

# Possibilities of in situ UV/Vis/near-IR spectroscopy in the catalysis research

## Investigations of n-butane isomerisation on modified zirconia

J. Melsheimer

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-5,  
D-14195 Berlin (Germany), E-Mail : [jm@FHI-Berlin.mpg.de](mailto:jm@FHI-Berlin.mpg.de)

Recent progress in the redox behaviour and the identification of intermediates during the alkane isomerization on modified zirconia by in situ UV/Vis/near-IR spectroscopy as an useful method in catalysis research will be described [1]. This method was applied successfully by improved spectroscopic equipment and a suitable flow-through microreactor. Sulfated zirconia (SZ) and Fe-promoted SZ (FeZ) have been shown to be very active for n-butane isomerization [2,3]. However, the first step in the reaction – the activation of the alkane and the role of surface intermediates during the reaction – has not been clarified.

A modified Perkin–Elmer Lambda 9 UV/Vis/near-IR 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. The calcined SZ or FeZ catalyst was loaded into the cell and activated with 30 ml/min O<sub>2</sub> 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.

The evolution of spectra during the reaction at = 378 K evidences the growth of different types of allylic carbocations and enylic carbenium ions [4] which cause a quick catalyst deactivation. Bands were, e.g., located at 310 nm (Fig. 1) on sulfated zirconia and are assumed to arise from allylic carbocations [5]. It will be revealed that the increase of allylic species concentration is directly proportional to the increase of catalyst activity during the induction period. After this period the high concentration attained is irreversibly deposited and leads to fast catalyst deactivation. FeZ samples with Fe contents of 1, 2, and 5 wt% were all active for n-butane conversion. Products included small amounts of butenes at 523 K, suggesting that the formation of butenes may even be possible at temperatures below 523 K, although the butenes may not desorb or be too few to detect.

UV/Vis spectra taken after activation show a band at 290 nm that is attributed to ZrO<sub>2</sub>. The ligand to metal charge transfer (LMCT) bands of the Fe species of the various FeZ catalysts differ considerably in shape and position. Evidently, the lower the Fe content, the more blue shifted the LMCT band.



fated zirconia at 378 K. Evolution of peak at 310 nm.

### References

1. R. Ahmad, J. Melsheimer, F.C. Jen-toft, and R. Schlögl, to be published.
2. M. Hino, S. Kobayashi, K. Arata, J. Am. Chem. Soc. **101** (1979) 6439.
3. F.C. Lange, T.-K. Cheung, B.C. Gates, Catal. Lett. **41** (1996) 95.
4. D. Spielbauer, G.A.H. Mekheimer, E. Bosch, H. Knözinger, Catal. Lett. **36** (1996) 59.
5. C. Pazè, B. Sazak, A. Zecchina, J. Dwyer, J. Phys. Chem. B **103** (1999) 9978.