeneration at higher temperatures is not advisable due to the rapid evaporation of the acid. The graph, however, also shows that even at 130°C drying temperature sulfuric acid will be completely removed from the support if the duration of the treatment is prolonged.

3.6. Solvent-free operation

In mixed acid nitrations, the ratio of mixed acid to aromatic can be adjusted at any desired value since both are liquids. Using solid acids, this ratio has to be kept at a value sufficiently low in order to permit stirring of the reaction mixture. From the results obtained above, complete conversion of NT to DNT is not expected when NT also serves as its own solvent. The limitations of solvent-free operation for the production of DNT from NT using sulfuric acid supported on silica are assessed in Fig. 7, which shows the results of the step-wise nitration of an equimolar mixture of 2-NT/4-NT using an aromatic-to-catalyst weight ratio of 1.9 and HNO_3 as the limiting reactant. After addition of 0.05 equivalents of HNO_3 (based on the total amount of NT), 5% conversion were obtained within a relatively short reaction time of less than 30 min at ambient temperature. The initial rate of DNT production was determined as 0.35 g DNT/g catalyst/h from the extrapolated slope of the conversion-time curve. Addition of another 0.06 equivalents of HNO_3 increased the conversion to about 11–12%. The initial rate for this step dropped to 0.11 g DNT/g catalyst/h. The smaller initial rate reflected the effects of 'dilution' of the solid acid by water uptake. Further addition of 0.05 equivalents of HNO_3 affected only a slight increase in the conversion to about 13%. From these observations we estimated that upon further reduction of the aromatic-to-catalyst weight ratio to a minimum value of about 0.8 still providing a stirrable mixture, a maximum conversion of about 30% could be expected in one nitration cycle. Based on the sulfuric acid loading of our silica-supported sulfuric acid we further estimated that a site density of about 10 mmol/g catalyst would be required to affect complete conversion of NT to DNT in a solvent-free process.

4. Conclusions

The water present in the reaction mixture either as reaction product or contained in 65 wt.% nitric acid remains strongly adsorbed on the acid sites of the solid acids at ambient temperatures which leads to a mediating effect of acidity. Therefore, a high density of acid sites is required to maintain the solid acid active for a sufficiently long period. A continuous flow pro-

cess based on solid acids is hardly possible under such conditions because frequent regeneration of the solid acid is required by thermal treatment.

Only supported liquid acids were capable of providing the required high density of acid sites per unit weight of solid acid. Supported sulfuric acid on silica gel and preshaped silica beads was the preferred solid acid studied. Genuine catalytic behavior was not obtained under these conditions because, as is the case in the common mixed acid process, sulfuric acid amounts greater than stoichiometric were required to bind the water in the reaction mixture. Based on the amount of sulfuric acid present on the impregnated solid acid, the performance was somewhat lower than rates, yields-per-pass, and selectivity with liquid H_2SO_4/HNO_3. Due to the weight of the inactive carrier material, however, the impregnated acid was only half as active on a weight basis compared to liquid sulfuric acid. The solid acid could be easily separated by filtration or drainage of the product mixture. Regeneration for water removal was affected by thermal treatment, i.e., flowing hot nitrogen over the solid acid. The solid acid could be reused after regeneration without significant loss of performance.

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