

Combining results from XAS, Raman, STEM and TEOM to obtain reliable information about propane dehydrogenation catalysts

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Dehydrogenation of propane (DHP) has been studied over a series of Cr-SBA-15 and Cr-Al₂O₃ catalysts, prepared by incipient wetness impregnation, to gain a better understanding of the nature and distribution of Cr species and their catalytic function. To this end, the catalysts were characterized by N₂-physisorption, X-ray diffraction (XRD), UV-Raman spectroscopy, scanning transmission electron microscopy – energy dispersive X-ray spectroscopy (STEM – EDXS) and X-ray absorption spectroscopy (XANES and EXAFS). All these characterization techniques support that ≤ 1 wt.% Cr, SBA-15 contains a highly uniform distribution of chromium as isolated Cr(VI) species in tetrahedral (T_d) coordination whilst on γ -Al₂O₃ a fraction of oligomers (including dimers) is present along with isolated species. At ≥ 5 wt.% Cr, SBA-15 is dominated with crystalline α -Cr₂O₃ particles besides a fraction of isolated Cr(VI) species in T_d coordination. In contrast, Cr on γ -Al₂O₃ contains mainly oligomers with different degrees of nucleation and a fraction of isolated species but no Cr₂O₃ particles. Among Cr-SBA-15 catalysts, those containing exclusively isolated Cr species (i.e., ≤ 1 wt.% Cr) exhibit higher activity and selectivity per mole of Cr than the catalyst dominated with crystalline α -Cr₂O₃ particles (≥ 5 wt.% Cr). The intrinsic activity of these isolated Cr species is higher than those observed on γ -Al₂O₃ (≤ 1 wt.% Cr). Among Cr-Al₂O₃ catalysts dominated by oligomeric species show the highest activity indicating the important role of the species in the reaction. In situ XAS studies evidence that active Cr sites are apparently generated on site during the reaction and that Cr is typically in (III) oxidation state. Based on ex situ and in situ characterization results and catalytic data, it appears that the activity of Cr species is different in x Cr-SBA-15 and x Cr-Al₂O₃. For x Cr-SBA-15, isolated Cr(III) sites with coordination number greater than four are more active, selective and stable than Cr sites on the surface of crystalline Cr₂O₃. In contrast, for x Cr-Al₂O₃, oligomeric Cr species are more active and selective than the isolated Cr sites.