

Oxygen Species Regulating Carbon Monoxide Oxidation with Multi-Reaction Pathways over a Silver Catalyst*

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Abstract

The reaction route of CO oxidation by nitrous oxide and oxygen over a silver catalyst has been studied from the analysis of their transient behavior at 20°C. Half of the total surface sites are active for the adsorption of oxygen and one third of them are active for the decomposition of N₂O, indicating the heterogeneity of the silver surface. At a reaction steady state of CO oxidation in the N₂O-CO and the O₂-CO systems, the surface in the N₂O-CO reaction is in a more reduced state than that in the O₂-CO reaction. The activation energy is evaluated to be 14 kcal/mol for the O₂-CO reaction and 10 kcal/mol for the N₂O-CO reaction, suggesting a different rate controlling step between both reactions.

The adsorbed oxygen (presuming diatomic oxygen) from gaseous oxygen, not from N₂O, is responsible for the oxidation of CO. In a Eley-Rideal type mechanism, the rate of CO oxidation with diatomic oxygen is estimated to be about fourteen times faster than that of N₂O decomposition. The graphical analysis of transient response curves obtained in the two reactions leads us to a conclusion that the formation rate of the diatomic oxygen species is a sort of rate-controlling step in the N₂O-CO reaction.

1. Introduction

Silver is the only one catalyst heterogeneously producing ethylene oxide from ethylene, so many investigators have studied its catalytic behavior. A reasonable explanation of the specificity of this catalyst might be characterized by adsorbed oxygen. It seems to be accepted that there are two typical types of oxygen species for the adsorbed oxygen on metals and metal oxide: monoatomic and diatomic. According to the view-point concerning the reactivity of adsorbed oxygen species which has been proposed for some metal oxides by using ESR technique¹⁻³⁾, atomic oxygen species are supposed to be active for CO oxidation. However, in the case of silver, Clarkson and Cirillo⁴⁾ first proposed that diatomic

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oxygen species or some precursor which became in equilibrium with diatomic oxygen species should be responsible for the oxidation of CO, differing from other metal oxides. They used an ESR technique for the study, directly detecting the active oxygen species.

The present study is focused to elucidate how the two oxygen species, monoatomic and diatomic, can contribute to the oxygen of CO. For this purpose, N_2O and O_2 may usefully be employed because the former can yield a monoatomic form and the latter can give a diatomic form, at the first stage of their adsorption on reduced silver. Furthermore, the transient response method⁵⁾ was also used to develop the reaction mechanism and kinetic structure.

2. Experimental Method

The silver catalyst used was prepared from silver oxide by the same procedure as the catalyst used for ethylene oxidation.¹⁰⁾ The catalyst contained a small amount of K_2SO_4 and was supported on $\alpha-Al_2O_3$ of 20~40 mesh. The composition of this sample was 154 g-Ag, 0.827- K_2SO_4 /40 g- Al_2O_3 . The BET surface area was 0.3 m²/g-Ag. The stable activity of the fresh catalyst was obtained by treating it with a stream of CO (3.3%)– O_2 (20%)–He (76.7%) mixture at 20°C for 40 hrs.

An ordinary tubular flow-type reactor made from Pyrex glass was used. The catalyst bed was heated in a water bath controlled to within 0.2°C of the desired temperature. Oxygen (O_2 99%), carbon monoxide (CO 99.7%), nitrous oxide (N_2O 99.99%), carbon dioxide (CO_2 99.9%), and helium (He 99.999%) from commercial cylinders were purified through a dry-ice methanol trap to remove water vapor. When it was necessary to remove oxygen as an impurity from He and N_2O , the two gases were passed through a John-Mathey Deoxo type D.

The total gas flow rate was 160 (± 2) ml (NTP)/min. The total conversion in both the N_2O -CO and the O_2 -CO reaction never exceeded 10% and thus the system could be treated as a differential reactor. The reaction gas composition was varied by changing the concentration of helium as a diluent. The step function for the concentration jump was confirmed to be negligible at 400°C by comparing the rate data for catalysts with different sizes, 12~14 mesh and 20~42 mesh. The experimental mass transfer effect was also found to be negligible at 400°C by examining rate data at constant W/F with different flow rates and catalyst amounts.

Three gas chromatographs were used, each of which was kept at a different temperature and to which various columns with different lengths were attached. A Porapak Q column was used for the analysis of CO_2 and N_2O and a Molecular Sieves 5A column was used for the analysis of O_2 , N_2 and CO. A further detailed explanation for the transient response method used in this study can be found elsewhere.⁵⁾

3. Experimental Results and Discussion

3-1. Dynamic Behavior of Reaction Components Regulated by Adsorbed Oxygen Species

Let us first consider the behavior of the gases on the reduced surface. After the catalyst had been completely reduced by a pure hydrogen stream at 50°C for 24 hrs, the CO (inc., 0)-CO and the CO (dec., 0)-CO response or the CO₂ (inc., 0)-CO₂ and the CO₂ (dec., 0)-CO₂ response were separately followed at 20°C. All the responses obtained instantaneously responded to a steady state value, indicating that these gases had not been adsorbed on the surface, as has been reported by Drake and Benton⁶⁾ and Czanderna.⁷⁾

The O₂ (inc., 0)-O₂ response on the reduced surface clearly showed a delay, whereas the O₂ (dec., 0)-O₂ response indicated no delay, typically showing irreversible adsorption of oxygen. The integrated amounts of adsorbed oxygen estimated from the obtained O₂ (inc., 0)-O₂ response curves (see Fig. 1) give an adsorption isotherm, from which the total amount of adsorbed oxygen is estimated to be 1.6×10^{-6} mol/g-Ag (0.64×10^{19} oxygen atoms/m²) with no dependence upon the concentration of O₂. Sholten, Konvalinka and Beek⁸⁾ estimated the total number of surface silver atoms to be 1.31×10^{19} atoms per m² based on Sanquists data⁹⁾, and also estimated the number of adsorbed oxygen atoms at 50°C to be about 0.7×10^{19} . Thus the total amount of adsorbed oxygen is close to Sholten et al's estimation at 50°C, and the value would correspond to 53% of the surface coverage, assuming a monoatomic form of adsorbed oxygen on one silver atom.

N₂O can easily be decomposed on a reduced surface at 20°C. The N₂O (inc., 0)-N₂ response curve obtained indicated a typical overshoot mode with an instantaneous maximum, and finally reaching zero at 130 min. This characteristic mode strongly suggests the direct decomposition of N₂O on active sites, and that

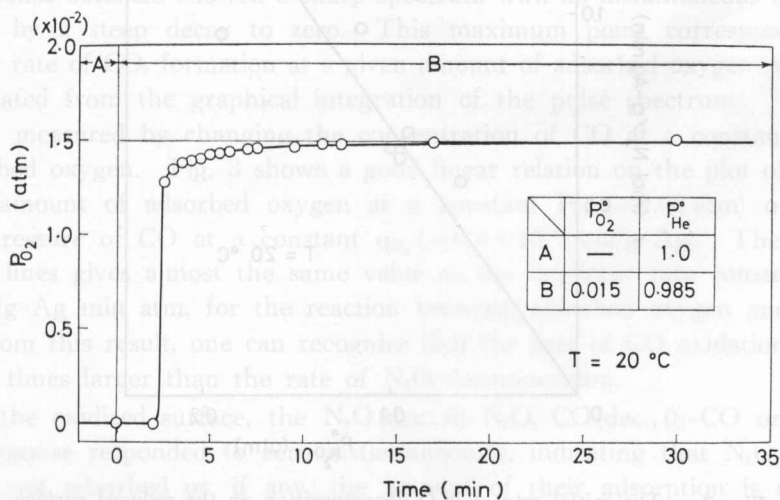


Fig. 1. The O₂ (inc., 0)-O₂ response on the reduced surface.

no regeneration of active sites results from the irreversible adsorption of formed oxygen atoms. In fact no oxygen is detected in the effluent gas stream. The integrated amount of the adsorbed oxygen is estimated to be $0.50 \times 10^{-6} (\pm 0.1) \text{ mol/g-Ag}$ with no dependence upon the concentration of N_2 introduced. This is about one third the total number of active site for O_2 -adsorption. For an explanation of this difference, the blocking effect of oxygen adsorption being contained in a $\text{N}_2\text{O-He}$ stream as an impurity may be considered. It can be estimated, however, to be at most $0.1 \times 10^{-6} \text{ mol/g-Ag}$ which is an estimated amount in the period of the $\text{N}_2\text{O}(\text{inc., } 0)\text{-N}_2$ response (130 min) in Fig. 3. The total number of active sites for N_2O decomposition should therefore be smaller than the total number of active site for O_2 -adsorption, even though there is an additional explanation that the rate of recombination of the formed atomic oxygen to generate two species, one molecular oxygen and one vacant site, is very slow. Since N_2O cannot be decomposed on the oxidized surface, it may be concluded that the reduced surface is heterogeneous for the decomposition of N_2O . A certain fraction of the active sites for oxygen adsorption is not active for the decomposition of N_2O . This heterogeneity will give rise to the difference of reaction mechanism between the $\text{N}_2\text{O-CO}$ and $\text{O}_2\text{-CO}$ reactions.

The maximum value of the $\text{N}_2\text{O}(\text{inc., } 0)\text{-N}_2$ response curve on the reduced surface corresponds to the rate of N_2 decomposition, since N_2 is not adsorbed. This rate is measured at different pressures of N_2O and is plotted as a function of $P_{\text{N}_2\text{O}}$ as shown in Fig. 2. The result gives a straight line and from its slope

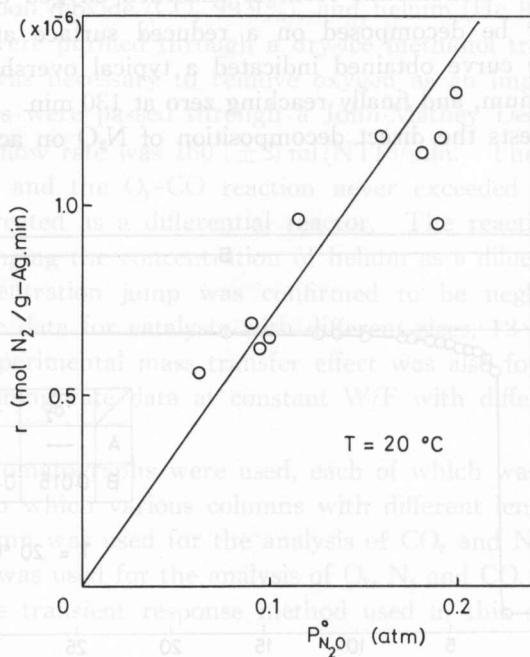


Fig. 2. The initial rate of N_2O decomposition on the reduced surface as a function of $P_{\text{N}_2\text{O}}$.

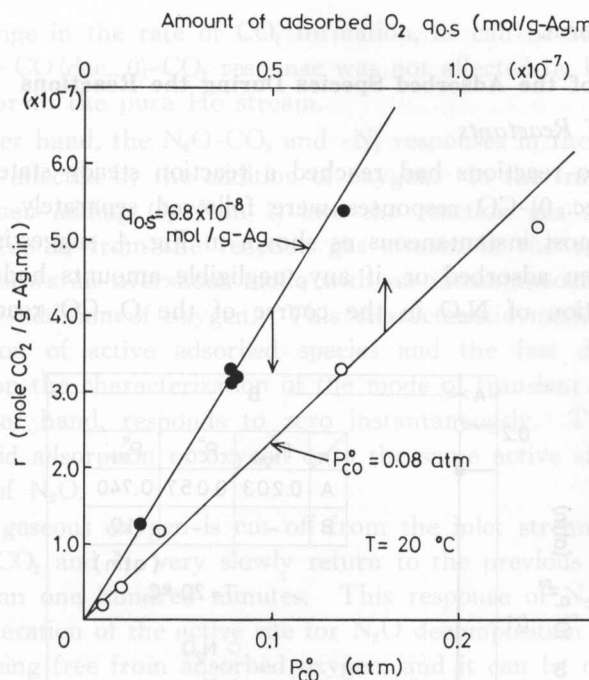


Fig. 3. The rate of CO_2 formation as a function of P_{CO} ; closed circle: by the pulse of 6.8×10^{-8} mol/g-Ag of oxygen gas onto the reduced surface amounts in various P_{CO} ; open circle: by the pulse of oxygen in various in the constant $P_{\text{CO}} (=0.08 \text{ atm})$.

an apparent rate constant for N_2O decomposition is estimated to be 6.7×10^{-6} mol/g-Ag·min.

After the reduced surface had been exposed in a CO-He stream, oxygen was pulsed into the inlet of the reactor, in various amounts. The O_2 (pulse)- CO_2 response obtained showed a sharp spectrum with an instantaneous maximum, followed by a steep decay to zero. This maximum point corresponds to an apparent rate of CO_2 formation at a given amount of adsorbed oxygen (which can be estimated from the graphical integration of the pulse spectrum). This rate was also measured by changing the concentration of CO at a constant amount of adsorbed oxygen. Fig. 3 shows a good linear relation on the plot of the rate vs. the amount of adsorbed oxygen at a constant $P_{\text{CO}} (=0.08 \text{ atm})$ or vs. the partial pressure of CO at a constant $q_{\text{O}_2} (=6.8 \times 10^{-8} \text{ mol/g-Ag})$. The slope of the two lines gives almost the same value as the apparent rate constant, 9.6×10^{-3} mol/g-Ag min atm, for the reaction between adsorbed oxygen and gaseous CO . From this result, one can recognize that the rate of CO oxidation is about fourteen times larger than the rate of N_2O decomposition.

On the oxidized surface, the $\text{N}_2\text{O}(\text{dec.}, 0)\text{-N}_2\text{O}$, $\text{CO}(\text{dec.}, 0)\text{-CO}$ or $\text{O}_2(\text{dec.}, 0)\text{-O}_2$ response responded to zero instantaneously, indicating that N_2O , CO and O_2 were not adsorbed or, if any, the amount of their adsorption is negligible. CO_2 , in contrast, was clearly adsorbed on the oxidized surface with reversible

and irreversible form.

3-2. Regulation of the Adsorbed Species During the Reactions

(1) Behavior of Reactants

After the two reactions had reached a reaction steady state, the N_2O (dec., 0)- N_2 and CO (dec., 0)- CO responses were followed separately. The responses obtained were almost instantaneous as shown in Fig. 4, suggesting that the two gases had not been adsorbed or, if any, negligible amounts had been adsorbed. In fact, the addition of N_2O in the course of the O_2 - CO reaction caused no

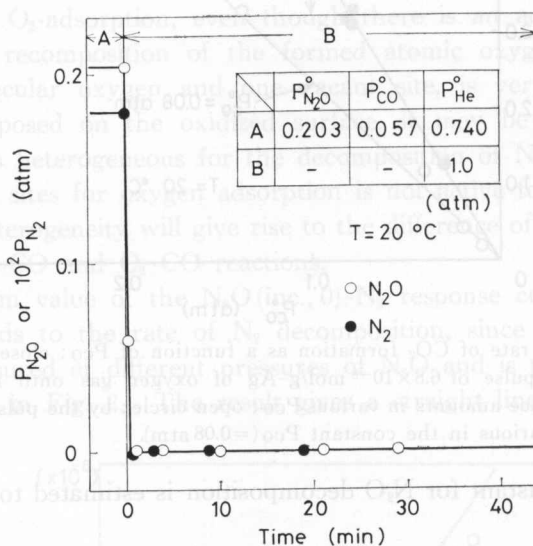


Fig. 4. The N_2O , CO (dec., 0) - N_2O and - N_2 responses.

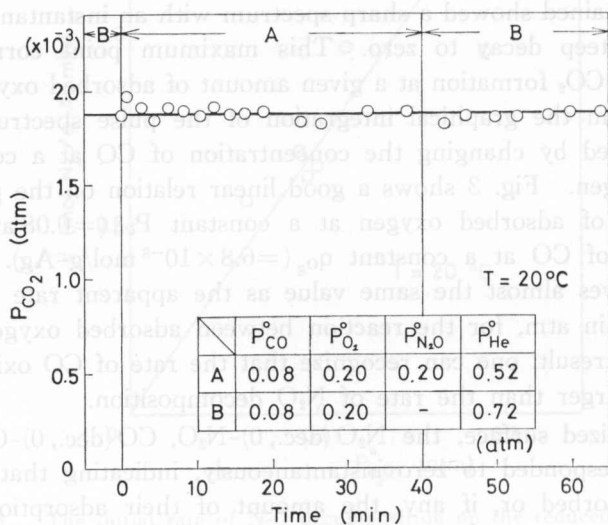


Fig. 5. The effect of N_2 on the oxidation of CO by O_2 .

appreciable change in the rate of CO_2 formation, as can be seen in Fig. 5, and furthermore the $\text{CO}(\text{dec.}, 0)\text{-CO}_2$ response was not affected by being either in the $\text{O}_2\text{-He}$ stream or in the pure He stream.

On the other hand, the $\text{N}_2\text{O-CO}_2$ and $-\text{N}_2$ responses in the $\text{N}_2\text{O-CO}$ reaction are significantly affected by the addition of oxygen. In the transient behavior of CO_2 and N_2 when adding O_2 (Run 1) into the reaction gas stream, and when removing O_2 (Run 2) from the reaction gas stream in the course of $\text{N}_2\text{O-CO}$ reaction, CO_2 shows an overshoot mode with an instantaneous maximum corresponding to the addition of oxygen. This characteristic mode results from the slow regeneration of active adsorbed species and the fast desorption of CO_2 formed, based on the characterization of the mode of transient response curves¹⁰. N_2 , on the other hand, responds to zero instantaneously. This is due to the competitive rapid adsorption of oxygen onto the same active site as that for the decomposition of N_2O .

When the gaseous oxygen is cut off from the inlet stream, one can clearly recognize that CO_2 and N_2 very slowly return to the previous steady state level, taking more than one hundred minutes. This response of N_2 might be caused by the slow generation of the active site for N_2O decomposition: the active site is a vacant site being free from adsorbed oxygen, and it can be regenerated by the recombination of two monoatomic oxygens to form one diatomic oxygen (which is active for the reaction with gaseous CO as discussed in our previous paper¹¹). This gives rise to an idea that the recombination of monoatomic oxygen is very slow, meaning that the fraction of the surface coverage of diatomic oxygen in the $\text{N}_2\text{-CO}$ reaction is smaller than that in the $\text{O}_2\text{-CO}$ reaction. This is consistent with the experimental finding that the apparent rate constant in the $\text{N}_2\text{O-CO}$ reaction, estimated from the linear plot of the rate of CO_2 formation vs. the amount of adsorbed oxygen existing under the reaction steady state (see Ref. 11), is about half of that in the $\text{O}_2\text{-CO}$ reaction.

(2) Behavior of Products

The amount of CO_2 reversibly adsorbed during the reaction can be estimated from the graphical integration of the $\text{CO}(\text{dec.}, 0)\text{-CO}_2$ response curve. The amount of adsorbed CO_2 being in equilibrium, $q^r_{\text{CO}_2}$ corresponding to the averaged partial pressure of CO_2 formed in the reactor which may be calculated from half the partial pressure of CO_2 at the outlet of reactor, is estimated by using the adsorption isotherm. The equilibrium amount estimated thus is designated as $q^e_{\text{CO}_2}$. A comparison between $q^r_{\text{CO}_2}$ and $q^e_{\text{CO}_2}$, shows the former is lower than the latter in the two reactions. This means that the surface under the two reactions is in a reduced state, since CO_2 is adsorbed only on adsorbed oxygen not bare silver. $q^r_{\text{CO}_2}$ in the $\text{N}_2\text{O-CO}$ reaction is lower than that obtained in the $\text{O}_2\text{-CO}$ reaction, indicating the surface in the former to be a more reduced state rather than the surface in the latter, under reaction steady states. This oxygen-deficient surface gives rise to no linear relation of reaction rate against the partial pressure of CO .

CO₂ is also irreversibly adsorbed in the following experiment. The catalyst used for the reaction had been flushed by a pure helium stream until no desorption of CO₂ was observed, and then the surface was reduced by a pure hydrogen stream. The H₂(inc., 0)-CO₂ response clearly showed the fast desorption of an appreciable amount of CO₂. This resulted from the rapid removal of adsorbed oxygen (which is the active site for the adsorption of CO₂) by H₂. The integrated amount of the irreversibly adsorbed CO₂ is evaluated at various partial pressures of CO and the results are presented in Fig. 6. The amount is estimated to be 0.66 (0.1) × 10⁻⁶ mol/g-Ag independent of both the concentration of CO and the kind of reaction system (O₂-CO or N₂O-CO reaction). Assuming that one irreversibly adsorbed CO₂ atom occupies one adsorbed oxygen, one fifth the surface active site is blocked by this irreversibly adsorbed CO₂ during the reaction.

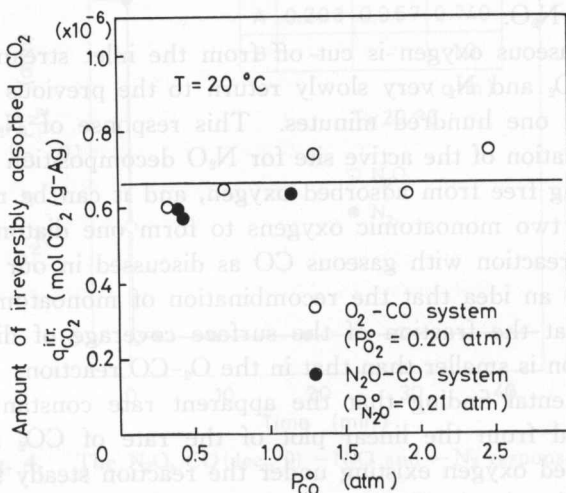


Fig. 6. The amount of irreversibly adsorbed CO₂ as a function of P_{CO} .

3-3. Proposed Model for the Multi-Reaction Pathways

One can roughly estimate the reaction mechanism from the mode of the transient response curve of products caused by the concentration jump of reactants¹⁰. On the O₂-CO reaction, the CO-CO₂ response caused by the stepwise increase or the stepwise decrease in the concentration of CO shows a simple mode with gradual increase or gradual decrease, being called a monoatomic mode. Based on the classification of the mode of transient response curves, this is a typical type suggesting a surface reaction controlling, with the fast readsorption of CO₂ formed, taking into account that the reaction rapidly responds to a new steady state within two minutes. Since CO is not adsorbed, gaseous CO reacts directly with adsorbed oxygen, which may be presumed to be diatomic oxygen, suggesting an Eley-Rideal type mechanism.

It seems to be accepted that gaseous oxygen is adsorbed on silver to form

diatomic oxygen followed by the successive dissociation into monoatomic oxygen. This consecutive two-step reaction strongly affects the mode of the CO, O₂ (inc., 0)-CO₂ response curve according to whether the catalyst surface has been oxidized or reduced. Typical examples are shown in Fig. 7. Although the CO, O₂ (inc., 0)-CO₂ response curve obtained shows an overshoot type before achieving a steady-state level which is the same as that on the oxidized surface, the value of the maximum point is more than two times that of the oxidized surface. This difference in the maximum value in the two cases may be attributed to the amount of adsorbed diatomic oxygen, because diatomic oxygen is formed first prior to the formation of monoatomic oxygen by the adsorption of gaseous oxygen

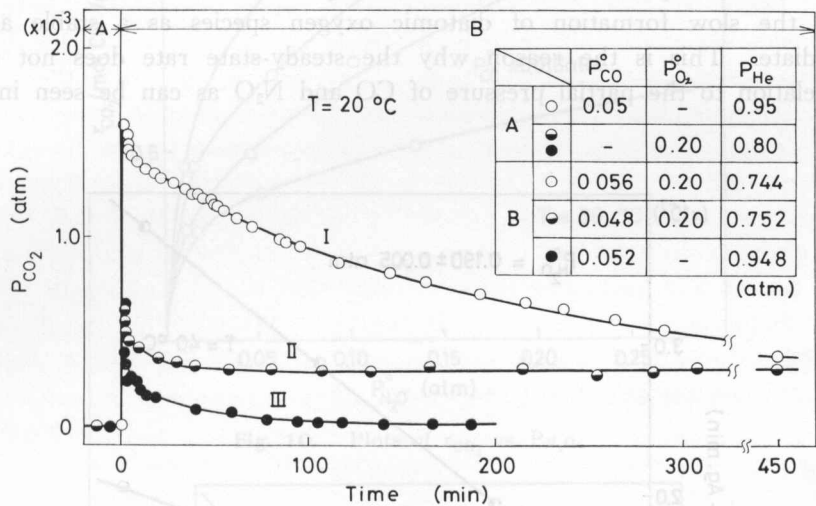


Fig. 7. The CO (inc., 0)-CO₂ and O₂ (inc., 0)-CO₂ responses.

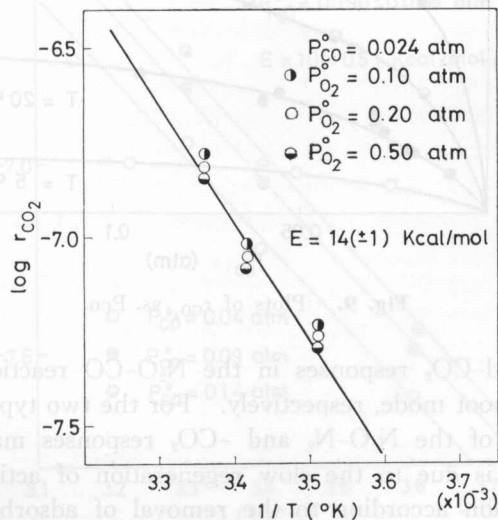


Fig. 8. Arrhenius plots for r_{CO_2} .

at the initial stage of the oxidized surface. The overshoot mode is due to two reasons: (1) the slow regeneration of diatomic oxygen and (2) the accumulation of CO_2 irreversibly adsorbed on adsorbed oxygen. At the steady state of reaction the activation energy is estimated to be 14 kcal/mol independent of the concentration of O_2 and CO as shown in Fig. 8.

On the N_2O - CO reaction, on the other hand, the N_2 (inc., 0)- N_2 and $-\text{CO}_2$ responses show an overshoot mode (type III) and a S-sharp mode (type IV) respectively. Applying the classification of the mode of transient response curves, the two characteristic modes lead us to two reasonable explanations: (1) the overshoot mode of the N_2 curve results from the slow regeneration of the active site for N_2O decomposition, and (2) the S-sharp mode of the CO_2 curve is attributed to the slow formation of diatomic oxygen species as a stable adsorbed intermediate. This is the reason why the steady-state rate does not show a linear relation to the partial pressure of CO and N_2O as can be seen in Fig. 9 and 10.

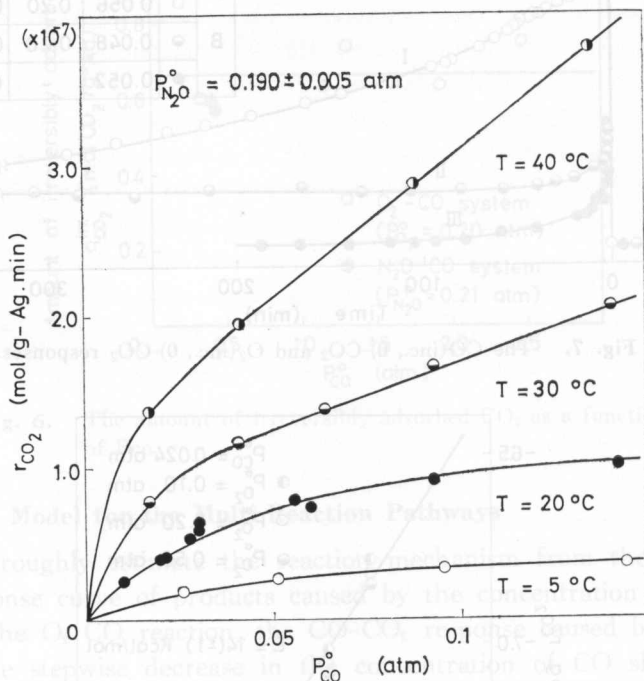


Fig. 9. Plots of r_{CO_2} vs. P_{CO} .

The CO - N_2 and $-\text{CO}_2$ responses in the N_2O - CO reaction give the S-shape mode and the overshoot mode, respectively. For the two types of curve, a similar explanation to that of the N_2O - N_2 and $-\text{CO}_2$ responses may be available: the S-shape type of N_2 is due to the slow regeneration of active sites (bare silver) for N_2O decomposition according to the removal of adsorbed oxygen with the concentration jump of CO , and the overshoot type of CO_2 results from the slow

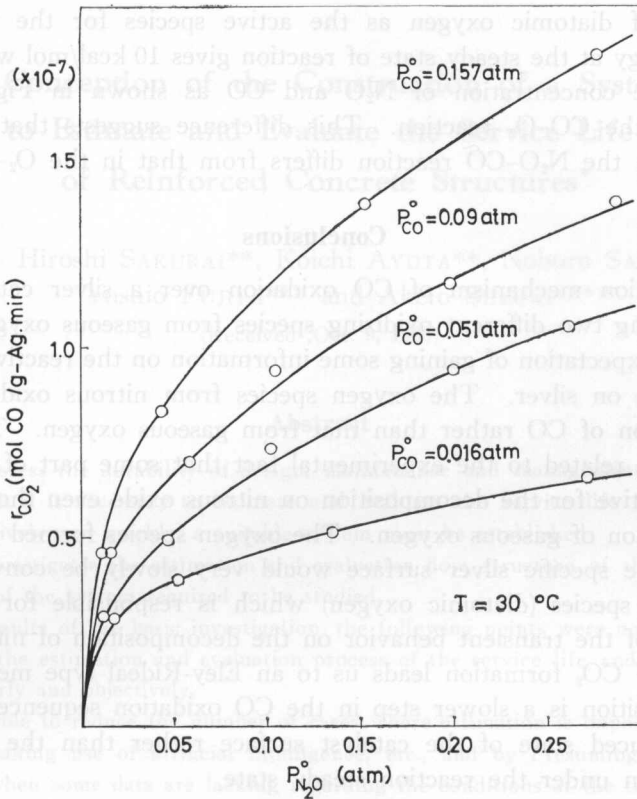


Fig. 10. Plots of r_{CO_2} vs. P_{N_2O} .

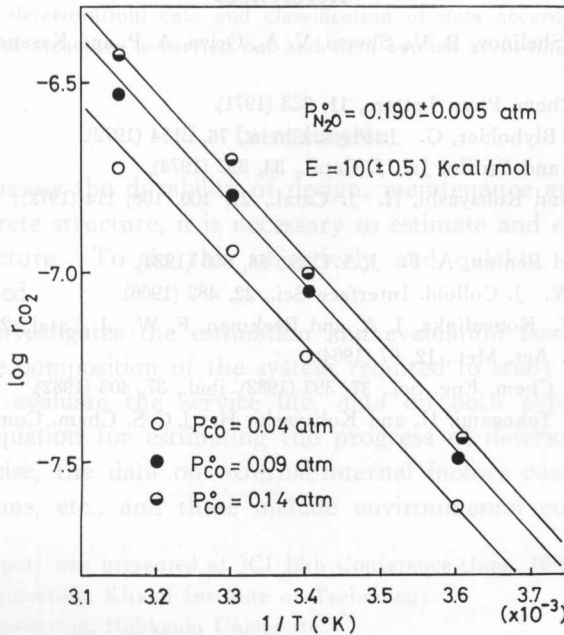


Fig. 11. Arrhenius plots for the steady state rate of CO₂ formation.

regeneration of diatomic oxygen as the active species for the reaction. The activation energy at the steady state of reaction gives 10 kcal/mol with no dependence upon the concentration of N_2O and CO as shown in Fig. 11, differing from that in the $CO-O_2$ reaction. This difference suggests that the rate controlling step in the N_2O-CO reaction differs from that in the O_2-CO reaction.

Conclusions

The reaction mechanism of CO oxidation over a silver catalyst has been studied by using two different oxidizing species from gaseous oxygen and nitrous oxide, in the expectation of gaining some information on the reactivity of adsorbed oxygen species on silver. The oxygen species from nitrous oxide is less active in the oxidation of CO rather than that from gaseous oxygen. This interesting view might be related to the experimental fact that some part of the bare silver surface is inactive for the decomposition on nitrous oxide even though it is active in the adsorption of gaseous oxygen. The oxygen species formed by N_2O decomposition on the specific silver surface would very slowly be converted into the active oxygen species (diatomic oxygen) which is responsible for CO oxidation. The analysis of the transient behavior on the decomposition of nitrous oxide and on the rate of CO_2 formation leads us to an Eley-Rideal type mechanism. The N_2O decomposition is a slower step in the CO oxidation sequence, giving rise to the more reduced state of the catalyst surface rather than the surface in the O_2-CO reaction under the reaction steady state.

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