New Catalyst of γ-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 γ-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 γ-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.

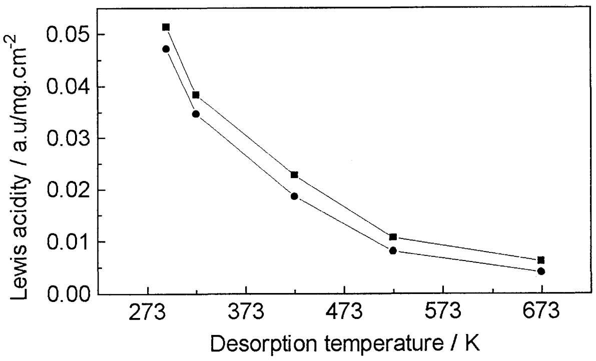

Figure 1. Amount of Lewis acidity at different desorption temperatures (■)60%SZ/Al_2O_3 (•) SO_4^{2-}/ZrO_2.

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 γ-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

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