JOURNAL OF CATALYSIS **38**, 514–515 (1975)

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

In an article by Vannice (*1*) a kinetic rate expression was developed for carbon monoxide hydrogenation to methane over group VIII transition metals. The measured rate form taken as [Eq. (1)]:

$$\text{rate} = k \cdot P_{H_2}{}^{X} \cdot P_{CO}{}^{Y} \qquad (1)$$

is compared with a model expression [Eq. (2)]:

$$\text{rate} = k' P_{H_2}{}^{n} P_{CO}{}^{[n-(y/2)]}, \qquad (2)$$

where y = number of hydrogen atoms involved in the rate determining step (RDS) [Eq. (3)]:

$$CHOH(ad) + y/2\ H_2(ad) \rightarrow CH_y(ad) + H_2O \qquad (3)$$

and n is the power law exponent for the approximation in [Eq. (4)]:

$$\frac{K \cdot P_{CO} \cdot P_{H_2}}{1 + K \cdot P_{CO} \cdot P_{H_2}} \sim (K\ P_{CO}P_{H_2})^{n}. \qquad (4)$$

Two implications of Eq. (4) are then that

(a) $0 \leqslant n \leqslant 1.0$ and

(b) $K\ P_{CO}P_{H_2}$ must be comparable to 1.0 if n is not near 1.0 or zero.

The values of n deduced from comparison of Eq. (3) with Eq. (2) were found to be greater than unity for 3 of the 10 alumina-supported metal catalysts.

Although Fe($n = 1.1$) and Co($n = 1.2$) have values of n near unity within experimental error, Ru($n = 1.6$) has a value of n well outside any experimental uncertainty. This is a violation of restriction (a) above. The particularly irregular behavior of Ru is removed if the assumption of quasi-equilibrium in step (IIIa) of reference (1) is voided and is then considered as a reversible step. This may be appropriate since the RDS was fastest on Ru and could make this rate comparable to that of the reverse reaction of step (IIIa).

However, the following discussion provides a much more unifying approach. The discrepancies with all three metals are eliminated by a slight modification of the original treatment.

Since $\theta_c = K\ P_{CO}P_{H_2}/(1 + K\ P_{CO}P_{H_2})$, the general expression for $(1 - \theta_c)$ consistent with restriction (b) above is:

$$(1 - \theta_c) = (1 + K\ P_{CO}P_{H_2})^{-1}$$

rather than the term $(1 - \theta_c) \simeq (K\ P_{CO}P_{H_2})^{-1}$. Then the hydrogen coverage, θ_{H_2}, is given by [Eq. (5)]:

$$\theta_{H_2} = \frac{K_{H_2}\ P_{H_2}}{1 + K\ P_{CO}P_{H_2}}$$

(neglecting $K_{H_2}P_{H_2}$ in the denominator)

$$= \frac{K_{H_2}\ P_{H_2}}{(K\ P_{CO}P_{H_2})} \cdot \frac{K\ P_{CO}P_{H_2}}{(1 + K\ P_{CO}P_{H_2})}$$

$$\simeq \frac{K_{H_2}\ P_{H_2}}{K P_{CO}P_{H_2}} (K\ P_{CO}P_{H_2})^{n}$$

$$= (K\ P_{CO}P_{H_2})^{n-1} K_{H_2}P_{H_2}, \qquad (5)$$

the rate of reaction then becomes [Eq. (6)]:

$$\begin{aligned} \text{rate} &= k_2 \cdot \theta_c \cdot (\theta_{H_2})^{y/2} \\ &= k_2[K\ P_{CO}P_{H_2}]^{n} [(K\ P_{CO}P_{H_2})^{n-1} K_{H_2}P_{H_2}]^{y/2} \\ &= k_2 K^{\{n+[(n-1)y/2]\}} K_{H_2}{}^{y/2} P_{CO}{}^{\{n+[(n-1)y/2]\}} P_{H_2}{}^{[n+ny/2]}. \end{aligned} \qquad (6)$$

The measured pressure exponents now are related to the parameters n and y by

TABLE 1

	X	Y	y	n	y^*	n^*	$\bar{X}^*$	Y^*
Pd	0.7	0.2	1.0	0.475	1	0.5	0.75	0.25
Pd	0.8	0.3	1.0	0.532	1	0.5	0.75	0.25
Ni	0.8	−0.3	2.2	0.38	2	0.5	1.0	0.0
Ir	1.0	0.1	2.2	0.475	2	0.5	1.0	0.0
Pd	1.0	0.0	2.0	0.50	2	0.5	1.0	0.0
Pt	0.8	0.0	1.6	0.445	2	0.5	1.0	0.0
Rh	1.0	−0.2	2.4	0.455	2	0.5	1.0	0.0
Fe	1.1	−0.1	2.4	0.50	2	0.5	1.0	0.0
Co	1.2	−0.5	3.4	0.445	3	0.5	1.25	−0.25
Ru	1.6	−0.6	4.4	0.50	4	0.5	1.5	−0.50

the expressions

$$X = n(1 + y/2),$$
$$Y = n(1 + y/2) - y/2 = X - y/2,$$

or

$$y = 2(X - Y), \tag{7a}$$
$$n = X/(1 + y/2), \tag{7b}$$

The values of y are identical to those used before since Eq. (7a) is unchanged from the original treatment. Whereas $n = X$ originally, under the present derivation $n = X/(1 + y/2)$ which leads to the values of y and n shown in Table 1. Now n is between 0 and 1.0 for all metals and appears to be nearly 0.5 for all cases. If n is fixed at exactly 0.5, the values of X and Y calculated (indicated by an asterisk) are given in the last two columns. The sum of absolute deviations between Y_{expt} and Y^* is 1.15 here vs 1.20 in the original paper (*1*), thus both simplified treatments give equal fit to the exponent Y_{expt}. The final form for the rate over all metals is that for $n = 0.5$ in Eq. (6) above:

$$\text{rate} = k_2[K^{[1-y/2]}K_{\text{H}_2}{}^{y}P_{\text{CO}}{}^{[1-y/2]}P_{\text{H}_2}{}^{[1+y/2]}]^{1/2}$$
$$= k_2\left(k \cdot P_{\text{CO}} \cdot P_{\text{H}_2}\left[\frac{K_{\text{H}_2}P_{\text{H}_2}}{K\ P_{\text{CO}}}\right]^{y/2}\right)^{1/2} \tag{8}$$

ACKNOWLEDGMENT

D. F. O. is pleased to thank the National Science Foundation (NSF-GK-38575).

REFERENCE

1. Vannice, M. A., *J. Catal.* **37**, 462 (1975).

David F. Ollis
Chemical Engineering Department
Princeton University
Princeton, New Jersey 08540

M. Albert Vannice
Corporate Research Laboratories
Exxon Research and Engineering Company
Linden, New Jersey 07036
Received November 25, 1974