# New Catalyst of $\gamma$-$Al_2O_3$ Supported $SO_4^{2-}/ZrO_2$ for *n*-Butane Isomerization

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A series of new catalysts γ-$Al_2O_3$ supported $SO_4^{2-}/ZrO_2$ was prepared by the modified impregnation method using $Zr(NO_3)_4$ decomposition on a γ-$Al_2O_3$ carrier. The most active sample 60%SZ/$Al_2O_3$ is not only low expensive compared to the traditional bulk SZ due to the high price of $ZrO_2$, but also increases the steady activity about 50% for n-butane isomerization in the presence of $H_2$ at 523 K in comparison with the bulk SZ catalyst.

The isomerization of n-butane to isobutane is an important process in refining industry. On strong acid catalysts n-Butane can be converted to isobutane , which is a valuable precursor for the production of MTBE and alkylated gasoline. The $SO_4^{2-}/ZrO_2$ (SZ) was reported to be a good n-butane isomerization catalyst by many papers.[1,2] However, because SZ was usually prepared by the precipitation method from hydrolyzing a zirconium salt, such as $ZrOCl_2 \bullet 8H_2O$, which results in a higher costs, it seems difficult to use this bulk SZ catalyst in industry. Further more, the particles of unsupported sulfated metal oxides, which are generally very small, makes operation difficult.[3] Only a few papers[4] reported on preparation supported sulfated zirconia on silica. No literature report on γ-$Al_2O_3$ supported SZ using as a n-butane isomerization catalyst is known to the present authors. In this work, the γ-$Al_2O_3$ supported SZ catalysts was prepared and its catalytic behavior of n-Butane isomerization was studied in flow system at 523 K.

A series of γ-$Al_2O_3$ supported SZ catalysts was prepared by impregnating a desired amount of $Zr(NO_3)_4$ onto γ-$Al_2O_3$ (Shanghai Chemical Reagent Corporation, surface area 120 $m^2g^{-1}$) from aqueous solution. After drying at 383 K, decomposing in air at 573 K for 3 h, the obtained material was treated with 0.5 mol/l $(NH_4)_2SO_4$ solution for 30 min. Then it was calcined at 923 K for 3 h after filtration and drying. The obtained catalysts are labeled as x%SZ/$Al_2O_3$ (x% = weight of $ZrO_2$ / total weight of catalyst). The "standard" SZ catalyst was obtained with a technique described in literature.[5] The isomerization of n-butane was carried out in a flow-type fixed bed reactor under ambient pressure at 523 K in presence of $H_2$. 1.0 g catalyst was loaded, and a mixture of butane and $H_2$ (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 723 K for 3 h. The reaction products were analyzed by a gas chromatography equipped with FID.

**Table 1.** Activity for n-butane isomerization at 523 K[a]

| Sample | Conversion / % | | | | | |
|---|---|---|---|---|---|---|
| | 2 min | 10 min | 60 min | 120 min | 180 min | 360 min |
| 15%SZ/$Al_2O_3$ | 17.3 | 13.6 | 9.1 | 7.6 | 6.9 | 5.6 |
| 30%SZ/$Al_2O_3$ | 36.1 | 31.7 | 27.4 | 21.8 | 20.1 | 15.2 |
| 60%SZ/$Al_2O_3$ | 41.8 | 37.1 | 30.5 | 29.4 | 28.8 | 26.6 |
| 90%SZ/$Al_2O_3$ | 43.3 | 35.4 | 24.8 | 23.0 | 21.5 | 17.1 |
| $SO_4^{2-}/ZrO_2$ | 27.7 | 25.2 | 24.5 | 21.6 | 20.4 | 17.5 |

[a] The reaction was done as described in the text.

The variations of the conversions of n-butane isomerization at 523 K with time on stream for the series of SZ/$Al_2O_3$ and bulk SZ catalysts are given in Table 1. The initial activity of SZ/$Al_2O_3$ catalysts increases along with the increasing zirconia content. When the $ZrO_2$ contents of SZ/$Al_2O_3$ samples were above 30%, much higher initial activities of them were observed comparing with bulk SZ. After reaction on stream for 6 h, the steady activity of sample 90%SZ/$Al_2O_3$ and SZ are comparable, whereas 30%SZ/$Al_2O_3$ performs a little bit low. It is worth noting that, the steady activity of 60%SZ/$Al_2O_3$ is much higher and it was increased about 50% comparing with SZ. The steady selectivities of SZ and all of the SZ/$Al_2O_3$ samples are above 90% after on stream for 1 h. Because of the introduction of the cheaper carrier γ-$Al_2O_3$ , the cost of the SZ/$Al_2O_3$ catalysts is decreased greatly in comparison with the traditional bulk SZ catalyst. And, considering the high activity and selectivity, the most active sample 60%SZ/$Al_2O_3$ can be regarded as a good candidate for a commercial-scale n-butane isomerization catalyst.

To explain the reason why the 60%SZ/$Al_2O_3$ sample exhibits such a marked increase in activity, many physical chemical characterization methods such as XRD, BET, IR of adsorbed pyridine were used.

XRD patterns of SZ/$Al_2O_3$ catalysts were obtained after calcination the samples at 923 K. The SZ/$Al_2O_3$ samples with lower zirconia content did not show any diffraction peak from zirconia. A small quantity of poorly crystallized zirconia giving reflections in the 2θ ranges of 25-35° appears in the 15%SZ/$Al_2O_3$ sample. The peak characteristics of the tetragonal phase becomes larger when the $ZrO_2$ content increases, while the monoclinic phase was not observed when the zirconia content is below about 70%. The reasons why the SZ/$Al_2O_3$ samples exhibited better stability of the tetragonal phase are as follows. On one hand, the crystallization and phase transformation of zirconia were delayed due to the interaction of zirconia with the γ-$Al_2O_3$ carrier and the dispersion of the zirconia phase. On the other hand, the enhancement of the quantity of the sulfate groups on the oxide surface will also retard the phase transformation of $ZrO_2$. Many literature[6,7] reports point out that the tetragonal phase is the active phase and necessary to obtain activity of sulfated zirconia in n-alkane isomerization, but the monoclinic phase is almost inactive. So, it seems that the activity increase of the sample is related to the increase of the tetragonal phase.

**Table 2.** Surface area, pore volume and $SO_3$ content of various samples

| Sample | Surface area / $m^2g^{-1}$ | Pore volume /$cm^3g^{-1}$ | $SO_3$ content[a] / wt% |
|---|---|---|---|
| 15%SZ/$Al_2O_3$ | 142.4 | 0.43 | 3.90 |
| 30%SZ/$Al_2O_3$ | 107.2 | 0.21 | 3.84 |
| 60%SZ/$Al_2O_3$ | 106.0 | 0.16 | 4.06 |
| 90%SZ/$Al_2O_3$ | 85.0 | 0.13 | 3.93 |
| $SO_4^{2-}/ZrO_2$ | 113.0 | 0.09 | 3.30 |

[a] $SO_3$ content of samples were analyzed by $BaSO_4$ gravimetric method.

However, when $ZrO_2$ content is about 90%, the monoclinic phase appears. At the same time, we observed that the steady activity of 90%SZ/$Al_2O_3$ is lower than that of 60%SZ/$Al_2O_3$.

The results of BET surface areas and $SO_3$ content of the samples are shown in Table 2. The surface area of SZ/$Al_2O_3$ samples are about 100 $m^2/g$ and mostly a little bit lower than bulk SZ. Relating to the data of the reaction, it seems that the surface area is not a very important factor to affect the activity. The pore volume of the sample is decreasing with increasing zirconia content. The $SO_3$ contents of all SZ/$Al_2O_3$ samples are higher than that of bulk SZ and the $SO_3$ content of 60%SZ/$Al_2O_3$ is the highest in all of the samples. However, the increase of the $SO_3$ content was not comparable to that of the activity, because the result from chemical analysis represents only the total sulfate concentration on the oxide surface but not the effective active sites. From the data of sulfur content, we suggest that the $\gamma$-$Al_2O_3$ carrier could help to stabilize the surface sulfate complexes remarkably. According to the literature[8], Zr-O-Al bonds were formed when zirconia was supported on $\gamma$-$Al_2O_3$ . Since the electronegativity of $Al^{3+}$ is larger than that of $Zr^{4+}$, the partial charge on Zr is increased after the formation of the Zr-O-Al bonds, which may help to stabilize the surface surfur complex and to increase the number of strong acid sites.

IR spectra of the samples were recorded on a Perkin-Elmer 983G infrared spectrometer. The self-supported wafers were outgassed at 673 K for 2 h under a vacuum of $10^{-3}$-$10^{-4}$ Pa. Pyridine was adsorbed and then outgassed for 0.5 h at every designed temperature.

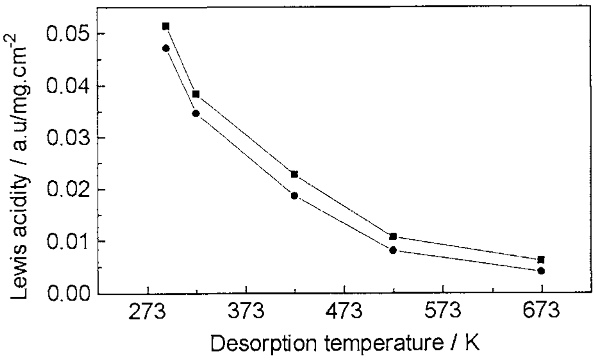

**Figure 1.** Amount of Lewis acidity at different desorption temperatures (■)60%SZ/$Al_2O_3$ (•) $SO_4^{2-}/ZrO_2$.

All the SZ/$Al_2O_3$ samples and the bulk SZ give only pyridine species adsorbed on Lewis acid sites with IR band at 1444 and 1608 $cm^{-1}$. The variations of the 1444 $cm^{-1}$ band intensities of the pyridine species as a function of outgassing temperature are given in Figure 1. It is clear that the amount of Lewis acid sites on 60%SZ/$Al_2O_3$ sample is higher than that of the bulk SZ. We suggest that the increasing of acid sites is the reason why the activity of the former is better than that of the latter.

In conclusion, the activity of SZ/$Al_2O_3$ catalyst could be adjusted by changing the zirconia content. The 60%SZ/$Al_2O_3$ was the most active sample and its steady activity increased about 50% compared to the bulk SZ catalyst. After supporting $SO_4^{2-}/ZrO_2$ on $\gamma$-$Al_2O_3$ carrier, the $SO_3$ content and the quantity of the tetragonal phase were increased. As a result, the amount of acid sites of the catalyst was also improved, which may be the reason for the increasing activity. Further more, the most valuable point is that the cost of the catalysts is lower than that of SZ, which is essential for its practical use in industry.

## References and Notes

1 M. Hino, S. Kobayashi, and K. Arata, *J. Am. Chem. Soc.*, **101,** 6439 (1979).
2 H. Matsuhashi, M. Hino, and K. Arata, *Chem. Lett.*, **1988,** 1027.
3 T. Yamaguchi, T. Jin, T. Ishida, and K. Tanabe, *Mater. Chem. Phys.*, **17,** 3 (1987).
4 T. Ishida, T. amaguchi, and K. Tanabe, *Chem. Lett.*, **1988,** 1869.
5 Yongde Xia, Weiming Hua, and Zi Gao, *Catal. Lett.*, **55,**101 (1998).
6 R. L. White, E. C. Sikabwe, M. A. Coelho, and P. E. Resasco, *J. Catal.*, **157,** 755 (1995).
7 C. Morterra, A. Cerrato, F. Pinna, and M. Signoretto, *J. Catal.*, **157,** 109 (1995).
8 S. Damyanova, P. Grange, and B. Delmon, *J. Catal.*, **168,** 421 (1997).