

Summary

The main focus of this work was putting into operation, testing, and optimizing an apparatus for *in situ* observation of the surface structure of zirconia catalysts. Surface species and reactions occurring during *n*-butane isomerization were studied by means of diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The catalytic activity (conversion, rate) and selectivity were determined in the DRIFTS cell and in a tubular fixed-bed reactor by on-line gas chromatography.

The self synthesized catalysts based on sulfated zirconia (SZ) isomerize *n*-butane at temperatures below 100°C where branched alkanes are thermodynamically favored. The selectivity to *i*-butane was always above 95%.

The catalytic results in the IR cell are reproducible and similar to the catalytic behaviour in the fixed-bed reactor. The positions of the bands obtained by DRIFTS are reproducible to $\pm 1 \text{ cm}^{-1}$.

The mostly monoclinic zirconia (Z) used as a reference substance is not active in *n*-butane isomerization. The X-ray diffraction patterns before and after reaction point to a phase transformation under reaction conditions (slight increase of the monoclinic modification).

Sulfated zirconia (SZ) showed an interaction between sulfate and *n*-butane during reaction. The band shifts in the IR spectra indicate a weakening of the S=O double bond and a strengthening of the S-O single bond.

While pure SZ reaches a maximum conversion of only 0,1% during the catalytic experiments at 85°C in the IR cell, iron or manganese promoted SZ (FeSZ / MnSZ) have a maximum conversion of several percent even at 50°C. FeSZ causes a twice as high maximum conversion (7%) to *i*-butane as MnSZ (4%). MnSZ can be regenerated under oxygen at conditions analogous to the activation (heating to 500°C, 30 min hold, cooling to 50°C; nominal heating rate 25 K/min). If nitrogen is used instead of oxygen, the regeneration of the deactivated catalyst fails. The investigations suggest that the oxygen content and possible oxygen defects are relevant for the activity.

Possible effects of the promoters were studied by DRIFTS of FeSZ, MnSZ, and reference substances. Number and position of the bands in the IR spectra of iron or manganese promoted catalysts differ only little from unpromoted SZ or from each other. An influence of the SZ surface by iron as promotor is not visible. The addition of manganese as promotor however leads to changes of the surface as indicated by the IR spectra: The band at 1300 cm^{-1} is missing for MnSZ, at 1260 cm^{-1} an additional band occurs, which cannot be observed for SZ or FeSZ. An interaction of the S=O double bond with the feed gas was detected whereby the shift of the S=O band at 1400 cm^{-1} correlates with the conversion.