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Reply to Comments by Dan-Chu, Bakhshi and Mathews

The note by Dan-Chu, Bakhshi and Mathews shows that the same equation (Eq. (14)) can be obtained whether step (3) or step (4) is taken as the controlling step in the methanation sequence. However if step (4) were the slow step, most of the surface would be covered with deposited carbon, and the values of θ_{CO} and θ_H would be quite small. It is then inconsistent to derive equations for θ_{CO} and θ_H ignoring θ_C, as the authors have done, and their final equation, Eq. (15), is not correct.

In our original derivation, we ignored θ_C because tests showed that a large fraction of the surface was covered with adsorbed carbon monoxide. Furthermore, the measured activation energy for gasification of deposited carbon was much less than that for methanation. However, as pointed out in our paper, extrapolation of the data indicates that gasification of the deposited carbon would probably be the limiting step at high temperatures.

The kinetic equations for methanation with two slow steps are derived below. Dissociative adsorption of hydrogen is assumed to require only one site. It is interesting that when step (4) controls, the overall rate depends on the product of k_4 and the ration (k_4/k_3), rather than just k_4.

Kinetic Equations for Methanation of Carbon Monoxide with Two Slow Steps

$$CO + s \rightleftharpoons CO_s, \quad (1)$$

$$H_2 + s \rightleftharpoons 2H_s, \quad (2)$$

$$CO_s + 2H_s \rightarrow C_s + H_2O \quad \text{slow}, \quad (3)$$

$$C_s + 2H_s \rightarrow CH_{2s} \quad \text{slow}, \quad (4)$$

$$CH_{2s} + 2H_s \rightleftharpoons CH_4, \quad (5)$$

$$r_3 = k_3\theta_{CO}\theta_H{}^2, \quad (6)$$

$$r_4 = k_4\theta_C\theta_H{}^2 . \quad (7)$$

At steady state,

$$r_3 = r_4 \quad \text{or} \quad \frac{\theta_{CO}}{\theta_C} = \frac{k_4}{k_3}. \quad (8)$$

From the normal solution for competitive adsorption on sites not covered by carbon:

$$\theta_{CO} = \frac{K_{CO}P_{CO}}{(1 + K_{CO} + K_{H_2}P_{H_2})}(1 - \theta_C), \quad (9)$$

$$\theta_H{}^2 = \frac{K_{H_2}P_{H_2}}{(1 + K_{CO}P_{CO} + K_{H_2}P_{H_2})}(1 - \theta_C). \quad (10)$$

From Eqs. (8) and (9)

$$\theta_{CO} = \frac{K_{CO}P_{CO}}{(1 + K_{CO}P_{CO} + K_{H_2}P_{H_2})}\left(1 - \theta_{CO}\frac{k_3}{k_4}\right), \quad (11)$$

$$\theta_{CO} = \frac{K_{CO}P_{CO}}{(1 + K_{CO}P_{CO} + K_{H_2}P_{H_2} + (k_3/k_4)K_{CO}P_{CO})}, \quad (12)$$

$$\theta_{CO} = \frac{K_{CO}P_{CO}}{(1 + K_{H_2}P_{H_2} + K_{CO}P_{CO}(1 + (k_3/k_4))}. \quad (13)$$

0021-9517/81/100445-02$02.00/0

From (9) and (10)

$$\frac{\theta^2_{H_2}}{\theta_{CO}} = \frac{K_{H_2}P_{H_2}}{K_{CO}P_{CO}}, \quad (14)$$

$$\theta_H{}^2 = \frac{K_{H_2}P_{H_2}}{1 + K_{H_2}P_{H_2} + K_{CO}P_{CO}\,(1 + (k_3/k_4))}. \quad (15)$$

From (6)

$$r = \frac{k_3K_{CO}P_{CO}K_{H_2}P_{H_2}}{(1 + K_{H_2}P_{H_2} + K_{CO}P_{CO}\,(1 + (k_3/k_4)))^2}. \quad (16)$$

When

$$\frac{k_3}{k_4} \ll 1,$$

step (3) controls:

$$r \cong \frac{k_3K_{CO}P_{CO}K_{H_2}P_{H_2}}{(1 + K_{H_2}P_{H_2} + K_{CO}P_{CO})^2}. \quad (17)$$

When

$$\frac{k_3}{k_4} \gg 1,$$

step (4) controls:

$$r \cong \frac{k_3K_{CO}P_{CO}K_{H_2}P_{H_2}}{(1 + K_{H_2}P_{H_2} + (k_3/k_4)K_{CO}P_{CO})^2}. \quad (18)$$

Since $K_{CO}P_{CO}$ usually exceeds $(1 + K_{H_2}P_{H_2})$,

$$r \cong \frac{k_3K_{CO}P_{CO}K_{H_2}P_{H_2}}{(k_3/k_4)K_{CO}P_{CO})^2}$$

$$= k_4\,(k_4/k_3)\frac{K_{H_2}P_{H_2}}{K_{CO}P_{CO}}. \quad (19)$$

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