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Investigation of the cobalt/support interface in thin-film model catalysts for Fischer-Tropsch reaction using XPS

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Abstract

The cobalt catalyzed Fischer-Tropsch (FT) reaction is gaining interest for the sustainable production of fuels and chemicals via converting renewably derived CO and H_2. It is reported in literature that the interaction of cobalt with the support materials commonly used in FT catalysis (e.g., SiO_2, TiO_2) plays a crucial role for the formation of active sites [1]. The investigation of the Co/support interface is challenging; employing chemical and electronic structure-sensitive surface science techniques usually requires suitable model systems and necessitates high vacuum conditions and control of the (surface) contamination level. In our contribution, we report on the *in-system* study of the interface of Co with SiO_2 and TiO_2 using well-defined thin-film model catalyst systems and studying these samples before and after operation-mimicking conditions with advanced spectroscopic techniques without the need to break vacuum conditions. A series of samples were prepared using physical vapor deposition of a few monolayers of Co on SiO_2 and TiO_2. The prepared thin-film samples were subjected to oxidation and reduction treatments mimicking realistic operation conditions (i.e., simulating calcination and activation treatments, respectively) which are typically applied during a lifecycle of real-world catalysts. The pristine and treated samples were characterized by XPS; by making use of the vacuum transfer in-between preparation, reactor, and analysis chambers unwanted sample surface contamination was avoided. The effect of both the oxidation and reduction steps on the chemical structure (i.e., oxidation state) of the Co atoms was influenced by metal/support interactions. More specifically, during the oxidation step Co atoms near the interface were oxidized to an oxidation state of +2 while those far from the interface have a mixed oxidation state between +2 and +3, most probably forming the spinel phase. The reducibility was also lower for the Co atoms interacting with the support which remained in the +2 oxidation state instead of converting to metallic Co as observed for the Co atoms located further from the support. Thus, according to our results, a Co (+2) oxide interlayer forms between the support and the active metallic Co (surface) phase formed during the reduction step. Differences observed in Co reducibility implied that the strength of metal-support interactions is higher in the case of TiO_2 compared to SiO_2. Mixed oxide compounds formed from the Co and the support species were also detected, which are known to be largely unreducible. DFT calculations carried out for the same systems agree with the experimental findings, suggesting that during the reduction step a portion of the Co oxide reacts with the support, forming a mixed-oxide interlayer that regulates the Co-support interactions. The present study provides experimental evidence and new insights on the nature of the metal/support interface during catalysts preparation and can assist to the rational design of more efficient F-T catalysts.

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