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CO Desorption from Supported Ruthenium Catalysts

In a recent article, Low and Bell reported on the desorption of CO from alumina-supported ruthenium surfaces and its interaction with hydrogen. They have extrapolated the interpretation of their results to the reaction mechanism of the Fischer–Tropsch synthesis (*1*). The purpose of this letter is to point out that the conclusions might be more extensive than proposed by the authors.

Analogous desorption experiments have been carried out by myself, mainly on Ru-faujasites and Ru on silica (Aerosil) catalysts. In these experiments, however, the TPD (temperature-programmed desorption) was started after a relatively long period of Fischer–Tropsch synthesis at elevated growth probabilities. The latter condition may be very important, as was pointed out in my earlier work with Jacobs (*2*, *3*). After putting an abrupt end to the reaction, TPD under helium at 5 K $\min^{-1}$ was followed by multichannel single-ion monitoring. It was reasoned that under such conditions it would be more likely that the nature of the surface species during Fischer–Tropsch synthesis could unequivocably be established.

From these experiments desorption curves were obtained which are very much in line with the results of Low and Bell for both adsorbed CO and CO_2. The amounts of desorbed hydrocarbons and H_2 were several orders of magnitude lower, which indicates that during reaction the surface is mainly covered by CO or a closely related reaction intermediate.

The most remarkable feature of the CO desorption experiments, however, was the occurrence of two very distinct peaks. In our experiments it was found that the relative area of the second peak depended on the average metal particle size and hence was related to the length of the hydrocarbons produced during synthesis. Moreover, it was noticed that the ratio between the total area of the second and the first peak could vary between 0 and 3. Furthermore the color of the samples after reaction varied from bright yellow to dark grey also depending on Ru particle size and hydrocarbon chain length.

It is well known that thermal decomposition *in vacuo* of the yellow complex $Ru_3(CO)_{12}$ proceeds in two distinct steps, the first in which three molecules of CO are desorbed and the second in which nine molecules are released. It therefore seems very likely that upon adsorption of CO on Ru two differently adsorbed species are formed, depending on the geometrical configuration of the site. The number of sites responsible for the CO desorbed at high temperatures seems to diminish with metal sintering.

Furthermore, it was observed that catalysts which were practically black after reduction turned yellowish during high-pressure synthesis, particularly the zeolite-supported samples. This would indicate that high synthesis gas pressures could cause redispersion of the metal phase, probably due to the generation of more, apparently very stable, Ru–CO species at low-coordination sites. More detailed studies of these phenomena might lead to very interesting results.

In conclusion, I would like to state that under normal Fischer–Tropsch conditions two different CO species are formed on a

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Ru surface and their relative abundance depends on particle size, i.e., the relative abundance of low-coordinated Ru atoms. On the other hand, the occurrence of the Boudouard reaction at the surface and the concurrent evolution of small amounts of C_2 hydrocarbons are not in contradiction with the mechanism proposed in Ref. (*3*). Indeed, at the given temperature it is very likely that enough water is present on the catalyst support to account for the formation of some C–C bonds. It might be interesting to do an analogous experiment on unsupported Ru.

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