

Formation of carbon-containing deposits on chromia/alumina during isobutane dehydrogenation

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Light alkenes, such as propene and butenes, are important intermediates in the manufacture of polymers and chemicals. The most selective way to produce these short-chain alkenes is the direct catalytic dehydrogenation of the corresponding alkanes. Industrial dehydrogenation processes frequently use alumina-supported chromia catalysts. Oxidised chromia/alumina contains chromium mainly as Cr³⁺ and Cr⁶⁺, and in trace amounts as Cr⁵⁺. At the beginning of the alkane feed, or during prereduction, the higher oxidation states reduce mainly to Cr³⁺, which is generally considered to be the active species in the reaction [1]. One problem related to these catalysts is their rapid deactivation during dehydrogenation due to coke formation. However, the carbon-containing species formed have been discussed only briefly [2].

The purpose of this work was to investigate the formation of the carbon-containing species during isobutane dehydrogenation on a chromia/alumina catalyst with 13.5 wt-% chromium. The measurements were done by *in situ* DRIFT spectroscopy combined with mass spectrometry (MS). The effect of hydrogen prereduction was studied, also. Previously, H₂ prereduction has been observed to result in formation of OH groups [3] and in decrease of the dehydrogenation activity of chromia/alumina [4].

Temperature programmed DRIFTS-MS measurements with isobutane suggested that the isobutane reacted at temperatures below 100°C to adsorbed acetone and formate. At the same time, reduction of the catalyst took place. With increasing temperature, also acetate/carbonate species were observed. Above 450°C where dehydrogenation products were detected by MS the formates disappeared whereas the acetates/carbonates were still present. Simultaneously, first aliphatic and then olefinic/aromatic hydrocarbon deposits appeared. Therefore, at low temperatures the carbon-containing deposits are mostly oxygen-containing ones formed in the reduction of the catalyst, whereas at dehydrogenation conditions also hydrocarbon-type species form.

Isobutane dehydrogenation measurements at 580°C were done for non-prereduced and H₂-prereduced catalysts. Acetates/carbonates formed rapidly on the non-prereduced sample at the start of the isobutane feed, and more slowly on the H₂-prereduced sample. Also aliphatic hydrocarbon species were present from the start. Olefinic/aromatic deposits formed gradually with increasing time on stream on both of the samples. This agreed with the continuous decrease in activity observed by MS and may suggest that the olefinic/aromatic deposits contributed to the deactivation more than the acetates/carbonates or the aliphatic species.

References

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