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Reply

In the preceding letter (*1*), the validity of an earlier kinetic model for methanation is discussed (*2, 3*). It was consistent with the best available information at the time; however, studies since then have provided much additional information about the state of the catalytic surface and have indicated quite clearly that this model does not appear to describe the predominant reaction over the metals that readily dissociate CO (Ru, Fe, Co, and Ni) (*4–6*). In addition, the assumption of a unique CH_2O species on the surface existing as the most abundant surface intermediate does not appear to be appropriate although much evidence exists for a cooperative interaction between adsorbed CO and adsorbed hydrogen (*2, 6*). These considerations in themselves argue against the model proposed by one of us (*2*).

However, the analysis provided in Ref. (*1*) is far too simple and incorrect in its approach. First, the metallic properties which result in a variation in the heat of adsorption of CO also simultaneously change this property for hydrogen; therefore, the parameter $\Delta H_{a,CO}$ cannot be varied holding all others (such as $\Delta H_{a,H_2}$) constant, as inferred. Second, a rate maximum as a function of this property (ΔH_a) can be predicted (*7*) and has already been reported (*8*); therefore, a positive slope does exist over an appropriate range of $\Delta H_{a,CO}$. Third, a compensation effect frequently exists in kinetic rate expressions, and one has been shown for this reaction (*2*); therefore, the K_0 term in Eq. (2), Ref. (1), is also dependent on $\Delta H_{a,CO}$, and the actual partial derivative has the form $(-b/R + 1/RT)(0.5)(1 - y/2)$ if a reasonable relationship between the entropy and enthalpy of adsorption is used (*9, 10*). As a consequence, the temperature range utilized can cause this expression to be negative.

In summary, ample evidence exists from recent studies to warrant a revision of the assumptions made in this early model (*5, 6*), but the approach taken by Takoudis is not sufficiently valid to justify this conclusion.

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