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LETTERS TO THE EDITORS

Activity Patterns in Methanation

When it appeared that the dissociation of CO could be a necessary step in the methanation reaction (*1–3*), some authors (see, e.g., Vannice (*4*) and Ponec and van Barneveld (*5*)) tried to rationalize the activity patterns of the metals in the Periodic System. In doing so, the authors of Ref. (*5*) divided the metals into three groups:

1. Metals which do not dissociate CO, such as the IB or IIB metals, and those which dissociate it only slowly, like Pd (and most probably Pt and Ir). These metals are inactive in the methanation reaction.
2. Metals which do dissociate CO, but form stable surface oxides. These oxides are hardly reducible at the temperature of the methanation reaction (500–600°K), so that the surface of these metals becomes covered by oxygen, and the activity of the catalyst decreases.
3. The group of metals which dissociate CO at the temperature of the methanation reaction and form surface oxides reducible under reaction conditions, namely Fe, Co, Ni, Ru, and Rh. These are the most active metals in the methanation reaction, and their order of activity depends among other things on the reaction conditions, because also factors such as the rate of carbon deactivation play a role.

Vannice (*4*) made predictions of which the results are similar to those reported by Ponec and van Barneveld (*5*). However, his basis was a completely different reaction mechanism, in which nondissociative chemisorption of CO takes place. In order to correlate the methanation activity, Vannice (*4*) used the heat of adsorption of CO as the correlation parameter. The similarity between the results of both predictions is to be expected, since the heats of adsorption of various gases on metals are mutually correlated (*6, 7*) and they can also be related to the heat of formation of surface oxides and carbides (*8*).

Whatever the correct correlation might be, according to both predictions Mo and W are expected to be poorly functioning methanation catalysts. However, recently Kelley *et al.* (*9*) reported that their W catalyst was about as active as Ni. If the discrepancy were confirmed both correlations mentioned above should be reconsidered. Because of the importance of reliable information on the activity patterns of metals, we decided to make a short study in order to compare the methanation activity of Mo, W, and Ni.

The catalysts have been prepared in the form of films by UHV sublimation of the metals. This procedure is known to be a suitable way to prepare clean metal surfaces, and the choice enabled an easy comparison with previous results on Ni films (*1*).

Prior to the evaporation of the metal from the sources by Joule heating, the metal filaments were thoroughly cleaned by a 16-h oxidation in 5×10^{-7} Torr of O_2 at a temperature of 1300°K. This oxidation step was reported to be suitable to remove impurities like S and C (*10*). This procedure was followed by a high-temperature outgassing up to the evaporation temperature in order to remove oxides. Indeed, a W filament cleaned in this way in a separate experiment, showed no contaminants detectable by Auger electron spectroscopic analysis. After the evaporation was finished, the clean metal films of a thickness of about 20 nm were annealed at 670°K during 1½ h. The surface area of the films was taken to be equal to their geometrical area; earlier experiments showed that the surface rough-

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ness factor of well sintered films does not differ very much from 1 (*11*).

All experiments were carried out at a relatively low pressure of 0.5 Torr in order to prevent diffusion limitations in the static reactor system used. The catalyst temperature in the experiments to be described below was 530°K, and where needed some additional data at 680°K are also presented.

In the first type of experiment, carbon was deposited on both metals by CO disproportionation. Assuming that the surface oxygen formed in this dissociative adsorption is at least partly removed by CO, the lower limit of the number of surface carbon atoms can be calculated from the number of CO_2 molecules being formed in the disproportionation reaction:

$$2\,CO \rightarrow C_s + CO_2.$$

With W, no formation of CO_2 could be observed, within the limits of detection. Since W is known to dissociate CO (*12*), evidently CO was unable to reduce the surface tungsten oxide. The upper limit for the rate of the Boudouard reaction on W is estimated to be about 3×10^9 molecules s^{-1} cm^{-2}. On Mo only small amounts of CO_2 were formed; the reaction rate of the Boudouard reaction at 520°K is estimated to be about 3×10^{10} molecules s^{-1} cm^{-2}, and at 680°K the reaction rate is 3.5×10^{11} molecules s^{-1} cm^{-2}. Since the dissociation of CO does not seem to be a problem, it is obviously the reduction of adsorbed oxygen by CO which is slow.

In the second type of experiment the carbon deposited onto the metal surface was hydrogenated by hydrogen, admitted to the reactor after evacuation of the CO. With W no formation of CH_4, or any higher hydrocarbon, and also no formation of H_2O was observed. From the limit of detection the reaction rate of surface carbon hydrogenation on W was estimated to be about 1×10^{10} molecules s^{-1} cm^{-2} at most, with an unknown amount of carbon atoms on the surface. With Mo, the formation of small amounts of CH_4 and again no formation of H_2O was observed. The reaction rate for the methanation of surface carbon on Mo was about 3×10^{10} molecules s^{-1} cm^{-2} at 520 and at 680°K (subsequent reactions on the same surface), with at least 3×10^{13} C atoms cm^{-2} present on the metal surface.

For comparison, the reaction rates of the Boudouard reaction and of the hydrogenation of the surface carbon on a Ni film prepared in the same apparatus, were at least 70 times as large (*1*). It should be remembered at this point that while on Ni the dissociation of CO needs some activation, on Mo and W it proceeds readily, even at room temperature (*12*).

In a last type of experiment a mixture of CO and H_2 (1:4) was admitted to a clean Mo film, in order to check whether under these reaction conditions the methanation reaction does occur. The reaction rate of the CH_4 formation was found to be low, about 3×10^{10} molecules s^{-1} cm^{-2}. The reaction rate with the CO/H_2 mixture and a Mo film after a CO disproportionation reaction was about 10 times as low as with a virgin film. This points again to an incomplete reduction, and a self-poisoning by oxygen of the catalyst surface in this reaction. The reaction rate for the methanation reaction from a CO/H_2 mixture over a Ni catalyst, under the same experimental conditions ((*1*) and this work) was about 2×10^{12} molecules s^{-1} cm^{-2} at 573°K.

According to all three aspects checked, Mo and even more so W, are worse functioning methanation catalysts than is Ni. This is in agreement with results obtained with powder catalysts (*13*). Also according to this reference, the order of activities is Ni > Mo (carbide) > Mo (metal) at 620°K, 1 atm total pressure and a H_2/CO ratio of 3.1. The question which arises now is what causes this discrepancy with the results of Kelley *et al.* (*9*).

Since we made the necessary checks by AES of the Mo and W filaments, and the evaporation has been performed at sufficient vacuum conditions, we believe that mere contamination of the surface of our films cannot be the cause of the difference in activity. This is also confirmed by the results of the experiments of the last type. Also a different structure of the surface cannot cause the difference, since the surface of well-tempered polycrystalline samples like films, filaments, and foils mainly consists of the most densely packed crystal faces (*14*). A possible reason for the high activity of the W catalyst of Kelley *et al.* (*9*) could be the presence of some undetected catalytic active component on the surface of their W ribbon, e.g., the Re of the thermocouple used in their experiment, or something similar.

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