

## **Labile sulfate species as key active components in sulfated zirconia for activating n-butane**

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### **Introduction**

Sulfated zirconia and other sulfated metal oxides have been studied for over 2 decades owing to their high catalytic activity for activation of short alkanes at low temperature. The surface structure of sulfated zirconia has been studied widely in order to elucidate the nature of active sites since the discovery of its catalytic property for alkanes conversion at low temperature. Nevertheless, no consensus has been reached so far.

Here, we report that the labile sulfate, which can be removed from sulfated zirconia by water washing, acts as crucial component for the active site of sulfated zirconia.

### **Experimental**

Sulfate-doped zirconium hydroxide was obtained from Magnesium Electron, Inc. (XZO 1077/01), which was heated up to 873 K with a ramp rate of 10 K/min in static air and kept at 873 K for 3 h, denoted as SZ. Water washing technique was applied to the above calcined sulfated zirconia. 20 g of SZ were suspended in 400 mL bi-distilled water and then filtered. Repeated the washing procedure for 3 times, then the cake was dried at room temperature. The resulting powder is denoted as SZ-WW. The materials were characterized by IR spectroscopy, (including the sorption of probe molecules such as pyridine and CO<sub>2</sub>), TAP measurements, XRD and the sulfate content was determined. n-Butane isomerization reactions were carried out in a quartz micro tube reactor under atmospheric pressure. Prior to the reaction, the catalyst was activated at 473 K for 2 h in He flow (10 ml/min).

## Results and Discussion

The calcined sulfated zirconia, SZ, showed a catalytic activity of 0.015  $\mu\text{mol/g/s}$  for n-butane skeletal isomerization with an initial iso-butane selectivity of 96 % at 373 K. It is interesting to note that the removal of water soluble sulfate by water washing treatment of the parent sample resulted in an inactive sample (SZ-WW).

The content of sulfate of the water washed sample (SZ-WW) is 0.25 mmol/g, which is much lower than that of the original calcined sulfated zirconia, 0.44 mmol/g. Thus, 43 % of the total sulfate of sulfated zirconia was removed by water washing. The water washing treatment not only removed the water soluble sulfate of SZ, but also the Brønsted acid sites leading to an increase of Lewis acid concentration.

The IR spectra of water washed sulfated zirconia (SZ-WW) and sulfated zirconia (SZ) samples showed pronounced difference in the region OH and S=O vibrations. In the IR region of OH group above  $3600\text{ cm}^{-1}$ , water washing increased the intensity of the OH band at  $3634\text{ cm}^{-1}$  and shifted it to higher frequency,  $3661\text{ cm}^{-1}$ . In addition, water washing reduced a fraction of sulfate groups at high frequency leading to sulfate stretching vibrations of water washed sample (SZ-WW) at  $1391\text{ cm}^{-1}$  compared to the parent sample (SZ) at  $1404\text{ cm}^{-1}$ . Note that the wavenumber of the S=O stretching vibration is related to the SO bond order [1, 2], indicating that fractions of highly covalent sulfate were removed. IR spectra recorded during adsorption of  $\text{CO}_2$  showed the formation of bicarbonate on the surface of the washed sample but not on the original sample. SZ-WW featured an about equal number of two different types of Lewis acid sites, while for SZ one type of Lewis acid sites was predominant. The data indicate that water washing produces domains of bare zirconia surface, free of sulfate.

The results show for the first time that the water soluble sulfate species are responsible for the formation of highly covalent sulfates as well as the Brønsted acid sites, which are essential for the alkane isomerization reaction on sulfated zirconia at low temperature. Elementary steps are discussed based on steady state and transient kinetic measurements.

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