

## Synthesis of 1-Bromooctane Catalyzed by Solid Super Acid $\text{SO}_4^{2-}/\text{ZrO}_2\text{-ZnO}$

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The solid super acid catalyst  $\text{SO}_4^{2-}/\text{ZrO}_2\text{-ZnO}$  was prepared by impregnation and characterized by infrared spectroscopy, X-ray diffraction, different scanning calorimetric and thermogravimetric analysis. Their performances were evaluated by the synthesis of 1-bromooctane. Under the condition of *n*-octanol/hydrobromic acid molar ratio of 1:3, a catalyst amount of 8 wt. %, reaction time of 7 h, temperature of 130 °C, produce 1-bromooctane (yield 70.22 %).

**Keywords:** Solid super acid, Impregnation, 1-Bromooctane.

### INTRODUCTION

1-Bromooctane is an important intermediate in organic synthesis. It is soluble in ethanol and ether, slightly toxic and narcotic<sup>1</sup>. The atom of bromine can be substituted by hydroxy, amino, alkoxy to generate corresponding alcohols, amines and ether. It is widely used for synthesis of pesticides, organic dyes, surfactants, ultraviolet absorbers, *etc.*<sup>2-4</sup>. Due to its broad spectrum of activity, the compound has received a great deal of attention in connection with their synthesis. Several methodologies of preparation of 1-bromooctane have been reported in the literatures<sup>5-7</sup>.

The bromine-phosphorus method causes environmental pollution because of the volatility and toxicity of bromine and the corrosivity and flammability of phosphorus. Some by-products are produced by sodium bromide-sulfuric acid method because of the dehydration and oxidation of concentrated sulfuric acid. Another hydrobromic aqueous solution method has long reaction time, too much raw material consumption and low yield.

Recently considerable attention has been devoted to the super solid acids. Generally, these catalysts offer several advantages, such as strong acid sites, nontoxicity, noncorrosive-ness, easily handling, mild reaction conditions, high selectivity, low cost and easy to recover and recycling<sup>8</sup>. In this work, a kind of solid super catalyst sulfated zirconia and zinc oxide was prepared and its performance applying in synthesis of 1-bromooctane was investigated. The solid base catalyst showed a good performance during the synthesis process, with a high purity and yield of 1-bromooctane product in a relatively short time.

### EXPERIMENTAL

Sulfuric acid (98 %), aqueous ammonia (25-28 %), hydrobromic acid (40%), sodium bicarbonate (A.R) were purchased from Kermel, Tianjin Chemical Reagent Co., Ltd. Zirconium(VI) oxychloride octahydrate ( $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$ ), *N*-octyl alcohol (99 %) and Silver nitrate (A.R) were purchased from Sinopharm Chemical Reagent Co., Ltd., Sanmenxia AOKE Chemical Co., Ltd. and Beijing chemical plant respectively.

**Preparation of catalyst:** 2:1 of the molar ratio of  $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$  and  $\text{Zn}(\text{NO}_3)_2$  was dissolved in distilled water. To this solution, aqueous concentrated ammonia (25-28 %) was added drop-wise from a burette with vigorous stirring until the pH of the solution reached 10 and then left for 24 h. The obtained precipitate was washed several times with deionized water and filtrated by pump until a neutral filtrate and the absence of chlorine ion, detected by  $\text{AgNO}_3$  (0.1 mol/L). The cake after filtration was dried at 110 °C for 16 h. The sample thus obtained was ground into powder under 120 mesh. To prepare the targeted catalyst, the powdered complex oxides were impregnating with sulfuric acid of 0.5 M for 6 h followed by filtration. The sample was oven dried at 110 °C for 12 h then calcined at 650 °C for 4 h to obtain  $\text{SO}_4^{2-}/\text{ZrO}_2\text{-ZnO}$ <sup>9,10</sup>.

**Characterization of catalyst:** Infrared spectroscopy spectrogram of the sample showed the support of  $\text{H}_2\text{SO}_4$  on  $\text{ZrO}_2\text{-ZnO}$ . X-ray diffraction (XRD) analysis revealed the presence of zirconia crystal phases and zinc oxide crystal phases. DSC-TG measurements indicated temperature from the tetragonal phase to the monoclinic phase of zirconia rises.

**Synthesis of 1-bromooctane:** The synthesis reaction was carried out in a 250 mL three-necked flask, with a thermostat and mechanical stirring. A prescribed amount of *n*-octanol and sulfated zirconia-zinc oxide were put into three-necked flask and hydrobromic acid (40 %) was slowly added to the mixture in a stirred. Then temperature was raised to the preset degree while stirring. Saturated sodium bicarbonate solution was added to the reaction mixture after the reaction when the three-necked flask was cooled to room temperature. The obtained mixture was separated and washed several times with deionized water until a neutral liquid. Then the production 1-bromooctane was tested by gas chromatography.

## RESULTS AND DISCUSSION

Solid super acid  $\text{SO}_4^{2-}/\text{ZrO}_2\text{-ZnO}$  was characterized by IR spectra. In Fig. 1, there is a strong and broad vibration peak in  $3600\text{-}3000\text{ cm}^{-1}$  assigned to physisorbed and coordinated water, accompanied by a broad band at  $1628.05\text{ cm}^{-1}$ , assigned to the bending mode ( $\delta$  HOH) of coordinated water. Weak vibration peaks at  $1372.53$  and  $1138.29\text{ cm}^{-1}$  are assigned to vibration peaks of  $\text{O}=\text{S}=\text{O}$ , while the weak peaks at  $1058.41$  and  $967.99\text{ cm}^{-1}$  belong to symmetric vibration peaks of  $\text{O}-\text{S}-\text{O}$ . These typical peaks are assigned for chelating bidentate sulfate ions coordinated to the zirconia and zinc oxide<sup>11,12</sup>.

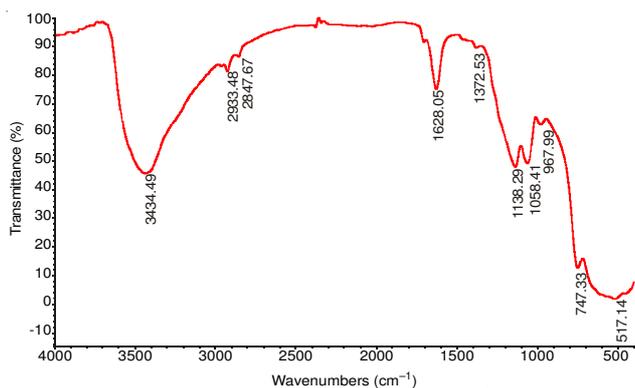


Fig.1. IR spectrogram of the solid super acid  $\text{SO}_4^{2-}/\text{ZrO}_2\text{-ZnO}$

**X-ray diffraction:** The structures of sulfated zirconia and zinc oxide we prepared at  $650\text{ }^\circ\text{C}$  was measured by XRD. Both tetragonal (t) and monoclinic (m) zirconia crystal phases and zinc oxide crystal phases were found in the sample according to the XRD spectrum in Fig. 2. It indicated that zirconia and zinc oxide were uniformly dispersed in the solid super acid<sup>13,14</sup>.

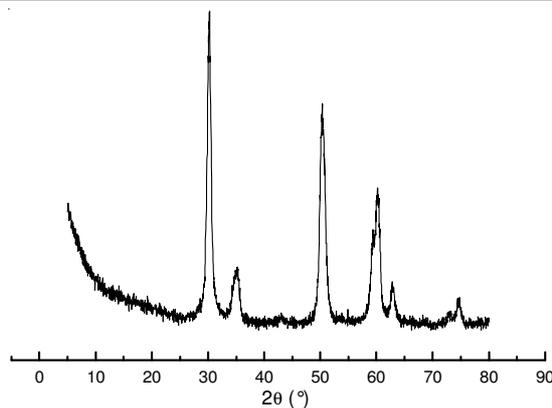


Fig. 2. XRD patterns of the solid super acid  $\text{SO}_4^{2-}/\text{ZrO}_2\text{-ZnO}$

**Different scanning calorimetry and thermo gravimetry:** From the DSC-TG scans shown in Fig. 3. The weight losses are concentrated in two ranges:  $25\text{-}400$  and  $700\text{-}1000\text{ }^\circ\text{C}$ . The weight loss occurred at  $379.3\text{ }^\circ\text{C}$  and the weight loss occurred at  $834\text{ }^\circ\text{C}$  are most likely due to the desorption of molecular water and the decomposition of sulfate, respectively. Therefore, the solid acid catalyst should calcined below  $800\text{ }^\circ\text{C}$ . It also indicated that the temperature from the tetragonal phase to the monoclinic phase of zirconia rises due to the added of zinc oxide, which means less sulfate loss<sup>11,14,15</sup>.

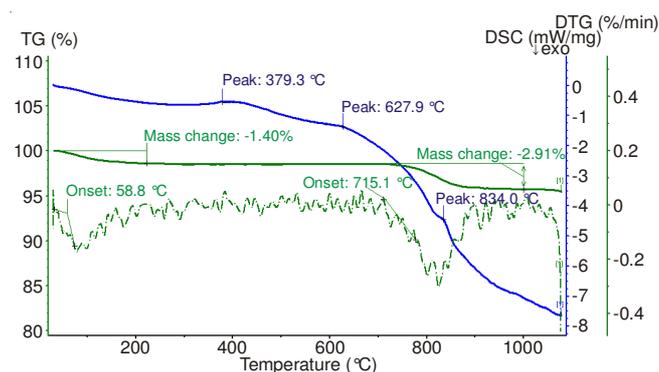


Fig. 3. DSC-TG curves of the solid super acid  $\text{SO}_4^{2-}/\text{ZrO}_2\text{-ZnO}$

**Result of orthogonal design:** Factors of the experiment were reaction time, reaction temperature, mole ratio of *n*-octanol to hydrobromic acid and amount of catalyst. Orthogonal design was adopted to afford better conditions. The results are listed in Table-1.

TABLE-1  
RESULT OF ORTHOGONAL DESIGN ( $L_93^4$ )

Entry.	Mole ratio (A)	Amount of Catalyst (%) (B)	Reaction temperature ( $^\circ\text{C}$ )	Reaction time (h)(D)	Yield (%)
1	1:2	4	120	5	68.05
2	1:2	6	130	6	69.15
3	1:2	8	140	7	68.81
4	1:2.5	4	130	7	68.73
5	1:2.5	6	140	5	66.91
6	1:2.5	8	120	6	68.41
7	1:3	4	140	6	68.82
8	1:3	6	120	7	69.93
9	1:3	8	130	5	69.13
Mean value K1	2.0601	2.0560	2.0639	2.0409	
Mean value K2	2.0405	2.0599	2.0701	2.0638	
Mean value K3	2.0788	2.0635	2.0454	2.0747	
Range R	0.0383	0.0075	0.0247	0.0338	

The factors followed the order mole ratio of *n*-octanol to hydrobromic acid > reaction time > reaction temperature > amount of catalyst by the mean values. The optimum combination was A3, B3, C2, D3.

**Results of orthogonal design under the optimal experiment conditions:** The optimum combination was not presented in the orthogonal design. So another two experiments were carried out according to the optimum combination. The results were listed in Table-2.

TABLE-2  
RESULTS OF ORTHOGONAL DESIGN UNDER  
THE OPTIMAL EXPERIMENT CONDITIONS

1	70.13
2	70.22

### Conclusion

SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>-ZnO was prepared by impregnation. It is widely used in organic synthetic processes due to its reliability, high activity and repeatability. It showed a good performance during the synthesis process of 1-bromooctane. The optimal experiment conditions were obtained by orthogonal designs. When molar ratio of *n*-octanol to hydrobromic acid was 1:3, the catalyst amount was 8 wt. %, the reaction time was 7 h and the temperature was 130 °C, the yield can reach 70.22 %

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