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Reply to Comment by Xuezhi Zhang

The comment offered by Xuezhi Zhang that the rate-determining step in the nickel-catalyzed methanation reaction is not the formation of Ni≡C—H would be impeccable logic if it were not for the fact that (a) we did not say that NiCH is the most abundant surface species, and (b) experimental observations of catalyst deactivation show unequivocally that it is not realistic to postulate a steady state at the catalyst surface.

Evidence accumulated by means of infrared reflectance spectroscopy points to NiCH as the most abundant surface hydrocarbon species. This does not imply that NiC is not in abundance. We conclude from both the infrared and the microreactor experiments that NiCH is in greater abundance than either of the surface species

$$\begin{matrix}\mathrm{Ni}\\ \mathrm{Ni}\end{matrix}\!\!>\!\mathrm{CH_2} \quad \text{and} \quad \mathrm{NiCH_3}.$$

We had no experimental means available to us to determine whether or not NiC is present in greater concentrations at the surface than NiCH. We cannot therefore draw the conclusion, as Xuezhi Zhang suggests, that the subsequent hydrogenation of NiCH to methane is rate determining. Indeed, the fact that Ni_2CH_2 and $NiCH_3$ could be removed from a Ni surface by hydrogen at lower temperatures than NiCH militates against the conclusion of Zhang. Furthermore, the important experiment in which it was demonstrated that CH_4 continued to be formed (but the formation of H_2O ceased) after the CO supply to the microreactor was interrupted, when considered together with the evidence that the surface concentration of NiCH is greater than either Ni_2CH_2 or $NiCH_3$ species, suggests that it is the formation of NiCH which is the rate-determining step in the sequence of events. Thus, the experimental evidence provided by infrared reflectance and microreactor studies supports the conclusion that the rate-determining step in the nickel-catalyzed methanation reaction is the formation of Ni≡C—H.

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