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Metal Crystallite Size Effects and Low-Temperature Deactivation in Carbon Monoxide Oxidation over Platinum

The effect of particle size on the activity of platinum for carbon monoxide oxidation is a question of both practical and fundamental importance. McCarthy *et al.* (*1*) studied this reaction for three alumina-supported preparations containing platinum particles with estimated average diameters of 28, 78, and 1000 Å, respectively. They reported that the reaction was facile (i.e., surface structure insensitive (*2*)) for CO pressures such that the reaction was inverse order in this reactant but demanding (i.e., structure sensitive) for low CO pressures when this kinetic order was positive. The dichotomy was attributed to two different reaction mechanisms although it is not possible definitely to equate their suggestions with those defined under ultrahigh vacuum conditions, most recently by Golchet and White (*3*). Hopster *et al.* (*4*) have shown that the various elementary processes operative in this system do show different dependencies on step size for Pt(111) planes. They generalize that for irregular surfaces (e.g., particles) these different functional dependencies will always manifest themselves in demanding behavior, with small particles able to exhibit higher or lower specific activities than large ones depending upon reaction conditions.

These conclusions seem of sufficient importance to warrant further checks on the rather limited data of McCarthy *et al.* (*1*) and here we wish to report such measurements in the high CO/O_2 ratio region. The catalysts used represent a selection of the $Pt–SiO_2$ series described by Burwell *et al.* (*5*) and well characterized with respect to particle size by hydrogen absorption, X-ray diffraction, and electron microscopy. The activity of 100–200 mg of each was tested under differential flow conditions in a system similar to that described earlier (*6*) using gas mixtures containing approximately 2% CO and 0.8% O_2 with the balance helium. Under these conditions the reaction is first order in O_2 and fractional negative order in CO (*6*). The pretreatment conformed to that used prior to surface area determination (i.e., successive treatments in O_2, H_2, and He near 630 K). After cooling in helium the reaction was commenced (generally near 450 K). The subsequent time dependence of the rate of CO_2 formation is shown for the 81–SiO_2–IonX catalyst as (a) in Fig. 1 (The semilogarithmic plot is used as a convenient method of representing the data and is not meant to imply that such a relationship necessarily holds.) We will return to possible causes for the activity loss later, it being sufficient to point out here that since deactivation over a

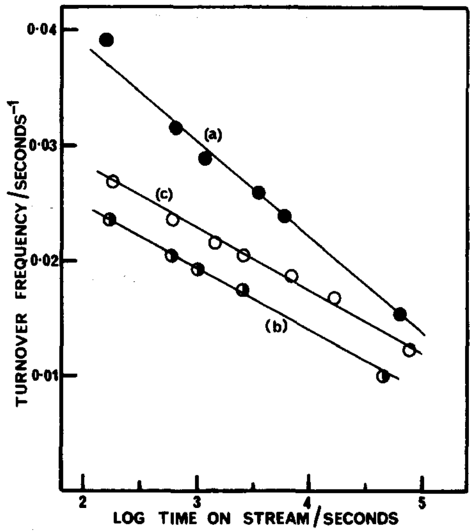

FIG. 1. Variation in turnover frequency (molecules CO_2 per surface Pt atom per second) with time on-stream at 450 K for 81–SiO_2–IonX–S catalyst (a) following standard pretreatment at 630 K; (b) following O_2 treatment for 1.5 hr at 630 K and flushing in He; (c) following restart after flushing with He for 1 hr subsequent to (a).

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range of temperatures followed a similar course with all the other catalysts, it was immaterial which time was chosen to compare relative activities. We prefer to use 16-hr activity since by that time deactivation was sufficiently slow so that the activation energy could be determined in a time span such that corrections for any activity loss during it could be accurately applied.

As may be seen from Table 1, activation energies so determined were in the range 76 ± 4 kJ mole^{-1} for each catalyst. Given the experimental error the corresponding turnover frequencies at 450 K also agreed fairly closely although repeated tests with the 27–SiO_2–IonX material always showed that its activity was the lowest. Thus we conclude, in agreement with McCarthy *et al.* (*1*), that under these conditions site activity varies little with particle size. Conversely the results fail to show the higher activity for small particles anticipated by Hopster *et al.* (*4*). However it must be pointed out that while their predictions do cover the CO/O_2 ratio we used, it is quite possible that the operative mechanism is *not* the one for which their calculations apply (*6*). Unfortunately trial experiments indicated that the second pressure regime where the reaction is first order in CO could not be obtained with these catalysts in our system before the intervention of mass and heat transfer limitations.

However, the absence of particle size effects does not enable the assigning of a unique turnover frequency for all Pt catalysts to any set of external conditions. It is evident that under the mild conditions we employed continual deactivation was taking place while if this were avoided by accelerated aging there could be no guarantee that all sizes of particles would be affected equally. Indeed changes brought about by varying pretreatments may be in part the cause of the variety of activation energies that we have previously pointed to in the literature (*6*).

We have studied the effect of many system variables on the activity decline. In the first place both the initial activity (i.e., in the first minutes) and the subsequent decline were unaffected by prior treatment for some hours at reaction temperture (450 K) in H_2, CO, or O_2. However as exemplified by (b) of Fig. 1, prior treatment in O_2 at 630 K did lower the entire deactivation curve by 40%. Second, the original activity could be fully recovered by the standard pretreatment and substantial recovery was attained by simple flushing with H_2, He, or O_2 for periods as short as a few minutes at reaction temperature (Fig. 1c). Subsequent activity decline over a further 16-hr period was to a value simply reflecting the extra time onstream. Third, deactivation followed a similar course whether or not the feedstream was passed through silica gel at −80°C (which would remove all potentially

TABLE 1

Catalyst designation[a]	wt% Pt[a]	Percentage Pt atoms[a] exposed	Activation energy (kJ mole^{-1})	Turnover[b] frequency
6.3–SiO_2–PtCl–L	1.89	6.0	79 ± 4	0.0118–0.0135
27–SiO_2–IonX–S	1.48	27(27.5)	80 ± 4	0.008–0.011
40–SiO_2–PtCl–L	1.10	40	72 ± 4	0.0137–0.0159
63–SiO_2IonX–S	0.48	63(63.5)	76 ± 4	0.0118–0.0135
81–SiO_2–IonX–S	0.825	81	72 ± 4	0.012–0.017

[a] As per Ref. (*5*). Figures in parentheses calculated from our own measurements of static hydrogen chemisorption at 273.2 K.

[b] Expressed as molecules (CO_2)/surface Pt atom/sec for 16 hr onstream adjusted to 450 K and CO pressure = 2000 Pa and O_2 pressure = 800 Pa. Range covers several experiments with at least two samples of each catalyst.

reactive impurities except H_2, CH_4, and perhaps C_2H_4, C_2H_6, and N_2O). Furthermore it was independent of total flow rate over a wide range provided the feed was dried by passage over activated silica gel at ambient temperature.

The above observations rule against the supposition that impurities (or product CO_2) cause the activity decline, but given the extraordinary sensitivity of this reaction to impurities as revealed by the recent work of Varghese *et al.* (*7*) that possibility should perhaps not be ruled out entirely. However, it seems more likely that deactivation stems from a parallel side reaction in manner similar to that observed by Ostermaier *et al.* (*8*) for ammonia oxidation over Pt. They attribute deactivation to build-up of a nonreactive oxygen species and, given the lower activity we find following oxygen pretreatment at 630 K, the same effect seems likely here. It is perhaps significant that infrared studies (*9–11*) have shown that repeated cycling of Pt catalysts in CO/O_2 mixtures, or their high-temperature exposure to oxygen prior to CO adsorption, results in the formation of a second CO absorption band at 2120 cm^{-1} in addition to that normally observed at 2070 cm^{-1} for adsorption on bare metal. The 2120 cm^{-1} band is assigned to CO molecules attached to a single Pt atom simultaneously associated with an adsorbed oxygen species (*10*). This type of oxygen is *unreactive* toward gas phase CO in contrast to oxygen initially adsorbed at room temperature. There seems no reason to suppose that such build-up of unreactive oxygen should not take place under our conditions and indeed the formation of both forms of CO infrared absorption bands has been noted recently under reaction conditions during the oxidation of CO over Pt/Al_2O_3 and $Pt/CeO_2/Al_2O_3$ catalysts by Summers and Ausen (*12*). Whatever the exact nature of the deactivating oxygen species it is evident that the blocking can be relieved in part by reaction and/or rearrangements within surface layers since considerable reactivation was achievable by short pretreatment with inert gas alone.

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