

NOTE

Kinetics of Carbon Monoxide Oxidation on Solid Oxide Solution and Platinum on Alumina—A Comparative Study

Catalytic oxidation of carbon monoxide on supported and unsupported noble metal catalysts has been the subject of numerous studies aimed at elucidating reaction mechanism and quantifying its kinetic parameters (1–10). We studied the kinetics of CO oxidation in excess oxygen (99% O₂) on supported Pt catalyst and solid oxide solution La_{0.8}Sr_{0.2}CrO_{3-δ} (NDI) as a function of CO concentration. The comparison between the kinetics of the catalytic behavior of Pt/alumina and solid oxide solution La_{0.8}Sr_{0.2}CrO_{3-δ} and the dependency of the turnover velocity coefficient of CO oxidation upon dispersion on Pt/alumina catalysts with different sintering severity are reported.

Experiments were performed in the integrated-external recycle reactor designed for reaction kinetic studies and *in situ* measurement of gas chemisorption by pulse technique. A detailed description of the apparatus has been presented elsewhere (11). The gas composition was analyzed before and after reaction by an on-line gas chromatograph interfaced with an automatic integrator. Kinetic studies were performed in the recycling mode under isothermal condition at a feed flow rate of 100 cm³ min⁻¹. The gas recirculation rate was kept at 10 liter min⁻¹. Thus, the recycle ratio is 100, well above 25, the minimum ratio required for gradientless, CSTR, performance.

La_{0.8}Sr_{0.2}CrO_{3-δ} was prepared by solid state processing. The required amount of component oxides were mixed, pressed, and sintered in an alumina crucible between 1173 and 1223 K for 12 h (12, 13). Cycles of grinding, pelletizing, and heating were repeated three times to ensure complete reaction. X-ray diffraction, SEM, and EDX showed the formation of a homogeneous single phase. Uniform mesh size of powder (sieve fraction between 10 and 35 μm) was used for the catalytic studies.

The supported Pt catalyst (0.5% Pt on gamma alumina) was supplied by Engelhard Industries, Inc. The dispersion of fresh catalyst (Pt 1) as measured by hydrogen titration and CO chemisorption is 95%. Heat treatment at 873 K in constant air flow for 4 and 8 h resulted in 40% dispersion (Pt 2) and 10% dispersion (Pt 3), respectively.

Specific Pt atom exposure was determined by Benson–Boudart hydrogen–oxygen titration (14), as well as

by CO chemisorption at room temperature by pulse flow technique. Pretreatment was as follows: samples of 5 g of the catalyst were outgassed for 30 min at room temperature and 3 h at 423 K; hydrogen at 75 ml/min was passed over the samples and the temperature was raised to 773 K. Reduction was carried out for 12 h at this temperature after which the samples were outgassed at 773 K for 1 h and then cooled to room temperature. CO chemisorption was measured after He flushing. For hydrogen titration the reduced sample was exposed to oxygen and then flushed with He before measuring hydrogen uptake at room temperature by quantitative pulses. Surface area of the catalysts was measured by the BET N₂ adsorption technique.

Table I lists the total number of exposed catalyst (Pt) atoms of the Pt/alumina catalyst. It is interesting to note that the exposed sites counted by hydrogen titration of chemisorbed oxygen (\bar{A}_1) is about two times the number inferred from CO chemisorption (\bar{A}_c) upon the same sample; i.e., $\bar{A}_1/\bar{A}_c = 1.75$ at all levels of dispersion, a result not in conflict with the findings of Benson and Boudart (14). This could be due to bridged CO chemisorption where each CO counts a site pair instead of a single Pt site. Evidence for the latter seems not to be on hand for Pt/alumina.

For any kinetic scheme, global rate (R_g) is defined as

$$R_g = C_f X / \theta \quad [1]$$

for feed concentration C_f , conversion X , and contact time θ . The global rates (moles of CO converted per g catalyst per time) of CO oxidation over fresh and sintered supported Pt catalyst at 383 K and on solid solution La_{0.8}Sr_{0.2}CrO_{3-δ} at 368–393 K are displayed in Figs. 1 and 2. It is generally acknowledged that CO oxidation over Pt can be adequately described by a kinetic model rooted in the Langmuir–Hinshelwood postulate

$$R_g = \frac{k_o C_c}{(1 + KC_c)^2} \quad [2]$$

in excess oxygen concentration.

TABLE 1

Kinetic Parameters of CO Oxidation on Pt/Alumina Catalyst with Different Crystallite Size at 383 K

Pt Dispersion	\bar{A}_t (10^{-17})	\bar{A}_c (10^{-17})	k/\bar{A}_t (10^{20})	k/\bar{A}_c (10^{20})	\bar{K}/\bar{A}_t (10^{18})	\bar{K}/\bar{A}_c (10^{18})
Pt 1 ($d = 0.95$)	94	54	3.1	5.4	8.3	14
Pt 2 ($d = 0.4$)	23	13.5	5	8.5	36.9	63
Pt 3 ($d = 0.1$)	8.03	4.66	7.7	14	56	101

Note. \bar{A}_t = exposed catalyst site counted by hydrogen-oxygen titration. \bar{A}_c = exposed catalyst site counted by CO-chemisorption.

The genesis of this rate expression is, of course, the assumption that the rate determining step is that of surface reaction between chemisorbed CO and O_2 . Indeed, Eq. [2] adequately describes CO oxidation over a wide range of CO concentration (positive and then negative order in CO with increasing CO concentration). Note, however, that the L-H postulated model fails to predict the observed zero order in CO at high CO concentrations. The zero order kinetic behavior is observed on solid oxide solution $La_{0.8}Sr_{0.2}CrO_{3-\delta}$ at higher CO concentration at various temperatures (a representative point is given in Fig. 2b). The issue of positive, negative, and zero order behavior with increasing CO concentration inspired the speculation that two parallel routes to CO_2 exist, a Langmuir-Hinshelwood and an Eley-Rideal route (15-17). A similar observation was made earlier for Pt/alumina catalyst (15); i.e., in excess oxygen

$$R_g = \frac{k_o C_c}{(1 + KC_c)^2} + \frac{\bar{k}_o C_c}{(1 + KC_c)}, \quad [3]$$

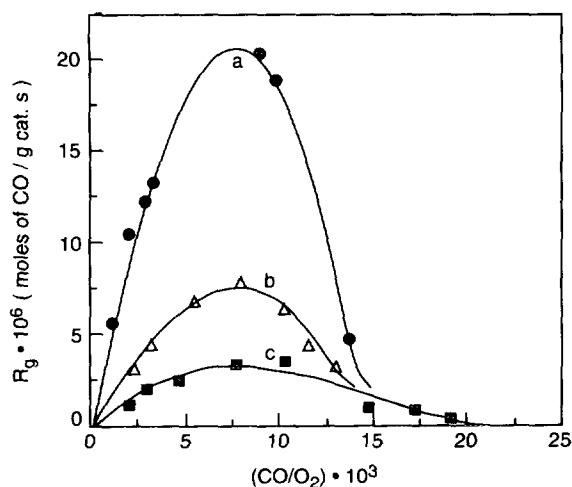


FIG. 1. Global rate of catalytic oxidation of CO on (a) Pt 1, (b) Pt 2, and (c) Pt 3 at 383 K.

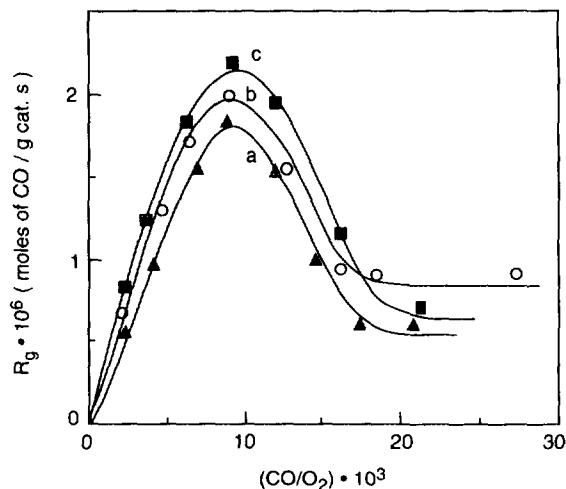


FIG. 2. Global rate of catalytic oxidation of CO on $La_{0.8}Sr_{0.2}CrO_{3-\delta}$ at (a) 368 K, (b) 383 K, and (c) 393 K.

where at higher values of KC_c

$$R_g \rightarrow \frac{k'_o}{C_c} + \bar{k}'_o \rightarrow \bar{k}'_o \quad [4]$$

or zero order, in the limit, as is observed (15). It is to be noted that an Eley-Rideal step and that of CO chemisorption yield identical kinetic forms; however, the Eley-Rideal step is a parallel one, while that of CO chemisorption a serial one.

Our data analysis is confined largely to the region of positive and negative order behavior and constancy of O_2 concentration. The candidate rate equation (L-H) is then

$$R_g = \frac{kK_oK_c \cdot C_c \cdot C_o}{(1 + K_oC_o)^2(1 + K_cC_c/(1 + K_oC_o))^2}, \quad [5]$$

where K_o and K_c are chemisorption equilibrium constants for oxygen and CO, respectively.

If $K_oC_o \gg 1$, then

$$R_g = \frac{k\bar{K}(C_c/C_o)}{(1 + \bar{K}(C_c/C_o))^2}, \quad [6]$$

where $\bar{K} = K_c/K_o$.

Values of k , \bar{K} at three levels of Pt dispersion are obtained by linearization of Eq. [6] and hence the values of k/\bar{A}_t , \bar{K}/\bar{A}_t , k/\bar{A}_c , \bar{K}/\bar{A}_c are estimated (Table 1).

$$\sqrt{\frac{C_c/C_o}{R_g}} = \frac{1}{\sqrt{k\bar{K}}} + (C_c/C_o) \sqrt{\frac{\bar{K}}{k}} \quad [7]$$

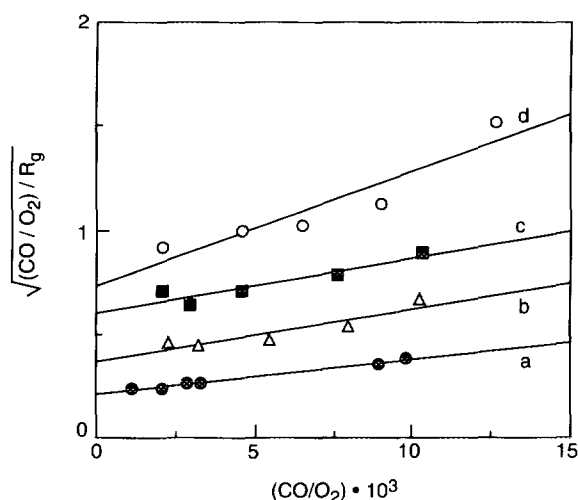


FIG. 3. Linearized kinetic data of CO oxidation in accord with L-H model (a) Pt 1, (b) Pt 2, (c) Pt 3, and (d) $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_{3-\delta}$ at 383 K.

The linear concentration dependence of the global rate at CO concentration on supported Pt and solid oxide solution (Fig. 3) clearly indicates that the reaction kinetics strictly follows L-H model at a lower CO concentration limit.

An unambiguous examination of the influence of \bar{A} (dispersion) upon \bar{K} and k is possible since three dispersions were studied.

The turnover velocity (N_c) defined by Carberry (18, 19) is

$$N_c = N_b/f(\text{concentration}), \quad [8]$$

where N_b is the conventional turnover number.

$$N_b = \frac{R_g}{\bar{A}} = k_v(a/\bar{A})C$$

$$N_c = k_v(a/\bar{A}), \quad [9]$$

where \bar{A} is the exposed catalyst area or number of catalyst sites per g or volume of catalyst, a is the catalytic area or number of active catalyst sites per g or volume of catalyst, and k_v is the reaction velocity coefficient.

We invoke a recently suggested relationship (19) between exposed catalyst \bar{A} and catalytic sites a

$$a/\bar{A} = D_0(\bar{A})^d. \quad [10]$$

Then Eq. [9] becomes

$$N_c = k_v D_0(\bar{A})^d = k/\bar{A}. \quad [11]$$

The linear dependency of the turnover velocity coefficient k/\bar{A} gives a value of site discrimination order $d =$

-0.4 which is to say that the turnover velocity coefficient is structure sensitive. Also we observed the linear dependency of \bar{K}/\bar{A} upon dispersion, i.e., $d = -0.8$. As \bar{K}/\bar{A} is inversely proportional to \bar{A} we do expect the observed sensitivity of \bar{K}/\bar{A} with different dispersion.

We have been unable to count *catalytic* as opposed to *catalyst* sites. Topsoe *et al.* (20) have done so in the case of supported Fe ammonia synthesis catalyst. They measured \bar{A} by CO chemisorption and found structure sensitivity ($d = 3.8$) in the Carberry equation [11], but structure insensitivity ($d = 0$) was found when N_2 chemisorption was employed as the site counter. In sum, N_2 chemisorption granted a , whilst CO chemisorption provided \bar{A} . In our study of Pt catalyzed oxidation of CO we have not been able to find the proper catalytic site counter. Perhaps this is to be expected if indeed the rate determining step is that of surface reaction between chemisorbed CO and O_2 , whereas in NH_3 synthesis the rate determining step is generally agreed to be N_2 chemisorption.

A comparison of specific activity for CO oxidation over Pt and $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_{3-\delta}$ is set forth in Table 2. Specific activity is reaction velocity (moles per contact time) per exposed catalyst area at a definite CO conversion. While we use the total number of exposed catalyst (Pt) atoms for the Pt catalysts, we are obliged to use the BET area for the solid oxide solution, as we do not at this time know what portion of the total (BET) area of SOS is the actual catalyst area. The comparison of the specific activity calculated with the total BET area shows that solid solution $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_{3-\delta}$ surely rivals Pt/alumina (Table 2).

The major facts manifested in this study are:

(i) The kinetics of CO oxidation on solid oxide solution $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_{3-\delta}$ results in a Langmuir-Hinshelwood model identical to that of the Pt/alumina catalyst in the low CO concentration region whilst it follows the Langmuir-Hinshelwood, Eley-Rideal mixed kinetics in the high CO concentration levels.

TABLE 2
Specific Activity of the Oxidation Catalysts for CO Conversion at 383 K

Catalyst	Wt. of the catalyst (g)	BET Area (m^2/g)	Exposed area (m^2)	Specific activity (mol CO/ m^2 h) 50%
Pt/Alumina (Pt 1)	0.12	249	0.27 ¹ 0.47 ²	0.04 0.02
ND1 ($\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_{3-\delta}$)	0.25	0.33	0.08 ³	0.02

¹ Specific surface area of Pt measured by CO chemisorption.

² Specific surface area of Pt measured by hydrogen-oxygen titration.

³ BET area.

(ii) The turnover velocity, N_c (cm/time per active catalytic site per exposed catalyst site), shows the CO–O₂ reaction is structure sensitive at low CO concentration region ($<5 \times 10^{-4}$ mol/liter). The turnover velocity coefficient and the ratio of CO/O₂ adsorption equilibrium coefficient show linear dependency upon dispersion with a site discrimination order $d = -0.4$ and -0.8 , respectively.

ACKNOWLEDGMENT

The authors are indebted to the Mobil Oil and Exxon Education Foundation for support of our catalysis studies.

REFERENCES

1. Su, E. C., Rothschild, W. G., and Yao, H. C., *J. Catal.* **118**, 11 (1989).
2. Cho, B. K., and Stock, C. J., *J. Catal.* **117**, 202 (1989).
3. Herz, R. K., and Marin, S. B., *J. Catal.* **65**, 281 (1980).
4. Yao-En Li, Boecker, D., and Gonzalez, R. D., *J. Catal.* **110**, 319 (1988).
5. Papp, H., and Kamp, P., *Surf. Interface Anal.* **12**, 253 (1988).
6. Plath, P. A., Moeller, K., Jaeger, N. I., *J. Chem. Soc. Faraday, Trans. 1* **84**, 1751 (1988).
7. Rumpf, F., Poppa, H., and Boudart, M., *Langmuir* **4**, 722 (1988).
8. Sant, R., and Wolf, E. E., *J. Catal.* **110**, 249 (1988).
9. McCarthy, E., Zahradnik, J., Kuczynski, G. C., and Carberry, J. J., *J. Catal.* **39**, 29 (1975).
10. Boudart, M., and Rumpf, F., *React. Kinet. Catal. Lett.* **35**, 95 (1987).
11. Serrano, C., and Carberry, J. J., *Appl. Catal.* **19**, 119 (1985).
12. Rajadurai, S., Carberry, J. J., Alcock, C. B., and Li, B., *J. Catal.* **131**, 582 (1991).
13. Carberry, J. J., Rajadurai, S., Alcock, C. B., and Li, B., *Catal. Lett.* **4**, 43 (1990).
14. Benson, J. E., and Boudart, M., *J. Catal.* **4**, 704 (1965).
15. Carberry, J. J., *Acc. Chem. Res.* **18**, 358 (1985).
16. Cameron, P., Scott, R. P., and Watts, P., *J. Chem. Soc., Faraday Trans. 1* **82**, 1389 (1986).
17. Dwyer, S. M., and Bennett, C. O., *J. Catal.* **95**, 275 (1982).
18. Carberry, J. J., *J. Catal.* **114**, 277 (1988).
19. Carberry, J. J., *J. Catal.* **107**, 248 (1987).
20. Topsoe, H., Topsoe, N., Bohlbro, H., and Dumesic, J. A., in "Proceedings, 7th International Congress on Catalysis, Tokyo 1980" (T. Seiyama and K. Tanabe, Eds.), p. 247. Elsevier, Amsterdam, 1981.

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Received January 25, 1993; revised November 9, 1993

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