

## LETTERS TO THE EDITORS

## Effect of Metal Dispersion in CO Oxidation on Supported Pt Catalysts

The effect of the degree of metal dispersion on the activity and selectivity in various reactions is receiving increased study (1, 2). Recently Otero-Schipper *et al.* (1) investigated the effect of dispersion on the activity and selectivity of a series of Pt/SiO<sub>2</sub> catalysts for the hydrogenation of cyclopropane, methylcyclopropane, and propene. Hydrogen pretreatment and the percentage of Pt exposed, from 7 to 81%, were found to yield various types of structure sensitivity. The energy of activation was found to be structure insensitive.

Dispersion effects on the activity of catalysts for oxidation reactions have not yet been widely studied, but of these the behaviour of carbon monoxide over Group VIII metals is of particular interest given both its importance in the treatment of car engine exhaust gases and the observations of multiple states and limit cycle behaviour (3). Cant *et al.* (4, 5) have reported power law kinetic expressions and turnover numbers over a series of Group VIII metals and supports, and recently described metal crystallite size effects using the Pt/SiO<sub>2</sub> series prepared by Otero-Schipper *et al.* (1). Professor Butt has kindly provided us with

samples of some of these catalysts and this note extends the data obtained by Cant. In some respects our conclusions differ although our findings are largely in agreement.

The kinetic data were obtained using a gradientless reactor operating at atmospheric pressure with oxygen mole fraction of 1 to 4% and carbon monoxide mole fractions of 1 to 6%.

Gas analyses were carried out with gas chromatography and also using infrared analysers for carbon monoxide and carbon dioxide and a paramagnetic oxygen analyser. The apparatus operates completely under the control of a PDP 11/45 computer and is described elsewhere (6). It is an improved version of an earlier computer-controlled kinetic apparatus (7) and permits the rapid collection of a large number of data points.

The pretreatment of the catalysts included 0.5 h in O<sub>2</sub> at 573 K, 1 h in H<sub>2</sub> at 573 K, and 1 h in Ar at 723 K. Flowing argon was passed over the catalyst.

Rates of reaction were measured over a wide range of CO and O<sub>2</sub> concentrations, the operation conditions being listed in Ta-

TABLE I  
Operating Conditions

Catalyst		No. of data points	Concn range (10 <sup>-6</sup> mole/cm <sup>3</sup> )		Temp. range (K)
% Pt/SiO <sub>2</sub>	% Dispersion		CO	O <sub>2</sub>	
1.97	6.2	50	0.11-1.7	0.23-1.1	390-437
1.17	40.	129	0.10-1.5	0.22-1.1	383-450
0.48	63.	16	0.17-1.0	0.50-1.0	437
0.825	81.	70	0.17-1.1	0.19-1.1	380-437

TABLE 2  
Values of Parameters in Eqs. (1) and (2)

Parameter	Catalyst, % Dispersion (wt% Pt)			Average <sup>a</sup>
	6.2 (1.97% Pt)	40. (1.17% Pt)	81. (0.825% Pt)	
$\alpha$	-0.32	-0.39	-0.38	-0.38
$\beta$	0.51	0.55	0.64	0.58
$E/R$ (K)		8600	7900	8100
$A^b$	$1.43 \times 10^5$	$1.68 \times 10^5$	$7.46 \times 10^4$	

<sup>a</sup> Calculated from data of the three catalysts.

<sup>b</sup> Calculated with average values of  $\alpha$ ,  $\beta$ , and  $E$ .

ble 1. Runs performed over long periods of time (2–3 days) with each of the four catalysts indicated no loss of activity. Furthermore, the rates measured before and after repacking the reactor with fresh catalyst were in good agreement.

The results are correlated here by a simple power law expression:

$$r = kC_{CO}^\alpha C_{O_2}^\beta, \quad (1)$$

$$k = A \exp(-E/RT). \quad (2)$$

A multivariable linear regression was employed in the computations.

First, each set of data obtained for three catalysts (1.97, 1.17, and 0.825% Pt) was analyzed independently yielding the values of  $\alpha$ ,  $\beta$ , and  $E$  listed in Table 2. Then those data sets were combined to give average values of the parameters  $\alpha$ ,  $\beta$ , and  $E/R$ . These are also listed in Table 2, along with derived values for  $A$  for each catalyst. The goodness of fit of data is illustrated in Fig. 1 (at constant temperature), and in Fig. 2, at temperatures between 390 and 437 K.

The parameters  $\alpha$ ,  $\beta$ , and  $E$  appear to be essentially independent of metal dispersion, in agreement with previous findings (1, 3, 5). Furthermore the energy of activation calculated from our data (67 kJ/mole) agrees with the value reported by Cant *et al.* (5) (56 KJ/mole) and Cant (4) (75 KJ/mole).

However, our results, in contrast to those of Cant, indicate that the activity of

the catalysts does depend on crystallite size. The magnitude of  $A$  in Table 2 is approximately the same for the 6.2 and 40% dispersion catalysts but is lower for the 81% dispersion catalyst.

The relative slopes of the lines of Fig. 1 depend on the values assumed for the mag-

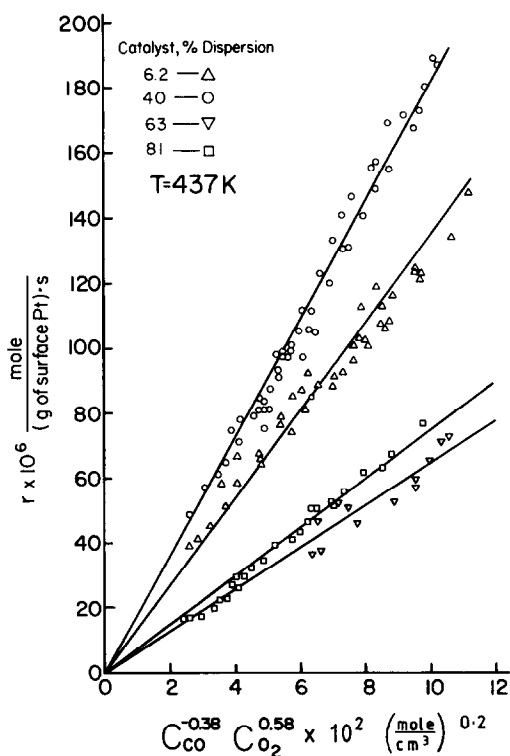


FIG. 1. Effect of reactant concentration and metal dispersion on the rate of reaction.

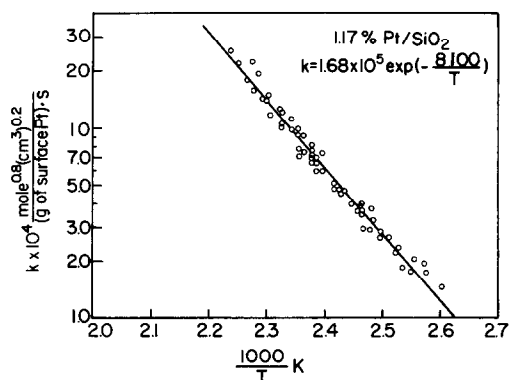


FIG. 2. Temperature influence on reaction rate constant.

nitude of the dispersion of the platinum catalysts and it has been shown (1) that chemisorption and titration lead to different estimates. These and other errors may account, in part, for the relative slopes of the catalysts with 6.2 and 40% dispersion but we consider the observed lower activity of higher-dispersion catalysts cannot be attributed solely to experimental errors. Moreover, the results show the same trend as those reported in other studies of carbon monoxide oxidation (4, 8) and in other reactions (2).

Turnover numbers are also comparable with those obtained by Cant but our experiments differ markedly in that deactivation was at no time apparent and activity was constant over periods of several days. Similar reproducibility has also been observed using a recycle reactor for transient experiments and studies of oscillatory behaviour with Pt/Al<sub>2</sub>O<sub>3</sub> catalysts (9, 10). These techniques clearly provide a greater insight into the reaction mechanism. The data treated here, which can be closely correlated with a power law expression, clearly lie in the range of high, and rate-inhibiting, surface

coverage of carbon monoxide. A more extensive analysis of these and other data in terms of kinetic models is in progress and will be published separately.

#### ACKNOWLEDGMENTS

One of the authors (M.H.) would like to express his thanks to the Rothschild Foundation for a fellowship which made possible his stay at the University of Cambridge. Another (R.H.) is grateful to the Science Research Council for the award of a Research Studentship.

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Received July 13, 1981

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