

## Reply to Comments by Dan-Chu, Bakhshi and Mathews

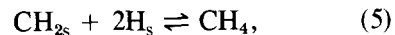
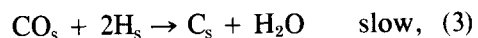
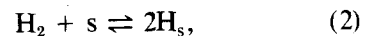
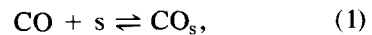
The note by Dan-Chu, Bakhshi and Mathews shows that the same equation (Eq. (14)) can be obtained whether step (3) or step (4) is taken as the controlling step in the methanation sequence. However if step (4) were the slow step, most of the surface would be covered with deposited carbon, and the values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

In our original derivation, we ignored  $\theta_C$  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 ratio  $(k_4/k_3)$ , rather than just  $k_4$ .

### *Kinetic Equations for Methanation of Carbon Monoxide with Two Slow Steps*



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

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

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)

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

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

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

From (9) and (10)

$$\frac{\theta_{\text{H}_2}^2}{\theta_{\text{CO}}} = \frac{K_{\text{H}_2} P_{\text{H}_2}}{K_{\text{CO}} P_{\text{CO}}}, \quad (14)$$

$$\theta_{\text{H}_2}^2 = \frac{K_{\text{H}_2} P_{\text{H}_2}}{1 + K_{\text{H}_2} P_{\text{H}_2} + K_{\text{CO}} P_{\text{CO}} (1 + (k_3/k_4))}. \quad (15)$$

From (6)

$$r = \frac{k_3 K_{\text{CO}} P_{\text{CO}} K_{\text{H}_2} P_{\text{H}_2}}{(1 + K_{\text{H}_2} P_{\text{H}_2} + K_{\text{CO}} P_{\text{CO}} (1 + (k_3/k_4)))^2}. \quad (16)$$

When

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

step (3) controls:

$$r \cong \frac{k_3 K_{\text{CO}} P_{\text{CO}} K_{\text{H}_2} P_{\text{H}_2}}{(1 + K_{\text{H}_2} P_{\text{H}_2} + K_{\text{CO}} P_{\text{CO}})^2}. \quad (17)$$

When

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

step (4) controls:

$$r \cong \frac{k_3 K_{\text{CO}} P_{\text{CO}} K_{\text{H}_2} P_{\text{H}_2}}{(1 + K_{\text{H}_2} P_{\text{H}_2} + (k_3/k_4) K_{\text{CO}} P_{\text{CO}})^2}. \quad (18)$$

Since  $K_{\text{CO}} P_{\text{CO}}$  usually exceeds  $(1 + K_{\text{H}_2} P_{\text{H}_2})$ ,

$$r \cong \frac{k_3 K_{\text{CO}} P_{\text{CO}} K_{\text{H}_2} P_{\text{H}_2}}{(k_3/k_4) K_{\text{CO}} P_{\text{CO}})^2}$$

$$= k_4 (k_4/k_3) \frac{K_{\text{H}_2} P_{\text{H}_2}}{K_{\text{CO}} P_{\text{CO}}}. \quad (19)$$

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