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The Role of Hydrogen in the Reaction of Water with Surface Carbon to Form Methane

In the synthesis of methane from carbon monoxide and hydrogen the importance of an active form of surface carbon on such metals as Ni and Ru has been known for some time (*1*). Recently, however, Rabo *et al.* (*2*) have reported that this active carbon also reacts readily with water to form equimolar amounts of CO_2 and CH_4 according to reaction 1.

$$2C + 2H_2O \xrightarrow[\text{Ni,Co,Ru}]{300^\circ\text{C}} CH_4 + CO_2. \quad (1)$$

Since H_2 was not reported as an intermediate, the implication of this work is that there may be a *direct* reaction between water and surface carbon to form methane. The possibility of such a direct reaction becomes more attractive when one considers the observation by Cabrera *et al.* (*3*) that graphite which contains potassium as a catalyst reacts with water at ca. 250°C to produce methane, but no methane was observed when water was replaced by hydrogen.

On supported nickel the reaction of H_2 with the active form of surface carbon is known to be rapid at 300°C. Thus, if H_2 were formed as an intermediate, the results of Rabo *et al.* (*2*) could be explained without invoking a direct reaction between carbon and water to form methane. The purpose of this study was to determine whether the reaction of water with surface carbon indeed produced H_2, which is an intermediate in the formation of methane.

Reaction conditions closely approximating those of Rabo *et al.* (*2*) were adopted for this investigation. A recirculating batch reactor system constructed of Pyrex was used at moderate pressures and a stainless-steel reactor was employed at higher pressures. Analysis of the reactants and products was achieved by on-line gas chromatography using He as a carrier gas. In order to improve sensitivity H_2 was converted to H_2O over CuO before the gases entered the thermal conductivity detector.

A nickel–zirconia catalyst (88% Ni) was prepared by co-precipitation of the hydroxides from a basic solution of the nitrate salts (*2*). After filtration and drying the catalyst was oxidized in air for 2 h at 200°C, followed by 2 h at 400°C. The oxidized catalyst was then reduced under 700 Torr hydrogen at 450°C for 15 h. Other catalysts, except for the Engelhard 0.5% Ru/Al_2O_3, were prepared by impregnation from aqueous solutions of either the chloride or nitrate salts. Metal loadings are reported as weight percentage.

The number of surface metal atoms was determined by hydrogen chemisorption at 25°C, making the usual assumption that one hydrogen atom is chemisorbed per surface metal atom. The amount of H_2 adsorbed was plotted as a function of pressure over the range 50–250 Torr, and the linear portion of the plot was extrapolated to zero pressure. The extrapolated amount of adsorbed hydrogen at zero pressure, which is taken as the chemisorbed amount, is given in Table 1 for several of the catalysts used in these experiments.

In a typical experiment at moderate pressures the carbon layer was formed at 250°C by recirculating a 15% CO in He mixture (700 Torr) over the catalyst (0.25–8 g, 20–40 mesh) for 4 min. After evacuation of the gas phase to a residual pressure of 5×10^{-5} Torr a mixture of H_2O (25 Torr) and

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TABLE 1

Activity of Surface Carbon

Catalyst	Carbon (μmole C/g metal)	H_2 chemisorption (μmole H_2/g metal)	Initial rate of product formation[a] (μmole/g catalyst · min)				CH_4 turnover frequency (min^{-1})
			CH_4	CO_2	CO	H_2	
Nickel–zirconia	91	15.7	6.2	15.4	0.16	11.6	4.0×10^{-1}
K^+-impregnated nickel–zirconia	44	72.7	0.003	1.46	0.90	19.6	4.1×10^{-5}
10% Ni on SiO_2	570	550	3.6	13.4	0.6	3.2	6.5×10^{-2}
10% Ni on Harshaw Zr-304	1280	—	1.0	0.4	10.4	2.2	—
10% Co on SiO_2	300	87	0.05	0.46	1.56	0.28	5.7×10^{-3}
0.5% Ru on Al_2O_3 (Engelhard)	256	2260[b]	0.013	0.32	1.04	0.8	1.2×10^{-4}

[a] 370 μmole H_2O/g catalyst.

[b] Value supplied by Engelhard.

He (675 Torr) was introduced to the catalyst which was at 300°C.

The amount of surface carbon was estimated from the amount of gas-phase CO_2 which was produced by the Boudouard reaction ($2CO \rightarrow C + CO_2$). Good agreement was found between the amount of carbon determined in this manner and the amount of CO_2 produced by extended reaction of the carbided nickel–zirconia catalyst with O_2. The rate of carbon formation was initially fast (>40 μmole g^{-1} min^{-1}) but decreased after 0.5 min. After 5 min about 66 μmole of carbon/g of catalyst was

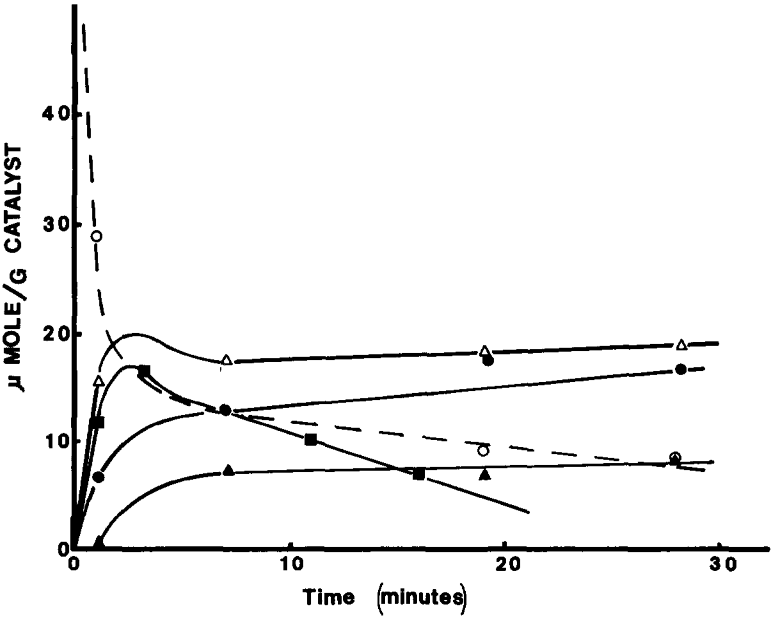

FIG. 1. Product distribution from carbon–water reaction on Ni–Zr catalyst: ○, H_2O; △, CO_2; ■, H_2; ●, CH_4; ▲, CO.

formed, which corresponds to an equivalent coverage of two monolayers. Surprisingly, only 30% of the surface nickel was deactivated for hydrogen chemisorption. This suggests that either the carbon forms multilayer structures on part of the surface or that it penetrates below the surface. At the temperatures used in these experiments we favor the latter alternative; however, we will continue to refer to this material as "surface carbon."

Upon exposing the carbided catalyst to the H_2O/He mixture at 300°C the results shown in Fig. 1 were obtained. Initially there was a very rapid uptake of H_2O which corresponds to 55% of the original amount of water in the gas phase. Experiments with pure nickel–zirconia (no carbon) indicate that this rapid uptake is due to adsorption. It is important to note that early in the reaction with surface carbon H_2 was formed more rapidly than CH_4. In addition, the concentration of H_2 soon went through a maximum, suggesting that it is an intermediate in the formation of CH_4. These results are more graphically demonstrated in Fig. 2a where the amount of product, H_2 or CH_4, is plotted as a function of the percentage of H_2O consumed. Greater amounts of hydrogen than methane were observed until more than 85% of the initial water had reacted. In a blank experiment it was demonstrated that when water vapor was passed over a clean nickel–zirconia catalyst, neither hydrogen nor methane was formed. The amount of CH_4, CO, and CO_2 formed in Fig. 1 corresponds to 87% of the surface carbon, and ultimately 96% of the carbon reacted upon further addition of water.

The order of the reaction with respect to H_2O was determined by adding different amounts of water to individual samples of equal mass which contained essentially the same amount of carbon. When up to 84 μmole H_2O/g catalyst was added no CH_4 was formed, but thereafter the initial rate of CH_4 formation exhibited a first-order dependence upon initial water concentration.

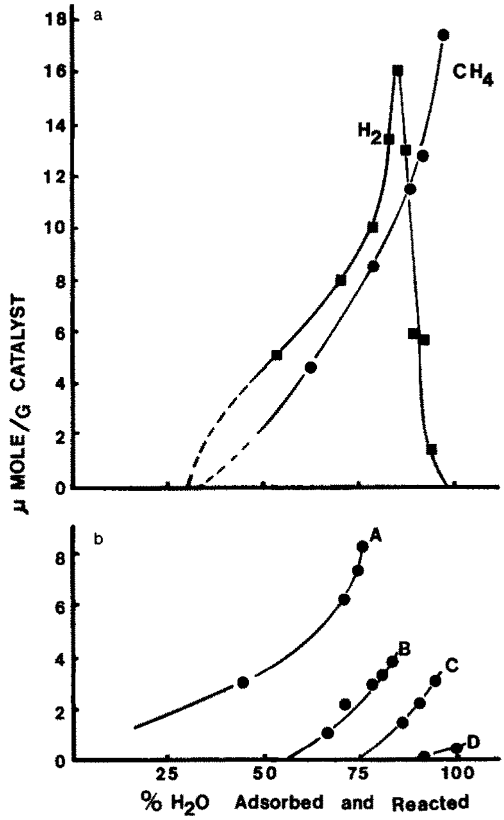

FIG. 2. Methane and hydrogen formation from carbon and water: (a) ■, H_2; ●, CH_4. (b) A, 10% Ni on SiO_2; B, 10% Co on SiO_2; C, 10% Ni on Harshaw Zr-304; D, 0.5% Ru on Al_2O_3.

On the basis of catalyst mass nickel–zirconia was clearly the most active material for the initial production of CH_4 and H_2 as indicated in Table 1. This phenomenon is even more pronounced when one compares the turnover frequencies for the formation of CH_4 over the several catalysts. The conversion to CH_4, depicted in Fig. 2, generally follows the trend in initial activity. The inactivity of supported ruthenium is not surprising in view of the sensitivity of this metal to poisoning by surface carbon (*4*).

The small amount of CO formed early in the reaction (Fig. 1 and Table 1), except for the 10% Ni on Harshaw Zr-304 catalyst, indicates that the water gas shift reaction ($CO + H_2O \rightleftharpoons H_2 + CO_2$) is not the primary source of H_2; however, this reaction may result in the formation of H_2 later in the reaction. The oxidation of Ni by water ($Ni + H_2O \rightleftharpoons NiO + H_2$) cannot be a significant source of H_2 if one considers that the *equilibrium* partial pressure of H_2 is only 0.01 Torr when the partial pressure of H_2O is 2 Torr (*5*). The value of 2 Torr H_2O is equivalent to 30 μmole/g catalyst in Fig. 1; at the corresponding time the H_2 partial pressure was 1.2 Torr. The small equilibrium amount of H_2 from the oxidation of Ni is consistent with the observation that no H_2 was detected when water vapor was passed over a clean nickel–zirconia catalyst. One must conclude, therefore, that most of the H_2 is formed by the direct reaction of H_2O with the surface carbon.

In order to determine the effect of potassium on the reaction a nickel–zirconia catalyst was impregnated with 2% by weight K as KNO_3, calcined in air at 420°C, and reduced under H_2 at the same temperature. This catalyst exhibited a 2.2-fold increase in hydrogen chemisorption, but had a drastic decrease in activity for methane formation as listed in Table 1. The origin of this decrease in activity is uncertain, but the results establish that unlike the case with graphite, potassium does not promote the formation of CH_4 from the reaction of carbon with H_2O on a nickel surface.

Finally, water at high pressures was reacted with surface carbon on nickel–zirconia in the stainless-steel batch reactor, without recirculation, and the products were expanded and analyzed after a predetermined time. The results are given in Table 2 for different amounts of water, but the same amount of surface carbon. Again, H_2 was formed in amounts comparable to or greater than the amount of methane after 10 min of reaction.

The results of this study confirm the conclusions of Rabo *et al.* (*2*) that surface carbon can be converted to methane using water as a source of hydrogen. Moreover, nickel–zirconia has superior activity for this reaction. The present work, however, provides evidence for sequential reactions in which H_2 is first formed and the methane is produced mainly by the usual hydrogenation of surface carbon, rather than by the direct reaction of water with carbon.

TABLE 2

Reactions of Carbon[a] and Water on Nickel–Zirconia Catalysts

Amount of water (mmole H_2O/g catalyst)	Product (μmole/g catalyst)			
	CH_4	CO_2	CO	H_2
44[b]	221	496	27	227
11	82	113	4	139

[a] The catalysts contained about 190 μmole surface carbon/g catalyst.

[b] This value corresponds to 8000 Torr of H_2O vapor.

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