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Comment

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

[by T. Fujitani and J. Nakamura]

K.C. Waugh

Department of Chemistry, UMIST, PO Box 88, Manchester M60 1QD, UK

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Fujitani and Nakamura recently reported on the effect of ZnO on Cu/ZnO methanol synthesis catalysts (Catal. Lett. 56 (1998) 119). Having measured the methanol synthesis activity of a series of Cu/ZnO catalysts of different Cu/ZnO ratios, they reported a linear relationship between the copper metal area and the methanol yield (implying a fixed value of the copper specific activity) and paradoxically they also reported a volcano-type relationship between the copper specific activity in methanol synthesis and the ZnO content. This paradox is resolved by showing that their Cu/ZnO catalysts fall into two groups: (i) the low-surface-area copper catalysts which have a specific activity of 10 mg CH_3OH/m^2-Cu h and (ii) the high-surface-area copper catalysts which have specific activity of 14.8 mg CH_3OH/m^2-Cu h. These different specific activities derive from different surface morphologies of the copper in these catalysts.

Keywords: methanol synthesis, copper metal area, copper morphology, copper specific activity

A recent paper by Fujitani and Nakamura examined the activity of a series of Cu/ZnO catalysts of different Cu/ZnO weight ratios ranging from 100 : 0 to 0 : 100 in the synthesis of methanol [1]. The activity was measured using a CO_2/H_2 (25/75) feed at 50 atm, 523 K with a specific velocity of 18000 cm^3/g-cat. h. The copper metal area of the catalysts was measured using N_2O reactive frontal chromatography [2]. The authors reported a linear relationship between the methanol synthesis activity and the copper metal area (figure 1(a)) [1] which would suggest a constant specific activity (activity/m^2-Cu). Paradoxically, however, they also reported a specific activity which was a function of the ZnO content of the catalyst (figure 1(b)). They reported zero methanol synthesis activity for Cu alone and for the Cu/ZnO catalyst containing 90 wt% ZnO. Their powder X-ray diffraction studies of re-reduced post-reaction catalysts showed that the Cu lattice constant increased in a step-wise fashion from 3.615 Å for pure Cu to 3.646 Å for Cu/ZnO catalyst containing >60 wt% ZnO. From these data, the authors concluded that the role of the ZnO was to increase not only the Cu dispersion but also the Cu specific activity, doing so by forming a Cu/Zn alloy evidenced by the increase in the lattice constant of Cu with increasing content.

The comments I should like to make on this paper are the following. In the paper in which we described the technique of N_2O reactive frontal chromatography, we also reported a linear relationship between copper metal area and methanol synthesis activity (figure 2) [2]. Our relationship, however, included not only $Cu/ZnO/Al_2O_3$ catalysts but Cu/MgO, Cu/Al_2O_3, Cu/MnO and Cu/SiO_2. We found the activity for unsupported Cu to lie on this linear relationship but

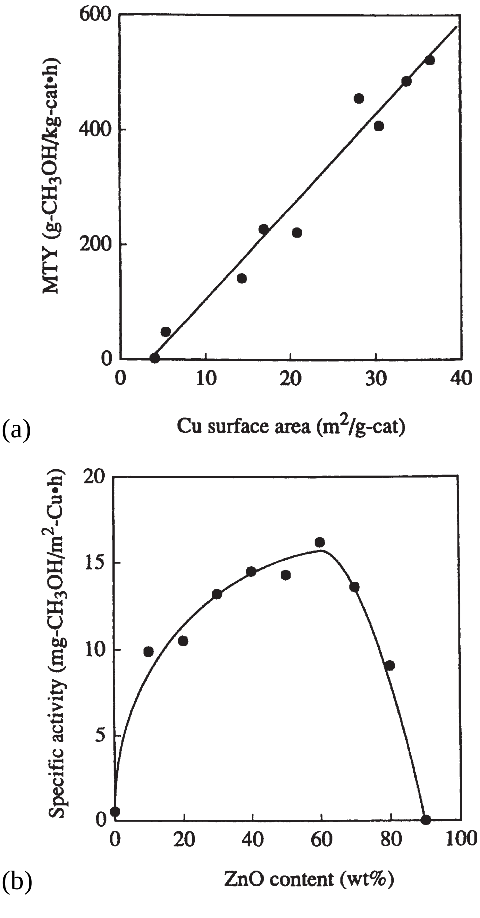

Figure 1. (a) Yield of methanol as a function of Cu surface area [1]. (b) Specific activity for methanol synthesis as a function of ZnO content in the Cu/ZnO catalysts [1].

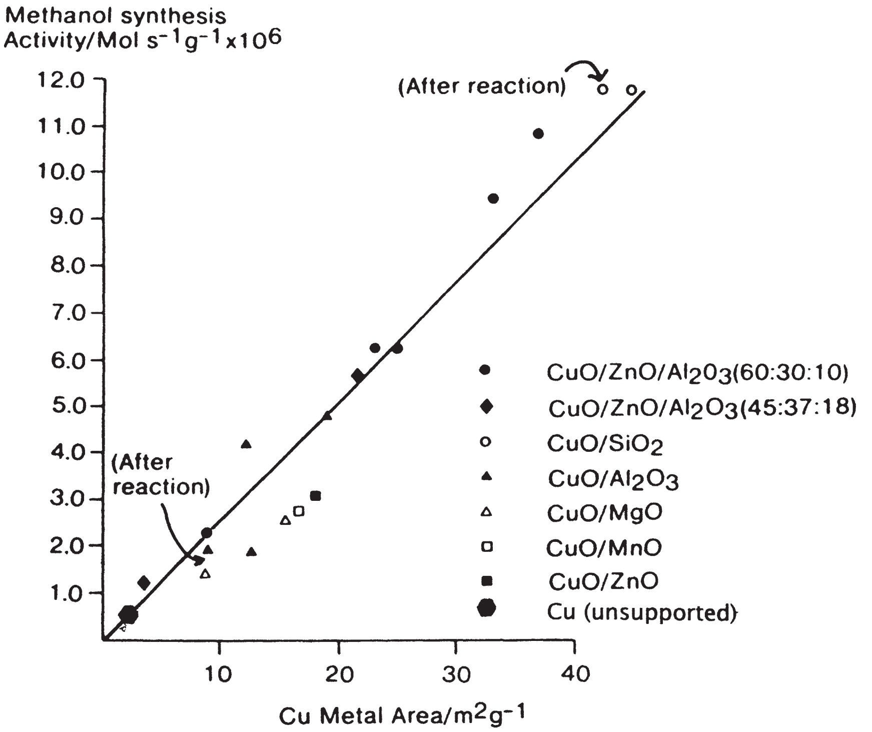

Figure 2. Methanol synthesis activity as a function of copper metal area [2].

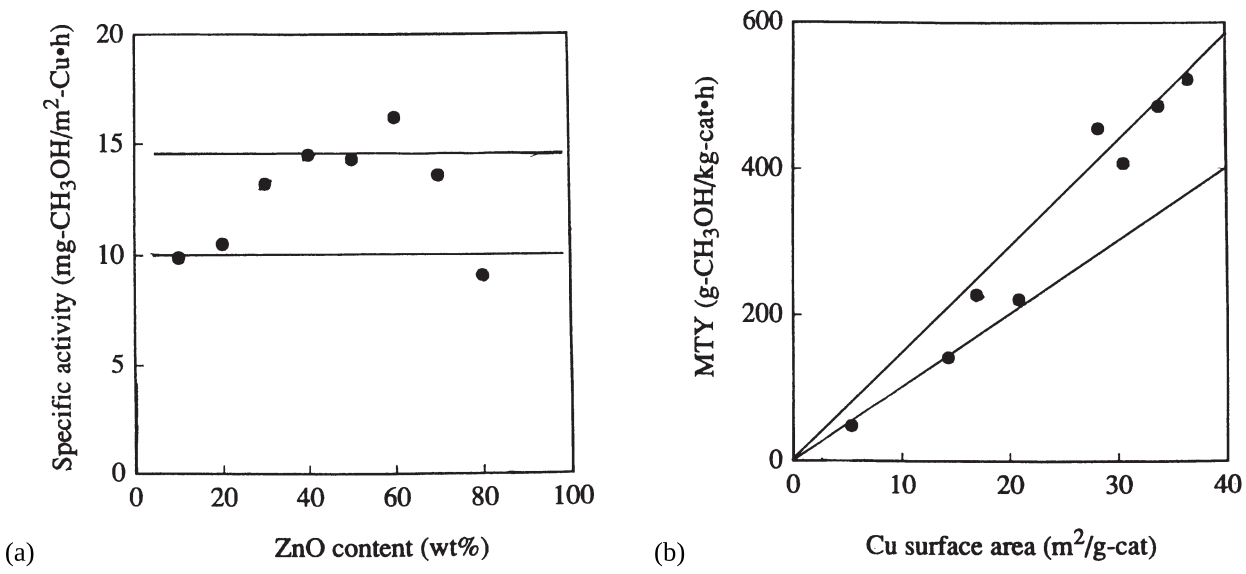

Figure 3. (a) Re-plot of the methanol specific activity/ZnO relationship with two specific activities, 10 mg and 14.8 mg CH_3OH/m^2-Cu h. (b) Re-plot of the methanol yield as a function of Cu surface area using the gradients of 10 and 14.8 mg CH_3/m^2-Cu h.

did not include it because of its proximity to the origin. (I have now included it.) We found this, in total, to be compelling evidence for not ascribing any unique role to the ZnO.

Close examination of Fujitani and Nakamura's data is revealing. There is the apparent conflict between their constancy of the specific activity of copper in methanol synthesis implied by figure 1(a) and the volcano-type dependence of their Cu specific activity on ZnO content in figure 1(b) [1]. It is possible to resolve this conflict by ignoring the points at 90 wt% ZnO and at 0 wt% ZnO in figure 1(b). The former had no copper area and the zero methanol activity of the latter could be within experimental error. (We had great difficulty in measuring the amount of methanol produced by unsupported Cu which was part of the reason for not including it in our original version of figure 2.) With these points removed, figure 1(b) shows that the catalysts fall into two groups: one with a specific activity of ~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 (figure 3(a)).

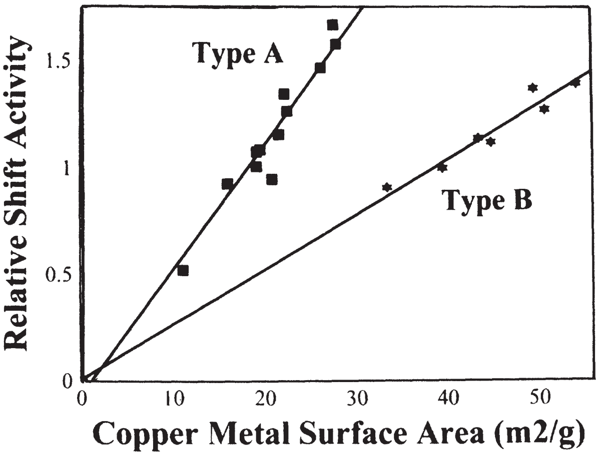

Figure 4. Relative shift activity as a function of copper metal area [3].

The data in figure 1(a) can now be replotted using these two specific activities as the gradients shown in figure 3(b). The fit is improved. We have therefore two families of Cu/ZnO catalyst of distinctly different Cu specific activities. Hadden and co-workers found the same effect for the activity in the shift reaction of a series of Cu/ZnO/Al_2O_3 catalysts as a function of Cu metal area (figure 4) [3]. They ascribed this result to different morphologies of the copper surface resulting from the two sets of catalysts being produced at different pH's, different ageing times and different ageing temperatures.

The low Cu surface area catalysts produced by Fujitani and Nakamura therefore appear to have a different morphology from that of their high Cu surface area catalysts. In my judgement, the authors appear to have shown that methanol synthesis activity on Cu from CO_2/H_2 is structure sensitive which is a unique and important result. Indeed, re-examination of our original methanol synthesis activity/copper metal area linear relationship shown in figure 2 suggests 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.

References

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