JOURNAL OF CATALYSIS 60, 167–168 (1979)

LETTERS TO THE EDITORS

Comments on Heterogeneous Methanation: Absence of H_2–D_2 Kinetic Isotope Effect on Ni, Ru, and Pt

In a 1977 note, Dalla Betta and Shelef (*1*) presented data which showed that substituting D_2 for H_2 in CO hydrogenations over supported Ni, Ru, and Pt catalysts caused no change in the rate of synthesis of methane or higher hydrocarbons. They concluded from these results that the rate-determining step (RDS) in the hydrogenation of CO is not a reaction involving H(D). This conclusion is at variance with that reached from studies of the kinetics of the synthesis reaction by Araki and Ponec (*2*) and by Ellgen *et al.* (*3*). Both the latter groups have shown that their results and the kinetics determined by Vannice (*4*) on other supported Group VIII metals, can be interpreted in terms of an initial rapid dissociative chemisorption of CO on the metal, followed by a series of additions of H_s to the C_s formed, with the RDS being one of the H_s additions. This note is intended to show that the reported absence of an isotope effect (*1*) is not inconsistent with the latter reaction mechanism.

The problem encountered in interpreting isotope effects observed in heterogeneous reactions has been pointed out in general terms by Ozaki (*5*), who states that the "isotope effect on the rate of reaction does not always arise from the rate-determining step but can also arise from a thermodynamic isotope effect on the concentration of a reaction intermediate." The argument can be made specific by consideration of the detailed mechanism proposed (*3*) for CO hydrogenation over a Rh catalyst, relevant portions of which are as follows:

$$H_2 \overset{K_H'}{\rightleftharpoons} (H_2)_s \overset{K_H''}{\rightleftharpoons} 2H_s, \tag{1}$$

$$CO \rightleftharpoons CO_s \rightleftharpoons C_s + O_s, \tag{2}$$

$$C + H \underset{(K_1)}{\overset{k_1}{\rightleftharpoons}} CH \underset{(K_2)}{\overset{k_2}{\rightleftharpoons}} CH_2 \underset{(K_3)}{\overset{k_3}{\rightleftharpoons}} CH_3 \xrightarrow{k_4} CH_3. \tag{3}$$

Here the k's represent rate constants and the K's, equilibrium constants. The kinetics for the Rh case (*3*) and for other Group VIII metals (*2*) are consistent with a mechanism of this sort in which the RDS is one of the four additions of H_s to a surface CH_x moiety. Which of the four H_s additions is rate determining would appear to depend on reaction conditions (*3*) and on the metal on which the reaction is occurring (*2*, *4*). Reactions prior to the RDS are presumed to proceed to equilibrium during synthesis. So long as the RDS is one of the H additions, the molar rate of product formation can be represented (*2*) by

$$R(\mathrm{P}) = k_x \theta_C \theta_H{}^x, \tag{4}$$

where x is the number of H atoms in the species CH_x formed in the RDS. A variety of results (*2*, *6–8*) suggest that the surface is largely covered by carbon even in operations at rather modest CO pressures, i.e., $\theta_C \simeq 1$ under most conditions. The value of θ_H, the fractional coverage by H_s of the potentially available surface, is determined by the equilibrium constant for dissociative hydrogen chemisorption, K_H, and by the competition between CO

0021-9517/79/130167-02$02.00/0

and H_2 for vacant surface sites (*3*). The appropriate Langmuir-type expression for θ_H, according to the assumptions set forth in Ref. (*3*), would be

$$\theta_H = K_H^{\frac{1}{2}} P_{H_2}^{\frac{1}{2}} (1 + bP_{CO})^{-\frac{1}{2}}. \qquad (5)$$

Combining (4) and (5), for the case where $\theta_C = 1$ and $x = 1$, the rate can be written as

$$R(P) = k_1 K_H^{\frac{1}{2}} P_{H_2}^{\frac{1}{2}} (1 + bP_{CO})^{-\frac{1}{2}}. \qquad (6)$$

Literature data indicate that substitution of D_2 for H_2 should affect both k_1 and K_H, but that the expected effects should be in opposite directions and might well compensate for each other, resulting in no overall change in the rate of methanation. The adsorption coefficient for D_2 chemisorption on Ni is 1.4 to 1.5 times that for H_2 chemisorption at 100 to 200°C (*9*, *10*). This result is not confined to Ni, as evidenced by Beebe's results with Cu powder (*11*). No comparable data appear to be available on other Group VIII metals, but qualitative evidence for the preferential chemisorption of D_2 in the presence of H_2 has been obtained on promoted iron synthetic ammonia catalysts (*12*), on a mixed manganous oxide–chromic oxide catalyst (*13*), and on chromic oxide (*14*).

The kinetic isotope effect expected for k_1 would be such that $k_H/k_D > 1$. The magnitude of that effect cannot be predicted quantitatively, but a range from 1.4 to 2.5 at 200°C would not be unreasonable ((*15*, *16*); see also the discussion in Chap. 6 of Ref. (*5*)).

The interpretation above has been limited to the case where $x = 1$, i.e., the first H addition is rate determining. Based on the kinetics observed by Vannice (*4*) (i.e., $X = 0.8$) this is nearly the case for a Ni/Al_2O_3 catalyst. The detailed arguments outlined above can be extended to cases where $X > 1$, and probably should be if they are to be applied to methanation over Ru catalysts. It should be noted that the effect of deuterium substitution on the stability of surface CH_x species could also become significant in that case (*17*). Such a response could account for changes in the overall isotope effect as changes in reaction conditions change the RDS. Proceeding with the details of the arguments would add little to the present semiquantitative discussion, though.

In general it appears impossible to decide what the RDS is in the hydrogenation of CO over Group VIII metals simply by substituting D_2 for H_2 in the synthesis gas and noting the change in kinetics. A more discriminating experiment will be needed to establish unequivocally the identity of that step.

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Received December 8, 1978