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LETTERS TO THE EDITORS

Comment on "A Study of the Nickel-Catalyzed Methanation Reaction"

In a recent paper Hayes *et al.* (*1*) discuss the experimental results obtained from the study of the nickel-catalyzed methanation reaction and attempt to provide an overall "self-consistent" model of the catalytic methanation process. Although the paper contains some interesting experimental information, the proposed mechanism is self-conflicting.

The mechanism they proposed is

$$2Ni + CO(g) \xrightarrow{k_1} Ni{-}C_{(ads)} + Ni{-}O_{(ads)} \quad (1)$$

$$Ni{-}C_{(ads)} + H_{(ads)} \xrightarrow{k_2} Ni{\equiv}C{-}H_{(ads)} \quad (2)$$

$$Ni{\equiv}C{-}H_{(ads)} \xrightarrow[+H]{k_3} CH_4(g) \quad (3)$$

Equation (3) is implied in their discussion but not written. Equation (3) is added for the convenience of discussion.

Hayes *et al.* claimed that the rate-determining step is the formation of $Ni{\equiv}C{-}H_{(ads)}$ (Eq. (2)). However, if Eq. (2) were the rate-determining step, one would expect the predominant species to be NiC instead of NiCH for the following reason.

At steady state, the rate of the production of CH_4, TOF can be expressed as

$$TOF = k_2 \cdot [NiC] = k_3 \cdot [NiCH]. \quad (4)$$

Thus

$$[NiC] = k_3/k_2 \cdot [NiCH]. \quad (5)$$

According to the authors, the rate-determining step is Eq. (2). In other words,

$$k_2 \ll k_3. \quad (6)$$

Substituting Eq. (6) into Eq. (5), one would obtain

$$[NiC] \gg [NiCH]. \quad (7)$$

This is obviously opposite to what they observed, i.e., $[NiCH] \gg [NiC]$.

To resolve this problem, one has to assume Eq. (3) to be the rate-determining step, i.e., the hydrogenation of NiCH to produce methane. However, this would change one of the conclusions Hayes *et al.* made in Ref. (*1*).

In summary, the mechanism proposed in Ref. (*1*) is self-conflicting. The rate-determining step is not the formation of NiCH but the hydrogenation of NiCH.

REFERENCE

1. Hayes, R. E., Thomas, W. J., and Hayes, K. E., *J. Catal.* **92,** 312 (1985).

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