

# In-Situ Spectroscopic Study of Isomerization of Light Alkanes over Sulfated Zirconia Catalysts

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Sulfated zirconia (SZ) is a potentially interesting catalyst for isomerization of light alkanes, because it is already active, e.g., for *n*-butane isomerization, at temperatures below 373 K [1]. However, the catalyst suffers from rapid deactivation. A typical profile of conversion vs. time on stream suggests that there may be (at least) two types of active sites present in the catalyst: one type is responsible for a short-term high activity, which deactivates during the reaction, while the other is less active but produces a stable long-term activity. It is known that the tetragonal crystalline ZrO<sub>2</sub> bulk of an SZ catalyst plays an important role for the isomerization activity. The aim of the present work is to find out, if any relationship exists between one of the two activity components and the bulk crystalline phase of the catalyst.

Sulfate-containing ordered mesoporous zirconia of MCM-41 structure can be considered as an SZ catalyst without the typical tetragonal ZrO<sub>2</sub> bulk. A comparison of the catalytic performance of this material with that of a crystalline SZ catalyst will be helpful to distinguish the bulk-related activity from that of surface sites. Catalysts used in the present work include a sulfate containing ordered mesoporous zirconia synthesized according to the literature procedure [2] and a commercial SZ with the typical tetragonal bulk, obtained by calcination of MEL XZO 682/01. In-situ UV/Vis spectroscopy and in-situ DRIFTS have been performed under atmospheric pressure at various temperatures around 373 K using *n*-butane and *n*-pentane as probe reactants.

The activity–time-on-stream profile of the mesoporous catalyst for *n*-butane isomerization differs significantly from that of the MEL catalyst. A maximum at short time on stream is absent, and the activity increases gradually with the reaction time and reaches the level of the “steady state” of the MEL catalyst. [3]. In-situ DRIFTS showed shifts of absorption bands of sulfate species for both materials under reaction conditions.

With in-situ UV/Vis spectroscopy, absorption bands at wavelengths > 280 nm with increasing intensity, which can be attributed to the formation of allylic species on the surface, have been observed simultaneously to the deactivation process of the MEL catalyst. On the mesoporous catalyst these bands are absent. Instead, a band emerged below 280 nm.

The results suggest, that the crystalline bulk of SZ catalysts is associated with the high activity. The bulk-related sites deactivate due to coke formation through allylic intermediates. The sulfated, ordered mesoporous zirconia that does not possess a crystalline bulk has a stable low activity. The bulk ZrO<sub>2</sub> containing MEL catalyst shows an overlap of these two functions. These findings may be helpful in developing an SZ catalyst with a low selectivity towards the side reactions that lead to coking during low temperature isomerization of light alkanes.

## References:

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