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Selectivity engineering in the nitration of chlorobenzene using eclectically engineered sulfated zirconia and carbon molecular sieve catalysts

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Selective synthesis of the *para*-nitro derivative from chlorobenzene by using nitric acid over an eclectically engineered sulfated zirconia carbon molecular sieve catalyst is reported. The $p : o$ ratio in chlorobenzene nitration was found to be very high with eclectically engineered sulfated zirconia and carbon molecular sieve catalyst.

Keywords: sulfated zirconia, carbon molecular sieve, nitration, chlorobenzene, selectivity

Industrial aromatic nitrations are carried out by employing a mixture of nitric acid and sulfuric acid predominantly yielding *ortho*- and *para*-substituted products from substituted benzenes as substrates. Nitro compounds find uses in many industries such as drugs and dye intermediates, explosives, and the use of *para* isomers is found commercially to be the most common. However, this mixed acid process has a major problem of the spent acid disposal which is environmentally unfriendly and can be costly. The formation of water during the reaction causes the dilution of the nitrating mixture thus reducing the rate of nitration as the reaction proceeds. At about 68% sulfuric acid, the nitration becomes extremely slow.

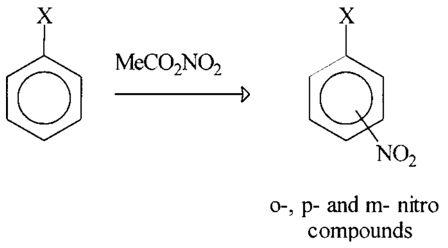
Attempts are being made to reduce the spent acid generated during this reaction and increase the *para* preference by properly substituting the type of catalyst with suitable solvents. Recent advances in solid acid and superacid catalysts have focused on the use of solid acids in nitrations [1–3].

In view of the drawbacks associated with the conventional nitration process such as disposal of spent acids, hazardous nature of sulfuric acid–nitric acid mixture, homogeneity of the reaction, non-selectivity and reusability it prompted us to explore the preparation of aromatic nitro compounds using novel selective and ecofriendly routes. Sulfated zirconia (S-ZrO_2) is found to be a very efficient solid acid catalyst in a number of reactions of industrial relevance [4–15]. Recently, we have reported the use of a novel modified S-ZrO_2 as a shape-selective catalyst in the cyclisation of citronellal to isopulegol [16]. Herein we present the use of S-ZrO_2 and its modified forms as catalysts for selective nitration of chlorobenzene using nitric acid and acetic anhydride as solvents.

Several catalysts have been reported for nitration of chlorobenzene which include $Cu(NO_3)_2$/K-10, HNO_3/silica–alumina, HNO_3 supported on H-ZSM-5, zeolite β and HNO_3 supported on SiO_2 molecular sieves [17–20] amongst which zeolite β was reported to give the best *para* selectivity of about 93% [20].

Nitration of aromatic compounds proceeds via the *in situ* formation of acetyl nitrate, obtained from the reaction of nitric acid and acetic anhydride, as shown below in reaction (a). Acetyl nitrate, thus formed, further reacts with the aromatic compound to form the corresponding nitro compound, as shown in reaction (b). We report here the efficacies of novel catalysts in the nitration of chlorobenzene leading to very high *para* isomer yields.

$$HNO_3 + (MeCO)_2O \rightarrow MeCO_2NO_2 + MeCO_2H \qquad \text{(a)}$$



(b)

Materials used. Zirconium oxychloride, 25% ammonia solution, 98% sulfuric acid, acetic anhydride and 70% nitric acid, all of A.R. Grade, and polyvinyl alcohol and dodecatungstophosphoric acid (DTP) were obtained from s.d. Fine Chemicals Ltd.

General procedure for the preparation of catalysts. In a typical method S-ZrO_2 was prepared by the conventional precipitation technique [4,5]. About 110 g of zirconium oxychloride was dissolved in about 2000 ml of distilled water. Zirconium oxychloride solution and 25% ammonia

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solution were simultaneously added, dropwise, under constant stirring, in a 5000 ml beaker. On addition of both the solutions, a white precipitate of zirconium hydroxide was obtained. The pH of the solution was maintained between 9 and 10. After complete precipitation, it was allowed to digest for 4 h. The precipitate was then washed and filtered through a buchner funnel. The precipitate was washed and made free of chloride ions and ammonia, which was confirmed by the phenolphthalein and the silver nitrate tests, respectively. This hydroxide was dried in an oven for 24 h at 110 °C. The dried cake was then crushed to obtain the desired particle size. Sulfation of this hydrous zirconia was carried out by percolating 1 M sulfuric acid solution through it (15 ml acid/g of solid hydrous zirconia). The sulfated zirconium hydroxide was then calcined in air at 650 °C for 3 h in a quartz tube to yield the S-ZrO_2 catalyst.

S-ZrO_2 was then modified by coating with polyvinyl alcohol solution by an incipient wetness technique followed by carbonisation at the desired temperature for 3 h to yield a novel shape-selective catalyst, designated as UDCaT-2.

General procedure for the preparation of nitro compounds. In a typical experiment, 70% nitric acid (0.1 g/mol) was added dropwise over a period of 90 min to a mixture of chlorobenzene (0.2 g/mol) and acetic anhydride (0.5 g/mol) containing the desired catalyst (2.24 g) at 30 °C in a fully baffled 100 ml glass reactor under constant stirring. Samples (1 ml) were removed periodically and washed with water (20 ml) to remove acetic anhydride and acetic acid, produced *in situ*. The organic layer was treated with sodium sulfate (0.05 g) and filtered to obtain a mixture of the reactant, chlorobenzene, and nitro products. The products were isolated by distillation. The catalyst was recovered for further use by washing with solvent and reused as such. Samples were analysed on a Chemito gas chromatograph (model 8510) equipped with a flame ionisation detector. A 2 m long stainless-steel column with 3 mm internal diameter packed with AT-1000 was used for the analysis. The carrier gas used was moisture-free pure nitrogen at a flow rate of 30 ml/min. The oven temperature was maintained at 150 °C for 6 min. The injector and detector temperatures were maintained at 300 °C.

It has been reported that when excess acetic anhydride is present, the only nitrating agent detectable by Raman spectral measurements is acetyl nitrate, whereas when nitric acid is in slight excess dinitrogen pentoxide is observed to be present [21]. The authors have also concluded that nitrating action is not obtained unless conversion to acetyl nitrate occurs. In the current studies, 70% nitric acid was added to the reaction mixture containing the aromatic compound dissolved in excess of acetic anhydride. Thus, the mole ratio of acetic anhydride to nitric acid would always be infinite at any instant of time. The acetyl nitrate, formed *in situ*, reacts with the aromatic substance and depending upon the rate of addition of nitric acid, the free concentration of acetyl nitrate will be decided.

Table 1
Nitration of chlorobenzene.[a]

Catalyst	Conversion of HNO_3[b] (%)	$p:o$ ratio[c]
No catalyst	No conversion	–
S-ZrO_2	47	10.6 : 1
UDCaT-2	45	13.2 : 1
5%DTP/S-ZrO_2[d]	41	8.6 : 1
5%DTP/S-ZrO_2/CMS[e]	21	10.2 : 1

[a] No dinitrated products detected.

[b] In a short while after the addition of nitric acid was complete. Conversion of nitric acid was calculated on the basis of chlorobenzene consumed.

[c] Analysed by GC and by GC-MS. Compared with authentic samples.

[d] 1 g of dodecatungstophosphoric acid (DTP) was dissolved in 10 ml of methanol and supported on 19 g of S-ZrO_2 by incipient wetness technique, dried at 120 °C in an oven for 24 h and calcined at 285 °C for 3 h to obtain 5%DTP/S-ZrO_2.

[e] 5%DTP/S-ZrO_2 was coated with polyvinyl alcohol solution using incipient wetness technique and calcined at 285 °C for 3 h.

Table 1 shows the effect of different catalysts on conversion and $p:o$ selectivity in nitration of chlorobenzene. As seen from the table the use of S-ZrO_2 for the nitration of chlorobenzene gave high selectivity towards the formation of *para* isomer. No formation of *meta* product was observed. Also, no formation of dinitrated by-products was observed in this reaction. Modification of S-ZrO_2 by coating it with carbon molecular sieve (CMS) to yield UDCaT-2 further enhanced the selectivity towards the formation of the *para* isomer though there was no considerable change in conversion. This can be attributed to the fact that the CMS around S-ZrO_2 acts as a barrier for the bulkier *ortho* isomer and, hence, favours the formation of kinetically smaller *para* isomer. This is further supported by the fact that the pore size of S-ZrO_2 was found to be in the range of 35–50 Å with maximum number of pores falling in the range of 38–45 Å and that of UDCaT-2 in the range of 9–28 Å with maximum number of pores in the range of 9–13 Å, as can be seen from the pore distribution plots of S-ZrO_2 and UDCaT-2 in figure 1. According to the network models of pore structure, not only the pore sizes but also the co-ordination number of the network matters and these results are in order. Table 2 shows the pore volumes and BET surface areas of S-ZrO_2 and UDCaT-2. It can be seen from the table that there is no significant difference in the pore volume of S-ZrO_2 and UDCaT-2. However, the BET surface area of UDCaT-2 was found to be lower than that of S-ZrO_2. This probably indicates blocking of some of the pores of S-ZrO_2 by the CMS around the former which results in the decrease in surface area. A possible reaction mechanism, explaining the efficacy of S-ZrO_2, is shown in figure 2. It can be seen from the mechanism that acetyl nitrate, formed *in situ*, gets chemisorbed onto the catalyst surface. When the substituted aromatic substance, in this case chlorobenzene, approaches these catalytic sites the catalyst readily loses the chemisorbed nitronium ion which attacks chlorobenzene either on the *para* or *ortho* position.

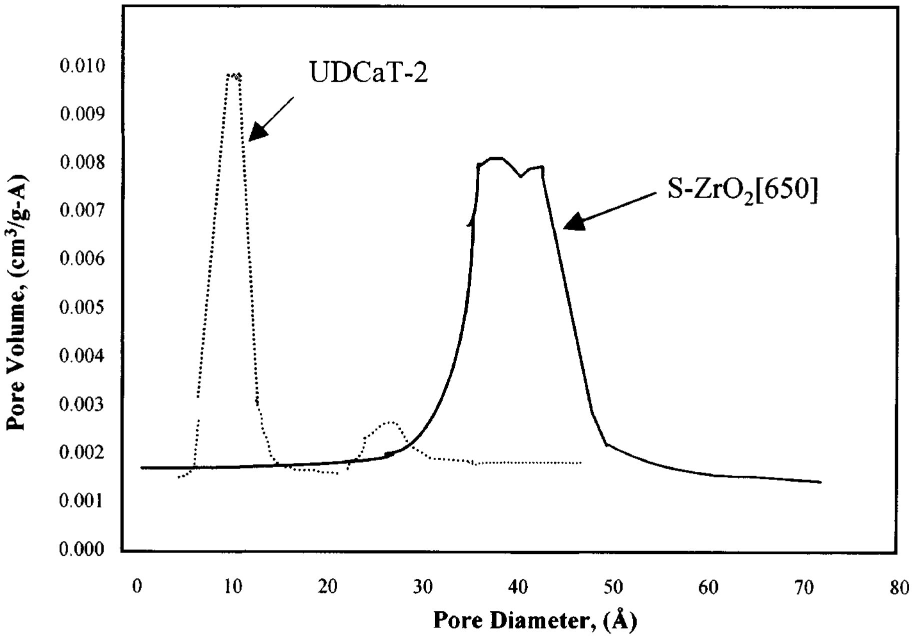

Figure 1. Pore size distribution plots of S-ZrO$_2$ and UDCaT-2.

Table 2
Physical characterisation of catalysts.

Catalyst	Pore volume (cm^3/g)	BET surface area (m^2/g)
S-ZrO$_2$	0.108	100
UDCaT-2	0.165	64

Hence, if the *ortho* position of chlorobenzene is attacked then the mechanism will follow path (a) or path (b), if the *para* position is attacked. The $p:o$ ratio is then governed by the CMS barrier surrounding S-ZrO$_2$, in case of UDCaT-2, as mentioned earlier. The proton, thus released, from the respective positions of the chlorobenzene, then combines with the acetyl group, which desorbs from the catalyst surface, to give acetic acid, thus regenerating the catalyst.

S-ZrO$_2$ was modified by supporting dodecatungstophosphoric acid (DTP), a heteropoly acid, on the former to give another synergistic catalyst, 5%DTP/S-ZrO$_2$. When this was used as a catalyst for nitration of chlorobenzene the $p:o$ ratio was found to decrease. DTP is a very well known heteropoly acid with a very huge Keggin structure. By supporting DTP on S-ZrO$_2$, the selectivity towards the formation of *para* product should increase due to the partial pore plugging. However, it showed a reverse trend, as mentioned earlier. It is probably because DTP, being a very large molecule, will not penetrate deep into the pores of S-ZrO$_2$ and will remain chemisorbed more on the external surface of S-ZrO$_2$ or it will diffuse into very large and accessible pores of S-ZrO$_2$. Also, the doping of S-ZrO$_2$ with DTP augments the catalytic activity but which in turn might also have blocked the pores of S-ZrO$_2$ thereby reducing the accessible sites and, hence, decreasing the overall activity of the catalyst. This has reflected in the marginal decrease of the activity of 5%DTP/S-ZrO$_2$. Hence, though

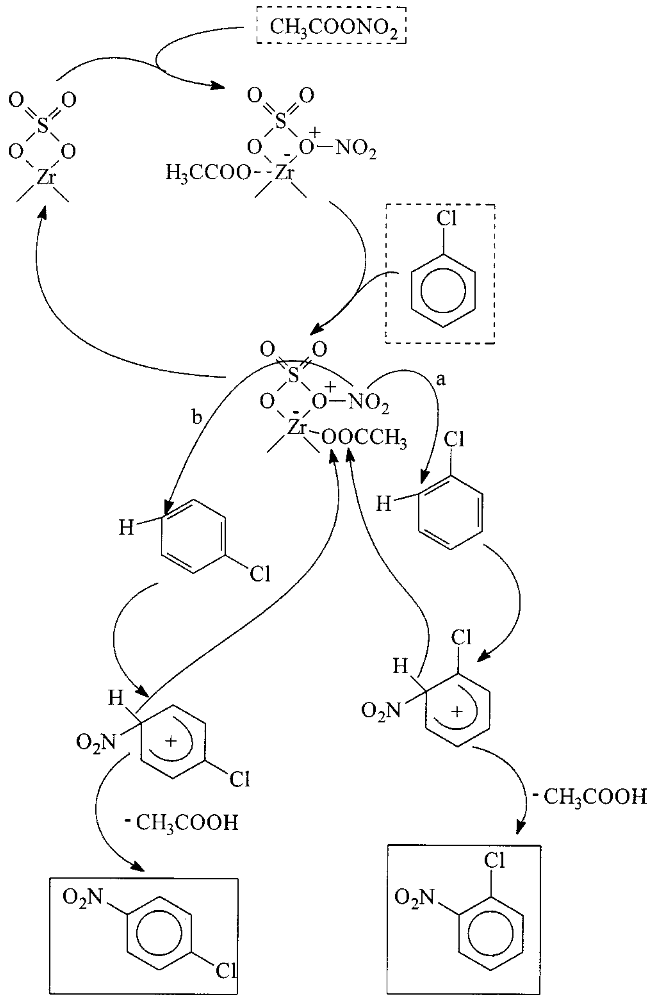

Figure 2. Reaction mechanism over S-ZrO$_2$.

the pore plugging may take place in DTP supported on S-ZrO_2, it is not so significant and the active sites of DTP are available more on the external surface of S-ZrO_2 or very large pores of S-ZrO_2 which will not lead to the increase in the *para* selectivity. This was also supported by the fact that when 5%DTP/S-ZrO_2 was coated with CMS, to get CMS/DTP/S-ZrO_2, there was a significant decrease in the activity of the latter. However, at the same time it shows higher selectivity towards the formation of *para* product due to the CMS barrier. This shows that DTP is present more on the external surface than inside the pores of S-ZrO_2 which are shielded to a significant extent by CMS coating.

Thus from the results obtained it can be concluded that: (a) very high selectivity is obtained for the *para* product in case of chlorobenzene using either S-ZrO_2 or UDCaT-2 as catalysts; (b) UDCaT-2 type of catalysts can be easily prepared using inexpensive materials; (c) selective formation of *para* product can be carried out by tailor making the catalyst using different polymeric materials to prepare the CMS coating around S-ZrO_2; (d) the spent acid disposal problem is completely eliminated; (e) the process is ecofriendly and heterogeneous in nature and, on further optimisation, has the capacity to get commercialised [22,23].

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References

[1] G.A. Olah, R. Malhotra and S.C. Narang, *Nitration: Methods and Mechanisms* (VCH, New York, 1989).

[2] P. Laszlo, ed., *Preparative Chemistry Using Supported Reagents* (Academic Press, London, 1987).

[3] J.M. Riego, Z. Sedin, J.M. Zaldivar, N.C. Marziano and C. Tortato, Tetrahedron Lett. 513 (1996).

[4] G.D. Yadav and T.S. Thorat, Ind. Eng. Chem. Res. 35 (1996) 721.

[5] G.D. Yadav, T.S. Thorat and P.S. Kumbhar, Tetrahedron Lett. 34 (1993) 529.

[6] G.D. Yadav and M.S. Krishnan, Ind. Eng. Chem. Res. 37 (1998) 3358.

[7] P.S. Kumbhar and G.D. Yadav, Chem. Eng. Sci. 44 (1989) 2535.

[8] T.S. Thorat, V.M. Yadav and G.D. Yadav, Appl. Catal. A 90 (1992) 73.

[9] G.D. Yadav and J.J. Nair, Micropor. Mesopor. Mater. (1999), in press.

[10] K. Tanabe, Y. Nakano, T. Eizuka and H. Hattori, J. Catal. 57 (1979) 1.

[11] K. Tanabe, T. Yamaguchi and J. Ishida, Mater. Chem. Phys. 17 (1987) 3.

[12] K. Arata and M. Hino, Appl. Catal. 59 (1990) 197.

[13] M. Hino and K. Arata, J. Chem. Soc. Chem. Commun. (1980) 851.

[14] M. Hino and K. Arata, J. Chem. Soc. Chem. Commun. (1979) 1148.

[15] T. Yamaguchi and K. Tanabe, Mater. Chem. Phys. 16 (1986) 67.

[16] G.D. Yadav and J.J. Nair, J. Chem. Soc. Chem. Commun. (1998) 2369.

[17] P. Laszlo and P. Pennetraeu, J. Org. Chem. 52 (1987) 2407.

[18] M. Furuya and H. Nakajima, JP 63,303,957 (1988).

[19] M. Furuya and H. Nakajima, JP 63,225,339 (1987).

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

[21] F.G. Bordwell and E.W. Garbisch, Jr., J. Am. Chem. Soc. 82 (1960) 3588.

[22] G.D. Yadav, J.J. Nair and V. Narendra, Indian Patent Appl. 3592/DEL/97 (1997).

[23] G.D. Yadav, J.J. Nair and V. Narendra, US Patent Appl. 09/211,500 (1998).