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Effect of Metal Dispersion in CO Oxidation on Supported Pt Catalysts. Reply to Herskowitz, Holliday, Cutlip, and Kenney

In the foregoing Letter to the Editors Herskowitz, Holliday, Cutlip, and Kenney (*1*), hereafter referred to as HHCK, presented rate data on the oxidation of carbon monoxide over a series of silica-supported platinum catalysts prepared and characterised by Uchiyama *et al.* (*2*). The results are in general agreement with our previous results (*3, 4*) on the same reaction over the same series of catalysts but differ in two significant respects. In the first place HHCK did not observe declines in activity with time. Secondly, they report lower activity for the catalyst with the smallest metal crystallite size whereas in our work no clear dependence of turnover number on metal dispersion existed.

The extent of difference can be seen in Table 1 which compares our turnover numbers with ones calculated from the parameters given by HHCK for the conditions of our experiments (450 K with CO pressure of 2000 Pa and O_2 pressure of 800 Pa). Given all the experimental factors which contribute to the accuracy with which these values can be determined the agreement is remarkably good for the 6.3 and 40% dispersed samples. Even for the 81% dispersed sample the difference of a factor of 2 is not large in the present context, although it probably does represent an actual discrepancy as HHCK claim.

In our view this discrepancy is probably related to the deactivation phenomena noted in our work but not in that of HHCK. As shown in Fig. 1 of our paper (*4*) the activity fell semilogarithmically with time and is thus concentrated in the initial period on stream. For example, the decline is 25% from 10 min to 2 h on stream but only 8% over the time from 16 to 24 h. Thus if HHCK employed a significant lining-out period then subsequent deactivation might well have been undetected over a subsequent period of several days as they state especially as intervening pressure and temperature changes were made. In our work it appeared that the 81% dispersed sample showed a slightly higher deactivation rate than the other samples although this was not investigated at length. We also pointed out that its activity could be lowered to about the level found by HHCK by prior exposure to oxygen at 630 K. Thus their results could have been obtained if there had been inadvertent exposure to oxygen

TABLE 1

Comparison of Turnover Numbers[a]

Catalyst designation[b]	Percentage metal atoms exposed[b]	Calculted from data of HHCK (*1*)	As reported by Cant (*4*)
6.3-SiO_2-PtCl-L	6.0	0.0139	0.0125
40-SiO_2-PtCl-L	40	0.0163	0.015
81-SiO_2-IonX-S	81	0.0073	0.0145

[a] In molecules CO_2 per surface Pt atom per second at 450 K with CO pressure of 2000 Pa and O_2 pressure of 800 Pa.

[b] As given by Uchiyama *et al.* (*2*).

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(e.g., as an impurity in the argon stream used to flush their system free of hydrogen at 723 K following reduction). Uchiyama *et al.* (*2*) have stressed the need for the use of oxygen-free carrier gases when working with these catalysts.

Thus we see no reason to doubt our previous data or our conclusion (*4*) that turnover numbers for carbon monoxide oxidation over this particular series of silica-supported platinum catalysts is independent of metal crystallite size. However, given the apparent sensitivity of the reaction to some deactivation during operation, and the likelihood that this process will not proceed in the same way in all circumstances, it is possible that the above conclusion will not carry over to other catalyst preparations.

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NOEL W. CANT

School of Chemistry
Macquarie University
North Ryde
NSW 2113
Australia

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