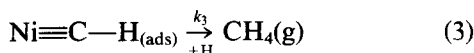
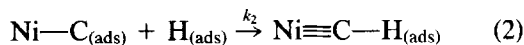
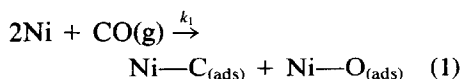


LETTERS TO THE EDITORS

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



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 $\text{Ni}\equiv\text{C}-\text{H}_{(\text{ads})}$ (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

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

Thus

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

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

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

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

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

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