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Sulphated zirconia: an efficient paraselective catalyst for mononitration of halobenzenes

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The nitration of halobenzenes (chlorobenzene, bromobenzene and iodobenzene) was carried out using sulphated zirconia (SO_4^{2-}/ZrO_2) as catalyst and stoichiometric quantities of nitric acid and acetic anhydride in CCl_4 medium at room temperature, 50 and 70°C. The isolated yield of the nitrated product after vacuum distillation was found to be nearly 99% for all the halobenzenes. The order of selectivity to para-isomer was found to be chlorobenzene > bromobenzene > iodobenzene. The catalyst can be recycled at least five times with little decrease in its activity.

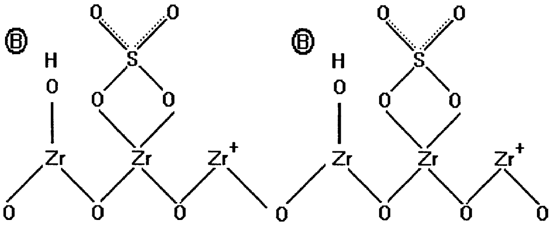
Keywords: sulphated zirconia, nitration, halobenzene, para-selectivity

1. Introduction

The mononitration of halobenzenes and especially that of chlorobenzene to chloronitrobenzenes is a widely studied reaction. Its products find use in pharmaceuticals, intermediates for dyes, perfumes, and many others [1–4]. Most of the aromatic nitration reactions as classically conducted with a mixture of nitric and sulphuric acids give a mixture of ortho- and para-products close to the statistical ratio 1 : 2 [5,6]. However, carrying out the reaction in the presence of acetic anhydride along with sulphuric and nitric acids, increased the para-selectivity at low reaction temperature [7,8]. This has been interpreted as the addition of acetic anhydride decreases the dielectric constant of the reaction medium, hence favouring the production of the more para-substituted product.

Recently, due to environmental concerns the traditional use of aggressive mixtures of sulphuric and nitric acids need be replaced by eco-friendly solid acid catalysts. In this respect solid acid catalysts such as zeolites, montmorillonite-clay-supported ferric nitrate (clayfen) and copper nitrate (claycop) have been used for the nitration of simple aromatics such as halobenzenes, toluene, etc. [9–11]. Sulphate-doped zirconia (SO_4^{2-}/ZrO_2) which is considered to be a solid superacid has recently attracted much attention by several researchers. This sulphated zirconium oxide has already been found to be very active in the isomerization of *n*-butane and aliphatic alkylation reactions even at room temperature.

Surface acidity characterization of sulphated zirconia shows that its surface contains very strong Brønsted as well as Lewis acid sites [12–14]. However, the number and the strength of these sites largely vary with parameters such as sulphur concentration, activation temperature and surface area of the precursor hydroxide or oxide [15–18]. Based on IR spectroscopy and XPS techniques Ward et al. [14] have given the following structure of SO_4^{2-}/ZrO_2 explaining the presence of both Brønsted and Lewis acid sites:



Ⓑ denotes Brønsted acid sites ; Zr^+ denotes Lewis acid centre

The Brønsted acid sites result from the weakening of the O–H bond by the neighbouring sulphate groups, whereas the Lewis acid sites are electronically deficient Zr^{4+} centers as a result of the electron-withdrawing nature of the sulphate group.

In the present work we report the nitration of halobenzenes using SO_4^{2-}/ZrO_2 as a catalyst. The activity and selectivity of the catalyst has been correlated with its surface acid sites. The proposed mechanism is well supported by our experimental observations.

2. Experimental

Catalyst preparation. The SO_4^{2-}/ZrO_2 catalysts were prepared from zirconium hydroxide following the controlled sulphur impregnation method, where the hydroxide was previously prepared from zirconium oxychloride (0.4 M) and aq. NH_3 (6.7 M) being added

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dropwise at a constant pH of 10 [18]. For impregnation, 1 N H_2SO_4 and dried hydrogel of zirconium ground to particle size less than 100 BSS mesh were used. For activation, all the impregnated samples were calcined at 600, 700 and 800°C for 3 h.

Catalytic activity test. The nitration of halobenzenes (chlorobenzene, bromobenzene and iodobenzene; CDH, AR) was carried out in carbon tetrachloride solution, taking 0.5 g of the calcined sample, 10 mmol of halobenzene and an equivalent amount of nitric acid, in the presence of acetic anhydride. The amount of acetic anhydride was chosen such as to be the minimum that would allow quantitative conversion to acetylnitrate. Time of reaction for most cases was 1 h; it was 2 h for the reaction at room temperature. Acetic acid, the only byproduct of the reaction, was separated from the nitration product by distillation. The percentage of ortho- and para-isomer of the nitrated products were analysed by gas chromatography using 15% FFAP on 80/100 mesh W(HP) column.

3. Results and discussion

It was revealed from preliminary experiments that a catalyst containing 3.22 wt% S is the most active for nitration of all the halobenzenes. The activities of SO_4^{2-}/ZrO_2 catalysts are largely affected by their sulphur content. The low activity at sulphur concentration more or less than 3.22 wt% is presumably due to the formation of inactive S–O–S type of bonds at higher concentration [15,17,19] and less number of Brønsted acid sites at lower concentration.

It can be seen from table 1 that the percentage yield as well as the selectivity to para-isomer gradually decrease with increase in the activation temperature of the catalyst. For all the halobenzenes the catalyst heated at 600°C was found most active and also selective to para-isomer. However, the para-selectivity decreases from chlorobenzene to iodobenzene. This is similar to the earlier report of Holleman [20], who had found that among the halobenzenes, fluorobenzene gives the highest para-substituted product and iodobenzene the lowest. This has been explained by the greater –I effect ($F > Cl > Br > I$) which affects the nearest ortho-position more than the more remote para-position, so the NO_2^+ ion will prefer to attack the para-position [20,21]. In the present case the decrease in activity as well as selectivity of the catalysts with increase in their activation temperature might be due to a decrease in the number of Brønsted and Lewis acid sites. The high activity and para-selectivity of the catalyst (SO_4^{2-}/ZrO_2, 3.22 wt% S) activated at 600°C might be due to the presence of a larger number of Brønsted and Lewis acid sites. The mechanism which we propose for the reaction is well supported by our experimental observations. This mechanism is given in scheme 1.

As we have already mentioned, the –I effect of halogens determines the para-substitution of the NO_2^+ ion in the nitration of halobenzenes. The Lewis acid sites on SO_4^{2-}/ZrO_2 would probably facilitate the increase of the electronegative properties of the halogens (Cl, Br and I) and hence the –I effect, thereby, consequently, affecting the ortho-position more, resulting in a high proportion of para-substituted product. Hence, the Brønsted acid sites are responsible for producing NO_2^+ ions while the Lewis sites favour formation of the para-substituted product.

When blank experiments were carried out without using a catalyst, a very small conversion, i.e., less than 5%, was observed. It is possible that the excess protons of the nitric acid react with acetyl nitrate to produce NO_2^+ ions and hence the conversion.

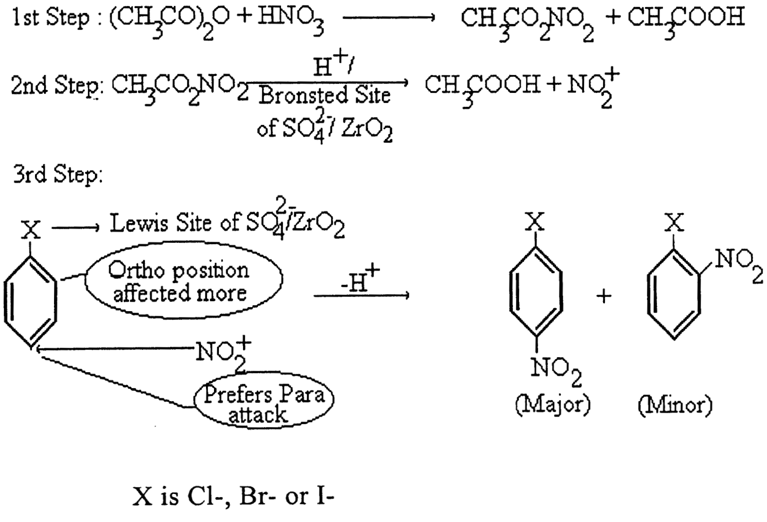
4. Conclusions

The SO_4^{2-}/ZrO_2 (3.22 wt%) calcined at 600°C was

Table 1
Nitration of halobenzenes using SO_4^{2-}/ZrO_2 (3.22 wt% S) catalyst in carbontetrachloride medium

Catalyst [a]	Reaction temp. (°C)	Chlorobenzene		Bromobenzene		Iodobenzene	
		yield [b] (%)	ortho : para (%)	yield [b] (%)	ortho : para (%)	yield [b] (%)	ortho : para (%)
SZ-600 [c]	70	94	15 : 85	95	18 : 82	94	24 : 76
SZ-600 [c]	RT [d]	95	14 : 86	94	17 : 83	95	23 : 77
SZ-600 [c]	50	99	14 : 86	99	18 : 82	99	25 : 75
SZ-700 [c]	50	80	18 : 82	82	20 : 80	80	27 : 73
SZ-800 [c]	50	10	21 : 79	11	23 : 77	10	30 : 70
SZ-600 [c] (recycled)	50	88	15 : 85	85	18 : 82	86	25 : 75
blank	50	5	30 : 70	4	32 : 68	4	35 : 65

[a] 0.5 g of catalyst; SZ, SO_4^{2-}/ZrO_2.
[b] Isolated yield of the nitrated product.
[c] Calcination temperature in °C.
[d] RT: room temperature.



Scheme 1.

found most active and selective to para-substituted product in the nitration of halobenzene. It is very interesting to note that the percentage yield approaches 99% in 1 h of reaction time. As we have argued, the Lewis acid sites of SO_4^{2-}/ZrO_2 are responsible for the high para-selectivity. Control over their number by changing the preparative method could help us to control the ortho-to para-ratio of the nitrated product even better.

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