



## Effects of calcination temperature and water-washing treatment on n-hexane hydroisomerization behavior of Pt-promoted sulfated zirconia based catalysts

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### ARTICLE INFO

#### Article history:

Received 13 March 2012

Received in revised form 11 July 2012

Accepted 22 July 2012

Available online 11 September 2012

#### Keywords:

Hydroisomerization  
Calcination temperature  
Sulfated zirconia  
Promoter  
Water washing

### ABSTRACT

Synthesis of Pt-promoted sulfated zirconia catalyst Pt/SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> (designated as PSZ), Pt/SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (designated as PSZA), and Pt/SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub> (designated as PSZAY) was reported. These catalysts were characterized by N<sub>2</sub> adsorption-desorption, thermal gravimetric (TG) analysis, NH<sub>3</sub>-temperature programmed desorption (NH<sub>3</sub>-TPD), and H<sub>2</sub>-temperature programmed reduction (H<sub>2</sub>-TPR) techniques. Effects of calcination temperature of the catalysts on the n-hexane hydroisomerization behavior were investigated in details. The experiment results revealed that the addition of Al and Y or Al promoter alone could improve the thermal stability of the catalysts. PSZA and PSZAY exhibited higher isomerization activity than unmodified PSZ as the calcination temperature of sulfated Zr(OH)<sub>4</sub> was relatively high, for example, between 650 °C and 750 °C. For the first time, it was found that water-washing treatment of PSZA and PSZAY at different preparation stages had considerably different impacts on their catalytic activity. Water-washing after calcination of the sulfated Zr(OH)<sub>4</sub>, the catalytic activity of PSZA and PSZAY was high, as indicated by approximately 80% of n-hexane conversion. However, water-washing before calcination of sulfated Zr(OH)<sub>4</sub> led to a significant decrease in the catalytic activity of PSZA and PSZAY, that is, the n-hexane conversion diminished to around 35%. It was proposed that the presence of excessive sulfur species over sample was favorable for keeping the active sulfur species in the catalyst surface.

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### 1. Introduction

The transformation of n-alkanes into iso-alkanes through hydroisomerization process is of practical importance in petrochemical industry. For example, n-butane can be converted into iso-butane and the latter can be alkylated with butene to produce iso-octane, which is an environmentally friendly high-octane gasoline booster. In addition, n-pentane and n-hexane can also be isomerized into their isomers and directly acted as blending components of clean high-octane gasoline. The n-hexane isomerization process was commercialized; however, the used conventional bifunctional catalyst presented some shortcomings, such as small amount of high octane number components in the products and low catalytic activity at reaction temperature below 280 °C. Since sulfated zirconia (SZ) was found to possess super or strong acidity

[1], it attracted much attention in acid-catalyzed field, especially in n-alkane isomerization reaction [2–6]. The isomerization activity of SZ or Pt-promoted SZ (PSZ) was greatly dependent on the preparation step or method. It is generally believed that the high isomerization activity of SZ and PSZ could be obtained only when amorphous zirconium hydroxide acted as the precursor of sulfation. In the preparing process of SZ and PSZ, the high calcination temperature was considered to be indispensable [7] and it strongly affected the catalytic activity of SZ and PSZ to a great extent [8–13]. The results from Arata et al. [12] and Sun et al. [13] indicated that the calcination temperature effect on the isomerization activity of SZ depended on the preparation method to some extent. Comelli et al. [8] examined the effect of calcination temperature on n-hexane isomerization catalytic performance of Pt-promoted SZ, and these authors considered that the isomerization activity reached maximum at the calcination temperature of 550–600 °C.

The influence of calcination temperature is usually related with different promoters. Hua and Sommer [9] once investigated the calcination temperature of sulfated Zr(OH)<sub>4</sub>-Al(OH)<sub>3</sub> on n-butane isomerization activity over Pt/SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (PSZA) and found that the optimized calcination temperature was 650 °C,

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in agreement with the previous investigation results from our groups [10]. Signoretto et al. [11] also reported the optimal calcination temperature of sulfated  $Zr(OH)_4$  modified with  $Ga_2O_3$  which depended on the content of  $Ga_2O_3$  promoter. Our previous results confirmed the important role of rare earth Y promoter in PSZA in the isomerization activity and stability [14]. The investigation from Xia et al. [15] demonstrated that the introduction of Al to PSZ could not improve the isomerization activity, but was helpful to catalyst shaping. In fact, the effect of the calcination temperature of sulfated  $Zr(OH)_4$  before and after the addition of Al or other promoters may be different, but there existed seldom systematic investigation about this aspect.

On the other hand, water-washing treatment usually plays an important role in the SZ catalyst preparation; it can partially remove sulfur species over catalyst, thus modify the surface acidity and catalytic activity [16]. However, for Pt-promoted SZ and SZA, update it is unclear whether or not only water soluble sulfur species over PSZ and PSZA are the catalytic active centers. According to the new isomerization reaction mechanism over PSZ suggested by Ebitani et al. and Manoli et al. [17,18] that the new strong acid sites could be created in the presence of gaseous hydrogen and acted as the catalytic active sites, after water washing, PSZ or PSZA may show certain catalytic activity in the hydroisomerization reaction.

The object of the present work is to further investigate the effect of calcination temperature of sulfated  $Zr(OH)_4$  on the n-hexane isomerization activity of the Al or Al and Y promoted  $Pt/SO_4^{2-}/ZrO_2$  catalysts. The role of water washing treatment at different preparing stages in the catalytic activities is also studied in detail.

## 2. Experimental

### 2.1. Catalyst preparation

A prepared 0.2 mol/L  $Zr(NO_3)_2$  solution was dropwise added into 5% ammonia solution with stirring. After precipitation, the slurry was stirred for additional 0.5 h and then aged statically at room temperature for 10 h. The obtained  $Zr(OH)_4$  white precipitate was repeatedly washed with deionized water by evacuation filtration till the pH value of the filtrate was ca. 7 and then dried at 110 °C for 20 h. The dried sample was crushed to very fine powder. Part of the dry powder was mixed with boehmite powder. The mixture powder was extruded with dilute  $HNO_3$  and dried again at 110 °C. Sulfating procedure was performed by impregnating separately the dry  $Zr(OH)_4$  powder and the extrudate with 0.5 mol/L of  $H_2SO_4$  solution (15 ml/g) at room temperature for 6 h. The sulfated samples were filtered without washing and dried overnight at 110 °C, denoted as SZ and SZA. Part of SZA sample was impregnated with yttrium nitrate solution to load Y and dried at 110 °C for 13 h, denoted as SZAY. Subsequently, the three dry sulfated solid samples were calcined at certain temperature for 3 h. Finally, the calcined samples were respectively impregnated in  $H_2PtCl_6$  solution to load with 0.5 wt% Pt, dried at 110 °C and calcined at 500 °C for 3 h. Thus, the prepared  $Pt/SO_4^{2-}/ZrO_2$ ,  $Pt/SO_4^{2-}/ZrO_2-Al_2O_3$  and  $Pt/SO_4^{2-}/ZrO_2-Al_2O_3-Y_2O_3$  catalysts were designated as PSZ, PSZA and PSZAY. The weight percentage of  $Al_2O_3$  and  $Y_2O_3$  in the support was 3%.

In order to investigate the water washing treatment, part of dry sulfated  $Zr(OH)_4$  was washed with water three times (30 ml/g), denoted as WSZ. Part of calcined sulfated  $Zr(OH)_4$  at 650 °C was washed with water three times (30 ml/g), denoted as SWZ. Then these samples were mixed with boehmite powder. The following preparation steps were the same as the above. The final catalysts were named as PWSZA and PSWZA.

### 2.2. Catalytic activity measurement

The n-hexane hydroisomerization reaction was carried out in a continuous flow-type fixed-bed stainless reactor (i.d. = 5 mm) loaded with 2.0 g of catalyst. The prepared catalyst was crushed and sieved to 40–60 mesh. Prior to the reaction, the catalyst sample was pretreated in flowing dry air (20 ml/min) at 400 °C for 3 h. The system was cooled to 250 °C and the catalyst was reduced with flowing hydrogen for 3 h at this temperature. After the reduction, the temperature of catalyst bed decreased to a set temperature. Hydrogen gas and n-hexane were simultaneously introduced into the reactor and the reaction pressure was controlled by hydrogen gas. The standard reaction conditions were as follows: the reaction total pressure = 2.0 MPa, n-hexane weight hourly space velocity (WHSV) =  $1.0\ h^{-1}$ , hydrogen/n-hexane molar ratio = 5, and the reaction temperature = 165 °C. Normal hexane feedstock was sent to the reactor by a double plunger micro pump and the hydrogen gas flow rate was controlled by a mass flow meter. The products were analyzed by on-line GC-920, equipped with an FID and an OV-101 capillary column. Since weight percentage of all kinds of isomers and the cracking products could be obtained by area normalization method in GC peaks, the conversion of n-hexane and the selectivity of iso-hexane were calculated according to the following formulas (1) and (2), respectively:

$$X \text{ (n-hexane conversion)} = 100\% - \text{wt\% of n-hexane in product} \quad (1)$$

$$S \text{ (iso-hexane selectivity)} = \frac{\text{wt\% of total iso-hexanes in products}}{X} \quad (2)$$

### 2.3. Catalyst characterization

#### 2.3.1. X-ray diffraction (XRD)

XRD patterns were obtained with a Philips MagiX X-ray diffractometer, using  $Cu\ K\alpha_1$  radiation and instrumental settings of 40 kV and 40 mA. The scanning was within a range of  $2\theta$  from 10° to 70° at a scanning rate of 6°/min.

#### 2.3.2. $NH_3$ -temperature programmed desorption ( $NH_3$ -TPD)

$NH_3$ -TPD was carried out at a homemade equipment. The sample (0.14 g) was loaded into a stainless steel U-shaped microreactor (i.d. = 5 mm) and pretreated at 600 °C for 0.5 h in flowing He. After the pretreatment, the sample was cooled to 150 °C and was exposed to  $NH_3$  atmosphere. As the catalyst was saturated with the adsorbed  $NH_3$ , helium was used as carrier to remove  $NH_3$  physically adsorbed until the baseline was stable.  $NH_3$ -TPD was then carried out in a constant flow of He (20 ml/min) from 150 °C to 650 °C at a heating rate of 18 °C/min. The concentration of ammonia in the exit gas was monitored continuously by a gas chromatograph (Shimadzu 8A) equipped with a thermal conductivity detector (TCD).

#### 2.3.3. $H_2$ -temperature programmed reduction (TPR)

TPR experiments were performed in a domestic apparatus. The sample (0.1 g) was loaded in a quartz tube and pretreated in helium for 0.5 h. After cooled to room temperature, a 5%  $H_2/He$  mixed gas passed through the sample with a flow rate of 30 ml/min. The sample began to be heated at a heating rate of 10 °C/min from room temperature to 800 °C. The hydrogen consumption was measured by using a thermal conductivity detector (TCD).

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