JOURNAL OF CATALYSIS 79, 281–285 (1983)

A Study of the Kinetics and Mechanisms of Heterogeneously Catalyzed Reactions with Power Rate Laws

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Received April 28, 1982; August 31, 1982

A new approach to the study of the kinetics and mechanisms of heterogeneously catalyzed reactions with power rate laws is discussed and applied to two reactions. This method may suggest experiments that can discriminate among rival kinetic mechanisms for this class of reactions. It can also provide information on whether assumptions and approximations usually made are justified.

INTRODUCTION

When kinetic data are obtained, they are fitted by a reaction rate expression. Then many mechanisms are tested until we obtain one that satisfactorily explains the experimental observations (*1*, *2*).

In many cases data are fitted in the form of a power rate law. Such examples are the carbon monoxide hydrogenations to methane (*3*, *4*) and to methanol (*5*). The kinetics and the mechanisms of these reactions were studied with an approach that involves "reasonable" assumptions, approximations, and reaction steps. This methodology leads to power rate laws that cannot predict any possible variations of an exponent of a partial pressure under varying conditions. Also, this approach can hardly provide any information that may lead to further discriminatory experiments among candidate mechanisms.

The purpose of this paper is to discuss another approach to the kinetics and mechanisms of reactions in heterogeneous catalysis in the case of power rate laws. This approach can suggest further experiments that can discriminate among rival mechanisms, predict changes of exponents under varying conditions (*5*), and provide information on whether assumptions, approximations, and/or reaction steps are reasonable (*6*).

METHOD–DISCUSSION

Let us assume that some data of a reaction are fitted by a power rate law of the form

$$r = k_0 \exp(-E/RT) \prod_{i=1}^{n} P_i^{X_i}, \qquad (1)$$

where $\prod_{i=1}^{n} P_i^{X_i} = P_1^{X_i} \cdot P_2^{X_2} \cdot \ldots P_n^{X_n}$. It is easily seen that Eq. (1) yields

$$\frac{\partial \ln r}{\partial \ln P_i} = X_i \qquad (2)$$

and

$$\frac{\partial \ln r}{\partial\left(-\frac{1}{RT}\right)} = E. \qquad (3)$$

Equations (2) and (3) are the only ones we use without any assumptions or approximations. To show the importance of Eq. (2) (and Eq. (3)), we consider two heterogeneously catalyzed reactions.

Reaction 1: Carbon monoxide hydrogenation to methane. Consider the methanation reaction mechanism proposed by Vannice (*3*),

$$\mathrm{CO} + \mathrm{S} \overset{K_{\mathrm{CO}}}{\longleftrightarrow} \mathrm{CO{-}S}, \qquad (4)$$

$$\mathrm{H_2} + \mathrm{S} \overset{K_{\mathrm{H_2}}}{\longleftrightarrow} \mathrm{H_2{-}S}, \qquad (5)$$

0021-9517/83/020281-05$03.00/0

$$\text{CO–S} + \text{H}_2\text{–S} \overset{K_1}{\longleftrightarrow} \text{CHOH–S} + \text{S}, \qquad (6)$$

$$\text{CHOH–S} + \frac{y}{2}\,\text{H}_2\text{–S} \xrightarrow{k_2} \text{CH}_y\text{–S} + \text{H}_2\text{O}, \qquad (7)$$

and

$$\text{CH}_y\text{–S} + \text{H}_2 \xrightarrow{\text{rapid}} \text{CH}_4, \qquad (8)$$

where equilibrium is assumed for the first three reaction steps and Eq. (7) is the rate-determining step. Since Eqs. (4)–(6) are assumed to be in equilibrium, we obtain

$$\theta_{\text{CO}} = K_{\text{CO}} P_{\text{CO}} \theta_{\text{S}}, \qquad (9)$$

$$\theta_{\text{H}_2} = K_{\text{H}_2} P_{\text{H}_2} \theta_{\text{S}}, \qquad (10)$$

and

$$\theta_{\text{CHOH}} = K_1 K_{\text{CO}} K_{\text{H}_2} P_{\text{CO}} P_{\text{H}_2} \theta_{\text{S}}. \qquad (11)$$

Since $\sum_j \theta_j = 1$, Eqs. (9)–(11) yield

$$\theta_{\text{S}} = (1 + K_{\text{CO}} P_{\text{CO}} + K_{\text{H}_2} P_{\text{H}_2} + K_1 K_{\text{CO}} K_{\text{H}_2} P_{\text{CO}} P_{\text{H}_2})^{-1}. \qquad (12)$$

The rate-determining step, Eq. (7), yields the following rate expression for the methane production,

$$r_{\text{CH}_4} = k_2\, \theta_{\text{CHOH}}\, \theta_{\text{H}_2}{}^{y/2},$$

which, from Eqs. (10)–(12), becomes

$$r_{\text{CH}_4} = \frac{k_2 K_1 K_{\text{CO}} K_{H_2}^{1+y/2} P_{\text{CO}} P_{\text{H}_2}^{1+y/2}}{(1 + K_{\text{CO}} P_{\text{CO}} + K_{\text{H}_2} P_{\text{H}_2} + K_1 K_{\text{CO}} K_{\text{H}_2} P_{\text{CO}} P_{\text{H}_2})^{1+y/2}} \qquad (13)$$

Data were fitted by a power rate law of the form

$$r_{\text{CH}_4} = k_0' \exp(-E_{\text{m}}/RT) P_{\text{H}_2}{}^X P_{\text{CO}}{}^Y, \qquad (14)$$

where X and Y were determined experimentally.

One approach in obtaining Eq. (14) from Eq. (13) is the method discussed by Vannice *et al.* (*3, 4*). Here we use Eq. (2) (and Eq. (3)). Equations (2), (13), and (14) yield

$$X = \frac{\partial \ln r_{\text{CH}_4}}{\partial \ln P_{\text{H}_2}} = \frac{P_{\text{H}_2}}{r_{\text{CH}_4}} \frac{\partial r_{\text{CH}_4}}{\partial P_{\text{H}_2}} = \frac{\left(1 + \frac{y}{2}\right)(1 + K_{\text{CO}} P_{\text{CO}})}{1 + K_{\text{CO}} P_{\text{CO}} + K_{\text{H}_2} P_{\text{H}_2} + K_1 K_{\text{CO}} K_{\text{H}_2} P_{\text{CO}} P_{\text{H}_2}} \qquad (15)$$

and

$$Y = \frac{\partial \ln r_{\text{CH}_4}}{\partial \ln P_{\text{CO}}} = \frac{1 + K_{\text{H}_2} P_{\text{H}_2} - \frac{y}{2}(K_{\text{CO}} P_{\text{CO}} + K_1 K_{\text{CO}} K_{\text{H}_2} P_{\text{CO}} P_{\text{H}_2})}{1 + K_{\text{CO}} P_{\text{CO}} + K_{\text{H}_2} P_{\text{H}_2} + K_1 K_{\text{CO}} K_{\text{H}_2} P_{\text{CO}} P_{\text{H}_2}}. \qquad (16)$$

Thus, we have two equations and the "unknown" quantities y, $K_{\text{CO}} P_{\text{CO}}$, $K_{\text{H}_2} P_{\text{H}_2}$, and $K_1 K_{\text{CO}} K_{\text{H}_2} P_{\text{CO}} P_{\text{H}_2}$. Hence we can eliminate one of the unknowns, say, $K_1 K_{\text{CO}} K_{\text{H}_2} P_{\text{CO}} P_{\text{H}_2}$, as follows: Eqs. (15) and (16) yield

$$1 + \frac{y}{2} = \frac{X(1 + K_{\text{CO}} P_{\text{CO}} + K_{\text{H}_2} P_{\text{H}_2} + K_1 K_{\text{CO}} K_{\text{H}_2} P_{\text{CO}} P_{\text{H}_2})}{1 + K_{\text{CO}} P_{\text{CO}}}$$

$$= \frac{(1 - Y)(1 + K_{\text{CO}} P_{\text{CO}} + K_{\text{H}_2} P_{\text{H}_2} + K_1, K_{\text{CO}} K_{\text{H}_2} P_{\text{CO}} P_{\text{H}_2})}{K_{\text{CO}} P_{\text{CO}} + K_1 K_{\text{CO}} K_{\text{H}_2} P_{\text{CO}} P_{\text{H}_2}},$$

which yields

$$K_1K_{CO}K_{H_2}P_{CO}P_{H_2} = \frac{1 - Y}{X} + \frac{1 - Y - X}{X} K_{CO}P_{CO}, \quad (17)$$

because $1 + K_{CO}P_{CO} + K_{H_2}P_{H_2} + K_1K_{CO} K_{H_2}P_{CO}P_{H_2}$ is always positive. Now Eqs. (15)–(17) yield

$$y = -2Y + 2X\lambda, \quad (18)$$

where

$$\lambda \equiv \frac{1 + K_{H_2}P_{H_2}}{1 + K_{CO}P_{CO}}. \quad (18I)$$

Notice that Eqs. (15)–(18) were obtained with no approximations or further assumptions, once Vannice's mechanism was assumed.

Equation (15) yields $\partial X/\partial P_{H_2} < 0$. This suggests that under constant P_{CO} and T, X decreases when P_{H_2} increases. Equation (16) yields $\partial Y/\partial P_{CO} < 0$. This suggests that under constant P_{H_2} and T, Y decreases when P_{CO} increases. Also, under a constant ratio P_{H_2}/P_{CO} and temperature, it can be shown that $\partial X/\partial P_{tot} < 0$ and $\partial Y/\partial P_{tot} < 0$. These indicate that at these conditions, X and Y decrease when the total pressure, P_{tot}, increases. Hence Eqs. (15) and (16) suggest a number of further experiments, whose results may support, modify, or reject Vannice's mechanism.

We have shown some of the advantages of the method we introduced in the beginning of this section. Now we are going to discuss Vannice's results in the context of the methodology we introduced earlier.

Vannice's assumptions were that CHOH–S was the dominant adsorbed species on the surface and that $K_{H_2}P_{H_2} \ll 1$ and $K_{CO}P_{CO} \ll 1$. Hence it was

$$1 + K_{CO}P_{CO} + K_{H_2}P_{H_2} + K_1K_{CO}K_{H_2}P_{CO}P_{H_2} \approx 1 + K_1K_{CO}K_{H_2}P_{CO}P_{H_2}.$$

These and Eqs. (15) and (16) yield

$$K_1K_{CO}K_{K_2}P_{CO}P_{H_2} = \frac{1 - Y}{X} \quad (17a)$$

and

$$y = -2Y + 2X, \quad (18a)$$

because $\lambda = 1$ in this case. In Table 1, we summarize the values of y obtained from Eqs. (17) and (17a) and the values of $K_1K_{CO}K_{H_2}P_{CO}P_{H_2}$ obtained from Eqs. (18) and (18a), for the catalysts studied and reported in (*3*). In Table 1 we observe that the y values for Pt/Al_2O_3, 1.58, and Rh/Al_2O_3, 2.48, do not conclusively indicate whether y is equal to 1 or 2 for the first catalyst and to 2 or 3 for the second one. Also, Table 1 indicates that the quantity $K_1K_{CO}K_{H_2}P_{CO}P_{H_2}$ and hence the surface coverage

$$\theta_{CHOH} = \frac{K_1K_{CO}K_{H_2}P_{CO}P_{H_2}}{1 + K_1K_{CO}K_{H_2}P_{CO}P_{H_2}}$$

TABLE 1

Values of y and $K_1K_{CO}K_{H_2}P_{CO}P_{H_2}$ Obtained through Our Approach and Vannice's Approach

Catalyst	y	$y \mid$ Vann.	$K_1K_{CO}K_{H_2}P_{CO}P_{H_2}$	$K_1K_{CO}K_{H_2}P_{CO}P_{H_2} \mid$ Vann.
Pd/SiO_2	$-0.30 + 1.42\lambda$	1.12	$1.20 + 0.20\ K_{CO}P_{CO}$	1.20
Pd/H-Y zeolite	$-0.60 + 1.68\lambda$	1.08	$0.83 - 0.17\ K_{CO}P_{CO}$	0.83
Ni/Al_2O_3	$0.62 + 1.44\lambda$	2.06	$1.70 + 0.70\ K_{CO}P_{CO}$	1.70
Ir/Al_2O_3	$-0.20 + 1.92\lambda$	1.72	$0.94 - 0.06\ K_{CO}P_{CO}$	0.94
Pd/Al_2O_3	$-0.06 + 2.06\lambda$	2.00	$0.94 - 0.06\ K_{CO}P_{CO}$	0.94
Pt/Al_2O_3	$-0.08 + 1.66\lambda$	1.58	$1.16 + 0.16\ K_{CO}P_{CO}$	1.16
Rh/Al_2O_3	$0.40 + 2.08\lambda$	2.48	$1.15 + 0.15\ K_{CO}P_{CO}$	1.15
Fe/Al_2O_3	$0.10 + 2.28\lambda$	2.38	$0.92 - 0.08\ K_{CO}P_{CO}$	0.92
Co/Al_2O_3	$0.96 + 2.44\lambda$	3.40	$1.21 + 0.21\ K_{CO}P_{CO}$	1.21
Ru/Al_2O_3	$1.20 + 3.20\lambda$	4.40	1.00	1.00

has a constant value at any temperature. In particular, θ_{CHOH} is approximately equal to 0.5 for most catalysts. This suggests that Vannice's assumption $\theta_S = (K_1 K_{CO} K_{H_2} P_{CO} P_{H_2})^{-1}$ is not justified, because in his case it is

$$\theta_S = \frac{1}{1 + K_1 K_{CO} K_{H_2} P_{CO} P_{H_2}}$$

and $K_1 K_{CO} K_{H_2} P_{CO} P_{H_2} \approx 1$ (Table 1).

Similar analysis can be done with Eqs. (3), (13), and (14), and the apparent activation energy E_m can be expressed as a function of the heats of adsorption of CO and H_2, the activation energies E_1 and E_2, and the partial pressures of CO and H_2.

Reaction 2: Carbon monoxide hydrogenation to methanol. Lunsford *et al.* (*5*) recently proposed the following mechanism for this reaction over supported Palladium catalysts,

$$2H_2 + S \overset{K_I}{\longleftrightarrow} 4H\text{–}S, \qquad (19)$$

$$CO + S \overset{K_{II}}{\longleftrightarrow} CO\text{–}S, \qquad (20)$$

$$4H\text{–}S + SO\text{–}S \xrightarrow{k_r} CH_3OH + 2S, \qquad (21)$$

where adsorption–desorption equilibrium is assumed for Eqs. (19) and (20). These equilibria yield

$$\theta_{4H} = K_I P_{H_2}{}^2 \theta_S \qquad (22)$$

and

$$\theta_{CO} = K_{II} P_{CO} \theta_S. \qquad (23)$$

Therefore, the rate of formation of methanol is

$$r_{CH_3OH} = k_r \theta_{4H} \theta_{CO}$$
$$= k_r K_I K_{II} \frac{P_{H_2}{}^2 \mathrm{P}_{CO}}{(1 + K_I P_{H_2}{}^2 + K_{II} P_{CO})^2}. \qquad (24)$$

The same authors (*5*) fitted their data with a power rate law of the form

$$r_{CH_3OH} = k_0'' \exp(-E_a/RT) P_{H_2}{}^{\bar{X}} P_{CO}{}^{\bar{Y}}, \qquad (25)$$

where $\bar{X}$ and $\bar{Y}$ were determined experimentally.

Let us follow the procedure we used for the previous reaction. Equations (2), (24), and (25) yield

$$\bar{X} = \frac{2(1 - K_I P_{H_2}{}^2 + K_{II} P_{CO})}{1 + K_I P_{H_2}{}^2 + K_{II} P_{CO}} \qquad (26)$$

and

$$\bar{Y} = \frac{1 + K_I P_{H_2}{}^2 - K_{II} P_{CO}}{1 + K_I P_{H_2}{}^2 + K_{II} P_{CO}}. \qquad (27)$$

Equation (26) yields $\partial \bar{X}/\partial P_{H_2} < 0$ and $\partial \bar{X}/\partial P_{CO} > 0$. These suggest that under constant P_{CO} and T, $\bar{X}$ increases when P_{H_2} decreases, and under constant P_{H_2} and T, $\bar{X}$ increases when P_{CO} increases. Similarly, Eq. (27) implies $\partial \bar{Y}/\partial P_{H_2} > 0$ and $\partial \bar{Y}/\partial P_{CO} < 0$. These suggest further discriminatory experiments, whose results will support, modify, or reject the mechanism proposed in (*5*). Also, under constant ratio P_{H_2}/P_{CO} and temperature, it can be shown that $\partial \bar{X}/\partial P_{tot} < 0$ and $\partial(\bar{X} + \bar{Y})/\partial P_{tot} < 0$. Lunsford *et al.* (*5*) have found experimentally that $\bar{X}$ and $\bar{X} + \bar{Y}$ were decreased when they increased the total pressure. Hence these results corroborate their mechanism. However, notice that Eq. (26) implies $\bar{X} \leq 2$, and Eq. (27) yields $\bar{Y} \geq -1$ under any conditions for the mechanism described before. Since the uncertainties for the experimental values of $\bar{X}$ and $\bar{Y}$ were not reported in (*5*), we could not conclude whether these experimental values were within the limits of the bounds of $\bar{X}$ and $\bar{Y}$ reported above.

CONCLUSION

We introduced a new approach to studying the kinetics and mechanisms of heterogeneously catalyzed reactions, whose rate expressions were in the form of a power law. This approach may suggest further discriminatory experiments among rival kinetic mechanisms and may check whether the assumptions or approximations made are justified.

Global reaction kinetics do not provide a good way to establish reaction mechanisms for heterogeneously catalyzed reactions. Also, a preliminary agreement between reaction kinetics and a proosed mechanism may be misleading and may result in a premature acceptance of a mechanism. Hence a justification of assumptions made and discriminatory experiments among rival reaction mechanisms are required. The need for such experiments is particularly important for reaction mechanisms that include at least one lumped step as an elementary reaction.

APPENDIX: NOTATION

E, E_m, E_a	Activation energies
k_0, k_0', k_0''	Preexponential factors
k	Rate constant
K	Equilibrium constant
P_i	Partial pressure of the species i
P_{tot}	Total pressure
R	Universal gas constant
r	Reaction rate
T	Temperature
X, $\bar{X}$	Exponent of the partial pressure of H_2 in a power rate law
X_i	Exponent of the partial pressure of species i (Eq. (1))
Y, $\bar{Y}$	Exponent of the partial pressure of CO in a power rate law
y	Number of H_2 atoms involved in the rate determining step of reaction 1 (Eq. (7))

Greek Symbols

θ_i	Coverage (fraction of saturation density) of species i
λ	Dimensionless parameter defined by Eq. (18I)

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