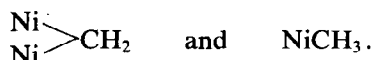


## Reply to Comment by Xuezhi Zhang

The comment offered by Xuezhi Zhang that the rate-determining step in the nickel-catalyzed methanation reaction is not the formation of  $\text{Ni}\equiv\text{C}-\text{H}$  would be impeccable logic if it were not for the fact that (a) we did not say that  $\text{NiCH}$  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  $\text{NiCH}$  as the most abundant surface hydrocarbon species. This does not imply that  $\text{NiC}$  is not in abundance. We conclude from both the infrared and the microreactor experiments that  $\text{NiCH}$  is in greater abundance than either of the surface species



We had no experimental means available to us to determine whether or not  $\text{NiC}$  is present in greater concentrations at the surface than  $\text{NiCH}$ . We cannot therefore draw the conclusion, as Xuezhi Zhang suggests, that the subsequent hydrogenation of  $\text{NiCH}$  to methane is rate determining. Indeed, the fact that  $\text{Ni}_2\text{CH}_2$  and  $\text{NiCH}_3$  could be removed from a Ni surface by hydrogen at lower temperatures than  $\text{NiCH}$  militates against the conclusion of Zhang. Furthermore, the important experiment in which it

was demonstrated that  $\text{CH}_4$  continued to be formed (but the formation of  $\text{H}_2\text{O}$  ceased) after the CO supply to the microreactor was interrupted, when considered together with the evidence that the surface concentration of  $\text{NiCH}$  is greater than either  $\text{Ni}_2\text{CH}_2$  or  $\text{NiCH}_3$  species, suggests that it is the formation of  $\text{NiCH}$  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  $\text{Ni}\equiv\text{C}-\text{H}$ .

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