

Activation of *n*-Butane by Modified Zirconia Catalysts Investigated with In Situ Diffuse Reflectance UV/Vis/NIR Spectroscopy

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- Introduction

Sulfated zirconia (SZ) and Fe-promoted SZ are highly active for *n*-butane isomerization [1,2], but neither has the first step in the reaction – the activation of the alkane - been clarified, nor is it understood which role surface intermediates play during the reaction and deactivation, nor has the function of promoters within the reaction scheme been identified. We investigated the interaction of *n*-butane with various zirconia catalysts at 378-573 K and followed the formation of surface species by UV/Vis/NIR-spectroscopy.

- Experimental and Summary of Results

For in situ diffuse reflectance measurements, a modified Perkin–Elmer Lambda 9 UV/Vis spectrometer and a home-made microreactor cell were used, with the quartz window of the reactor cell facing the integration sphere. All spectroscopic measurements were carried out sequentially with a scan speed of 240 nm/min, a slit width of 5.0 nm, a response time of 0.5 s, and with Spectralon® as a reference standard. Zirconium hydroxides (w and w/o sulfate) from MEL Chemicals were calcined in flowing air for 3 h at 823 K to produce ZrO₂ and SZ. Fe-ZrO₂ was obtained from zirconium hydroxide and Fe(NO₃)₃ through the incipient wetness method and subsequent calcination at 923 K for 3 h. The calcined catalyst (~1-2 g) was loaded into the cell and activated with 30 ml/min O₂ for 1.5 hrs at 723 K. The feed mixture was 5 vol-% *n*-butane in helium with a total flow of 50 ml/min for 6 hrs. Product analysis was performed by on-line gas chromatography with flame ionization detection.

At 378 K, ZrO₂ and Fe-ZrO₂ were inactive for the conversion of *n*-butane, and

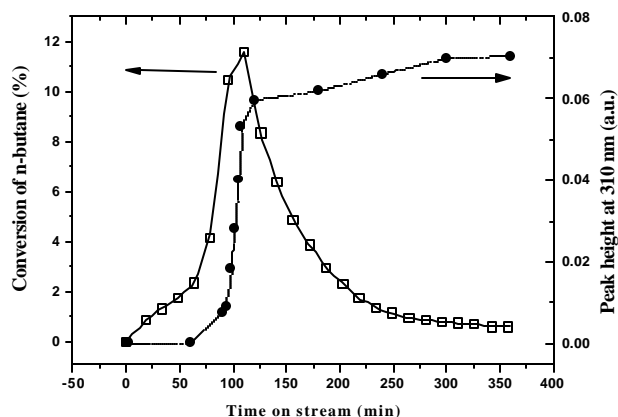


Fig. 1: Conversion of *n*-butane in the presence of sulfated ZrO₂ at 378 K. Evolution of peak at 310 nm.

surface species were not detected by UV/Vis-spectroscopy. Sulfated zirconia was active (Fig.1) at this temperature with isobutane being the predominant product. A sharp increase in activity after about 1 h on stream was accompanied by a strong intensity increase of a band at 310 nm. A rapid decline in activity followed along with further growth of the band. This band at 310 nm was previously observed [3] on deactivated sulfated zirconia and assigned

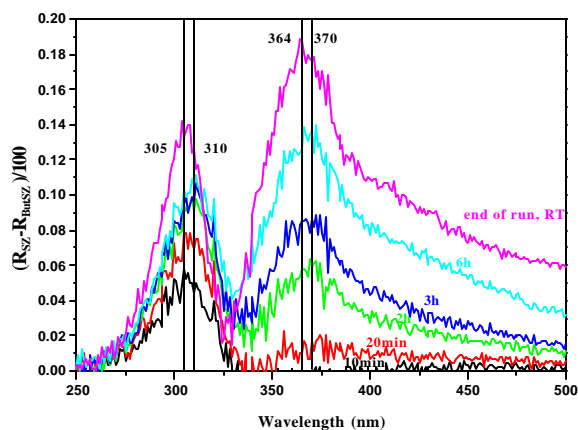


Fig. 2: Evolution of UV/Vis/NIR spectra during *n*-butane isomerization in the presence of sulfated zirconia at 523 K (difference spectra).

to allylic cations. At 523 K, sulfated zirconia showed declining conversion from the beginning and in addition to the band at 310 nm, a second band at 370 nm appeared (Fig 2), which can be attributed to dienic allylic carbocations [4], i.e. more highly unsaturated species. The band at 310 nm stopped growing after ~50 min on stream while the band at 370 nm increased further. At 573 K, ZrO_2 was inactive but Fe- ZrO_2 converted the *n*-butane into small amounts of butenes, but the activity ceased within 3 h. Concomittantly, a band at 1415 nm disappeared. This band is assigned to the overtone of an OH-stretching mode.

- Conclusions

On the surface of sulfated zirconia, allylic (378, 423, 523 K) and (only at 523 K) polyenylic species are formed during the reaction with *n*-butane. The rate of formation of allylic species is linked to the conversion to gas phase products, suggesting a connection (e.g. through a common intermediate) between reactions producing isobutane and reactions producing the surface deposits. Fe-promoted ZrO_2 converts traces of *n*-butane into butenes at 523 K. Butenes have a favorable influence on the isomerization activity of sulfated zirconia catalysts and the promoting effect of Fe could be explained, however, Fe-promoted SZ is very active already at RT.

- References

1. M. Hino, S. Kobayashi, K. Arata, *J. Am. Chem. Soc.* **101** (1979) 6439.
2. F.C. Lange, T.-K. Cheung, B.C. Gates, *Catal. Lett.* **41** (1996) 95.
3. D. Spielbauer, G.A.H. Mekhemer, E. Bosch, H. Knözinger, *Catal. Lett.* **36** (1996) 59.
4. C. Pazé, B. Sazak, A. Zecchina, J. Dwyer, *J. Phys. Chem. B* **103** (1999) 9978.