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Reply to Comments on Heterogeneous Methanation:

Absence of H_2–D_2 Kinetic Isotope Effect on Ni, Ru, and Pt

Wilson states (*1*) that the kinetic and thermodynamic isotope effects in the methanation reaction can be of opposite sign and equal magnitude and, therefore, can mutually cancel such that the rate for H_2 and D_2 will be identical, or almost so.

Assuming equilibrium (1) precedes rate-determining step (2), compensation may yield a negligible isotope effect.

$$\tfrac{1}{2}H_2 + * \overset{K}{\rightleftarrows} H* \tag{1}$$

$$C* + H* \xrightarrow{k} *CH + * \tag{2}$$

The question is: Will such an accident persist over the temperature range of the measurements? This depends on the exponential temperature dependence of the isotope effect. The latter is given by the following relation between vibrational temperatures θ (equal to $h\nu/k$).

$$-\frac{1}{2T}\left[\left(\frac{\theta_{H_2}-\theta_{D_2}}{2}\right) - (\theta_{CH^\ddagger} - \theta_{CD^\ddagger})\right] \tag{3}$$

Although we do not know $\theta_{CH^\ddagger}$ and $\theta_{CD^\ddagger}$ for the transition state of the controlling step, we can assume that they are equal to θ_{CH} and θ_{CD}, respectively, for characteristic CH and CD group stretching vibrations. Then quantity (1) becomes equal to $128/T$ with T in Kelvin. In the most favorable case, i.e., widest temperature range studied,

$$\frac{1}{T_1} - \frac{1}{T_2} = 0.4 \times 10^{-3},$$

the isotope effect at the upper and lower temperatures would differ by

$$\exp\left[128 \times 0.4 \times 10^{-3}\right] = 1.05,$$

which is clearly not measurable. Hence, the lack of an isotope effect is indeed not *proof* of the proposed mechanism according to which the dissociative chemisorption of CO is the limiting step although the observations are clearly *compatible* with the assumed mechanism.

In addition, the assumption by Wilson that $\theta_C = 1$ does not hold for all the catalysts examined. It has been shown by infrared spectroscopy that under reaction conditions similar to those explored in this work, the surface of Ru is covered almost entirely by adsorbed CO (*2*). Nickel is completely different, the steady-state surface exhibiting a very low surface coverage by CO and an apparently high surface carbon layer (*3*, *4*) although the actual chemical form of the carbon is not known. Cancellation of kinetic and thermodynamic isotope effects on different metals exhibiting such different behavior would be surprising, but it may occur. However, CO dissociation

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as the rate-determining step would be a simple, yet consistent, mechanism.

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