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NOTES

Some Observations on the Kinetics of the Hydrogenation of Carbon Monoxide

For the hydrogenation of CO a positive order in hydrogen and a slightly negative or a zero order in carbon monoxide are generally reported (*1*). The negative (or zero) order in carbon monoxide is often explained by assuming a strong adsorption of carbon monoxide on the same sites as used by the hydrogen. It is then assumed that the surface is "almost totally" covered by carbon monoxide (*2–4*). The fact that the heat of adsorption of carbon monoxide on catalytically active metals is higher than that of hydrogen is used as an argument. From infrared studies performed under reaction conditions on a ruthenium catalyst Ekerdt and Bell (*5*) recently concluded that a nearly saturation coverage by carbon monoxide was reached under reaction conditions. From our own experiments in which the surface products on an unsupported cobalt catalyst after the reaction were stripped off by a hydrogen treatment we concluded that more than 95% of the surface (as determined from the adsorption of carbon monoxide at room temperature) was covered by carbon-containing species (*6*). In the following we will show that "zero order in carbon monoxide" can be obtained already with much lower coverage of carbon-containing species in equilibrium with gas-phase carbon monoxide than indicated above.

The formation of methane will be used as an example. The following symbolism will be adopted:

$*$	surface site
K_i	equilibrium constant for reaction (*i*)
k_i	rate constant for reaction (*i*)
p_{H_2}	partial pressure of H_2
p_{CO}	partial pressure of CO
θ_i	surface fraction based on total surface
θ'_i	surface fraction based on active surface
e	empty site

According to recently published results (*7–11*) the formation of methane can be best described by a reaction sequence such as:

$$H_2 + 2* \rightleftarrows 2H*, \quad (1)$$

$$CO + * \rightleftarrows CO*, \quad (2)$$

$$CO* + * \rightleftarrows C* + O*, \quad (3)$$

$$C* + xH* \rightarrow CH_x* + x*, \quad (4)$$

$$CH_x* + (4 - x)H* \rightleftarrows CH_4 + (5 - x)*, \quad (5)$$

$$O* + yH* \rightarrow H_yO* + y*, \quad (6)$$

$$H_yO* + (2 - y)H* \rightleftarrows H_2O + (3 - y)*, \quad (7)$$

i.e., the reaction proceeds via dissociatively adsorbed carbon monoxide and hydrogen. Kinetic results can be described by such a reaction sequence if the hydrogenation of surface carbon (Eq. (4)) is taken as the rate-determining step (*6*). The rate of methane formation is then

$$r_4 = k_4\theta'_C\theta'^x_H, \quad (8)$$

where θ'_C and θ'_H are the fractions of the active surface covered by carbon and hydrogen, respectively. Here the term "active surface" is meant to denote all the surface that is available for or taking part in the reversible adsorption reactions. It should be noted that these fractions remain the same irrespective of the active surface area, i.e., the fractions are independent of

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the total number of sites available for reactions (1) to (7).

To evaluate further the rate equation (8) we assume that the surface fractions of adsorbed hydrogen and oxygen are small compared to the fraction of empty sites. The first assumption is justified by the heat of adsorption for H_2 being lower than that for CO and the second one by the fact that reaction (4) is the rate-determining step, i.e., $k_4 \ll k_6$. Applying the Langmuir adsorption model we can say that of the surface fractions $\theta'_e + \theta'_C + \theta'_{CO} + \theta'_O + \theta'_H$ (= 1) the latter two can be ignored and with $\theta'_{carbon} = \theta'_C + \theta'_{CO}$ we have $\theta'_e = 1 - \theta'_{carbon}$ and thus

$$\theta'_H = (K_1 p_{H_2})^{1/2}(1 - \theta'_{carbon}). \qquad (9)$$

If we assume as a first approximation that the quantity of dissociatively adsorbed carbon monoxide (θ'_C) is linearly proportional to the surface coverage of molecularly adsorbed carbon monoxide (θ'_{CO}), the rate equation (8) is

$$r_4 = k_4(k'\theta'_{carbon}) [(K_1 p_{H_2})^{1/2}(1 - \theta'_{carbon})]^x. \qquad (10)$$

At constant hydrogen pressure the rate equation (10) can be transformed into

$$r_4 = k'_4\theta'_{carbon}(1 - \theta'_{carbon})^x. \qquad (11)$$

In Fig. 1 this rate is given as a function of the surface coverage of carbonaceous species, θ'_{carbon}, for different values of x (a possible interpretation of x is that it is the number of hydrogen atoms taking part in the rate-determining step). It can be seen that the required surface fractions, θ'_{carbon}, for a zero or negative order in carbon monoxide are ≥ 0.5, ≥ 0.33, and ≥ 0.25 for $x = 1$, 2, and 3, respectively. These values are far from "almost total" coverage. In fact still lower values are calculated with the rate equation (12)

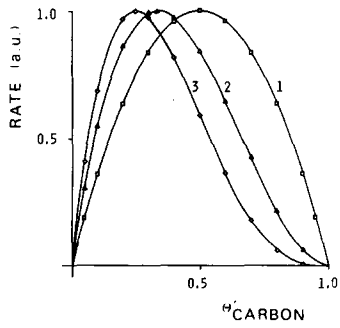

FIG. 1. The reaction rate (in arbitrary units) as a function of the surface coverage of carbonaceous species. (1) $x = 1$; (2) $x = 2$; (3) $x = 3$.

$$r_4 = k_4 \frac{(K_1 p_{H_2})^{x/2}}{1 + (K p_{CO})^{1/2}} \theta'_{carbon}(1 - \theta'_{carbon})^x. \qquad (12)$$

This equation, in which $K = (K_2/K_3) \cdot (k_4/k_6)$ and $x = y$, is derived from Eqs. (2), (3), and (4) without the assumption that a constant fraction of adsorbed CO is in a dissociated form, but that we have $\theta'_{carbon} = \theta'_C(1 + (K p_{CO})^{1/2})$. From Eq. (12) it can be seen that by increasing either K_2 or p_{CO}, both of which increase θ'_{carbon}, the reaction rate decreases.

The calculation also indicates that if the active surface were "almost totally" covered by carbon monoxide, much stronger negative orders in carbon monoxide than those found experimentally should be obtained.

In order to combine the calculations described above and the observations of the "almost totally" covered surface by carbon-containing species, we have to assume that there are two types of species:

(a) precursors of the rate-determining step, i.e., adsorbed carbon monoxide and surface carbon;

(b) all other (i.e., for the rate determination inactive) carbon-containing surface intermediates.

If the fraction of the total surface covered by the former species is denoted as θ_a and that by the latter as θ_b, the total surface coverage θ of carbonaceous species together, i.e.,

$$\theta = \theta_a + \theta_b, \qquad (13)$$

may easily form an "almost total" coverage.

TABLE 1

Fraction θ_a of the Catalyst Surface Covered by Active Carbon-Containing Species when the Reaction is Zero Order in CO

θ	θ_a		
	$x = 1$	$x = 2$	$x = 3$
0.90	0.10	0.050	0.033
0.95	0.05	0.025	0.017
0.99	0.01	0.005	0.003

On the basis of the calculations above, the surface coverage θ_a for a zero order in carbon monoxide with the value $x = 2$ is

$$\theta_a = 0.33(1 - \theta_b). \quad (14)$$

The value of θ_a can thus be calculated for a zero order in carbon monoxide for various values of θ and x. They are shown in Table 1.

We have included $x = 3$, realizing that the assumption $x = y$ must be invalid. Thus the results for $x = 3$ must be viewed as being indicative only.

The results suggest that only a small fraction of the catalyst surface is actively engaged in the hydrogenation of CO. This further suggests that the low turnover frequencies found for the Fischer–Tropsch synthesis (*1*) could be caused by a small number of sites which are active in the rate-determining step.

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