Reactivity of Oxygen Species Adsorbed on Silver for CO Oxidation

By MASAYOSHI KOBAYASHI,* HIROSHI TAKEGAMI, and HARUO KOBAYASHI
(*Department of Chemical Process Engineering, Hokkaido University, Sapporo* 060, *Japan*)

Summary Oxygen species adsorbed on silver from gaseous oxygen show higher activity for the oxidation of CO compared with those adsorbed from nitrous oxide at 20 °C.

IN recent work using e.s.r. techniques[1,2] it has been observed that monoatomic oxygen species adsorbed on some metal oxides react with CO while diatomic oxygen species do not. More recently, however, Clarkson and Cirillo[3] have reported that the diatomic oxygen species adsorbed on silver show high reactivity for CO oxidation. This discrepancy is attributed to the specificity of silver. We have studied the reactivity of oxygen species adsorbed on silver for CO oxidation further by applying the transient response method[4] using gaseous O_2 and N_2O which can produce, respectively, diatomic and monoatomic oxygen species at the initial stages of their adsorption.

The catalyst used was prepared by reducing silver oxide which was coated on α-Al_2O_3 with a small amount of K_2SO_4 as promoter. The composition of the catalyst was Ag, 154 g, and K_2SO_4, 0·827 g per 40 g of α-Al_2O_3. The total flow rate was maintained at 160 ml (N.T.P.) min^{-1} and gases were analysed by g.l.c.

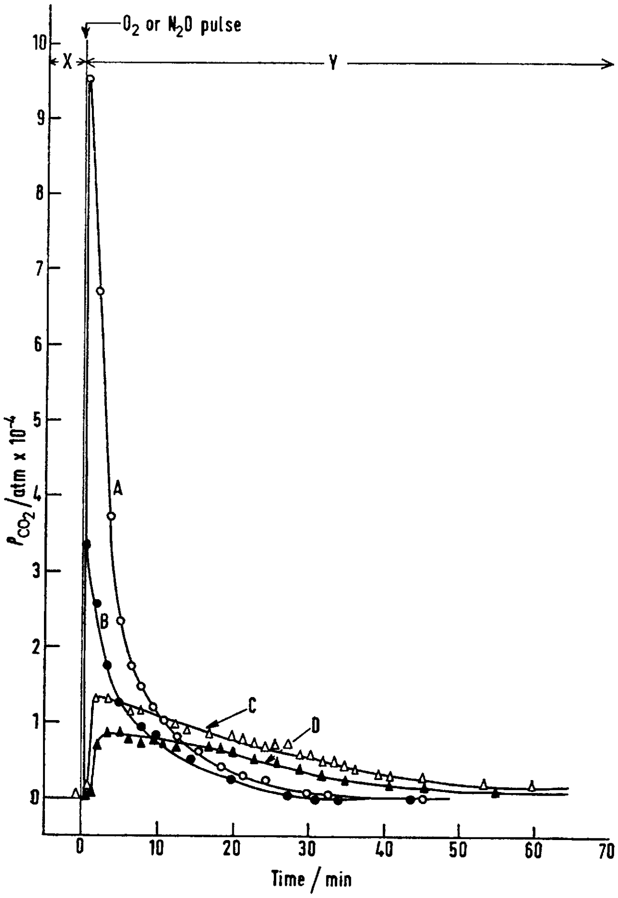

FIGURE 1. Transient responses of CO_2 by O_2 and N_2O pulses in a stream of CO–He at 20 °C: (A) O_2, 0·5 ml; (B) O_2, 0·25 ml; (C) N_2O, 3 ml; and (D) N_2O, 2 ml. Inlet gas mixture: X and Y, P_{CO} 0·08 and P_{He} 0·92 atm.

After the catalyst had been reduced by a stream of CO–He at 20 °C until no CO_2 was detected, O_2 and N_2O were separately pulsed into the inlet stream and the evolution of CO_2 in each case was measured. The responses obtained are presented in Figure 1. Curves A and B (O_2 pulses of 0·5 and 0·25 ml) show instantaneous maxima indicating the production of large amounts of CO_2 initially, followed by a steep decrease to none after 35 min. From integration of curves A and B, the amounts of oxygen adsorbed in both pulses were estimated to be $4{\cdot}9 \times 10^{-8}$ and $2{\cdot}4 \times 10^{-8}$ mol g^{-1} of Ag, respectively, indicating simple stoicheiometry. In contrast, curves C and D (N_2O pulses of 3 and 2 ml) show an induction period, followed by a gradual increase and then a decrease to nil over a period of 90 min. The integrated amounts of oxygen adsorbed were estimated to be $4{\cdot}1 \times 10^{-8}$ and $2{\cdot}7 \times 10^{-8}$ mol g^{-1} of Ag, respectively.

A comparison of curves A and C or B and D shows that the response curves for O_2 and N_2O differ from each other in spite of the fact that the difference in the amounts of oxygen adsorbed by the O_2 and N_2O pulses is small. This can reasonably be attributed to the difference in the reactivities of adsorbed oxygen species from O_2 and N_2O. The following results, obtained from separate transient experiments, show that there is no possibility of other factors contributing to the response curves: (i) CO and N_2O are not adsorbed on the reduced surface, (ii) gaseous CO reacts with oxygen which has been irreversibly adsorbed on the surface, (iii) the CO_2 produced is desorbed rapidly, and (iv) N_2O decomposes directly on the active sites which are free from adsorbed oxygen. The oxygen species adsorbed at the initial stage of each pulse are probably continuously distributed along the reactor length from the entrance to the exit of the catalyst bed without significant differences between the O_2 and N_2O pulses, since O_2 or N_2O which had not been adsorbed on the surface was detected in the effluent gas for all pulses.

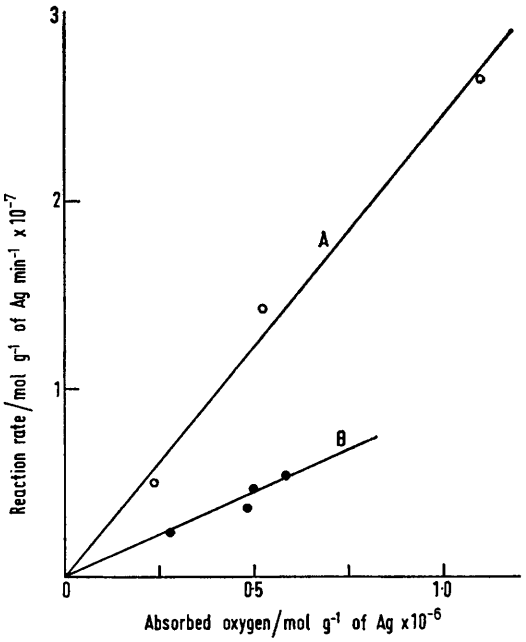

FIGURE 2. Plots of the reaction rate *vs.* the amount of oxygen adsorbed during the reaction at 20 °C and P_{CO} 0·10 atm: (A) oxidation of CO by O_2, and (B) oxidation of CO by N_2O.

The characteristic behaviour of the response in Figure 1 can be explained, assuming that only diatomic oxygen species react with CO as reported by Clarkson and Cirillo.[3] In the case of the O_2 pulse (curves A and B), diatomic oxygen species would be formed on the surface initially which would react with gaseous CO to produce a large amount of CO_2 resulting in the instantaneous maxima of the response; this suggests that the rate of dissociation of diatomic oxygen into monoatomic oxygen is not fast. On the other hand, in the case of the N_2O pulse (curves C and D), monoatomic oxygen is initially formed on the surface by decomposition of N_2O which is converted into diatomic oxygen and then reacts with CO. Thus curves C and D show an induction period.

Based on the above considerations, the following results can also be explained. The amount of adsorbed oxygen at the steady state of the oxidation of CO by O_2 (O_2–CO system) or N_2O (N_2O–CO system) can be estimated from integration of the response curve of CO_2 obtained by exposing the catalyst to a stream of CO–He under steady-state conditions. The amount of CO_2 adsorbed during the reaction can be separately estimated from the desorption curve of CO_2 obtained by exposing the catalyst to a stream of pure He instead of the mixture. When the amount of oxygen estimated in this way is plotted against the reaction rate at the steady state, a straight line is obtained for both systems as shown in Figure 2. The slope of the straight line indicates the apparent rate constant of the reaction between gaseous CO and the adsorbed oxygen. A comparison of the two straight lines shows that the value of the rate constant in the N_2O–CO system is *ca.* half that in the O_2–CO system, indicating that the amount of diatomic oxygen in the former is smaller than that in the latter. This suggests that the rate of recombination of monoatomic oxygen is slower than the rate of reaction of diatomic oxygen with CO.

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[1] V. V. Nikisha, B. N. Shelinov, V. A. Shvets, A. P. Griva, and V. B. Kasansky, *J. Catalysis*, 1973, **28**, 230.

[2] C. Naccache, *Chem. Phys. Letters*, 1971, **11**, 323.

[3] R. B. Clarkson and A. C. Cirillo, Jr., *J. Catalysis*, 1974, **33**, 392.

[4] M. Kobayashi and H. Kobayashi, *J. Catalysis*, 1972, **27**, 100; *Shokubai*, 1974, **16**, No. 2, 8; *Catalysis Rev.*, 1974, **10**, 139.