



Sulfated titania mediated regioselective nitration of phenol in solid state

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Abstract

Titania, sulfated titania and chromium loaded sulfated titania were prepared by sol–gel method and characterized using different technique. Phenol is nitrated regioselectively by nitric acid using chromium loaded sulfated titania catalysts. A remarkable *ortho* selectivity is observed in solid state nitration to yield exclusively *ortho*-nitrophenol. Compared to the conventional process, phenol nitration over solid acid catalyst is a clean and environment friendly process. Catalytic activity well correlates with the Brønsted acid sites of these catalysts.

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1. Introduction

Electrophilic aromatic substitution reactions are of considerable importance in the production of fine chemicals. Nitration of organic compounds has long been a very active and rewarding area of research and is the subject of a large body of literature. Extensive and well-documented reviews have been published by Ingold [1], Olah and co-workers [2,3], Schofield and co-workers [4,5] and Ione [6]. Nitrations in manufacturing process require the use of potent mixtures of concentrated or fuming nitric acid with sulfuric acid leading to excessive acid waste. The obvious disadvantages of the commercial manufacturing process currently used had led to a substantial effort to develop viable alternative, by using solid acid catalysts. Nitration using solid acids may be the answer to these problems. Recent advances in super-acid catalysts have brought considerable research importance to this reaction. Due to the attachment of

the acid function to a solid surface, corrosion would be less a concern. Solid acids effectively play the role of sulfuric acid in the reaction, assisting the formation of nitronium species. Attempts are being made to reduce the spent acid generated during this reaction and to increase the selectivity of the product by properly substituting the type of catalyst with proper solvents. Different solid acids tested so far include zeolites [6], partially dealuminated [7] or cation exchanged zeolites [8], sulfonated ion exchange resins (polystyrenesulfonic acid) [9], clay supported metal nitrates [10], Fe^{3+} on K-10 montmorillonite [11], modified silica [6], silica-alumina and supported acids [12,13].

Various nitration procedures have been described in the last few years making use of different nitrating agents like NO_2 (N_2O_4), N_2O_5 , molten nitrate salts, alkyl and acyl nitrates, etc. [3,14]. Currie et al. [15] reported the nitration of phenols and anisols in micro emulsion media based on the cationic surfactants. Smith et al. [16,17] have used H^+ form of zeolite β and acetyl nitrate for the highly regioselective *para* nitration of toluene. Catalytic performance of various solid acid catalysts for benzene nitration with nitric oxide (NO_2) as

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nitration agent in the vapor phase has been studied by Sato and Hirose [14]. Montmorillonite ion exchanged with multivalent cations and mixed metal oxides containing TiO_2 and ZrO_2 exhibited high activity. Recently, novel nitration systems composing of nitric acid, trifluoroacetic anhydride and H- β are reported for the nitration of deactivated aromatic compounds [16]. The *para*-selective nitration of halogenobenzenes using a nitrogen dioxide–oxygen–zeolite H- β /HY systems is also reported [17]. Yadav and Nair [18] proposed the selective synthesis of *para*-nitro derivative from chlorobenzene by using nitric acid over an electrically engineered sulfated zirconia carbon molecular sieve catalyst. Thomasz et al. [19] have recently achieved a high yield and selectivity for the nitration of phenol to *p*-nitrophenol over metal oxide catalysts. *o*-Nitrophenol is an important starting material used in multiple step synthesis of valuable compounds [20]. Mixed metal oxides treated with sulfuric acid were found to be efficient for the nitration reaction [21]. Nitration over sulfated metal oxides is not well studied. Different solid acids tested so far, mainly gives *para*-nitrophenol as the selective product. This paper is concerned with the effect of sulfation and the Cr content on the catalytic performance of the prepared system in the nitration of phenol. A remarkable *ortho* selectivity is observed in all the systems under study.

2. Experimental

Titania, sulfated titania and chromium loaded sulfated titania nano powders were prepared by sol–gel process. The experimental details regarding the preparation of the catalyst samples and the methods of characterization such as XRD analysis, FT-IR analysis, surface area and pore volume measurements, EDX, SEM, TG/DTG and UV–Vis diffuse reflectance spectral analysis have been described in our earlier paper [22]. The same is the case with the experimental details of acidity measurement using spectrophotometric monitoring of adsorption of perylene, thermogravimetric desorption of 2,6-dimethylpyridine (2,6-DMP) and temperature programmed desorption of ammonia. The samples, after overnight drying at 110 °C, were calcined for 5 h at 500 °C. The general sample notation STCr(*x*) stands for sulfated titania containing *x* (3, 6, 9 and 12) wt% of chromium, while T and ST stands for pure titania and sulfated titania.

Catalysts were kept at 500 °C for 2 h prior to each reaction for activation. In a typical experiment, to phenol (5 mL), activated catalyst (0.1 g) was added and the mixture was milled to get a paste. This is kept at 0–5 °C using an ice bath and nitric acid (5 mL) is added drop wise with continuous stirring. The reaction mixture is stirred for 30 min, while maintaining the temperature

at 0–5 °C. After bringing the reaction mixture to room temperature, it is extracted with dichloromethane, after 2 h. Products were analyzed by gas chromatography (Chemito-1000, BP-1 capillary column (12 m \times 0.32 mm), FID detector, high purity nitrogen as carrier gas, column temperature 90 °C, injection and detection port temperature 300 °C, using a temperature program 90–2–10–300 °C). Prior to injection in G.C. unreacted nitric acid in the reaction mixture was neutralized using sodium carbonate solution to a pH of 6–7. Identification of products was done by comparing the G.C. retention times of expected products with those of standard samples. Reaction was done under varying conditions to optimize the reaction parameters. The catalytic activity was expressed as the percentage conversion (wt%) of phenol and the selectivity for a product is expressed as the amount of the particular product divided by total amount of products multiplied by 100. *o*-Nitrophenol is found to be the major product.

3. Results and discussion

After calcination at 500 °C, anatase appears as a crystalline phase manifested by its 101 peak ($2\theta = 25.5^\circ$) in the XRD. The anatase–rutile transformation takes place at this temperature and is confirmed by the occurrence of the 110 peak of rutile at $2\theta = 27.5^\circ$. The sulfated titania possesses only diffraction lines, such as at $2\theta = 25.5^\circ$, 37.4° , 48° and 53° simply indicating the anatase type of TiO_2 . Diffraction lines for the rutile type of TiO_2 are observed at $2\theta = 27^\circ$, 36° , 41° and 54° in the case of pure titania.

Sulfation retards the transformation from anatase to rutile in comparison with the sample without sulfation. Absence of characteristic peaks of chromium implies the high dispersion of chromium particles on the titania surface. The average crystallite size is calculated using Scherrer equation from 101 reflection of anatase is given in Table 1. From our earlier studies it is noted that, crystallite size of titania decreases in the presence of sulfate ion [23]. This indicates that the crystallinity is more or less dependent on the presence of sulfate ion. At high loading and at low loading of sulfate ions, the crystallite size is found to be high, but at an optimum loading of 2 mL g^{-1} of titanium hydroxide, the crystallite size is found to be minimum. The average crystallite size of titania decreases in presence of sulfate ion and also by incorporation of chromium ions.

The surface area and pore volume (Table 1) of the sulfated samples are invariably higher than pure titania. The main reason of surface area increment is due to the retardation of crystallization of the support oxides by the sulfate groups present on the surface [22]. The lowering of degree of crystallinity, as evident from the XRD patterns, supports the increase in the surface area

Table 1
Surface parameters of the prepared systems

Catalyst	Surface area BET (m ² g ⁻¹)	Pore volume (mL g ⁻¹)	Crystallite size (nm)	Pore diameter (nm)	Elemental composition from EDX (%)		
					TiO ₂	SO ₄	Cr
T	35	0.09	12.7	102.8	100	-	-
ST	91	0.21	9.6	92.3	95.3	4.7	-
STCr(3)	100	0.18	5.9	72.0	88.1	9.1	2.8
STCr(6)	123	0.17	6.2	55.3	83.6	10.5	5.9
STCr(9)	128	0.17	6.4	53.1	81.6	10.6	7.8
STCr(12)	137	0.15	9.8	43.8	74.2	14.7	11.1

by sulfate treatment. Assuming the pores are cylindrical, the average pore diameter is calculated using the formula: $d = 4V_p/S_p$, where d is the average pore diameter, V_p is the pore volume, and S_p is the surface area. In TGA the weight loss in the temperature range 70–800 °C, for sulfated titania is due to the decomposition of the sulfate species and evolution of oxides of sulfur [24]. UV–Vis light excitation creates photogenerated electrons and holes. Characteristic band for tetrahedrally coordinated titanium appear at about 300–400 nm. The absorption is associated to the $O^{2-} \rightarrow Ti^{4+}$ charge transfer corresponding to electronic excitation from the valence band to the conduction band. The presence of the doping ions caused significant absorption shifts into the lower wavelength region compared to pure titania. In the case of chromium loaded samples additional band near 600 nm is observed, which is attributed to ${}^4A_{2g} \rightarrow {}^4T_{1g}$ transitions for Cr(III) ions in an octahedral environment [25]. However, Cr(III) \rightarrow Ti(IV) charge transfer transitions, which may be alternatively described as excitation of an electron of Cr(III) into the conduction band of TiO₂, cannot be ruled out [26]. A progressive shift in the band gap absorption onset to the visible region and a decrease absorbance in UV region are noticed with increasing metal content. FT-IR spectra shows a peak at 1200–1100 cm⁻¹ which can be assigned to S=O group [22]. The bands around 1636 and 3436 cm⁻¹ correspond to the bending and stretching modes of the –OH groups present in the catalysts. The bands near 595 and 467 cm⁻¹ are assigned to bending vibrations of Ti–O bonds [27]. In SEM pictures spherical aggregates of

small sub particles of approximate size 30–60 nm are observed. Particles present homogenous morphology and similar distribution in size and shape. The particles were clustered together due to the electrostatic effect of very fine particles. This is a very common phenomenon in the case of nanoparticles [28].

The ammonia thermodesorption results give clear evidence for the presence of surface acid sites of different strength going from weak to strong acidities. The distribution of acid sites and total acidity obtained from NH₃-TPD are shown in Table 2. Pure titania shows only low acidity and sulfation increases its acidity. Adsorption studies using perylene as electron donor gives information regarding the Lewis acidity in presence of Brönsted acidity [22]. The limiting amount of perylene adsorbed, which gives a measure of the Lewis acidity or the electron accepting capacity, was obtained from the Langmuir plot. Pure titania shows low adsorption which indicates lower electron accepting capacity and hence the lower Lewis acidity (Table 2). The thermodesorption study of 2,6-DMP was carried out with an intention of obtaining a comparative evaluation of the Brönsted acidity in the samples. Satsuma et al. [29] reported a complete elimination of the co-ordinatively adsorbed 2,6-DMP after purging at an appropriate temperature (above 300 °C). Thus, we presume the amount of 2,6-DMP desorbed at temperatures above 300 °C to be due to desorption from Brönsted acid sites and the results are given in Table 2.

The catalytic activity of titania system was tested by varying the percentage of nitric acid. As we expected, increase in the concentration of nitric acid increases the

Table 2
Surface acidity measurements by various methods

System	Ammonia desorbed (mmol g ⁻¹)				Perylene adsorbed (10 ⁻⁶ mol g ⁻¹)	Relative weight (%) loss from 2,6-DMP desorption
	Weak	Medium	Strong	Total		
T	0.31	0.20	0.01	0.52	5.23	0.77
ST	0.50	0.32	0.09	0.91	10.43	5.17
STCr(3)	0.56	0.59	0.29	1.44	22.53	5.60
STCr(6)	0.75	0.67	0.31	1.73	27.9	7.10
STCr(9)	0.42	0.47	0.02	0.91	26.45	6.04
STCr(12)	0.42	0.44	0.02	0.88	25.29	5.75

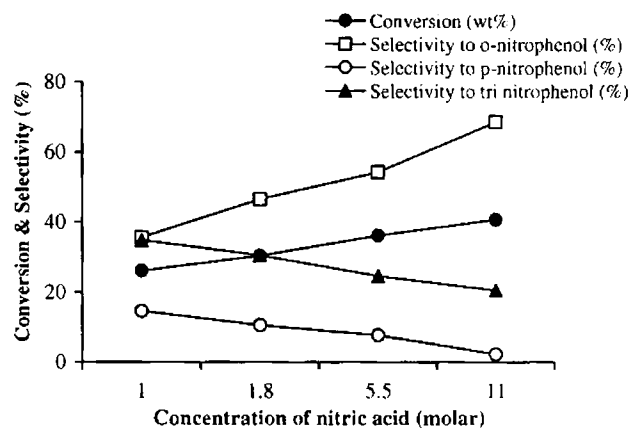


Fig. 1. Influence of concentration of nitric acid on conversion and product selectivity on phenol nitration. Amount of catalyst: 0.1 g; T , reaction temperature: 0 °C; reaction time: 2 h; phenol:nitric acid: 1:1.

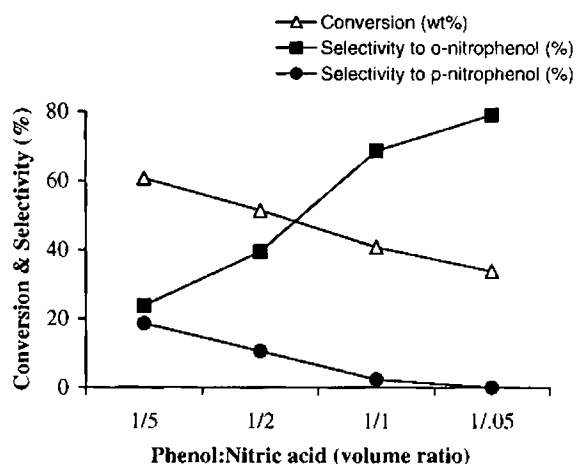


Fig. 2. Influence of volume ratio on the catalytic activity and product selectivity on phenol nitration. Amount of catalyst: 0.1 g; T , reaction temperature: 0 °C; reaction time: 2 h; phenol:nitric acid: 1:1.

conversion of phenol (Fig. 1). Selectivity towards *o*-nitrophenol increases as the concentration of nitric acid increases. Previous reports suggest the absence of any significant alteration of the product selectivity with change in the concentration of nitrating agent [30]. However, a slight alteration of product selectivities

was observed in this case when the nitric acid concentration was varied. Phenol to nitric acid ratio influences the percentage conversion and selectivity of the products. As the amount of nitric acid increases, conversion also increases (Fig. 2), but the selectivity towards *ortho* isomer decreases. An increase in the amount of nitric acid, though increases the percentage conversion, decreases the regioselectivity.

Nitration of phenol over these systems was done and the results are given in Table 3. Among the different systems, sulfated titania shows maximum conversion and selectivity. Sato et al. [31] examined various metal oxides and found that TiO_2 or ZrO_2 as an essential component for the vapor phase nitration of benzene using aqueous nitric acid. Esakkidurai and Pitchumani [32] reported regioselective nitration of phenol in solid state over modified zeolites. Among the chromium incorporated systems, maximum conversion is observed for the system with 6 wt% chromium content. The conversion then reduces slightly for 9 wt% loading. Preferential formation of *ortho* isomer is observed in all cases. When the reaction was carried out without catalyst, the conversion was low (34%) with nearly equal amounts of *ortho*- and *para*-isomers. This suggests the influence of solid acid catalysts on the conversion and selectivity. Sato et al. [21] reported that metal oxides treated by sulfuric acid at 500 °C such as $\text{SO}_4^{2-}/[\text{TiO}_2\text{-MoO}_3]$, $\text{SO}_4^{2-}/[\text{TiO}_2\text{-WO}_3]$ and $\text{SO}_4^{2-}/\text{TiO}_2$ show increase of nitration activity. The increase of the nitration activity is attributed to the increase in acidity of the catalysts by SO_4^{2-} treatment. In the present case also the acidity increases by sulfation and thus an increase in activity. Brei and co-workers [33] observed that the catalytic activity correlates with the acidic strength for the nitration of benzene over WO_3/ZrO_2 catalysts.

After the reaction, the products were extracted with dichloromethane at different time intervals for T and STCr(6). As the reaction time increases from 2 to 5 h there is an increase in the conversion for both the cases. In the case of pure titania, the selectivity to *o*-nitrophenol remains as such in the initial period. As time increases the *o*-nitrophenol selectivity decreases (Fig. 4). Meanwhile, 2,4,6-trinitrophenol selectivity increases and after 24 h, the major product is 2,4,6-trinitrophenol.

Table 3
Influence of amount of metal loading in the nitration of phenol

Systems	Conversion of phenol (wt%)	Selectivity (%)		
		<i>o</i> -Nitrophenol	<i>p</i> -Nitrophenol	2,4,6-Trinitrophenol
T	40.7	68.6	2.3	20.5
ST	85.6	92.4	3.9	1.4
STCr(3)	87.8	90.8	2.4	1.2
STCr(6)	90.0	97.5	-	1.4
STCr(9)	89.0	95.6	2.0	1.7
STCr(12)	88.4	91.7	2.3	1.5

Amount of catalyst: 0.1 g; T , reaction temperature: 0 °C; reaction time: 2 h; phenol:nitric acid: 1:1.

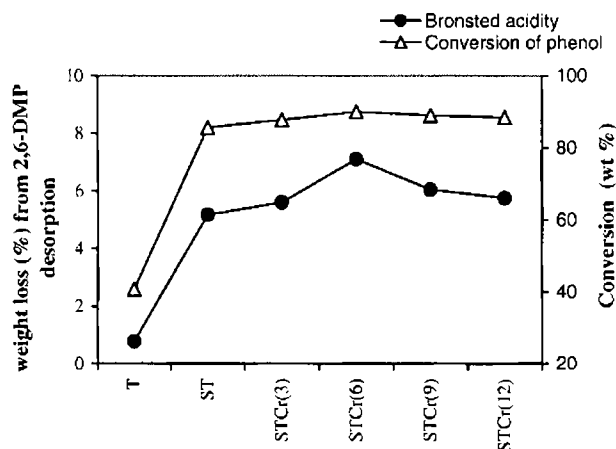


Fig. 3. Correlation between Brønsted acid sites and conversion of phenol.

In the case of modified catalyst, selectivity to *o*-nitrophenol remains constant even after 5 h. The reusability of the catalyst systems was also subject to investigation. The catalyst, STCr(6) was removed by filtration from the reaction mixture, washed thoroughly with acetone and then dried and activated. It was tested for catalytic activity and only a slight decrease in the conversion was observed for three cycles. This suggests the resistance to rapid deactivation. But from the fourth cycle onwards the decrease in conversion was much higher. To prove the heterogeneous character of the reactions, the catalyst was removed by filtration after a particular time (2 h) from the reaction mixture. The filtrate was subjected to qualitative analysis for testing the presence of leached metal ions. From the results, it is clear that chromium ions are not leaching from the metal oxide surface during the reaction.

The Brønsted acid sites were found to have an influence on the reaction. The nitration proceeds via nitronium ion mechanism, in which the nitronium ion is generated by the interaction of nitric acid with the Brøn-

sted acid sites and thus catalytic activity depends on Brønsted acidity. Sato et al. [21] proved that Brønsted acid sites are the active sites for the vapor phase nitration. The reason for the low activity for the titania is the low acidity of the system. The active site for the nitration by nitric acid is the Brønsted acid sites. However, the high activity cannot be explained simply by the solid acidity (acid strength and acid amount) of the catalyst. In the present study the catalytic activity can be very well correlate with the amount of Brønsted acid sites obtained from the thermodesorption studies of 2,6-DMP (Fig. 3).

In conclusion, the nitration proceeds via nitronium ion mechanism, and the increase of nitration activity can be attributed to the increase of Brønsted acidity by the sulfation of metal oxides. Regioselective nitration of phenol using HNO_3 over sulfated titania catalyst without any use of metal nitrates or H_2SO_4 is a comparatively clean and environmental friendly process. Incorporation of chromium ions increases the conversion and selectivity of *o*-nitrophenol. Maximum conversion and selectivity is shown by sulfated titania containing 6 wt% of chromium under milder reaction conditions. Thus, it is much eco-safer protocol of nitration.

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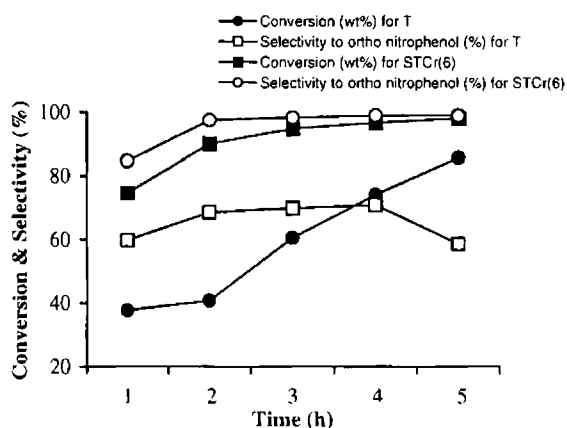


Fig. 4. Deactivation study over T and STCr(6).

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