

Reaction of Surface Deposits on Deactivated Sulfated Zirconia with O₂ and H₂O Monitored by In Situ DR UV-vis Spectroscopy and Mass Spectrometry

G. Tzolova-Müller, J. Melsheimer, F.C. Jentoft

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

Introduction

Unsaturated surface deposits have been detected by in situ UV-vis spectroscopy on tetragonal [1] and mesoporous sulfated zirconia (tSZ and mpSZ) during *n*-butane and *n*-pentane isomerization. The different bulk structures of the two materials appear to lead to a different deactivation behavior. In order to further identify the nature of these deposits on tSZ and mpSZ and to identify a procedure for catalyst regeneration, the deactivated materials were reacted at 298 K first with oxygen and then with water vapor. Changes to the catalyst and the deposits during the treatment with both reagents were monitored (in situ) by DR UV-vis spectroscopy, and the effluent stream was analyzed by MS.

Experimental

tSZ was obtained by calcination of a commercial precursor (MEL Chemicals) at 823 K, mpSZ was synthesized as reported in the literature [2, 3]. For in situ spectroscopy, a fixed bed flow reactor was placed in the sample position at the integrating sphere of a Lambda 9 spectrometer (PerkinElmer). Spectra were recorded using a scan speed of 240 nm min⁻¹, a slit width of 5 nm, and with Spectralon[®] as a white standard. *n*-Butane (5 vol%, 50 cm³ min⁻¹) isomerization was conducted at 378 K (tSZ) or 453 K (mpSZ), and *n*-pentane (1 vol%, 50 cm³ min⁻¹) isomerization at 298 K (tSZ) or 323 K (mpSZ); and the gas phase was analyzed by on-line GC. After 16 h on stream, the samples were cooled to 298 K in He, treated first with 20 vol% O₂ in He (50 cm³ min⁻¹) for 1.5 h, and then with water vapor in He (50 cm³ min⁻¹) for 1.5 h. The effluent gas stream was analyzed using a Pfeiffer ThermoStar mass spectrometer.

Results and discussion

During *n*-butane and *n*-pentane isomerization, unsaturated surface deposits (absorption band at 300-330 nm, allylic-type species [1]) were formed on the surface of tSZ and during *n*-pentane isomerization on mpSZ, while the catalysts deactivated

rapidly. Only during *n*-butane isomerization on mpSZ were nearly no changes in the UV-vis spectra with time on stream observed, and deactivation was slow.

The spectra of the SZ samples with allylic type deposits showed only minor changes in the *oxygen stream*. Oxygen treatment of the mpSZ sample caused an overall intensity decrease between 250 and 450 nm within the first 5 min but no further changes. Nevertheless, fragments of hydrocarbons and oxygenated derivatives were registered in the mass spectra of the effluent stream for all samples.

During *subsequent water vapor treatment* of the SZ samples with allylic deposits, intense bands at about 380, 455-460, and 550-560 nm developed and the original band at 310-330 nm was reduced in intensity (Fig. 1). Bands at 430-455 nm have been assigned to quinone-type compounds [4], the other

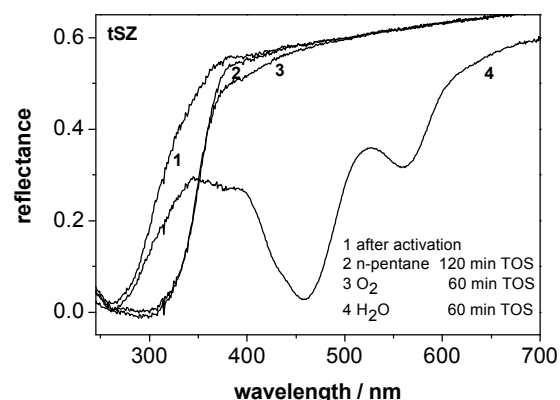


Fig. 1: UV-vis spectra of tetragonal SZ

spectrum of the mpSZ sample that had been deactivated in *n*-butane became similar to the spectrum of the activated state of this sample, with recovery of the overall intensity and the presence of absorption bands at 280 and 320 nm. The mass spectra of the gas phase during the water treatments showed the same fragments as during the oxygen treatment but with much lower intensity.

The nature of the surface deposits on tSZ and mpSZ can be different depending on reactant and conditions. Surface deposits formed during alkane isomerization react with the components of air and are partially volatilized. Color changes consistent with the UV-vis spectra in Fig. 1 have been observed when taking deactivated samples out of the reactor. Surface deposits must thus be studied in situ.

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