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The Role of Carbon in Methanation by Cobalt and Ruthenium

It has been shown recently that dissociation of CO is the necessary step in methanation on Ni and Ni–Cu alloys (*1*). The main evidence for it has been obtained by isotopic labeling of carbon (^{13}C) formed by disproportionation and deposited prior to methanation on the surface of the catalyst (*1*). There is also kinetic evidence available (*2, 3*) which convincingly shows that the "dissociative" route (with respect to CO) is either the fastest or even the exclusive one among the possible pathways on Ni. Experiments at higher pressures and comparison of Ni with Ni–Cu alloys revealed that CO dissociation is most probably an important step, also in the formation of higher hydrocarbons (*4*) (Fischer–Tropsch synthesis). Since Ni is not a typical Fischer–Tropsch catalyst, it is interesting to investigate whether also Co and Ru behave with regard to surface carbon in a way similar to Ni. We addressed ourselves to the two following questions:

(a) Can carbon deposited on Co and Ru surfaces be incorporated into CH_4 when a reaction mixture is admitted to the carburized surface?

(b) Is this the main pathway of CH_4 formation on Co and Ru?

The experimental procedure, the apparatus used and data evaluation were the same as in the previous paper (*1*). Evaporated films, UHV apparatus, and low pressures (<1 Torr) were used in this work.

The surface of Co was covered by ^{13}C to a high extent (almost a monolayer coverage) by disproportionation of ^{13}CO and brought into contact with $^{12}CO/H_2 = 1/5$ mixture afterwards. The production of various products was followed mass-spectrometrically. At 250°C both $^{13}CH_4$ and $^{12}CH_4$ were formed at comparable rates when the reaction mixture (^{12}CO) was admitted to the carburized (^{13}C) film. At the very beginning of the reaction, production of $^{13}CH_4$ was slightly faster than that of $^{12}CH_4$, as can be seen from Fig. 1.

Figure 1 shows that, as with Ni (*1*), incorporation of ^{13}C (predeposited) into $^{13}CH_4$ takes place. However, a comparison with Ni reveals also some differences. On Ni the initial rate of the $^{13}CH_4$ formation is clearly higher than that of the $^{12}CH_4$ formation, whereas on Co both rates are comparable; only at the very beginning of the reaction is $^{13}CH_4$ formed at a higher rate. On Ni the $^{12}CO_2$ formation is much slower than that of $^{12}CH_4$ (and $^{13}CH_4$); on Co the amounts of $^{12}CO_2$ and $^{12}CH_4$ are nearly the same. While on Ni water is formed upon methanation, no water was detected on Co in these initial stages of reaction and reaction conditions as described above. This indicates a relation between methanation and disproportionation. At low pressures and other conditions as in this paper, the stoichiometry of methanation is very near to $2CO + 2H_2 = CH_4 + CO_2$ (only at higher pressures is water formed as well).

Disproportionation of CO in the absence of hydrogen is of a comparable rate on Ni and Co but it is slower on Ru. It should

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be noticed that while with Ni and Ru the stoichiometry of disproportionation is exactly $2CO = C_s + CO_2$, on Co the number of CO_2 molecules detected in the gas phase indicates only the lower limit of the number of carbon atoms deposited because a small proportion of the oxygen atoms is retained by the Co film and not reduced during the experiment.

Analogous experiments with Ru at 300°C showed that also with this metal incorporation of the predeposited ^{13}C into $^{13}CH_4$ is possible. However, the results differed still more from those obtained with Ni: The $^{12}CH_4$ production was even faster here than that of the $^{13}CH_4$. The $^{12}CO_2$ production is again of a comparable rate with that of the $^{12}CH_4$ production. No water was detected upon reactions performed under the conditions described.

The results presented give a clear answer to the first question (see (a) above), namely, that with all metals studied up to now incorporation of the predeposited ^{13}C into $^{13}CH_4$ is possible. However, there is no definite answer as yet to the second question (b) above).

The difference between Ru, Co, and Ni can be explained in two ways:

(i) On Ni and Ru (two extremes) *different intermediates* are responsible for the CH_4 formation, viz., carbon on Ni and an oxygen-containing complex on Ru (no positive evidence for such complexes was found in this study, but in compliance with suggestions in the literature this could be something like Ru = CH·OH).

(ii) Carbon ^{13}C undergoes *deactivation* which is more important on Ru than on Ni (Ru > Co > Ni). On the other hand the supply of fresh ^{12}C by disproportionation of ^{12}CO is more important on Ru than on Ni. These two factors lead to a varying extent of incorporation of the predeposited ^{13}C into methane (Ni > Co > Ru).

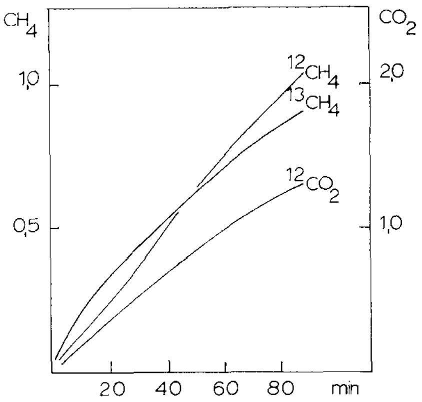

FIG. 1. Methanation on Co covered by ^{13}C. $^{13}CH_4$, $^{12}CH_4$, and $^{12}CO_2$ formed when a synthesis mixture is admitted to the surface covered by ^{13}C. For the calculation of these curves the primary MS data were plotted as continuous curves and evaluated for intervals of 1–3 min by a computer.

There are some indications that the explanation in (ii) should be favored. Kinetic pulse experiments at lower temperatures than in this paper (200°C) revealed less difference between Ni and Ru (*3*). Deactivation of the deposited carbon has been proven and studied by several authors (Ni (*3*, *5*), Fe (*6*, *7*)). Last but not least, the fact that at the conditions applied here the overall equation for the reaction is apparently $2CO + 2H_2 = CH_4 + CO_2$ (there is no detectable water formation) is support for a mechanism with carbon as an intermediary and favors an explanation as formulated in (ii) above.

Moreover, Van Barneveld (*8*) investigated how alcohols (oxygen-containing compounds) and olefines influence the production of higher hydrocarbons on Ni and Ru. Ruthenium did not show any preference in incorporating an oxygen containing compound as compared with Ni.

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