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Sulfuric Acid on Silica-gel: an Inexpensive Catalyst for Aromatic Nitration

Juan M. Riego, Zeno Sedin, José M. Zaldívar*, Nunziata C. Marziano† and Claudio Tortato†

Joint Research Centre of the C. E. C., Safety Technology Institute, Process Engineering Div. T.P. 680, 21020-Ispra (VA), Italy

†Università degli Studi di Venezia, Dipartimento di Chimica, Calle Larga-S. Marta 2137, 30123-Venezia, Italy.

Abstract: Solid acidic catalysts made of sulfuric acid supported on silica-gel and their application to the nitration of aromatics with nitric acid and isopropyl nitrate are described. Substrates with very different levels of activation were investigated. Methods to overcome the poisoning produced by water and to tune the catalyst activity according to the reactivity of the substrate are outlined.

The nitration of aromatics by nitric acid in concentrated aqueous sulfuric acid is a common reaction in the preparation of bulk and fine chemicals.

$$ArH + HNO_3 \xrightarrow{H_2SO_4} ArNO_2 + H_2O \qquad (1)$$

Sulfuric acid is the catalyst for the formation of nitronium ion, recognised as the actual nitrating agent.[1]

$$HNO_3 + H^+ \rightleftarrows H_2O + NO_2^+ \qquad (2)$$

The acid strength, i.e. the "acidity" of the medium, is the key parameter for the conversion of reagents to products.[2]

Industrially, a large excess of sulfuric acid is required because the water by-produced slows the reaction down by diluting the acid. At the end of the process, a large amount of "spent acid"[3] is obtained which, in batch processes, is usually neutralised and disposed of, while, in continuous processes, has to be recycled by complex techniques. Also, the separation of the products from the acid is often a difficult and energy consuming process that habitually implies a basic aqueous work-up. Moreover, sulfuric acid is corrosive and is dangerous to transport and handle. So, any reduction in the amount of sulfuric acid needed and/or any simplification in handling procedures would be highly convenient in terms of risk reduction, economic advantage and environment protection.

Some heterogeneous liquid-solid methods for aromatic nitration have been described[4-10] that use either a solid acid as catalyst or a supported catalyst.[1a,11] These solids are easier to handle because they hold the acidity internally, they are also readily separable from the products by simple filtration and they are recyclable. Moreover, constraining a reaction to the surface of a solid habitually allows to use milder conditions and increases its selectivity.

Continuing our interest on reactions using supported reagents,[12] we report in this paper the application of catalysts made of sulfuric acid supported on silica-gel to the nitration of aromatic compounds. Our preliminary results are summarised in Table 1, showing the substrates and reagents used as well as some experimental details.

The catalysts were easily prepared by soaking 20 g of silica-gel[13] with 25 ml of sulfuric acid of an appropriate concentration, followed by 5 h water pump drying at r.t. and oven drying at 130 °C for 24 h. Concentrations of sulfuric acid below 70% yielded solid acids that had high acidity[14] without too much hygroscopicity.[15] These easy to handle catalysts can be stored indefinitely in a desiccator with blue-indicating silica-gel and re-activated when needed by heating in the oven for 12 h.

In a typical run 25 ml of a solution of 5 mmol of substrate in dry dichloromethane (containing n-decane, n-dodecane or nitrobenzene as internal standard) were poured onto 4 g of activated catalyst and stirred in a thermostated reactor at 25 °C for 10 min. Then, 5.2 mmol of nitrating agent were added dropwise and the obtained slurry was stirred for an appropriate time. The supernatant solution was analysed by GC and GC-MS to determine the conversion and isomer distribution. The products were isolated by filtration and evaporation of the solvent. Anticipating its application to bulk chemicals production, the reaction was also carried out using the substrate concurrently as solvent instead of dichloromethane. This procedure increased the rate but yielded also small amounts of dinitrated products. The catalyst was recovered for further use by washing with solvent, water pump drying and oven re-activation. A minimal loss of acidity was found after 3 runs, ranging from 0.1 to 3%. For larger amounts of substrate, the reaction can be carried out with azeotorpic removal of the water formed, e.g. 15 mmol of either benzene, toluene or chlorobenzene were almost quantitatively converted to their respective mononitro derivatives with 70% HNO_3 and 4 g of G-70 just by refluxing until no more water was recovered in a Dean-Stark trap.[16]

Table 1 shows our results using isopropyl nitrate and 70% nitric acid as nitrating agents. Concentrated nitric acid (90%) gave analogous results with net increases of the reaction rates, providing 100% conversions in less time. However, formation of dinitrated by-products was found for xylenes and mesitylene. Likewise, toluene and xylenes showed decreased para selectivity. The test reactions using isopropyl nitrate as nitrating agent, confirmed that the reaction takes place smoothly on the catalyst, but some alkylation (1-10%) was always observed for activated substrates, an effect that worsened at higher temperatures (for instance some alkylation was observed when nitration of toluene was carried out with $^{i}PrONO_2$ at 50 °C).

The solid designed as G-70 (derived from 70% H_2SO_4, acidity=10±0.5 mmol H^+/g) is the catalyst of choice for medium activated substrates as benzene, toluene of chlorobenzene. It induced dinitration of activated substrates as xylenes or mesitylene that was avoided by using a less active catalyst. E.g. p-xylene or mesitylene in dichloromethane were quantitatively and exclusively converted to their mononitro derivatives in 40 min and 2 min, respectively, using a catalyst derived from 40 % H_2SO_4 (G-40, 7.4 mmol H^+/g). Anisole was always too reactive.[6,17]

Similarly, satisfactory results for progressively deactivated compounds were found by increasing the "acidity" of the solid catalysts. Bromobenzene was nitrated to 98 % in 1 h using G-80 as catalyst (from 80 % H_2SO_4,10.5 mmol H^+/g) and p-dichlorobenzene was nitrated to 97% in 20 h by catalyst G-90 (from 90% H_2SO_4, 11 mmol H^+/g). For a extremely deactivate substrate as nitrobenzene, a catalyst (G+20) was *in situ* generated from 4 g of dry[18] silica-gel and 1.5 ml 20% oleum (SO_3 acted as water scavenger). Using this system and concentrated (90%) nitric acid, 5 mmol of NO_2Ph in CH_2CCl_2 were converted in 80 min to a mixture of o- (7%), m- (81%) and p- (1%) dinitro-benzenes. A conversion of 90% was observed instead of the poor 3% obtained when using G-70.

Likewise, quinoline, a compound with a basic site (that with G-70 yielded only a 30 % of nitrated products) was cleanly and completely converted in 4 h to a mixture of 5- (51.5), 6- (0.5) and 8- (44.0) nitroquinolines when G+20 was used as the catalyst. Adequate modifications of the sampling and isolation procedures (washing the catalyst with water followed by dichloromethane extraction of the aqueous phase) were implemented on account of the basic character of the products.

Table 1. Nitrations over H_2SO_4-silica gel at 25 °C. Catalyst was G-70 unless otherwise stated.

Substrate	Solvent	Nitrating agent			
		70 % HNO_3		i-Propyl nitrate	
		Time (h)/ Conversion(%)[a]	Isomer Distribution [b] Mononitro Dinitro (% 2-; % 3-; % 4-)	Time (h)/ Conversion(%)[a]	Isomer Distribution[b] Mononitro (% 2-; % 3- ; % 4-)
anisole[c]	---	---	---	---	---
mesitylene	neat	1.3 / 100	93 (mono) 7	0.4 / 60	---[e]
	CH_2Cl_2	0.03 / 100[d]	100 (mono) ---	2.0 / 50	---[e]
o-xylene	neat	0.25 / 100	--- 48 51 <1	---	---
	CH_2Cl_2	1.0 / 97	--- 42 58 ---	---	---
m-xylene	neat	0.25 / 100	14 85 --- <1	---	---
	CH_2Cl_2	1.0 / 100	17 83 --- ---	---	---
p-xylene	neat	1.5 / 100	99 (mono) 1	3.0 / 60	---[i]
	CH_2Cl_2	0.7 / 100[d]	100 (mono) ---	4.0 / 50	---[i]
toluene[f]	neat	0.1 / 100	57 4 40 ---	3.0 / 94	56 4 40[i]
	CH_2Cl_2	1.5 / 99	57 3 40 ---	2.0 / 25	56 4 40[i]
benzene	neat	1.0 / 98	---	3.5 / 100	---
	CH_2Cl_2	3.0 / 96	---	4.0 / 40	---
chlorobenzene	neat	1.5 / 100	31 <1 68 ---	15.0 / 20	32 <1 68
	CH_2Cl_2	24.0 / 50	31 <1 68 ---	15.0 / 8	32 <1 68
bromobenzene	neat	8.0 / 50	37 1 62 ---	---	---
	CH_2Cl_2	1.0 / 98[h]	37 1 62 ---	---	---
1,4-dichlorobenzene	CH_2Cl_2	20.0 / 97[j]	---	3.0 / 31	---
nitrobenzene[g]	CH_2Cl_2	1.3 / 90	8 90 1 ---	---	---
quinoline[g]	CH_2Cl_2	5.0 / 100	k	---	---

a) Based either on starting material (CH_2Cl_2) or on added nitrating agent (neat). Determined by GC with internal standards. b) Analysed by GC with internal standard and by GC-MS. Compared with authentic samples. c) Complex mixtures of mono and dinitro derivatives as well as tarry material were always obtained. d) Catalyst was G-40. e) A complex mixture of alkylated and nitroalkylated compounds was obtained. f) No dinitrated products detected, even when using 90% HNO_3 as nitrating agent. g) Catalyst was 20% SO_3 oleum and the nitrating agent 90% HNO_3. h) Catalyst was G-80. i) Some alkylated aromatics were also obtained. j) Catalyst was G-90. k) 5-NO_2 (52%), 6-NO_2 (<1%), 7-NO_2 (44%).

From the obtained results, some experimental observations are of practical interest: a) catalytic systems can be prepared using inexpensive materials; b) the performance of such solid acids can easily be modified in accordance to the reactivity of the aromatic substrate; c) 70% nitric acid, as suggested by industrial requirements, can be used for most of the aromatics to be nitrated; d) conversions and isomer distributions are similar to those obtained over Nafion-H[7] but our catalysts are advantageous because cheaper and the reactions occur at room temperature. They are also vastly easier to prepare and handle than the clayfen and claycop described by Lazslo *et al.*[9]

Of course, solid acids prepared by supporting sulfuric and other strong acids on silica gel[19] can be applied to many acid catalysed reactions and research on this topic is underway.

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References and Notes

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13. GRACE GmbH Silica Gel Catalyst Carrier 239/ 30-100 micron.
14. The total acidity was measured by thoroughly extracting an aliquot of the acidic solid with water followed by titration of the joined extracts with 0.1 N aqueous NaOH in an automated titrator.
15. Total acidity was proportional to the concentration of the solution of H_2SO_4 used. Catalysts made from sulfuric acid of concentration >70% were better handled under an inert atmosphere.
16. Only a minimal amount of HNO_3 and no H_2SO_4 were detected in the distillate water. The azeotrope of cyclohexane and water was used for chlorobenzene.
17. Even when less active catalysts were used (G-10: 2.4 mmol H^+/g), complex mixtures of mononitro, dinitro and tarry materials were obtained.
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