

CO as an active spectator species in hydrocarbon conversions related to Fischer-Tropsch synthesis

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Cobalt-based catalysts show a high selectivity to long chain aliphatic hydrocarbons in the Fischer-Tropsch synthesis (FTS) process making them the catalyst of choice in the gas-to-liquids process. With a large number of elementary steps taking place on the catalyst surface the reaction mechanism can be ranked among the most complex in the chemical industry. Hydrocarbon adsorbates are key intermediates in the Fischer-Tropsch synthesis. The selectivity of the catalyst depends on the relative rates of the various elementary reaction steps, e.g. the competition between chain growth versus chain termination determines the average length of the hydrocarbon product.

By making use of a well-defined Co(0001) single crystal surface under UHV conditions we systematically explore the stability of the different hydrocarbon species and look at elementary reaction steps such as hydrogenation and dehydrogenation reactions. In our work we look at the influence that CO adsorbates have on the C_xH_y species that participate in the chain growth reaction. We find that ethene and propene both decompose <200 K, forming acetylene and propyne, respectively [1]. The hydrogen atoms produced remain adsorbed until they leave the surface as H_2 around 300 K. Instead, when the alkyne- H_{ad} layer is heated in the presence of CO we find rehydrogenation of the alkyne species around 250 K forming the corresponding alkylidyne species. Figure 1 shows TPD and IR data where 1-butene was used. Like for ethene and propene we see that decomposition yields the 1-alkyne, which, when heated in the presence of CO, is rehydrogenated to form 1-butylidyne. These experiments show that CO_{ad} , present in abundance during FTS, not only acts as a reactant but it also affects the reactivity of chain growth intermediates. The observed CO-induced conversion of alkyne to alkylidyne is of particular interest in the FTS context: in the alkylidyne chain growth mechanism [2,3] a new chain is created via $CH + CH = HC-CH$. This alkyne coupling product has to be hydrogenated to the alkylidyne, $C-CH_3$ so that further growth, via CH insertion to form $H-C-C-CH_3$, can proceed. And it is exactly this step that is facilitated by CO, making CO an active spectator species that is essential for the growth of long chains.

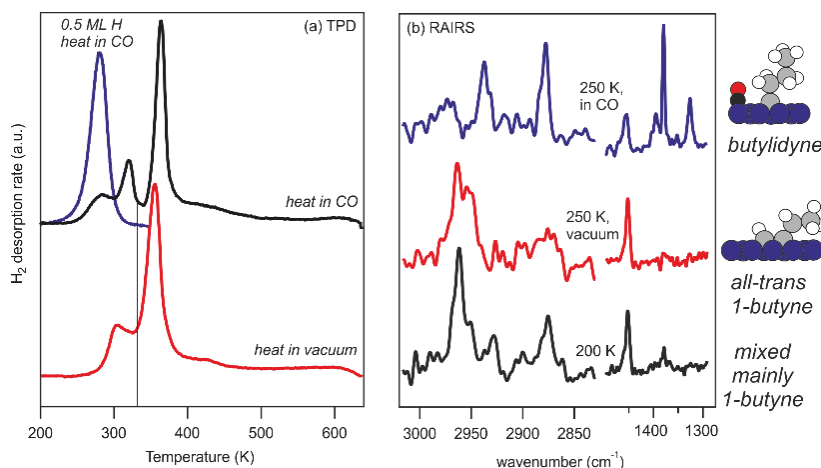


Figure 1: (a) H_2 desorption during heating of a 1-butene/ H_{ad} layer in vacuum and in the presence of CO (g), respectively. (b) IR absorption spectra of a 1-butene/ H_{ad} layer in the presence of CO (g), showing that 1-butyne is hydrogenated to butylidyne after heating to 250 K due to the presence of CO.

References:

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