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The Catalytic Synthesis of Hydrocarbons from H_2/CO Mixtures over the Group VIII Metals: Comments on Methanation Kinetics

Vannice (*1*) proposed a kinetic rate expression for carbon monoxide hydrogenation to methane over Group VIII transition metals. Later, in another publication, Ollis and Vannice (*2*) made additional comments on the rate expression developed in (*1*). However, their only concern in (*2*) was the exponents of P_{H_2} and P_{CO}, X and Y, respectively. Since Vannice's kinetics and mechanism were being used until recently (*3*), we find it appropriate to make further comments on the capabilities and predictions of this methanation kinetics.

Our starting point is Eq. (8) of (*2*) that is,

$$r_{CH_4} = k_2 K_1^{0.5(1-y/2)} K_{CO}^{0.5(1-y/2)} K_{H_2}^{0.5(1+y/2)} P_{CO}^{0.5(1-y/2)} P_{H_2}^{0.5(1+y/2)}. \quad (1)$$

If the equilibrium adsorption coefficients K_{CO} and K_{H_2} are represented by

$$K_{CO} = K_{0,CO} \exp(-\Delta H_{a,CO}/RT) \quad (2)$$

and

$$K_{H_2} = K_{0,H_2} \exp(-\Delta H_{a,H_2}/RT), \quad (3)$$

where $\Delta H_{a,i}$ is the enthalpy of adsorption of species i, then Eqs. (1), (2), and (3) yield

$$\frac{\partial \ln r_{CH_4}}{\partial(-\Delta H_{a,CO})} = \frac{1}{RT} 0.5 \left(1 - \frac{y}{2}\right). \quad (4)$$

For the catalysts shown in Fig. 1 of (*1*), $y = 1$ or 2 except for Co where $y = 3$. Hence, with the only exception of Co, Eq. (4) yields

$$\frac{\partial \ln r_{CH_4}}{\partial(-\Delta H_{a,CO})} \geq 0, \quad (5)$$

where the inequality sign is valid for $y = 1$ and the equality sign is valid for $y = 2$. Equation (5) indicates that if we plot $\ln r_{CH_4}$ versus $(-\Delta H_{a,CO})$ we expect a line of positive or zero slope. This is not what Fig. 1 of (*1*) shows, because there clearly

$$\frac{\partial \ln r_{CH_4}}{\partial(-\Delta H_{a,CO})} < 0.$$

Therefore, the conclusion from this discussion is that the methanation kinetics developed in (*1, 2*) cannot predict the results shown in Fig. 1 of (*1*).

But, Eqs. (1)–(3) yield

$$\frac{\partial \ln r_{CH_4}}{\partial(-\Delta H_{a,H_2})} = \frac{1}{RT} 0.5 \left(1 + \frac{y}{2}\right) > 0 \quad (6)$$

which is in qualitative agreement with Fig. 4 of (*1*). Equation (6) indicates that as y increases, the slope of a plot of $\ln r_{CH_4}$ versus $(-\Delta H_{a,H_2})$ should increase. This may explain why the points corresponding to Co ($y = 3$) and Ru ($y = 4$) are off the correlation shown in Fig. 4 of (*1*).

In conclusion, we have shown that the methanation kinetics developed by Vannice (*1*) can predict the results shown in Fig. 4 of (*1*) but it cannot predict the results presented in Fig. 1 of (*1*).

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