

A Novel Way to Prepare γ -Al₂O₃ Supported SO₄²⁻/ZrO₂ Solid Superacid Catalysts for n-Butane Isomerization

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Abstract: Highly active solid superacid catalysts for n-butane isomerization, SZ/Al₂O₃-P, were prepared by supporting SO₄²⁻/ZrO₂ (SZ) on γ -Al₂O₃ carrier using a precipitation method. The activities of some catalysts were enhanced significantly. The activity of the most active sample, 60%SZ/Al₂O₃-P, was even about 2 times more active than that of the SZ catalyst.

Keywords: SO₄²⁻/ZrO₂, n-butane isomerization, γ -Al₂O₃, supported superacid catalysts.

The isomerization of n-butane to isobutane, which is a valuable precursor for the production of MTBE and alkylated gasoline, on strong acid catalysts is an important process in refining industry. Solid superacid, especially sulfated zirconia, has high catalytic activity in n-butane isomerization at comparatively low temperatures and therefore has attracted more attention of researchers in the past twenty years.¹ However, from the view point of practice, the activity of SZ needs to be improved further and the task of decreasing its cost is also important and challenging. Some researchers² suggested that supporting sulfated zirconia on a cheaper porous material may be a good way to enhance the amount of superacid site by increasing the surface area and lower the cost of catalysts. Besides, with the introducing of the porous support, the operation difficulties caused by the small particles in using traditional SZ, can be overcome easily. Up to now, however, only a few papers^{3,4} have been published in this area. In our previous work, we have reported⁵ preparing γ -Al₂O₃ supported SZ catalysts by an impregnation method, which has been proved an effective way to improve its n-butane isomerization activity. In this work, a series of γ -Al₂O₃ supported SZ catalysts were prepared by a precipitation method, and their catalytic activities were improved further in comparison with those of catalysts prepared by the impregnation method. The activity of the most active sample, 60%SZ/Al₂O₃-P, is about 2 times more active than that of the bulk SZ.

Experimental

Supported sulfated zirconia catalysts made from the precipitation method (SZ/Al₂O₃-P)

were prepared as follows. Appropriate amounts of zirconium nitrate were dissolved in water and γ -Al₂O₃ (Shanghai Chemical Reagent Corporation, surface area 120 cm²g⁻¹) was then added to this aqueous solution in a suspended state. After hydrolysis by adding aqueous ammonia, the precipitate was filtered, washed and then dried at 110 °C for 6 h. The obtained material was immersed in 0.5 mol/l H₂SO₄ solution for 30 min and then dried at 110 °C. The final calcination temperature of samples was 650 °C. The obtained catalysts are labeled as x%SZ/Al₂O₃-P (x% = weight of ZrO₂/ total weight of catalyst). The SZ/Al₂O₃-I catalysts were prepared by the impregnation method according to the literature.⁵ Appropriate amount of zirconium nitrate was dissolved in water and γ -Al₂O₃ was added to this solution. After stirring, evaporating water and drying at 110 °C as well as precalcinating at 300 °C for 3 h, the obtained material was treated with 0.5 mol/l (NH₄)₂SO₄ solution. The final calcination temperature of samples was also 650 °C. The preparation method of SZFM and SO₄²⁻/ZrO₂ (SZ) catalysts were described in literature⁶ and literature⁷, respectively.

The isomerization of n-butane was performed at both low and high temperatures. At 35 °C a closed reaction system was used. 0.5 g catalyst was placed in a glass cell, and 5 ml (S.T.P.) of n-butane of 99.9% purity was injected for each test. The reaction at 250 °C was carried out in a flow-type fixed bed reactor under ambient pressure. 1.0 g catalyst was loaded and a mixture of butane and H₂ (1:10 molar ratio) was fed at a rate of WHSV 0.3 h⁻¹. The catalysts were preheated *in situ* in dry air at 450 °C for 3 h. The reaction products were analyzed by a gas chromatography equipped with FID.

Results and Discussion

Since the rate of n-butane isomerization on SZ at low temperature, such as 35 °C, obeys the rate law of a first-order reversible reaction, and the rate constants correlate fairly well with the superacidities of the catalysts⁸, this reaction is often used as a test reaction for estimation of superacidity of the catalysts. The rate constants k_1 of supported sulfated zirconia catalysts (SZ/Al₂O₃-P and SZ/Al₂O₃-I) with different zirconia content and SZ as well as SZFM are listed in **Table 1**. As illustrated, the superacidities of both SZ/Al₂O₃-P and SZ/Al₂O₃-I samples increases rapidly with the increasing of the zirconia content up to 60% and then decreases as zirconia content further increases. The optimum zirconia content to produce the strongest superacidity is 60% for both SZ/Al₂O₃-P and SZ/Al₂O₃-I catalysts. In addition, it was found that the superacidities of SZ/Al₂O₃-P catalysts are generally higher than those of SZ/Al₂O₃-I catalysts with the same zirconia content, indicating that the precipitation method is more effective to improve the superacidity than impregnation method. Moreover, it is worth notice that the catalytic activity of the most active sample prepared by precipitation method, 60%SZ/Al₂O₃-P, is even about 2 times more active than that of SZ.

The major reaction product of n-butane isomerization at 250 °C is isobutane and the steady selectivity to isobutane for all catalysts is above 90 % after on stream for 2 hours. The variations of the conversion of n-butane at 250 °C with time on stream for the SZ/Al₂O₃-P catalysts are depicted in **Figure 1(a)** and the comparison of the activities of 60%SZ/Al₂O₃-P, 60%SZ/Al₂O₃-I, SZ, and SZFM is given in **Figure 1(b)**.

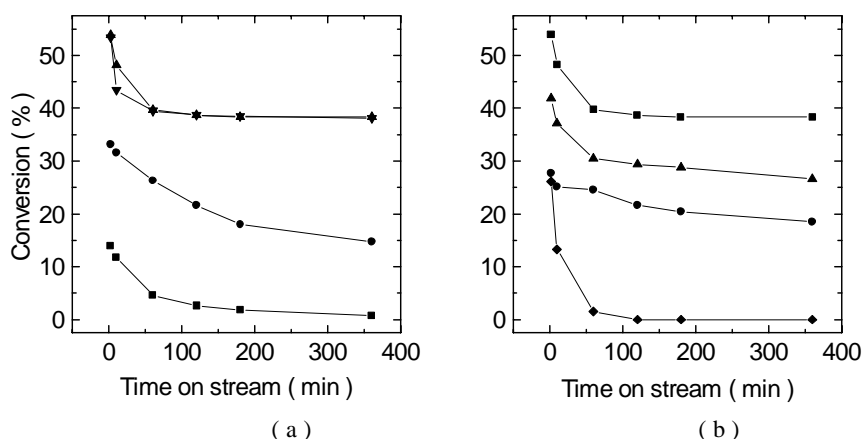
Similar to the reaction at 35 °C, both of the initial and steady activities of SZ/Al₂O₃-P samples increase with the increasing of the zirconia content till 60%. The activity of the 60%SZ/Al₂O₃-P sample is the highest among this series of catalysts although that of the 90%SZ/Al₂O₃-P is close to it. Moreover, from **Figure 1(b)**, it was found that the 60%SZ/Al₂O₃-P sample showed the highest catalytic activity in comparison with the catalysts from other methods. Its steady activity is about 2 times more active than that of bulk SZ. The fact proves again that the precipitation method is a good way to prepare highly active superacid catalyst for n-butane isomerization. Furthermore, because 40% of the catalyst was substituted by a cheaper component, γ -Al₂O₃, its cost could be decreased greatly. Due to the high activity and lower cost, the 60%SZ/Al₂O₃-P sample could be considered as an excellent candidate for a commercial-scale n-butane isomerization catalyst. In the case of SZFM, although its activity at 35 °C is the highest among all of the samples, the initial activity at 250 °C is only at the level of SZ. And, because it is deactivated rapidly under high temperature reaction condition, it seems impossible to be considered as a potential commercial catalyst.

Table 1. Surface area, sulfur content and n-butane isomerization activity 35 °C of various samples

Sample	Surface area (m ² /g)	SO ₃ content (wt%)	Activity k ₁ x 10 ³ (h ⁻¹)
15%SZ/Al ₂ O ₃ -P	120.9	4.5	20.3
30%SZ/Al ₂ O ₃ -P	128.5	4.6	40.5
60%SZ/Al ₂ O ₃ -P	133.5	4.3	85.3
90%SZ/Al ₂ O ₃ -P	106.3	4.0	58.7
15%SZ/Al ₂ O ₃ -I	142.4	3.9	16.7
30%SZ/Al ₂ O ₃ -I	107.2	3.8	38.4
60%SZ/Al ₂ O ₃ -I	106.0	4.1	65.0
90%SZ/Al ₂ O ₃ -I	85.0	3.9	49.3
SZ	113.0	3.3	40.1
SZFM	105.0	4.2	134.8

Figure 1. Activity for n-butane isomerization at 250 °C in flow system.

(a): (□) 15%SZ/Al₂O₃-P (●)30%SZ/Al₂O₃-P (Δ) 60%SZ/Al₂O₃-P (▽) 90%SZ/Al₂O₃-P
(b): (□) 60%SZ/Al₂O₃-P (Δ)60%SZ/Al₂O₃-I (●)SZ (◆) SZFM



The significant enhancement of catalytic activities of SZ/Al₂O₃-P samples for n-butane isomerization is considered to be related to the improvement of stability of the zirconia tetragonal phase. Many papers have reported that the tetragonal phase is the active phase⁹ and the transformation from the metastable tetragonal phase to the monoclinic phase causes the deterioration of the superacidity of the sample¹⁰. In the case of our SZ/Al₂O₃-P catalysts, the tetragonal phase of zirconia was stabilized and the transformation from tetragonal to monoclinic was obviously delayed. The monoclinic phase even did not appear after calcinating 60%SZ/Al₂O₃-P at 750 °C. On the contrary, a portion of the monoclinic phase is present when the SZ was calcined at only 650 °C. On the other hand, the element analysis results showed that the sulfur contents of SZ/Al₂O₃-P samples were increased markedly in comparison with bulk SZ, which might also help to increase the amount of active sites.

In conclusion, these initial studies indicate that supporting solid superacid SZ on γ -Al₂O₃ carrier by the precipitation method reported in this paper is an excellent way to obtain highly active and low cost n-butane isomerization catalyst. The data obtained demonstrate the discovery of a new class of superacid catalysts for n-butane isomerization and may prove to be a starting point for the development of a new generation of practical catalysts.

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Received 26 July 1999