# A Modified Kinetic Expression for the Methanation of Carbon Monoxide over Group VIII Metal Catalysts

In 1975, Vannice (*1*) published data for the methanation of carbon monoxide over a series of supported metal catalysts, fitting his rate data to an equation of the form:

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

He established a theoretical rate equation based on the assumption that the rate-determining step in the reaction was the interaction of adsorbed hydrogen atoms with CHOH species adsorbed on the surface:

CHOH(ads) + $y/2$ H$_2$(ads) →

$$\text{CH}_y(\text{ads}) + \text{H}_2\text{O}(\text{g}). \qquad (2)$$
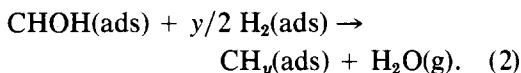
In a later note, Ollis and Vannice (*2*) presented a somewhat more satisfactory treatment in which they derived the expression

$$\text{Rate} = k_2 \left( k \cdot P_{CO} \cdot P_{H_2} \left[ \frac{K_{H_2} P_{H_2}}{K P_{CO}} \right]^{y/2} \right)^{1/2}, \qquad (3)$$

in which $k_2$ is the rate constant for reaction (2) above, $k$ is a constant, $K_{H_2}$ is the adsorption coefficient for H$_2$ on the surface and $K$ is that for CHOH(ads). In obtaining this equation, they used the commonly applied approximation to their Langmuir isotherm for CHOH(ads):

$$\frac{K P_{CO} P_{H_2}}{1 + K \cdot P_{CO} \cdot P_{H_2}} \simeq (K P_{CO} P_{H_2})^n, \qquad (4)$$
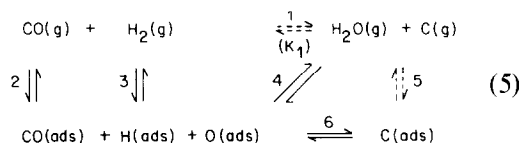
where $0 < n < 1$ and they also fixed $n = 0.5$.

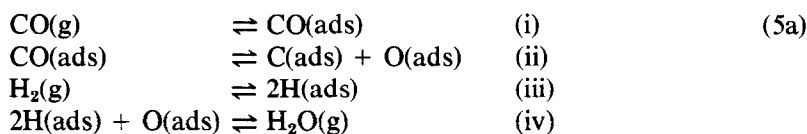Since 1975, it has become apparent that the previously accepted concept that CHOH species were intermediate in the methanation reaction is generally unfounded; see, for example, the review by Ponec (*3*) on the mechanisms of the methanation and Fischer–Tropsch reactions. It is now recognised, following the work of among others Araki and Ponec (*4*), Wentrcek *et al.* (*5*) and Rabo *et al.* (*6*) that the surface species taking part in the reaction are carbon atoms formed by the dissociative adsorption of carbon monoxide. That dissociative adsorption of CO occurs above about 80°C has been established, for example, using XPS, by Joyner and Roberts (*7*).

The object of this note is to show that a kinetic analysis of a scheme involving surface carbon atoms can be used to explain the results of Vannice and other workers (reviewed in Ref. (*8*)).

Consider the following equilibria and virtual equilibria (*9*):

$$
\begin{array}{ccc}
\text{CO(g)} + \text{H}_2\text{(g)} & \underset{(K_1)}{\rightleftharpoons} & \text{H}_2\text{O(g)} + \text{C(g)} \\
2 \updownarrow \quad\quad 3 \updownarrow & 4 \diagup \quad 5 \updownarrow & \\
\text{CO(ads)} + \text{H(ads)} + \text{O(ads)} & \underset{6}{\rightleftharpoons} & \text{C(ads)}
\end{array}
\qquad (5)
$$

In this scheme, virtual equilibria are shown as dotted arrows, actual equilibria as solid arrows. The virtual equilibria are included to enable a *pressure function* (*9*) to be established for the carbon atoms (see below). In step 1, H$_2$O(g) is shown on the right-hand side of the equilibrium. It is, however, in complete equilibrium with the surface species H(ads) and O(ads), through step (4). The sequence of events occurring may be depicted as follows:

$$CO(g) \qquad \rightleftharpoons CO(ads) \qquad (i) \qquad\qquad (5a)$$
$$CO(ads) \qquad \rightleftharpoons C(ads) + O(ads) \qquad (ii)$$
$$H_2(g) \qquad \rightleftharpoons 2H(ads) \qquad (iii)$$
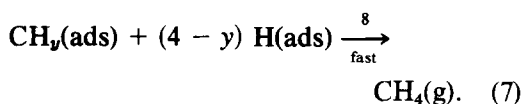$$2H(ads) + O(ads) \rightleftharpoons H_2O(g) \qquad (iv)$$

and by various combinations of these steps.

The slow step in the reaction is the subsequent reaction of C(ads) with $y$ atoms of H(ads) $(1 < y < 4)$:

$$C(ads) + y\ H(ads) \xrightarrow[\text{slow}]{7} CH_y(ads), \quad (6)$$
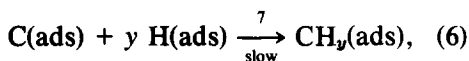
and this is followed by desorption of methane:

$$CH_y(ads) + (4 - y)\ H(ads) \xrightarrow[\text{fast}]{8}$$
$$CH_4(g). \quad (7)$$

Considering the virtual equilibrium (1) in Eq. (5), the pressure function for C(ads) is then $\dfrac{P_{CO}P_{H_2}}{P_{H_2O}}$.

Assuming a Langmuir isotherm for the adsorption of carbon on the surface:

$$\theta_c = \frac{b_c P_{CO} P_{H_2}/P_{H_2O}}{1 + b_c P_{CO} P_{H_2}/P_{H_2O}}, \quad (8)$$

where adsorption of other species is considered to be negligible and $b_c$ is an adsorption coefficient which is temperature dependent, including the heats of both steps (1) and (5) in Eq. (5). The rate of reaction is then given by:

$$\text{Rate} = k\theta_c \cdot \theta_H{}^y. \quad (9)$$

The hydrogen coverage, $\theta_H$, will depend on $P_{H_2}{}^{1/2}$ and will be given by a Langmuir isotherm of the form:

$$\theta_H = \frac{b_H P_{H_2}{}^{1/2}}{(1 + b_c P_{CO} P_{H_2}/P_{H_2O})}, \quad (10)$$

where the hydrogen is adsorbed competitively on the same sites as the carbon and the adsorption of hydrogen and other species is negligible compared with that of carbon.

Combining Eqs. (8), (9), and (10),

$$\text{Rate} = \frac{R \cdot B_c \cdot b_H{}^y \cdot P_{CO} P_{H_2}^{(1+y/2)}/P_{H_2O}}{(1 + b_c P_{CO} P_{H_2}/P_{H_2O})^{(1+y)}}$$
$$(11)$$

This expression assumes that only carbon is adsorbed on the surface to any appreciable extent and that the coverages of molecularly adsorbed carbon monoxide and hydrogen are small in comparison with that of the carbon. If the adsorption of either of these is appreciable, then appropriate terms will have to be included in the denominator. Equation (11) allows for the occurrence of a maximum in the rate of the methanation reaction at lower partial pressures of CO, as found by van Herwijnen et al. (10); it is not possible because of the lack of data on the partial pressures of water to test quantitatively the fit of Eq. (11) to their data but a semi-quantitative fit has been achieved. In what follows, the situation at intermediate partial pressures will be considered in order to derive a power rate expression equivalent to that derived by Ollis and Vannice (2). Multiplying Eq. (11) top and bottom by $P_{CO}{}^y \cdot P_{H_2}{}^{y/2} \cdot P_{H_2O}{}^{-y}$,

$$\text{Rate} = k \cdot b_c \cdot b_H{}^y$$

$$\cdot \frac{P_{CO}^{(1+y)} P_{H_2}^{(1+y)}/P_{H_2O}^{(1+y)}}{(1 + b_c P_{CO} P_{H_2}/P_{H_2O})^{(1+y)}}$$

$$\cdot \frac{P_{H_2O}{}^y}{P_{CO}{}^y P_{H_2}{}^{y/2}}. \quad (12)$$

With the approximation of Eq. (4),

$$\text{Rate} \approx k b_H{}^y (b_c P_{CO} P_{H_2}/P_{H_2O})^{(1+y)n}$$

$$\cdot \frac{P_{H_2O}{}^y}{b_c{}^y P_{CO}{}^y P_{H_2}{}^{y/2}} \quad (13)$$

which reduces to

$$\text{Rate} \approx k' P_{CO}^{\{n+y(n-1)\}}$$
$$P_{H_2}^{\{n+y(n-1/2)\}} P_{H_2O}^{-\{n+y(1-n)\}}, \quad (14)$$

where $k'$ is a constant including various powers of $k$, $b_c$, and $b_H$. Depending on the values of $n$ and $y$, this expression allows for a variety of different pressure dependencies. These are shown in Fig. 1 which illustrates the variation of the exponents for CO, $H_2$ and $H_2O$, as a function of n, for different values of y. It will be seen that a wide variety of exponents are permitted, ranging from about $-3$ to $+1$ for CO and from about $-1$ to $+2$ for $H_2$. The expression in Eq. (14) requires that the exponent in $H_2$ is $y/2$ greater than that in CO, which is the same requirement as the modified expression of Ollis and Vannice (2) shown in Eq. (3) for $n = \frac{1}{2}$. The obvious difference between the equations, apart from the more likely applicability of the model, is that Eq. (14) includes a term for the dependence on water pressure, not allowed for in Eq. (2). None of the work reviewed by Vannice (8) appears to demonstrate a dependence of the rate on water partial pressure; however, it is most unlikely that the experiments have been designed to show up such a dependence.

Several examples of the applicability of Eq. (14) will now be considered. For a 5% Ni/$\eta$-Al$_2$O$_3$ catalyst, Vannice (1, 11) gives the following kinetic expression:

$$\text{Rate} \propto P_{CO}^{-0.3} \cdot P_{H_2}^{0.8}. \qquad (15)$$

For other Ni catalysts (11), the exponents are slightly different, ranging from $-0.5$ to $-0.2$ for CO and from 0.6 to 0.8 for $H_2$. If values of $n = 0.57$ and $y = 2$ are inserted in Eq. (14), good agreement with Eq. (15) is obtained:

$$\text{Rate} \propto P_{CO}^{-0.3} P_{H_2}^{0.7} P_{H_2O}^{0.3}. \qquad (16)$$

It should be noted that the exponent $H_2O$ is small and therefore, as the kinetic measurements are generally carried out under differential conditions (i.e., product water $\sim 0$), the effect of water on the rate of reaction would be negligible. The results obtained by Vannice for other metals (1) are also explicable by Eq. (14). It is well
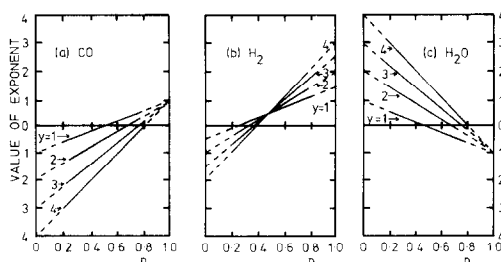


FIG. 1. The values of the exponents in Eq. (14) for (a) CO, (b) $H_2$ and (c) $H_2O$ as a function of $n$ for different values of $y$.

established that CO dissociation occurs readily on Ni (4), Co (12) and Ru (12) and probably also occurs relatively easily on Pd, Ir, Pt and Rh (13). Hence, the model proposed here is likely to be tenable for all these metals. With iron, the metal converts to a mixture of carbide, oxide and metal, and so the picture may be less clear (14). However, the results of Vannice (1) for a 5% Ru/Al$_2$O$_3$ catalyst are consistent with a value of $y = 4$; this requires that the rate-determining step involves the reaction of $C$(ads) with four hydrogen atoms, which seems improbable. Similarly, in the results of other workers summarized by Vannice (8), the only data which neither Eq. (3) nor Eq. (14) explain are those for a 1.5% Ru/Al$_2$O$_3$ catalyst reported by Dalla Betta et al. (14):

$$\text{Rate} \propto P_{CO}^{-1.1} P_{H_2}^{1.8}. \qquad (17)$$

It is therefore possible that, in the case of Ru, the rate determining step is different from that suggested here. It will be shown elsewhere (15) that the theory developed here can be used to explain results obtained, using a thermobalance as a differential microreactor, for the methanation reaction at atmospheric pressure over a commercial Ni/Al$_2$O$_3$ catalyst. In the treatment of the results, due allowance is made for the partial pressure of product water. As the applicability of this model depends critically on whether or not a term for the partial pressure of water enters into the

kinetic expression, further work on this point is in progress.

## REFERENCES

1. Vannice, M. A., *J. Catal.* **37**, 449 (1975).
2. Ollis, D. F., and Vannice M. A., *J. Catal.* **38**, 514 (1975).
3. Ponec, V., *Catal. Rev.* **18**, 151 (1978).
4. Araki, M., and Ponec, V., *J. Catal.* **44**, 439 (1976).
5. Wentrcek, P. R., Wood, B. J., and Wise, H., *J. Catal.* **43**, 363 (1976).
6. Rabo, J. A., Risch, A. P., and Poutsma, M. L., *J. Catal.* **53**, 295 (1978).
7. Joyner, R. W., and Roberts, M. W., *J. Chem. Soc., Faraday Trans., I* **70**, 1819 (1974).
8. Vannice, M. A., *Catal. Rev.* **14**, 153 (1976).
9. Kemball, C., *Disc. Faraday Soc.* **41**, 190 (1966).
10. Van Herwijnen, T., van Doesburg, H., and de Jong, W. A., *J. Catal.* **28**, 391 (1973).
11. Vannice, M. A., *J. Catal.* **44**, 152 (1976).
12. Sachtler, J. W. A., Kool, J. M., and Ponec, V., *J. Catal.* **56**, 284 (1979).
13. Ponec, V., and van Barneveld, W. A., *Ind. Eng. Chem., Prod. Res. Dev.* **18**, 268 (1979).
14. Dalla Betta, R. A., Piken, A. G., and Shelef, M., *J. Catal.* **35**, 54 (1974).
15. Ross, J. R. H., and Sarkar, J., to be published.

JULIAN R. H. ROSS

*School of Chemistry*
*University of Bradford*
*Bradford BD7 1DP*
*United Kingdom*