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LETTERS TO THE EDITORS

Comments on "The Kinetics of Methanation on Nickel Catalysts"

As far as mechanism of methanation is concerned a new model of intermediate was put forward by Araki and Ponec (*1*) in 1976. The main point is that the deposited carbon on the surface of the catalyst is the active intermediate which forms from dissociation of adsorbed CO. That is,

$$2\,CO + 2(\,) \rightarrow 2(CO) \rightarrow (C) + (CO_2).$$

Recently Sa Van Ho and Harriott (*2*) supported the carbon intermediate hypothesis but proposed another mechanism for formation of the carbon intermediate. They pointed out that, according to the reported data for activation energy or the rate of methanation, if carbon is an intermediate some steps other than simple dissociation of CO must be involved. So the modification they suggested was only to change the step of carbon formation. That is,

$$(CO) + 2(H) \rightarrow (C) + H_2O.$$

Also they proposed that this latter step was the slow step.

Though this mechanism is more reasonable than that of Araki and Ponec, the identification of the limiting step is doubted. If the formation of deposited carbon is a limiting step, it will be a problem to explain the deactivation of most methanation catalysts by deposited carbon. It might be better explained if the hydrogenation step were the slow one and then some of the active deposited carbon would become unreactive deposited carbon, since the active carbon is unstable (*3*). One of the hydrogenation steps might therefore be a reasonable limiting step.

If we consider that the step of (C) + 2(H) → (CH_2) is the slow step, then the mechanism would be the same as that of Sa Van Ho and Harriott, i.e.,

$$CO + (\,) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (CO), \qquad (1)$$

$$H_2 + 2(\,) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2(H), \qquad (2)$$

$$(CO) + 2(H) \xrightarrow{k_3} (C) + H_2O, \qquad (3)$$

$$\underline{(C) + 2(H) \xrightarrow{k_4} (CH_2)} \qquad (4)$$

$$(CH_3) + (H) \rightarrow (CH_4) \rightarrow CH_4 \qquad (5)$$

but the derived rate equation would be slightly different.

From (1) at equilibrium

$$k_1P_{CO}(1 - \theta_{CO} - \theta_H) = k_{-1}\theta_{CO}. \qquad (6)$$

Here k or k_{-1} is the constant of adsorption or desorption, P is the partial pressure of the gas, θ is the fraction of coverage of adsorbed gases.

From (6),

$$K_1P_{CO} = \frac{\theta_{CO}}{1 - \theta_{CO} - \theta_H}, \qquad K_1 = \frac{k_1}{k_{-1}}. \qquad (7)$$

From (2) at equilibrium,

$$k_2P_{H_2}(1 - \theta_{CO} - \theta_H)^2 = k_{-2}\theta_H{}^2, \qquad (8)$$

$$(K_2P_{H_2})^{1/2} = \frac{\theta_H}{1 - \theta_{CO} - \theta_H}, \qquad K_2 = \frac{k_2}{k_{-2}}. \qquad (9)$$

Combining (7) and (9),

$$\theta_{CO} = \frac{K_1P_{CO}}{1 + K_1P_{CO} + K_2^{1/2}P_{H_2}^{1/2}}, \qquad (10)$$

$$\theta_H = \frac{K_2^{1/2}P_{H_2}^{1/2}}{1 + K_1P_{CO} + K_2^{1/2}P_{H_2}^{1/2}}. \qquad (11)$$

Because (C) is an intermediate and using the steady-state method, θ_C can be evaluated

$$\frac{d(C)}{dt} = k_3(CO)(H)^2 - k_4(C)(H)^2 = 0, \qquad (12)$$

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$$\theta_C = (C) = \frac{k_3}{k_4}(CO) = \frac{k_3}{k_4}\theta_{CO}. \quad (13)$$

The limiting step is assumed to be step (4). Therefore the rate of methanation will be

$$r_{CH_4} = k_4\theta_C{\theta_H}^2 = k_4\frac{k_3}{k_4}\theta_{CO}{\theta_H}^2. \quad (14)$$

Substituting (10) and (11) into (14)

$$r_{CH_4} = k_3k_1k_2\frac{P_{CO}P_{H_2}}{(1 + K_1P_{CO} + K_2^{1/2}P_{H_2}^{1/2})^3}$$

$$= \text{Const.}\frac{P_{CO}P_{H_2}}{(1 + K_1P_{CO} + K_2^{1/2}P_{H_2}^{1/2})^3}. \quad (15)$$

This equation is similar to the one derived by Sa Van Ho and Harriott:

$$r_{CH_4} = kK_1K_2 \frac{P_{CO}P_{H_2}}{(1 + K_1P_{CO} + K_2P_{H_2})^2}. \quad (16)$$

The difference is only in the denominator.

It is difficult to see how (16) was derived, given that step (2) was written as a dissociative adsorption of hydrogen. It would seem that Eq. (16) should have the same denominator as Eq. (15).

Reported kinetics for the methanation reaction show a negative order with respect to P_{CO} and no retarding effect of hydrogen. Comparing the two rate equations, the denominator of Eq. (15) has a larger exponential number for P_{CO} and a smaller exponential number for P_{H_2}. Therefore it is suggested that Eq. (15) would represent the reported behavior better than Eq. (16).

REFERENCES

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