



## Selective Nitration of Chlorobenzene on Super-acidic Metal Oxides

Guangbin CHENG\*, Xiufang QI, Chunxu LU

*School of Chemical Engineering,  
Nanjing University of Science & Technology,  
Nanjing, 210094, China*

*\*E-mail: gcheng@mail.njust.edu.cn*

**Abstract:** The solid catalysts of  $\text{SO}_4^{2-}/\text{TiO}_2$ ,  $\text{SO}_4^{2-}/\text{TiO}_2\text{-ZrO}_2$ ,  $\text{SO}_4^{2-}/\text{WO}_3\text{-ZrO}_2$ , and  $\text{SO}_4^{2-}/\text{MoO}_3\text{-ZrO}_2$  have been prepared and regioselectivities of chlorobenzene mononitration on these catalysts were investigated. When the reaction was carried out at 30 °C for 30 min,  $\text{SO}_4^{2-}/\text{TiO}_2\text{-ZrO}_2(1:1)$  by a calcination step for 3 h at 550 °C enhanced the para-selectivity of chlorobenzene nitration by using nitric acid as nitrating agent, up to an *ortho-para* isomer ratio 0.17 in product distribution of chlorobenzene mono- nitration, and the yield of chlorobenzene mononitration was 55%. The catalysts could be reutilized for four times with a little decrease in activity.

**Keywords:** super-acidic metal oxides, chlorobenzene, regioselective nitration, catalysts

### Introduction

Nitrochlorobenzene is rather important intermediates, in which both functionalities can undergo further transformations used for the manufacture of fine chemicals. For instance, *p*-chloronitrobenzene is converted into the nitrophenol by aqueous sodium hydroxide and reduced into some amino-substituted compounds. Unfortunately, the commercial method for the preparation of nitrochlorobenzene involves nitric and sulfuric acids, performing the disposal of the large amount of exhausted acid unwanted reagents. The current environmentally economic considerations are increasingly unacceptable for the procedure. Inorganic solids can offer significantly industrial benefits due to the

easy work-up of separation, the nature of non-corrosion and superior recycling. For example, lanthanide triflates have been utilized to catalyze nitration with nitric acid [1, 2], which avoids the use of large volumes of sulfuric acid. In particular, some solids have represented an outstanding feature of nitration region-selection. Smith and cooperators have successfully applied zeolite HBEA for the selective nitration of simple arenas with nitric acid under Menke conditions [3]. We have also reported some progresses on clean and selective nitration using a combination of lower oxidations of nitrogen and ozone or molecular oxygen in the inorganic solids [4-7]. This work is a part of our efforts for renovating the conventional process of centuries-old using solid acid to replace liquid sulfuric acid. Metal oxides have proved efficient catalysts for the esterification and the conversion of hydrocarbons [8-9]. Here we strive to introduce the solid catalysts to solution nitration reaction, in the hope of avoiding the use of large volume of sulfuric acid and adjusting the isomer proportions of nitrochlorobenzenes in order to meet the desired markets. In industry, dilute nitric acid ( $d = 1.4$ ) is more economical compared with concentrated acid.

## Materials and Methods

All reagents used in this study were obtained from commerce with an AR level and used without further purification.

The analysis of product mixtures was performed using a Shanghai GC 1102 Gas Chromatography with a OV-101 capillary column (30 m  $\times$  0.32 mm) and a FID detector.

### Catalyst preparation

(1)  $\text{SO}_4^{2-}/\text{ZrO}_2$ : To 0.2 mol/L  $\text{ZrOCl}_2$  solution was added dropwise 28% aqueous ammonia at room temperature with vigorous stirring until PH 9.0-10.0. The precipitate formed was further aged at room temperature for 24 h, filtrated, washed to no  $\text{Cl}^-$ , dried at 110  $^\circ\text{C}$  for 14 h at air and ground into 100 mesh granules to obtain  $\text{ZrO}_2$  catalyst. Then this metal oxide was treated with 0.5 mol/L  $\text{H}_2\text{SO}_4$  at a ratio of 15 mL : 1 g (sulfuric acid : metal oxide). After separation, powder solid was dried overnight at 110  $^\circ\text{C}$  in the air, then calcined at various temperature for 3 h at air to obtain  $\text{SO}_4^{2-}/\text{ZrO}_2$ .

(2)  $\text{SO}_4^{2-}/\text{TiO}_2$ :  $\text{TiCl}_4$  was gradually dissolved to 0.2 mol/L  $\text{HCl}$ . 28% Aqueous ammonia was added to the solution dropwise to pH 9.0-10.0 at room temperature with vigous stirring. The later treatments are the same as above.

(3)  $\text{SO}_4^{2-}/\text{ZrO}_2\text{-TiO}_2$ : To the mixture solution of  $\text{TiCl}_4$  and  $\text{ZrOCl}_2$  in some

ratios 28% aqueous ammonia was added dropwise until pH 9.0-10.0 at room temperature with vigorous stirring. The same post-treatments are as before.

(4)  $\text{SO}_4^{2-}/\text{ZrO}_2\text{-WO}_3$ : To the mixture solution of  $\text{ZrOCl}_2$  and ammonium tungstenate 28% aqueous ammonia was added dropwise till pH 9.0-10.0 at room temperature with vigorous stirring. The same post-treatments are as before.

(5)  $\text{SO}_4^{2-}/\text{ZrO}_2\text{-MoO}_3$ : To 0.2 mol/L  $\text{ZrOCl}_2$  were added dropwise 5% aqueous ammonium molybdate and 28% aqueous ammonia till solution pH 9.0-10.0 at room temperature with vigorous stirring. The same post-treatments are as before.

### General nitration procedure

Into three-neck flask equipped with a magnetic stirrer and a dropping funnel  $\text{CCl}_4$  (15 mL), chlorobenzene (1.0 mL), acetic anhydride (1.5 mL), and metal oxide (1.0 g) were introduced. Nitric acid (1.0 mL,  $d = 1.4$ ) was added dropwise within ca. 5-10 min in a water bath. The reaction was carried out at 30-35 °C for 30 min.

## Results and Discussion

### Effect of solid acid $\text{SO}_4^{2-}/\text{ZrO}_2$ on nitration selectivity

A super acidity of Zirconium oxide can be formed by the treatment with sulfuric acid and by the following calcination at definite temperatures. The reactivity was related to the temperature for activation of solid.  $\text{SO}_4^{2-}/\text{ZrO}_2$  calcined at 500 °C for 3 h resulted in a 56% conversion of chlorobenzene, while the nitration regioselection was seldom observed, an 2-/4-nitro isomer ratio of around 0.21-0.23. The results were showed in Table 1.

**Table 1.** Nitration of chlorobenzene on solid acid  $\text{SO}_4/\text{ZrO}_2$ <sup>[a]</sup>

Calcined temperature of catalyst (°C)	Conversion (%) <sup>[b]</sup>	Production distribution(%)			<i>Ortho/para</i>
		<i>ortho</i>	<i>meta</i>	<i>para</i>	
400	36	17.8	0.5	81.7	0.22
500	56	18.6	0.8	80.6	0.23
600	52	17.2	0.6	82.2	0.21
700	23	18.4	0.9	80.7	0.23

<sup>[a]</sup> Reaction time 30 min; catalyst 1.0 g. <sup>[b]</sup> Calculated from GC.

**Table 2.** Influence of catalyst mass in the nitration of chlorobenzene<sup>[a]</sup>

Catalyst (g)	Conversion (%) <sup>[b]</sup>	Production distribution (%)			<i>Ortho/para</i>
		<i>ortho</i>	<i>meta</i>	<i>para</i>	
0.5	42	18.7	0.4	80.9	0.23
1.0	55	18.6	0.8	80.6	0.23
1.5	56	17.9	0.7	81.4	0.22
1.8	57	17.5	0.6	81.9	0.21

<sup>[a]</sup> Reaction time 30 min. <sup>[b]</sup> Calculated from GC.

**Table 3.** Nitration of chlorobenzene on the reused catalyst<sup>[a]</sup>

Run	Conversion (%) <sup>[b]</sup>	Production distribution (%)			<i>Ortho/para</i>
		<i>ortho</i>	<i>meta</i>	<i>para</i>	
1st	57	17.5	0.6	81.9	0.21
2nd	57	16.5	0.6	82.9	0.20
3rd	51	17.3	0.5	82.2	0.21
4th	44	18.1	0.7	81.2	0.22

<sup>[a]</sup> Reaction time 30 min, catalyst 1.8 g. <sup>[b]</sup> Calculated from GC.

An increase of catalyst amount could enhance the conversion of substrate and slightly improve the nitration toward para-substitution (indicated in Table 2). The use of 1.0 g amount of  $\text{SO}_4^{2-}/\text{ZrO}_2$  was a better run under the conditions employed considering all reaction economy.

The results listed in Table 3 show that recovered  $\text{SO}_4^{2-}/\text{ZrO}_2$  catalyst showed an activity that was comparable to the high activity.

### Effect of solid acid $\text{SO}_4^{2-}/\text{ZrO}_2\text{-TiO}_2$ on nitration selectivity

In a discussion there was paid attention to some other metal oxides and some mixed metal oxides, in the hope of finding more durable catalysts for improving the nitration selection. The  $\text{SO}_4^{2-}/\text{TiO}_2$ ,  $\text{SO}_4^{2-}/\text{TiO}_2\text{-ZrO}_2$ ,  $\text{SO}_4^{2-}/\text{WO}_3\text{-ZrO}_2$ , and  $\text{SO}_4^{2-}/\text{MoO}_3\text{-ZrO}_2$  systems were examined.

For the sulfuric acid-treated Titanium-Zirconium system with various compositions(molar ratios),  $\text{SO}_4^{2-}/\text{TiO}_2\text{-ZrO}_2(1:1)$  was effective for the para nitration selection, up to a lower 2-/4- isomer ratio of 0.17, while a 70% higher conversion was obtained on the  $\text{SO}_4^{2-}/\text{TiO}_2\text{-ZrO}_2(1:2)$  system under the other similar reaction conditions. For single oxide  $\text{SO}_4^{2-}/\text{TiO}_2$ , no effectiveness was observed in either regioselection or chlorobenzene conversion. These results were reflected in Table 4.

**Table 4.** Selective nitration of chlorobenzene over solid acids

Catalyst <sup>[a]</sup>	Conversion (%) <sup>[b]</sup>	Production distribution (%)			<i>Ortho/para</i>
		<i>ortho</i>	<i>meta</i>	<i>para</i>	
SO <sub>4</sub> <sup>2-</sup> /TiO <sub>2</sub>	15	23.1	0.2	76.7	0.30
SO <sub>4</sub> <sup>2-</sup> /TiO <sub>2</sub> -ZrO <sub>2</sub> (3:1) <sup>[c]</sup>	15	19.8	2.0	78.2	0.25
SO <sub>4</sub> <sup>2-</sup> /TiO <sub>2</sub> -ZrO <sub>2</sub> (2:1)	24	18.6	1.4	80.0	0.23
SO <sub>4</sub> <sup>2-</sup> /TiO <sub>2</sub> -ZrO <sub>2</sub> (1:1)	55	14.3	0.5	85.2	0.17
SO <sub>4</sub> <sup>2-</sup> /TiO <sub>2</sub> -ZrO <sub>2</sub> (1:2)	70	22.2	0.4	77.4	0.29
SO <sub>4</sub> <sup>2-</sup> /TiO <sub>2</sub> -ZrO <sub>2</sub> (1:3)	31	20.3	0.6	79.1	0.26

<sup>[a]</sup> Calcination temperature 550 °C, 3 h, 1.0 g. <sup>[b]</sup> Calculated from GC. <sup>[c]</sup> Molar ratio of TiO<sub>2</sub> to ZrO<sub>2</sub>.

### Effect of solid acid SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>-WO<sub>3</sub> on nitration selectivity

**Table 5.** Selective nitration of chlorobenzene over solid acids SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>-WO<sub>3</sub>

Catalyst <sup>[a]</sup>	Conversion (%) <sup>[b]</sup>	Production distribution (%)			<i>Ortho/para</i>
		<i>ortho</i>	<i>meta</i>	<i>para</i>	
SO <sub>4</sub> <sup>2-</sup> /WO <sub>3</sub>	15	23.5	1.8	74.7	0.31
SO <sub>4</sub> <sup>2-</sup> /WO <sub>3</sub> -ZrO <sub>2</sub> (0.10) <sup>[c]</sup>	20	17.8	0.7	81.5	0.22
SO <sub>4</sub> <sup>2-</sup> /WO <sub>3</sub> -ZrO <sub>2</sub> (0.15)	36	19.9	1.6	78.5	0.25
SO <sub>4</sub> <sup>2-</sup> /WO <sub>3</sub> -ZrO <sub>2</sub> (0.20)	33	21.7	0.9	77.4	0.28
SO <sub>4</sub> <sup>2-</sup> /WO <sub>3</sub> -ZrO <sub>2</sub> (0.25)	27	22.9	0.7	76.3	0.30
SO <sub>4</sub> <sup>2-</sup> /WO <sub>3</sub> -ZrO <sub>2</sub> (0.30)	23	22.3	2.1	75.6	0.29

<sup>[a]</sup> Calcination temperature 550 °C, 3h, 1.0g. <sup>[b]</sup> Calculated from GC. <sup>[c]</sup> Molar ratio of WO<sub>3</sub> to ZrO<sub>2</sub>.

The WO<sub>3</sub>-ZrO<sub>2</sub> system under the conditions employed afforded a lower conversion and a poorer region-selection, in particular, the characteristics became more obvious with an increase of a proportion of tungsten oxide in compositions.

### Effect of solid acid SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>-MoO<sub>3</sub> on nitration selectivity

A series of nitration reactions were carried out on solid acid SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>-MoO<sub>3</sub> with varied molar ratio of MoO<sub>3</sub> to ZrO<sub>2</sub> and the results were listed in Table 6. It could be seen that the MoO<sub>3</sub>-ZrO<sub>2</sub> system also afforded a lower conversion and a poorer region-selection.

**Table 6.** Nitration of chlorobenzene over solid acid  $\text{SO}_4^{2-}/\text{ZrO}_2\text{-MoO}_3$ 

Catalyst <sup>[a]</sup>	Conversion (%) <sup>[b]</sup>	Production distribution (%)			Ortho/para
		ortho	meta	para	
$\text{SO}_4^{2-}/\text{MoO}_3$	26	23.5	2.0	74.5	0.31
$\text{SO}_4^{2-}/\text{MoO}_3\text{-ZrO}_2$ (0.10) <sup>[c]</sup>	21	23.6	2.6	73.8	0.32
$\text{SO}_4^{2-}/\text{MoO}_3\text{-ZrO}_2$ (0.15)	35	23.4	1.6	74.9	0.31
$\text{SO}_4^{2-}/\text{MoO}_3\text{-ZrO}_2$ (0.20)	23	21.7	0.9	77.4	0.28
$\text{SO}_4^{2-}/\text{MoO}_3\text{-ZrO}_2$ (0.25)	22	22.3	0.8	77.1	0.28
$\text{SO}_4^{2-}/\text{MoO}_3\text{-ZrO}_2$ (0.30)	23	22.2	2.1	75.7	0.29

<sup>[a]</sup> Calcination temperature 550 °C, 3h, 1.0g. <sup>[b]</sup> Calculated from GC. <sup>[c]</sup> Molar ratio of  $\text{MoO}_3$  to  $\text{ZrO}_2$ .

## Conclusion

In conclusion, the metal oxide solid acid catalysts  $\text{SO}_4^{2-}/\text{TiO}_2$ ,  $\text{SO}_4^{2-}/\text{TiO}_2\text{-ZrO}_2$ ,  $\text{SO}_4^{2-}/\text{WO}_3\text{-ZrO}_2$ , and  $\text{SO}_4^{2-}/\text{MoO}_3\text{-ZrO}_2$  could catalyze the nitration of chlorobenzene with higher para-selectivity especially the  $\text{SO}_4^{2-}/\text{TiO}_2\text{-ZrO}_2$  system. These catalysts, which were prepared by a simple method, could be recycled easily and reused in the reaction with similar reactivity. With avoiding the generating of waste acid, this nitration system was more environmentally benign than the currently commercial method.

## References

- [1] Waller F. J., Barrett A. G. M., Braddock D. C. et al, Lanthanide(iii)triflates as Recyclable Catalysts for Atom Economic Aromatic Nitration, *Chem. Commun.*, **1997**, 613-614.
- [2] Barrett A. G. M., Braddock D. C., Ducray R. et al, Lanthanide Triflate and Triflide Catalyzed Atom Economic Nitration of Fluoroarenes, *Synlett*, **2000**, 57-59.
- [3] Smith K., Almeer S., Black S., *para*-Selective Nitration of Halogenobenzenes Using a Nitrogen Dioxide-Oxygen-Zeolite System, *Chem. Commun.*, **2000**, 1571-1572.
- [4] Guangbin Cheng, Chunxu Lu, Xinhua Peng, Regioselective synthesis of Mononitrochloro- benzene (II) Nitration with Nitrogen dioxide, *Chin. J. Appl. Chem.*, **2002**, 19(2), 181-183.
- [5] Guangbin Cheng, Chunxu Lu, Study on Regioselective Synthese of Mononitrobenzene on  $\text{SO}_4^{2-}/\text{WO}_3\text{-ZrO}_2$  Catalysts, *Chin. J. Energetic Materials*, **2002**, 10(4), 168-179.
- [6] Guangbin Cheng, Chunxu Lu, Xinhua Peng, Regioselective nitration of chlorobenzene with nitric acid on  $\text{TiO}_2$ -Pillared Clay Catalyst. *Chin. J. Fine*

- Chemicals*, **2001**, *18*(7), 426-427,431.
- [7] Guangbin Cheng, Chunming Shi, Xinhua Peng, Selective Nitration of Toluene with Nitric Acid in the Presence of Phosphomolybdic Acid Catalyst, *Chin. J. Energetic Materials*, **2004**, *12*(2), 110-112.
- [8] Yuling Zhang, Yingli Bi, Xianghao Cui et al, Isomerization of *n*-Butane over the Catalysts of SO<sub>4</sub>/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and Pt-SO<sub>4</sub>/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, *Chem. J. Chin. Universities*, **2000**, *21*(1), 112-115.
- [9] Li Zhang, Lin Wang, Jianmin Chen, Studies of peroxodisulfated zirconia solid superacid, *Chem. J. Chin. Universities*, **2000**, *21*(1), 116-119.

