

In Situ UV-vis-NIR Spectroscopic Investigation of Highly Reactive Surface Species Formed during Alkane Skeletal Isomerization

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Introduction

Catalyst deactivation is often caused by formation of stable surface compounds, which block access to active sites. Development of catalysts that are less prone to deactivation requires understanding the nature of such species and the formation routes. In situ methods are very informative in this respect, as they simultaneously deliver data on the catalytic reactivity and on the surface state including adsorbates, allowing correlations to be made. UV-vis-NIR spectroscopy offers great potential, providing not only information on unsaturated deposits and the oxidation state of catalyst components via their electronic transitions but also on functional groups and adsorbates via their overtone and combination vibrations.

Alkane isomerization catalysts such as chlorided alumina, mordenite and anion-modified zirconia require Pt doping and addition of H₂ to the feed to stabilize performance [1,2]. The role of the H₂/Pt combination is discussed controversially, proposed are (i) coke prevention by hydrogenation of unsaturated species [1], (ii) facilitation of dehydrogenation, isomerization via alkenes and re-hydrogenation [2], (iii) formation of additional acid sites [3]. For the present work we selected sulfated zirconia (SZ) and Mn-promoted sulfated zirconia as highly active low temperature isomerization catalysts [4] and investigated the nature of the surface species formed during alkane isomerization by in situ UV-vis-NIR spectroscopy. The deactivation characteristics and the effect of Pt and H₂ on performance were studied.

Materials and Methods

SZ was prepared by calcining a commercial precursor (MEL Chemicals XZO 682/01) for 3 h at 823 K. Mn-promoted SZ (0.5 or 2 wt% Mn) was obtained from the same precursor via the incipient wetness method and calcination at 923 K [4]. 0.5 wt% Pt were added afterwards. In situ UV-vis-NIR spectroscopy was performed in diffuse reflectance using a PerkinElmer Lambda 9 equipped with an integrating sphere and a reactor of in-house design, or a PE Lambda 950 equipped with a Harrick Praying Mantis™ DRP-P72 accessory and HVC-VUV reaction chamber. Reaction conditions were 5 kPa *n*-butane at 323–378 K or 1 kPa 1-butene at 303 K, with inert gas or H₂ added to reach atmospheric pressure. Effluent gases were monitored by on-line GC. Post-reaction treatment with O₂ or H₂O vapor was carried out in situ in the UV-vis reactor cell.

Results and Discussion

Figure 1 shows a reaction profile of SZ at 373 K. The usual induction period is passed so quickly that it is not observable under the selected conditions. Two phases of deactivation can be distinguished, a rapid decline for 2 h followed by a slow decrease. The

simultaneously recorded spectra show a band at 300 nm, according to the literature allylic species [5]. The NIR range reveals a H₂O combination mode. The concentration of the unsaturated species increases continuously, relating them to the slow decline, while water accumulates only for 2 h, relating it to the rapid loss in activity. Water could be a product of oxidative dehydrogenation, a suspected initiation reaction. Interaction of SZ with 1-butene however, resulted in bands at 320, 360 and 390 nm, indicating that the chemistry observed for butane is not a simple transition into the butene chemistry. Mn-promoted SZ samples were more active than SZ catalysts but fewer unsaturated species were detected.

High partial pressures of H₂ in the feed significantly reduced the isobutane formation rate over SZ. Using a butane/N₂ mixture, the catalytic activity for SZ doped with Pt was extremely low. Individually, Pt and H₂ do not seem to exert the desired effect of stabilizing the performance.

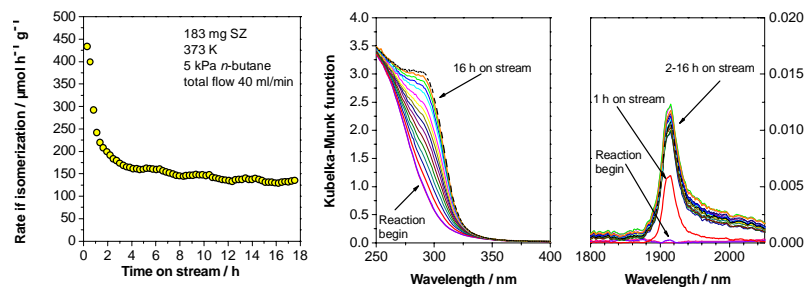


Figure 1. In situ spectroscopy during *n*-butane (5 kPa) isomerization catalyzed by sulfated zirconia at 373 K. Left: isobutane formation rate, center: UV-vis spectra, right: NIR spectra.

The unsaturated species on SZ were inert towards O₂ at 298 K, but H₂O vapor reduced the intensity of the band at 300 nm and produced new bands at 390, 455 and 550 nm. This reaction was also evident from a color change of used catalysts upon removal from the reactor into the air, demonstrating the high reactivity of the surface species.

Significance

Two deactivation pathways were identified for SZ materials, highlighting the complexity of stabilizing the activity of these catalysts. Surface species formed during isomerization were highly reactive towards air, and hence it is necessary to investigate their nature in situ.

References

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