Comment

Reply to the comment on “The effect of ZnO in methanol synthesis catalysts on Cu dispersion and the specific activity”

[by K.C. Waugh]

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We have reported the effect of ZnO in Cu/ZnO catalysts on Cu dispersion and the specific activity of the methanol synthesis from CO_2 and H_2, and have concluded that the role of ZnO is to increase both the Cu dispersion and specific activity [1]. This increase in specific activity has been ascribed to the creation of a Cu–Zn active site. Waugh [2] recently pointed out that “the linear relationship between the copper metal area and the methanol yield (figure 1(a)) is apparently in conflict with the volcano-type dependence of the Cu specific activity on ZnO content (figure 1(b))”. He commented that “it is possible to resolve this conflict by ignoring the points at 90 and 0 wt% ZnO in figure 1(b)”. That is, “with these points removed, figure 1(b) shows that the catalysts fall into two groups: one with a specific activity of $\sim$10 mg-CH_3OH/m^2-Cu h and a second with a specific activity of 14.8 mg-CH_3OH/m^2-Cu h”, which is due to “a different morphology” depending on the Cu surface area. He also suggested that “the copper of the Cu/ZnO, Cu/MgO and Cu/MnO catalysts could be of a different morphology from that of the Cu/ZnO/Al_2O_3 and Cu/SiO_2 catalysts”. He summarized that “these different specific activities derive from different surface morphologies of the copper in these catalysts”.

We should first answer that we have very reproducible data of the Cu surface area, the MTY, and the specific activity at 0 wt% ZnO, as shown in figure 1 (a) and (b). We are sufficiently confident about the data so that we cannot remove these points at 0 wt% ZnO. It is thus dangerous to classify the catalysts into the two different groups with different morphologies.

Secondly, we show unpublished results of the reverse water–gas shift (RWGS) reaction in figure 2, which were simultaneously taken during the measurement of the methanol synthesis activity reported in the cited paper [1]. The specific activity of the CO formation was similar regardless of the ZnO content or the Cu surface area. Clearly, the classification into the two types of catalysts made by Waugh for methanol synthesis cannot be applied to the correlation between the specific activity of the RWGS reaction and the Cu surface area. Note that the specific activity of the RWGS reaction at 0 wt% ZnO is comparable to those for the other catalysts. On the other hand, the specific activity of the methanol synthesis was promoted by an order of magnitude upon the addition of 10 wt% ZnO (figure 1(b)). This supports the fact that the addition of the small amount of ZnO does not significantly change the morphology, but creates active sites only for the methanol synthesis, as already reported [1].

Finally, we emphasize here a consistency of the powder catalyst and surface science results, which cannot be explained by the morphology effect, but can be well-explained by the Cu–Zn active site model created by the addition of Zn on the Cu surface. The methanol synthesis activity of a Cu/SiO_2 $+$ ZnO/SiO_2 physical mixture increased with reduction temperature, as previously reported [3]. On the other hand, the formation of CO by the RWGS reaction occurring in parallel with methanol synthesis on the physical mixture was found to be almost constant regardless of the reduction temperature [4], indicating that the morphology of the Cu does not change by H_2 reduction at different temperatures. We thus concluded that the Cu–Zn site being active only for methanol synthesis was created by the migration of Zn onto the Cu surface during the reduction of the physical mixture with H_2 ($ZnO + H_2 \rightarrow Zn + H_2O$), where the migration of Zn was confirmed by TEM-EDX and XRD.

We thus tried to establish a model catalyst by depositing Zn on single crystal surfaces of Cu. As shown in figure 3, only the methanol synthesis activity was significantly promoted by the Zn deposition on Cu(111), while the RWGS activity gradually decreased with Zn coverage, which is consistent with the powder results. Note that the Zn content that migrated to the Cu particles in the physical mixture of Cu/SiO_2 $+$ ZnO/SiO_2 was estimated to be below 15 at%, therefore, the TOF of the CO formation on Zn/Cu(111) is not so different from the TOF on clean Cu(111). Although we have consistently reported that the active site only for methanol synthesis should be created on Cu by the Zn deposition, we changed the model of the active site

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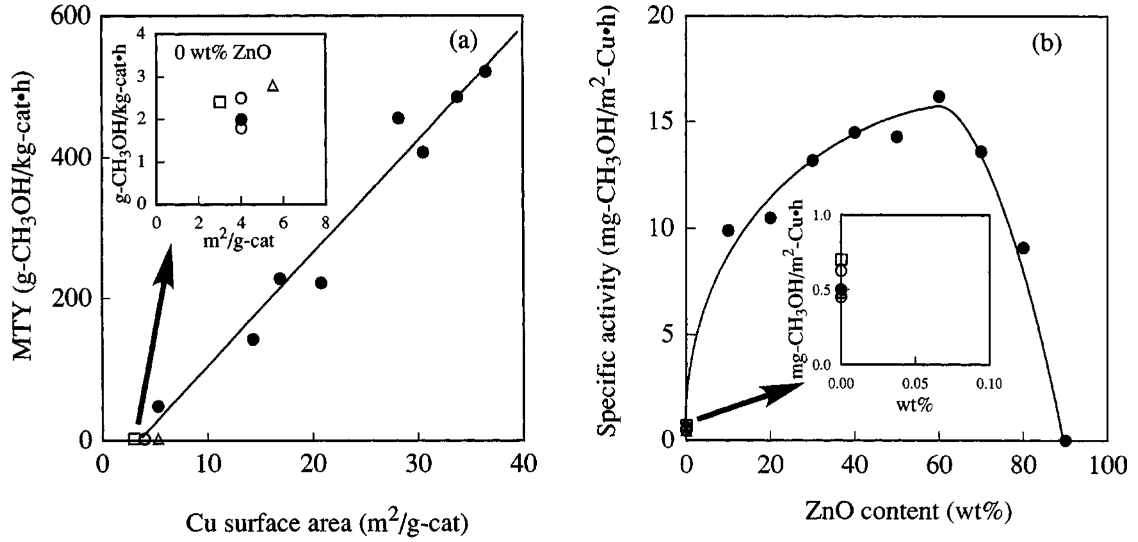

Figure 1. (a) Yield of methanol as a function of Cu surface area. (b) Specific activity for methanol synthesis as a function of ZnO content in the Cu/ZnO catalysts.

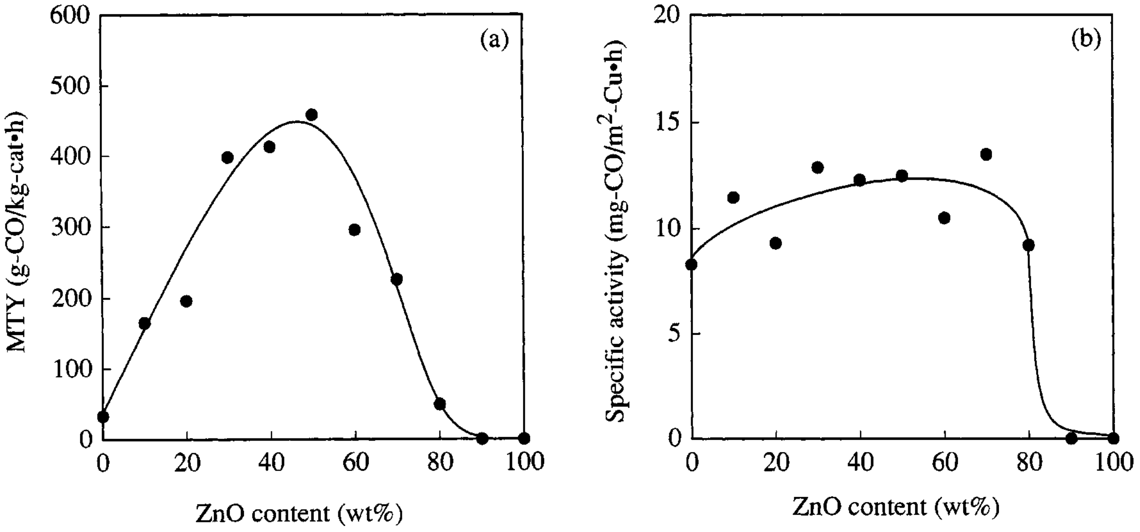

Figure 2. Yield of CO (a) and the specific activity for CO formation (b) as a function of ZnO content.

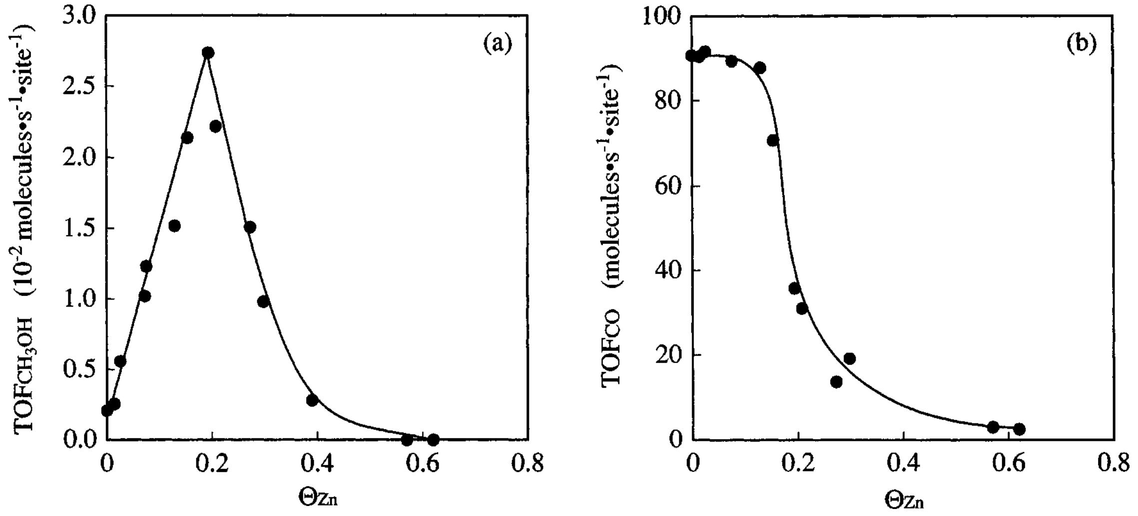

Figure 3. TOF for methanol synthesis formation (a) and CO formation (b) on Zn/Cu(111) as a function of Zn coverage [5].

from the Cu^+–O–Zn species to the Cu–Zn species in the study of Zn/Cu(111) (1997) [5] after the studies of Zn/poly Cu (1996) [6] and physical mixture, $Cu/SiO_2 + ZnO/SiO_2$, (1996) [3]. In the Zn/poly Cu paper, the Cu^+–O–Zn species was assigned to the active site at low Zn coverage. In later experiments, atomic oxygen was found to be formed by the decomposition of formate when the reaction mixture of CO_2 and H_2 was evacuated at the reaction temperature. On the other hand, no atomic oxygen was detected on the post-reaction Zn/Cu(111) ($\Theta_{Zn} < 0.2$) surface except for formate when the evacuation was carried out after cooling the sample to 373 K in the reaction mixture. We thus concluded that the atomic oxygen was not involved in the Cu–Zn active site. Note that we consider that the active site for methanol synthesis by the hydrogenation of CO is different from that by the hydrogenation of CO_2, which is currently under investigation.

In conclusion, our data concerning the promotion of Zn upon methanol synthesis cannot be explained by the morphology effect, but is well-explained by the creation of the Cu–Zn active site.

References

[1] T. Fujitani and J. Nakamura, Catal. Lett. 56 (1998) 119.

[2] K.C. Waugh, Catal. Lett. 58 (1999) 163.

[3] Y. Kanai, T. Watanabe, T. Fujitani, T. Uchijima and J. Nakamura, Catal. Lett. 38 (1996) 157.

[4] Unpublished data.

[5] T. Fujitani, I. Nakamura, T. Uchijima and J. Nakamura, Surf. Sci. 383 (1997) 285.

[6] J. Nakamura, I. Nakamura, T. Uchijima, Y. Kanai, T. Watanabe, M. Saito and T. Fujitani, J. Catal. 160 (1996) 65.