



In situ UV-vis-NIR Spectroscopy as a Tool to Understand Catalyst Deactivation



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Introduction

Catalyst deactivation is a frequently occurring problem, particularly in hydrocarbon conversion, and is often ascribed to the formation of “carbonaceous deposits”. Amount and nature of such deposits is usually determined by analysis of the spent catalyst after its removal from the reactor. In order to understand the formation and further transformation of surface species and to elucidate their effect on the catalytic performance, in situ measurements are compulsory. UV-vis-NIR spectroscopy is a powerful technique because it provides information on electronic and vibrational transitions simultaneously, facilitating spectral interpretation. Sulfated zirconia (SZ) is known to deactivate rapidly during alkane isomerization unless Pt is added to the catalyst and hydrogen to the feed, and presents a challenging study.

Experimental

Sulfated zirconium hydroxide (MEL Chemicals) was dried and calcined at 823 K to obtain SZ, or impregnated with 0.5 or 2.0 wt% Mn via the incipient wetness method and then calcined at 923 K [1,2]. UV-vis-NIR spectra were acquired with a Harrick Praying Mantis™ diffuse reflectance attachment DRP-P72, a HVC-VUV reaction chamber and a PerkinElmer lambda 950.

Results

Consistent with earlier results [3] obtained with a different setup, SZ deactivated during isomerization (5 kPa *n*-butane, 323 K) and an intense band at ≈ 300 nm grew with time on stream (Fig. 1). An additional band formed at 390 nm. Activated Mn-

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promoted SZ (0.5% Mn) exhibits already bands in the UV-vis range, namely at 305, 540 and 665 nm, which can be assigned to transitions arising from Mn^{2+} and Mn^{3+} ions. Mn-promoted SZ was more active than SZ under the same conditions and deactivated after the first hour on stream. Surprisingly, corresponding bands to those observed with SZ could not be detected, raising the question as to the causes of deactivation of the promoted SZ catalyst.

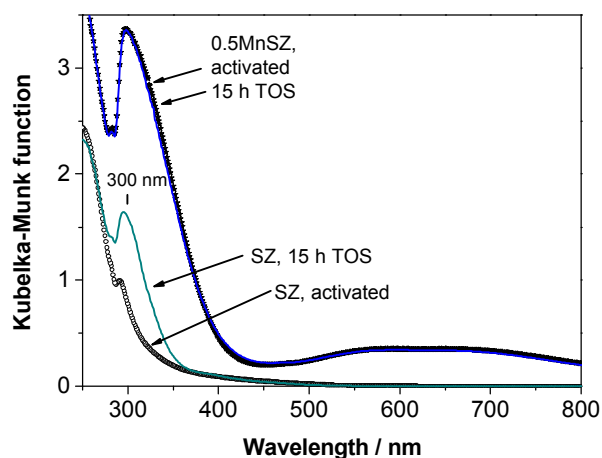


Figure 1: UV-vis spectra during isomerization, 1 kPa *n*-butane, 323 K.

In the NIR range, a band at 1910 nm (5235 cm^{-1}) indicated the accumulation of water (poisoning effect?) on the surface of both catalysts, consistent with oxidative dehydrogenation of butane [5]. Bands at 1695, 1715 and 1756 nm correspond to the double frequency of CH vibrations at 2950, 2915 and 2850 cm^{-1} , suggesting the presence of saturated hydrocarbons.

A dual strategy was pursued to interpret the bands that appear during isomerization, particularly to verify the literature assignment [4] of the band at 300 nm to allylic cations. 1. Reference spectra were recorded. Contact of activated SZ with 1-butene produced bands at 320, 360 and 390 nm and overtones of CH vibrations of saturated and unsaturated hydrocarbons. The surface species on SZ formed during isomerization are thus not simply secondary products of butane dehydrogenation. 2. Different reactants were used to convert the species on the surface of the deactivated catalyst and identify them based on the obtained products. The species absorbing at 300 nm proved highly reactive towards water.

UV-vis-NIR spectra demonstrate that deactivation of sulfated zirconia catalysts is not only caused by unsaturated hydrocarbon deposits. Currently we are trying to identify the nature of the highly reactive surface species formed during isomerization.

1. A. Hahn, T. Ressler, R.E. Jentoft, F.C. Jentoft, Chem. Commun. (2001) 537.
2. A.H.P. Hahn, R.E. Jentoft, T. Ressler, G. Weinberg, R. Schlögl, F.C. Jentoft, J. Catal. in print.
3. R. Ahmad, J. Melsheimer, F.C. Jentoft, R. Schlögl, J. Catal. 218 (2003) 365.
4. F.R. Chen, G. Coudurier, J.-F. Joly, J.C. Védrine, J. Catal. 143 (1993) 616.
5. B.S. Klose, F.C. Jentoft, R. Schlögl, J. Catal. 233 (2005) 68.