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Some Unique Aspects of CO Oxidation on Supported Pt

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Supported Pt catalyzed oxidation of CO was studied as a function of sintering severity. Specific rate data (moles CO oxidized/time · area of Pt) indicate the reaction to be demanding at low CO concentration and facile at higher CO concentrations. Further, sustained isothermal oscillations were observed. Overall kinetic behavior and the oscillations can be rationalized by viewing the oxidation process as one consisting of (a) an Eley–Rideal mechanism involving gaseous CO reacting with adsorbed O_2 at low CO concentrations, and (b) chemisorption of O_2 upon a surface partially covered with CO at higher CO concentrations. Global sintering kinetics in air are found to be second order in surface area with an activation energy of about 60 kcal.

INTRODUCTION

Catalysis of CO oxidation by noble metals (e.g., Pt, Pd, Rh, Ru) is kinetically unique in that negative first order dependency of CO concentration is manifested at CO concentrations above about 1% or less (*1–3*). For example, Tajbl *et al.* (*2*) and Mitani (*3*) correlate their phenomenological rate data, in excess oxygen, by the expression

$$r = \frac{\bar{k}}{[\mathrm{CO}]}. \qquad (1)$$

In fact, the rate–CO concentration behavior over a concentration range of from zero to several percent CO can be described by the rate law (*4*) (in excess O_2)

$$r = \frac{k[\mathrm{CO}]}{(1 + K[\mathrm{CO}])^2}. \qquad (2)$$

Equation (2) is generally thought to faithfully reflect the oxidation mechanism which suggests that the rate determining step (rds) is that of bimolecular surface reaction between adsorbed oxygen and CO.

Recent work of Nishiyama and Wise (*5*) clearly indicates that on a Pt foil (a) gaseous CO readily reacts with preadsorbed O_2, (b) gaseous O_2 chemisorbs prior to rapid surface reaction with a CO covered surface.

Thus it is known that in O_2 at low CO concentrations, Pt is largely covered with O_2 while CO populates the surface at higher CO partial pressures. Indeed in the range of CO partial pressures in which Eq. (1) is obeyed, one can argue that its form is a limiting one of a general model resting on the assumption that chemisorption of O_2 is the rds upon the CO-free portion of the surface, i.e.,

$$r = kO_2(1 - \theta_{\mathrm{CO}}) = \frac{\bar{k}\,O_2}{(1 + K[\mathrm{CO}])}. \qquad (3)$$

which, of course, reduces to Eq. (1) when $K\mathrm{CO} \gg 1$. The fact that Eq. (3) cannot apply as $[\mathrm{CO}] \to 0$, in which region the rate is observed to be linear in CO, does not preclude the possibility that Eq. (3) and its implied mechanism are operative at higher CO levels. Nor does the fact that Eq. (2) reduces to observed behavior at low CO levels ($r = k\mathrm{CO}$) and high levels ($r = \bar{k}/\mathrm{CO}$), justify the assertion that reaction between equilibrium adsorbed species is the rds over a wide range of CO partial pressures. Whereas a reaction model may well be formulated by Eq. (2) since it obeys the observed limiting behavior, conformity between reaction kinetics model and data proves not to be mechanistically persuasive. More severe, extrakinetic, evaluations are required to provide bases for mechanistic inferences.

Demanding-Facile Reactions

Taylor (*6*) provided a key insight into heterogeneous catalysis when he noted that, in essence, the behavior of the particular catalyst depends, perhaps, upon the nature of the reaction so catalyzed. Boudart (*7*) has crystallized this speculation by characterizing heterogeneous catalytic reactions as being (a) demanding, i.e., the specific velocity (moles reacted per unit time-per area of catalytic species) changes with said specific area and (b) facile, in which case specific activity is independent of specific area.

A derivative of Boudart's classification is: (c) should a reaction be governed by but one rds over the observed range of reactant partial pressure and temperature then the evidence of either demanding or facile behavior should prevail over that range of parameter variation. By inference, however, should the observed reaction be demanding in one range of species partial pressure and facile in another, then we must draw the inference that one rds *does not* characterize that reaction over the observed range of species partial pressure variation. In effect, Boudart's unique definition regarding demanding-facile reactions permits us the opportunity to detect nonuniqueness with respect to the rds. In other words, should a particular heterogeneous catalytic reaction exhibit both facile and demanding characteristics as a function of species partial pressure, we may then be allowed the freedom to suggest that that reaction is not determined by a unique rds but by at least two such steps—one operative in one range of key reactant partial pressure—the other in another range of key species partial pressure.

Goals of This Research

While recognizing that a phenomenological rate model [Eq. (2)] may well describe "overall" rate behavior for the CO oxidation system, we deemed it worthy that a more subtle inquiry be pursued to advance our understanding of the fundamental processes which determine this seemingly simple heterogeneous catalytic reaction.

Specifically, the rate of oxidation of CO in O_2 was measured as a function of not only CO partial pressure and temperature, but as a function of supported Pt crystallite size. Thus the primary goal of this research was that of ascertaining the influence of specific catalytic (Pt) area upon specific activity over a range of partial pressures of key reactant, CO.

EXPERIMENTAL DETAILS

The apparatus employed to measure reaction rates is identical to that detailed by Tajbl *et al.* (*2*). The Notre Dame CSTCR, "spinning basket," reactor was employed. However CO_2-effluent concentrations were herein determined instantaneously by infrared (Beckman Model 315A nondispersive ir CO_2 analyzer). It was thus possible to measure effluent CO_2 concentrations as a function of real time—with consequent unexpected yet fruitful dividends.

The usual metering schemes were employed to measure feed and effluent streams. Total reactor pressure was about 1 atm.

The catalyst consisted of 0.035% Pt deposited upon α-Al_2O_3 (BET area = $5 m^2/g$).

Specific Pt area was determined by the Benson–Boudart Hydrogen titration technique (*8*). While we are cognizant that that method is not absolute, it does provide a real measure of the *changes* in specific Pt surface atom availability as a consequence of sintering.

Said changes in specific Pt atom surface availability were created by sintering the particular catalyst sample in air in a furnace swept with air at 700, 750 and 800°C. Hydrogen titration was then employed at room temperature to estimate Pt catalytic site density at each level of sintering severity.

RESULTS

Sintering Kinetics

The phenomenological kinetics of sintering are displayed in Fig. 1, wherein reduced surface atom exposure, A/A_0, is displayed vs time of sintering in air at temperature levels of 700, 750, and 800°C.

These data are approximately correlated by second order kinetics, with an activation energy of about 60 kcal—a result not in conflict with earlier observations (*9*). However, the detailed, mechanistic, aspects of these sintering phenomena escape us at this time. Suffice it to note that by sintering in air, average crystallite sizes from between 30 and 1000 Å were obtained and then utilized in the determination of specific rate (moles CO oxidized/sec · area Pt) over a range of CO partial pressure (in O_2) of from 0 to 2% CO.

Catalytic Kinetics

The rates (moles CO_2 generated/time · g catalyst) of CO oxidation over fresh Pt/α-Al_2O_2 catalysts are displayed in Fig. 2 for various temperature levels. In Fig. 3 there is set forth the same measure of rate at constant temperature for various levels of sintering severity. No evidence of sintering during CO oxidation was noted.

From Fig. 2 we note rate–CO partial pressure behavior identical to that observed in earlier studies, namely (a) at low CO levels, rate is proportional to CO

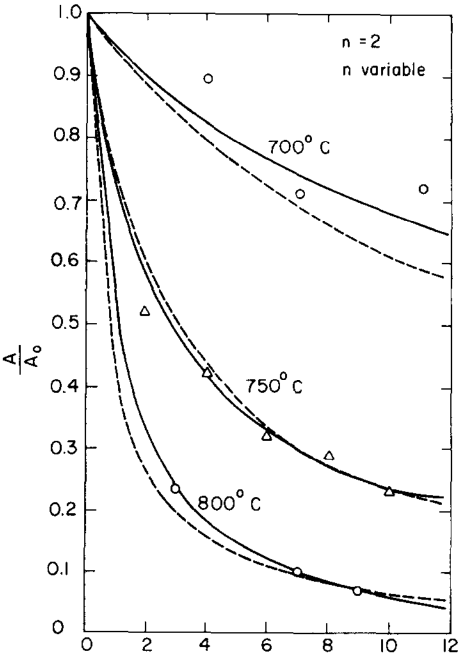

FIG. 1. Pt crystallite area vs time.

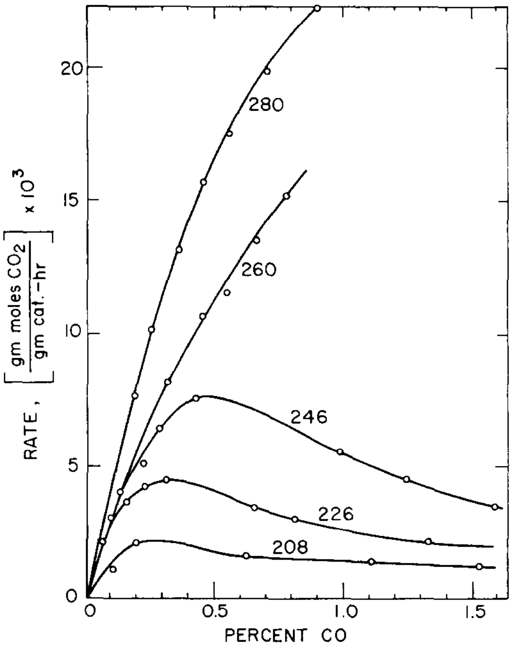

FIG. 2. CO oxidation rate vs % CO at various temperatures (°C).

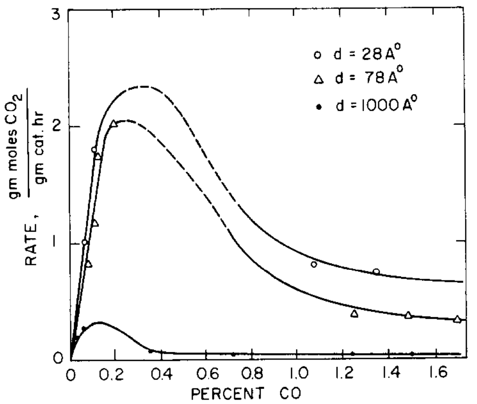

FIG. 3. CO oxidation rate vs % CO for various average Pt crystallite sizes.

while (b) at high CO levels the rate becomes inversely proportional to CO.

Figure 3 indicates that global rate (as opposed to specific rate) is drastically reduced as crystallite size increases. Note, however, that when the rate of Pt catalyzed CO oxidation is reported per square meter of surface exposed Pt, then that specific rate is (Fig. 4) (a) higher for low area (sintered) Pt than for highly dispersed (high specific area) Pt in the range of low CO partial pressure while (b) at higher CO partial pressure, specific rate is relatively insensitive to particle size (Fig. 5).

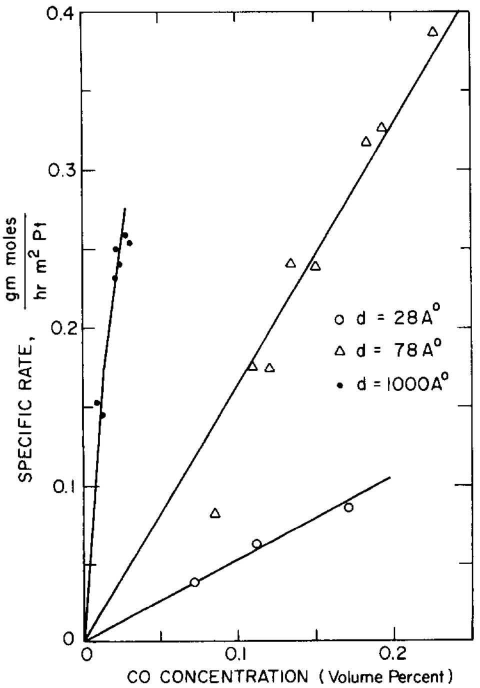

FIG. 4. Specific rate of CO oxidation vs % CO for various average crystallite sizes in region of low CO concentration.

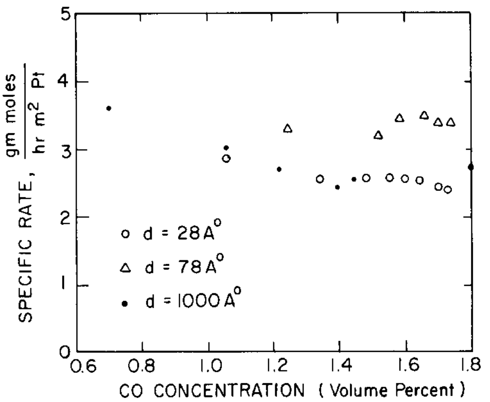

FIG. 5. Specific rates of CO oxidation vs % CO in region of high CO concentration.

These data suggest that the supported Pt catalyzed reaction of CO oxidation in pure oxygen is (a) demanding at low CO partial pressures, i.e., in the normal kinetic regime where specific rate increases with reactant CO partial pressure, (b) facile in the abnormal kinetic regime where specific rate decreases with reactant CO partial pressure.

Oscillations

Under certain conditions of reactant feed rate and temperature, sustained oscillations were observed as displayed in Fig. 6 which is an exact reproduction of instantaneous CO_2 effluent concentration,

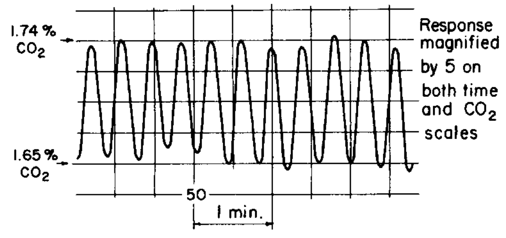

FIG. 6. Record of oscillatory behavior.

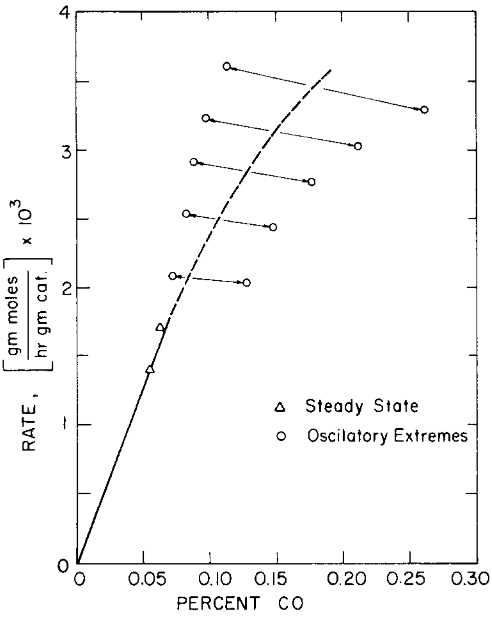

FIG. 7. Limits of oscillatory extremes.

as measured by ir, vs time. Figure 7 reveals the region of said oscillations and their magnitudes. Significantly these oscillations occur in the neighborhood of maximum rate.

DISCUSSION

Two significant facts are manifested in this study:

a. the Pt catalyzed reaction of CO oxidation is demanding at low CO partial pressures and facile at higher CO partial pressures,

b. in the vicinity of maximum rate, sustained oscillations are observed.

One must anticipate that oscillations may be thermal in nature, i.e., inter–intraphase temperature gradients may be responsible for the oscillatory behavior. Utilizing the criterion set forth earlier (*10*), it was determined that, at most, a reduced temperature difference between gas phase and catalyst bulk of 0.001 is predicted between rates commensurate with the maximum and minimum CO_2 concentrations shown in Fig. 6. The observed oscillations are, therefore, *isothermal.* The cause or causes of the noted oscillations must be sought in terms of the intrinsic kinetic mechanism which characterizes this reaction.

It is readily shown that if Eq. (2) and its implied mechanism truly describes the intrinsic catalytic events, oscillatory behavior is impossible (*11,12*).

In point of fact, isothermal oscillations will only occur by an autocatalytic process (*13*), or, if more than one step in a catalytic sequence proves to be rate determining.

An autocatalytic step within a surface catalyzed sequence is envisioned with difficulty, unless one invokes a mechanism involving bridged and linear CO chemisorption on Pt. However, as Eichens notes (*14*) Pt on Al_2O_3 reveals very little bridge structure.

The existence of oscillations *and* demanding-facile behavior which depends upon CO partial pressure strongly suggests that CO oxidation as catalyzed by supported Pt cannot be fundamentally characterized by one mode of rate control as is implied by Eq. (2).

Indeed, consider the following facts:

a. at high partial pressure of O_2, one can anticipate virtually total coverage of surface Pt by oxygen. This assertion is, of course, the basis of the H_2 titration technique (*8*) and the CO titration technique (*15*) for determination of exposed (surface) Pt atoms. Colliding CO molecules can thus be expected to react in accord with the Eley–Rideal mechanism, i.e.,

$$CO_{gas} + PtO \rightleftarrows Pt + CO_2. \qquad (4)$$

b. at high CO partial pressures, the Pt surface will be largely occupied by a CO–Pt chemisorbed complex. Reaction of gaseous molecular O_2, via an Eley–Rideal mechanism is not here possible as the O_2 must first be dissociated. The Pt surface unoccupied by CO provides the sites of O_2

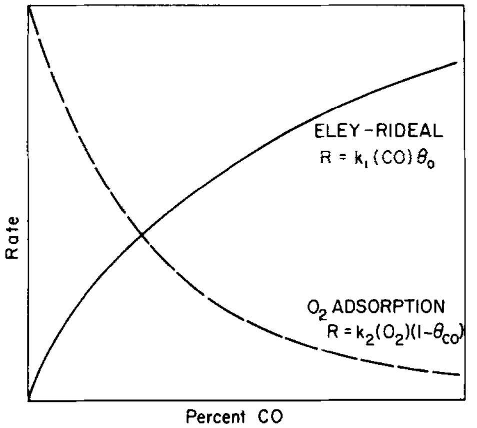

FIG. 8. Schematic of two modes of rate control.

dissociation. Hence at high CO partial pressures either chemisorption of O_2 or surface reaction between adsorbed coreactants must be rate controlling. In the light of Wise's work (*4*), O_2 chemisorption would seem to be the rds. In either case, a rate law in accord with observation is derivable from Eqs. (2) or (3).

In Fig. 8 there is set forth in schematic fashion the intrinsic rate vs CO partial pressure for

1. Eley–Rideal kinetics involving gaseous CO with chemisorbed O_2 and
2. O_2 chemisorption kinetics as a function of CO partial pressure.

Invoking by way of qualitative approximation the concept of additivity of surface resistances, the overall observed rate is given in terms of rate processes (1) and (2) above by

$$R_0 = \frac{1}{(1/k_1\text{CO}) + (\text{CO}/k_2)}, \quad (5)$$

which expression exhibits linearity at low CO partial pressures and negative order in CO with increasing CO partial pressure. A maximum is evidently predicted.

Further, the model which is suggested here, namely nonunique surface reaction rate control, is in accord with our observations of demanding-facile behavior and the oscillatory phenomena. For surely k_1 in Eq. (5) can be sensitive to crystallite size while k_2 may be insensitive. Thus the demanding-facile nature of the observed rate will depend upon CO partial pressure, as is indeed observed.

The oscillations can be attributed to the fact that in the region of near-maximum rate both mechanisms compete at a comparable velocity, a requirement for oscillatory behavior (*16*).

Our observations relate to a crucial issue of the influence of catalyst crystallite size upon catalytic activity. We speculate that small Pt crystallites may exhibit an understandably strong tenacity for O_2, to yield PtO, from which entity O is extracted by CO with difficulty. With an increase in crystallite size by sintering ease of O extraction is increased, thus the observed increase in specific rate with crystallite size is rationalized.

In the region of facile behavior (high CO concentration), the rate depends solely upon availability of surface to O_2 (surface not occupied by chemisorbed CO). The observed facility of specific rate is thus understandable.

REFERENCES

1. Langmuir, I., *Trans. Faraday Soc.* **17**, 621 (1922).
2. Tajbl, D. G., Simons, J. B., and Carberry, J. J., *Ind. Eng. Chem. Fundam.* **5**, 171 (1966).
3. Mitani, T., MS thesis in Chem. Eng., Univ. of Notre Dame, 1969.
4. Voltz, S. E., Morgan, C. R., Liederman, D., and Jacob, S. M., Ind. Eng. Chem. Prod. Res. Devel. **12**, 294 (1973).
5. Nishiyama, Y., and Wise, H., *J. Catal.* **32**, 50 (1974).
6. Taylor, H. S., *Proc. Roy. Soc. Ser. A* **108**, 105 (1925).
7. Boudart, M., *J. Catal.* **6**, 92 (1966).
8. Benson, J. E., and Boudart, M., *J. Catal.* **4**, 704 (1965).
9. Herrmann, R. A., *J. Phys. Chem.* **65**, 2189

(1960).
10. Carberry, J. J., and Kulkarni, A., *J. Catal.* **31,** 41 (1973).
11. Schmitz, R. A., private communication.
12. Aris, R., private communication.
13. Frank-Kamenetskii, D. A., "Diffusion and Heat Exchange in Chemical Kinetics." Princeton Univ. Press, Princeton, NJ, 1955.
14. Eichens, R., private communication.
15. Wentrcek, P., Kimoto, K., and H. Wise, *J. Catal.* **31,** 279 (1973).
16. Wicke, E., *Chem. Ing. Tech.* **46,** 365 (1974).