

## In Situ Diffuse Reflectance UV/Vis Spectroscopy Investigations of Alkane Activation Catalyzed by Sulfated Zirconia

*Rafat Ahmad, Jörg Melsheimer, Friederike Jentoft,*

*Department of Inorganic Chemistry, Fritz Haber Institute of the Max Planck Society,  
Faradayweg 4-6, 14195 Berlin, Germany*

### Introduction

Sulfated zirconia (SZ) is highly active for *n*-butane isomerization [1,2] but deactivates rapidly. Because isomerization and disproportionation of *n*-butane seem to occur concomitantly it is not possible to recognize if deactivation is the result of one or the other reaction. For *n*-pentane, isomerization and disproportionation activity reach their maximum at different times on stream, allowing the separate observation of mono- and bimolecular reaction pathways. In situ UV/Vis spectroscopy has been used to study the interaction of *n*-butane and *n*-pentane with SZ.

### Experiments and Summary of Results

In situ diffuse reflectance measurements during alkane reaction were conducted using a home-made microreactor cell with a quartz window facing the integration sphere. The setup was fitted into a modified Perkin–Elmer Lambda 9 UV/Vis spectrometer, operated at 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. SZ was obtained by calcining sulfated zirconium hydroxide (MEL Chemicals) in flowing air for 3 h at 823 K. The calcined catalyst (~1.3 g) was loaded into the cell and activated in 30 ml/min O<sub>2</sub> for 1.5 h at 723 K. The feed mixture was 5 vol-% *n*-butane in He or 0.25 or 0.50 vol-% *n*-pentane in He with a total flow of 50 ml/min at reaction temperatures of 358 – 523 K for *n*-butane and 298 – 308 K for *n*-pentane. Product analysis was performed by on-line GC with FID.

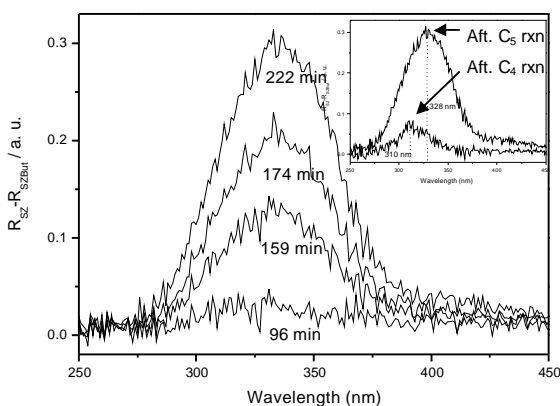
UV/Vis spectra showed a single broad band centered at 328 nm, which started to form after about 90 min of *n*-pentane reaction; the final intensity of this band (after 13 h) was independent of *n*-pentane concentration and reaction temperature. The formation of a band at 310 nm was detected during *n*-butane reaction (all temperatures, inset in Fig. 1). This band was previously observed [3] on deactivated sulfated zirconia and assigned to monoenic allylic cations. At 523 K, additional bands appeared at 370 nm and 430 nm after 20 min and 6 h on stream, respectively.

Analysis of the product stream during *n*-pentane reaction revealed an initial carbon loss of 16 to 44 %, suggesting considerable adsorption without the formation of

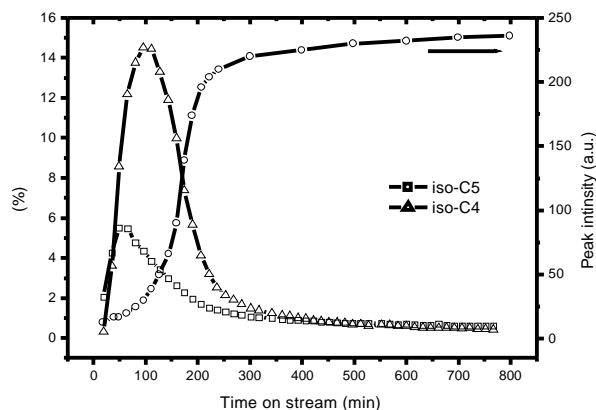
spectroscopically detectable species. At 298 K and 0.25 vol-% *n*-pentane, the maximum rate of formation of *n*-pentane preceded the maximum in production of *i*-butane (Fig. 2). Hexanes, *n*-butane, and propane were byproducts. Increasing the *n*-pentane concentration to 0.50 vol-% did not change the conversion but led to an increase in *i*-pentane selectivity and a decrease in *i*-butane selectivity. Interestingly, as the rate of disproportionation became significant (Fig. 2), a band at 330 nm appeared in the UV/Vis spectrum (Fig. 1). In the reaction of *n*-butane, the maximum conversion and the rate of deactivation increased with increasing temperature while the selectivity towards *i*-butane decreased (range 70 to 99 %).

## Conclusions

The broad UV/Vis absorption band formed during *n*-pentane reaction is presumably composed of two bands, maybe representing different isomers of monoenic allylic cations. These bands reach significant intensity only after the rate of *i*-pentane formation passes through a maximum, excluding these allylic species from being identified as isomerization intermediates (Figs. 1 & 2). During the induction period, *i*-pentane is predominantly formed through a monomolecular mechanism. The formation of *i*-butane at longer times on stream indicates a bimolecular mechanism, i.e. the disproportionation of C<sub>10</sub>-intermediates, which are formed in an alkylation step requiring alkenes. However, this bimolecular pathway is disadvantageous because the alkenes generated by the catalyst are precursors for site-blocking species.



**Fig. 1:** UV/Vis difference spectra recorded during *n*-pentane reaction with time on stream as parameter. SZ, 0.25 vol-% *n*-pentane, 298 K. Inset: end of reaction (butane / pentane).



**Fig. 2:** Conversion of *n*-pentane to *i*-pentane and *i*-butane and peak intensity at 330 nm vs. time on stream. SZ, 0.25 vol-% *n*-pentane, 298 K.

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