Catalysis Letters 6 (1990) 151–156

'GOOD' CORRELATIONS IN METHANOL SYNTHESIS CATALYSIS, A COMMENT ON A LETTER BY BURCH, GOLUNSKI AND SPENCER

Received 4 June 1990

An important debate is currently in progress on the mechanism of catalytic methanol synthesis, and very different views on the role of copper in Cu/metal oxide catalysts have been expressed, [1–3]. There appears to be insufficient experimental data to decide some crucial questions, and it is particularly important to determine whether catalytic activity relates directly to copper metal surface area and what is the role of the support. A recent paper by Burch, Golunski and Spencer, (ref. [4], subsequently referred to as BGS), contributes to this discussion by collecting results from eight unnamed publications. These authors choose a set of reaction conditions as a reference, calculate a 'standardised specific activity', (SSA), and plot this versus copper metal area. BGS conclude that their figure, (ref. [4], fig. 1), shows "a *good correlation* between activity and metal surface are", (my italics). Cursory inspection of the figure suggests that this claim is nonsense, indeed, a sceptical observer might conclude that their plot provided prima facie evidence that there is little if any correlation between activity and metal surface area. BSG argue that the correlation they obtain is good, since their plot contains results obtained under a wide range of conditions and in eight laboratories. This may be so, but it is an assertion which in the nature of things cannot be proved. It could be that the extrapolation and use of data from different laboratories accentuates the apparent correlation between SSA and metal surface area. In claiming a good correlation, BGS appear to have assumed their answer and to persist in the face of very equivocal evidence.

The extent of the correlation between SSA and copper metal area can be assessed by standard statistical techniques, [5]. I calculate the correlation coefficient R, between the standardised specific activity and copper metal area to be 0.73, which certainly does not represent a good correlation. However it is high enough to suggest that SSA and metal surface are are significantly related, since it passes the test:

$$|R| > 3/(n+7)^{1/2}. \tag{1}$$

n is the number of observations, 33 in this case, so the right hand side of eq. (1) yields a threshold value of ca 0.5, which is comfortably exceeded, [5].

Having placed BGS's data on firmer statistical ground, we may ask what might be the meaning of the relatively poor but statistically significant correlation

between SSA and copper metal surface area which is observed? The explanation may indeed be that given by BGS, namely variability between laboratories, but another possibility should be considered. It seems very probable that copper metal surface area is only one of a number of variables which determines the activity of the catalyst. One might then anticipate observing a level of correlation between SSA and metal surface are which falls short of perfection, as is observed. BGS and others may like to examine their data this possibility in mind.

The result is that the debate has not been advanced. If BSG are right and there really is a unique correlation between activity and metal surface area, then the ideas of Chinchen et al., [1] are correct. If metal surface area is only one of a number of variables determining catalytic activity, then either the views of Frost, [2], or of Burch et al., [3], could be correct. We cannot make a choice without more reliable experiments, carefully constructed to address the crucial points at issue.

King has recently remarked that the standard of proof required in surface science is greater than that which, through force of circumstance, often prevails in catalysis, [6]. The onus is of course on any community of scientists to treat their data as rigorously as possible. The cavalier approach adopted by BGS cannot be regarded as acceptable.

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REPLY TO THE COMMENT BY JOYNER ON A LETTER BY BURCH, GOLUNSKI AND SPENCER

Received 14 June, accepted 15 June 1990

The mechanism of methanol synthesis and the nature of the active centres is currently the subject of vigorous debate. In a recent Catalysis Letter [1] we have

analysed data for Cu/ZnO catalysts and proposed that the active centre is located on the Cu but that the overall rate of reaction may be enhanced by incorporating ZnO into the catalyst. In that Letter [1] we summarised results from 8 laboratories on the activity of Cu/ZnO catalysts for the synthesis of methanol from $CO/CO_2/H_2$ mixtures. The original results were obtained using a wide range of different experimental conditions and, in order to compare them directly, a simple kinetic model was used to convert the data to a standard set of conditions. The standardised specific activity for methanol synthesis was plotted against the Cu surface area reported in the original publications. We concluded that the results produced a "good" correlation, particularly when account was taken of the range of experimental conditions used by the original authors and the simple kinetic model chosen.

Joyner [2] has disputed our claim that there is a "good" correlation and examined our plot from a statistical point of view. Although he has demonstrated that the results are statistically significant he questions whether, what he describes as, a "relatively poor" correlation has any meaning. In some respects his analysis of the results shown in our Letter is not valid since it does not, and indeed could not, take account of the fact that some of the results shown were the average of many separate experiments and so should have a different weighting from other points corresponding to single measurements. However, in responding to his comments we do not wish to enter into a debate concerning the relative values of statistical correlations. Instead we should like to address two relevant points: first, is there good evidence of a correlation between activity and copper surface area for methanol synthesis on catalysts which contain both Cu and ZnO; second, is there a good correlation for results accumulated from different laboratories and transposed to a standard set of experimental conditions?

With regard to the first point, evidence of a possible correlation between activity and Cu area was reported a decade ago [3–5] and this has been supported by more recent work. The correlation between activity and copper surface area is best answered by reference to the original published work. As an example, in fig. 1 we have replotted sets of data from 4 completely independent laboratories [6–9]. In our view there is a good correlation in each of these cases. There seems to us little doubt that the activity of copper catalysts containing ZnO is related to the copper surface area. It should be noted that results for copper catalysts which do not contain zinc oxide do not necessarily fit on lines such as those shown in fig. 1. Where sufficient data have been reported it is found that there may also be a correlation between activity and Cu surface area for other supports but the activity per unit copper area is dependent on the choice of support.

The second point raised by Joyner concerns the validity of describing our original correlation as "good". In our Letter it was not our intention to demonstrate for the first time a correlation between activity and Cu surface area. Indeed it was our purpose to offer a possible interpretation of what we believed to be a well established experimental fact. We tried to simplify the discussion of a

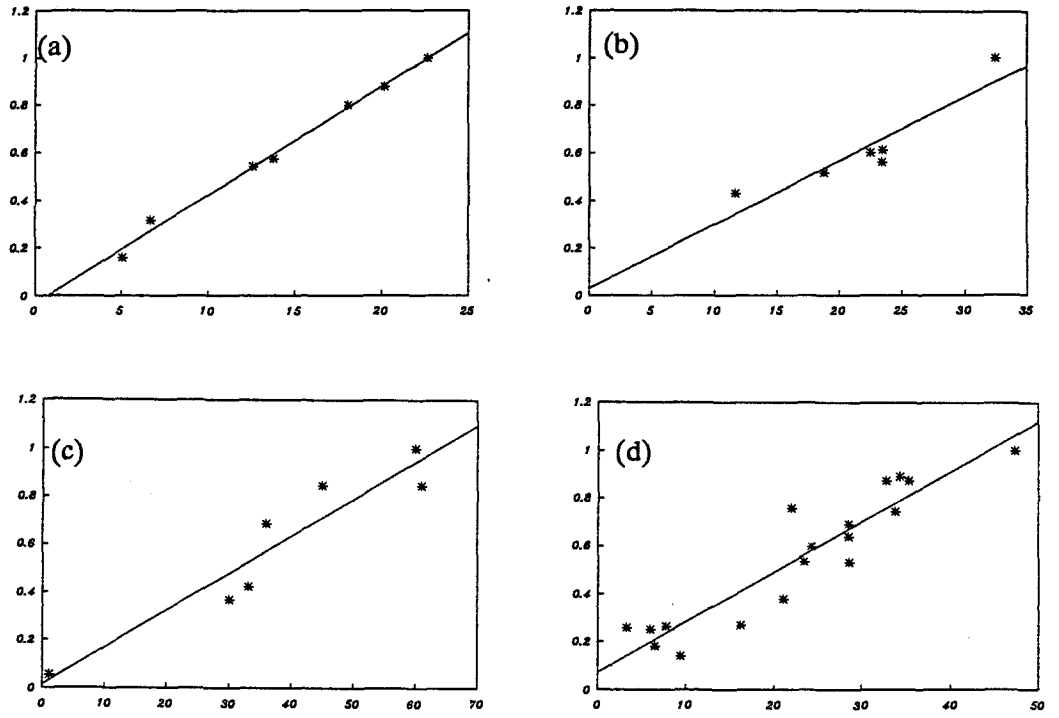

Fig. 1. Methanol activity as a function of Cu surface area. The original data have been normalized with respect to the most active catalyst in each individual case. (a) after ref. [6]; (b) after ref. [7]; (c) after ref. [8]; (d) after ref. [9].

mechanism for methanol synthesis by condensing many sets of results into a single plot, on the assumption that readers would be familiar with the relevant recent literature. We now accept that this may not have been the best way to proceed, and so we now include a list of the papers used [7,10–17], to which the reader is referred for further details.

We are still inclined to find our original correlation convincing, but would not wish to enter into a debate concerning the literal meaning of "good". The results shown in fig. 1 of the present paper would seem to support our contention [1] that a major reason why the points shown in our original Letter deviate from a straight line is the inaccuracy introduced into the original data by the transposition to standard reaction conditions rather than because of a fundamental deficiency in our hypothesis. This point is reinforced by consideration of table 1 which summarises the range of experimental conditions used in the original research and perhaps underlines the difficulty of comparing such a wide range of

Table 1

Range of catalysts and conditions used for fig. 1 in ref. [1].

Property	Range
Catalyst:	
Cu content (wt.%)	5.0–86
Cu area ($m^2\ g^{-1}$)	0.44–46
ZnO content (wt.%)	1.0–93
preparation methods	co-precipitation; impregnation; Raney
Test conditions:	
Temperature (K)	493–543
Total pressure (bar)	1.0–70
CO/CO_2 ratio	0.77–10.7
Space velocity (h^{-1})	6,000–60,000
Number of laboratories	8

catalysts. It seems to use hardly surprising that there should be some scatter in the final results.

Finally, we wish to emphasis that the correlations shown clearly in the present Reply, and perhaps less convincingly in the original Letter, refer only to catalysts in which ZnO is a component. Therefore, it is not correct to state, as Joyner has done, that such a correlation means that the ideas of Chinchen et al. [10] are correct. Indeed, the main purpose of our model is to point to the important role of ZnO. We thus repeat the proposal in our previous Letter, namely, that the rate determining step in methanol synthesis on Cu catalysts occurs on the Cu surface but that the rate of reaction can be enhanced by using ZnO as a support. This statement refers to catalysts in which both Cu and ZnO are present, and for which the reaction mixture includes both CO and CO_2. A quite different mechanism may operate in the absence of CO_2 [18]. We believe that a crucial role for ZnO is to raise the effective partial pressure of hydrogen on the catalyst under reaction conditions.

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