Modeling of Slow Dynamics in the Oxidation of CO over Supported Silver

The oxidation of CO over aluminum-supported Ag was studied at 147°C using transient experiments. Long-time-scale dynamics were observed that could not be explained by previously postulated kinetic mechanisms for this reaction system. A model is presented with kinetic parameters estimated from steady state and transient data that is able to reproduce a variety of cycled feed stream experiments. The model incorporates a slow reversible step which forms an adsorbed oxygen species that blocks reaction sites.

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Introduction

Silver catalysts have received a large amount of attention due to their ability to selectively catalyze ethylene epoxidation (reviewed by Sachtler, 1970; Verykios et al., 1980; Sachtler et al., 1981). The most elusive aspect of this reaction is the form or forms of adsorbed oxygen on the silver catalysts. While the existence of at least two oxygen species on silver is generally accepted, less equanimity has been reported as to the oxygen species that participate in oxidation reactions on silver. Czanderna (1964) has postulated that at temperatures of 0 to 100°C lower surface coverages are dominated by a monatomic oxygen form and higher coverages give predominately a diatomic oxygen species. For higher temperatures, 150–250°C, Force and Bell (1975b) suggest that any diatomic oxygen formed on the silver will readily decompose. Several studies suggest that while both diatomic and monatomic oxygen are present on silver and both are active for ethylene adsorption, one form promotes epoxidation and the other complete oxidation to CO_2 and H_2O (Sachtler et al., 1981).

While oxygen adsorption on silver has been studied with a variety of techniques, the oxygen species contributing to the reaction mechanism at reaction conditions are difficult to analyze. Adding to the analysis problems is the relative complexity of the ethylene epoxidation reaction. One approach for reducing the system to a more manageable form is to use carbon monoxide oxidation as the model oxidation system on silver. Keulks and Outlaw (1972) studied CO oxidation over silver in a recirculation reactor operating at 100°C. Oxygen was preadsorbed on the silver catalyst in small quantities to maintain fractional surface coverages of less than 10% of a monolayer, and both CO and CO_2 were found to adsorb. CO and CO_2 did not adsorb without the preadsorption of O_2. Keulks and Outlaw conclude that a monatomic oxygen species is active for CO and CO_2 adsorption. Using the initial stage of adsorption of N_2O and O_2 as sources for monatomic and diatomic oxygen species, respectively, Kobayashi and Takegami (1984) presented transient data for CO oxidation over alumina-supported silver. Differences in the observed activation energies for the $CO—O_2$ and $CO—N_2O$ reactions were attributed to different rate-controlling steps. since diatomic oxygen was assumed to be the active site for CO adsorption, the slower rate for the $CO—N_2O$ reaction relative to the $CO—O_2$ reaction was postulated to be due to the slow formation of diatomic oxygen from a monatomic oxygen source.

In previous work with the CO oxidation reaction studied at 147°C, Shanks and Bailey (1987) report a slow transient when oxygen is introduced to a reduced silver catalyst. The present study uses transient experiments to examine in more detail the source of the long-time-scale dynamics. Experimental data are compared with simulation results to test the validity of a proposed reaction model for CO oxidation over Ag/Al_2O_3.

Experimental System

The catalyst used in the experimental reactor was 2.3 g of 1 wt. % silver on 3 mm cylindrical $\alpha—Al_2O_3$ pellets (Engelhard). A dispersion of 13% for the silver catalyst was determined from oxygen chemisorption experiments based on the method of Seyedmonir et al. (1984). In addition to the catalyst, 2 mm glass beads were used to pack the reactor (≈ 10 cm^3 total volume). For this packing and for the conditions used in all of the experiments, 100 sccm total flow rate and 147°C, the reactor behaved as an ideal continuous stirred-tank reactor (CSTR) with a residence time of 4.7 s.

Gas flow rates of carbon monoxide (99.99%), oxygen (99.5%), hydrogen (99.9995%), and helium (99.995%) into the reactor were set and monitored by two banks of identical mass flow controllers (Tylan). A carbonyl trap operating at 500°C was used upstream of the CO mass flow controllers. Also, the CO, O_2, and He inlet lines contained desiccant columns. Computer-controlled, high-speed solenoid valves were used to switch between the two mass flow controller banks. The effluent CO and CO_2 concentrations were measured with two infrared analyzers (Wilkes Miran I) operating at 4.6 and 4.2 μm, respectively. Mixing due to the IR cells was found to be negligible. More specific details of the experimental apparatus have been presented by Prairie et al. (1987).

Pretreatment of the catalyst consisted of introducing 10% oxygen in helium for 2 h at 250°C and then reducing with 20% hydrogen also at 250°C. The catalyst activity stabilized after approximately 36 h of exposure to a feed of 10% CO and 10% O_2 at 147°C. By reducing again with 20% hydrogen at 250°C, the unstable catalytic activity could be reproduced, which then required a similar length of time to reach a stable value. Kobayashi (1982a) and Nowobilski et al. (1986) also report long initial stabilization transients for their studies of the ethylene epoxidation reaction over silver catalysts. In the work by Nowobilski *et al.* the long transient was attributed to slow oxidation of the initially reduced silver.

Internal diffusional and external mass transfer effects were found to be negligible for the operating conditions imposed in all of the experiments (Shanks and Bailey, 1987).

Reaction Model

Two kinetic models have been postulated previously in the literature for the CO—O_2 reaction on Ag. Keulks and Chang (1970) based their model on isotopic tracer experiments performed at 100°C in a recirculation reactor. The model contains no differentiation between various forms of adsorbed oxygen but in later work the monatomic oxygen species is regarded as the active site for CO adsorption and reaction (Keulks and Outlaw, 1972). Using transient response experiments in a differential reactor operating at 20°C, Kobayashi (1982b) has postulated a reaction mechanism in which diatomic oxygen is the reactive adsorbed species. In other work (Shanks and Bailey, 1987), these models were compared with dynamic experiments. Both models provided good descriptions of steady state rate data but failed to reproduce long transients that resulted when introducing oxygen to a reduced silver catalyst.

An alternative model represented by

$$O_2 + 2S \xrightarrow{k_1} 2OS \tag{A}$$

$$CO + OS \xrightarrow{k_2} CO_2S \tag{B}$$

$$CO_2S \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} CO_2 + S \tag{C}$$

$$OS \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} O'S \tag{D}$$

was used in the current work. The postulated existence of reaction step D, the formation of an inert oxygen species, results from observations in the transient experiments described later. Due to the long transient that was observed during catalyst stabilization, the exact nature of the vacant site, S, is not clear. Temkin (1979) and Sachtler et al. (1981) suggest that this site may be silver oxide. If this site is an oxide, then successive oxygen may be adsorbing on top of the surface oxide (Keulks and Outlaw, 1972). Preadsorption of oxygen on silver has been shown in several studies to be a necessary precursor for the adsorption of either CO or CO_2 (Keulks and Ravi, 1970; Lawson, 1968). Force and Bell (1975a) in transmission IR experiments have assigned a band to CO_2 that is weakly chemisorbed directly on silver.

The equations representing the model, steps A–D in an isothermal CSTR are

$$n\frac{dx_1}{dt} = F_{CO} - x_1F_o - k_2x_1\theta_1 \tag{1}$$

$$n\frac{dx_2}{dt} = F_{O_2} - x_2F_o - k_1x_2\theta_v^2 \tag{2}$$

$$n\frac{dx_3}{dt} = -x_3F_o + k_3\theta_2 - k_{-3}x_3\theta_v \tag{3}$$

$$n_s\frac{d\theta_1}{dt} = 2k_1x_2\theta_v^2 - k_2x_1\theta_1 + k_4\theta_1 - k_{-4}\theta_3 \tag{4}$$

$$n_s\frac{d\theta_2}{dt} = k_2x_1\theta_1 - k_3\theta_2 + k_{-3}x_3\theta_v \tag{5}$$

$$n_s\frac{d\theta_3}{dt} = k_4\theta_1 - k_{-4}\theta_3 \tag{6}$$

where x_1, x_2, and x_3 are the mole fractions of CO, O_2, and CO_2, respectively, θ_i is the fractional coverage of an adsorbed species, and F_{CO} and F_{O_2} are the inlet molar flow rates of CO and O_2, respectively. The fractional coverages θ_1, θ_2, and θ_3 correspond to OS, CO_2S, and $O'S$, respectively, with the fraction of vacant sites, θ_v, given by $1 - \theta_1 - \theta_2 - \theta_3$. Experimental data were taken under isothermal (147°C) and isobaric ($\approx$1 atm) conditions so the number of moles of gas in the reactor remains constant. Therefore, the exit molar flow rate, F_o, can always be determined from the equation

$$F_o = F_T - k_1x_2\theta_v^2 - k_2x_1\theta_1 + k_3\theta_2 - k_{-3}x_3\theta_v \tag{7}$$

Equation 7 can be used to remove F_o from the differential equations, Eqs. 1–3.

Kinetic parameters were determined for the model from an estimation scheme based on steady state rate data. Here estimation of the parameters used a finite-difference, Levenberg-Marquardt routine in conjunction with a minimization of the sum of squares objective function based on the difference between the observed and calculated reaction rates. Using various feed compositions of 2–20% CO and 2–20% O_2, 70 steady state reaction rates were determined. The observed rates were evaluated by monitoring the effluent CO concentration giving the amount of CO consumed. Accordingly, the simulated reaction rate was calculated using the theoretical consumption rate of CO:

$$r = k_2x_1\theta_1 \tag{8}$$

Table 1. Parameters Estimated from Steady State Data

k_1,	2.05×10^{-4} mol/s
k_2,	1.68×10^{-3} mol/s
k_3,	4.42×10^{-7} mol/s
k_{-3},	1.85×10^{-10} mol/s
K_e	9.74

From static experiments, k_4 and k_{-4} cannot be independently evaluated, so only the ratio $K_e = k_4/k_{-4}$ can be estimated from steady state rate data. The results of the parameter estimation are summarized in Table 1.

Two parameters are left undetermined from this procedure: n_s, the total moles of catalytic active sites in the reactor, and k_4 (or k_{-4}). Based on the oxygen chemisorption result, the number of sites available in the CSTR for oxygen chemisorption is 2.92×10^{-5} mol. This number is not necessarily equivalent to n_s because it was determined on the reduced silver catalyst. At reaction conditions n_s is probably less than the chemisorption result, as evidenced by the loss in activity of the catalyst during the initial stabilization period following the introduction of CO and O_2 to the H_2 treated silver. The value of k_4, and therefore k_{-4} (through K_e), must be determined from dynamic experiments.

Results

Transient experiments in which reactant concentrations were changed stepwise were performed while monitoring the effluent concentrations of CO and CO_2. Two characteristic time scales were observed: a rapid response when an oxygen-rich reaction environment was maintained, and a very slow response when stepping from only CO in He to O_2 and CO in He. The slow transient will be discussed later with the results from cycling experiments. The rapid response can be used to estimate a value for n_s. Figure 1 shows the transients in the CO and CO_2 effluent resulting from a step change of 1% CO, 10% O_2 to 10% CO, 10% O_2. Also shown in this figure are simulated responses of the model for three values of n_s between 7.5×10^{-6} and 5.0×10^{-5}. The value $n_s = 7.5 \times 10^{-6}$ mol gives the best reproduction of the experimental data. The simulated trajectories were calculated using Gear's method (IMSL routine DGEAR) to simultaneously solve Eqs 1–6. Due to the assumption of slow exchange for step D of the reaction sequence and the undetermined value of k_4, the fractional coverage of O^i was taken to be constant at its initial steady state value during the simulations used in estimating a value for n_s. The conditions for this step-response experiment were chosen so that the catalyst was always exposed to an oxygen-rich environment.

The slow transient observed when the catalyst was reduced in CO at reaction temperature was characterized using cycled reactant feed concentration experiments. Figures 2a and 3a

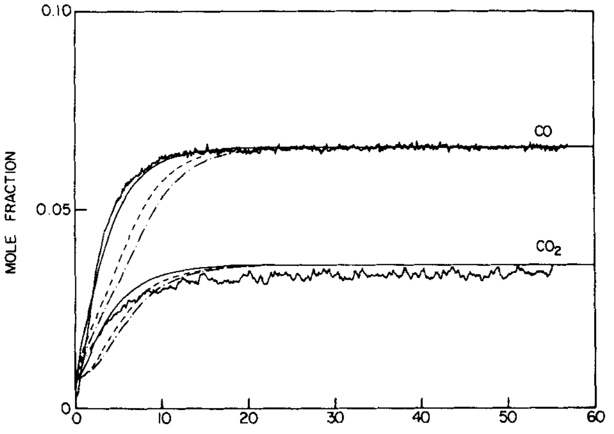

Figure 1. Effluent trajectories of CO and CO_2 for a step change of 1% CO, 10% O_2 to 10% CO, 10% O_2.
Simulation Results: —— $n_s = 7.5 \times 10^{-6}$, – – – $n_s = 3.0 \times 10^{-5}$, –·–·– $n_s = 5.01 \times 10^{-5}$

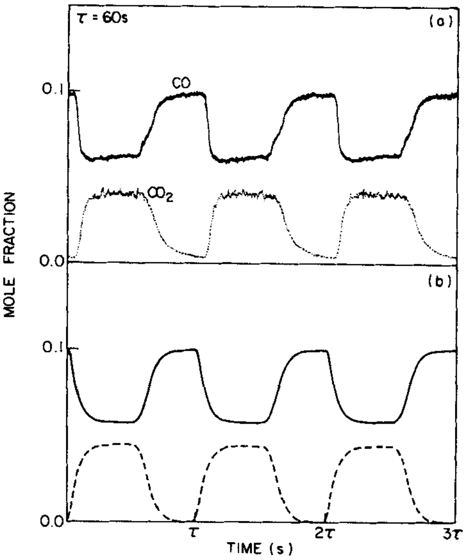

Figure 2. Trajectories for symmetric cycling of 10% CO to 10% CO, 10% O_2 with $\tau = 60$ s.
(a) experimental; (b) simulation

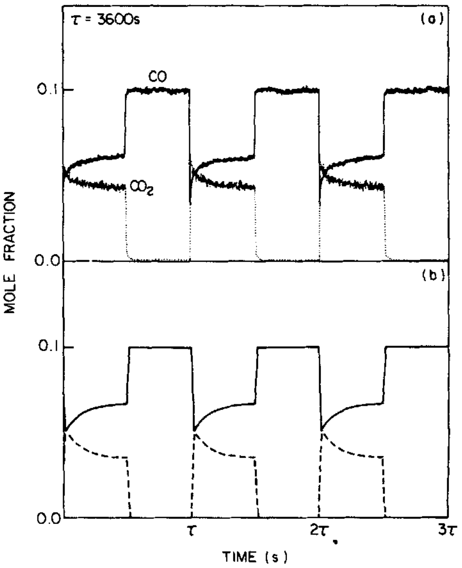

Figure 3. Trajectories for symmetric cycling of 10% CO to 10% CO, 10% O_2 with $\tau = 3{,}600$ s.
(a) experimental; (b) simulation

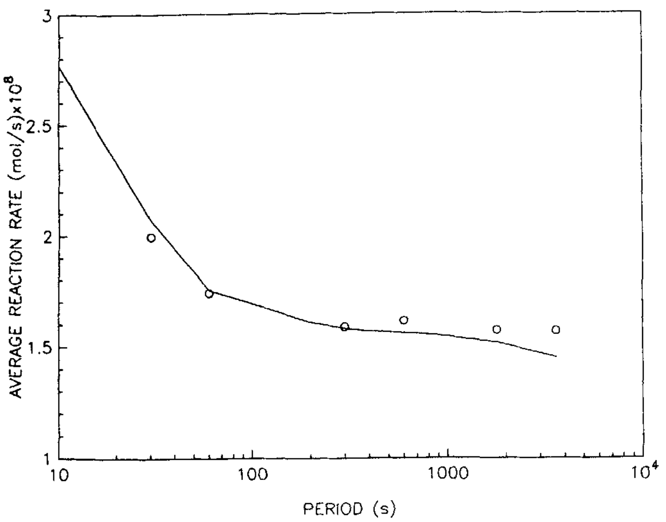

Figure 4. Time-average reaction rate for various cycling periods using 10% CO to 10% CO, 10% O_2.
O experimental; —— simulation

show the experimental effluent CO (top trajectory) and CO_2 (lower trajectory) for symmetric cycling between 10% CO, 10% O_2 and 10% CO for two periods, 60 and 1,800 s, respectively. In both cases, each of the indicated feed streams was introduced into the reactor for one-half of the period. The data were taken after the reactor had reached stable periodic operation. Of particular interest is the rate overshoot in CO_2 production when the O_2-containing feed stream is introduced. This relatively high instantaneous rate, as compared with the steady state rate for 10% CO, 10% O_2, is not as high a rate as is first observed when a similar feed stream is introduced to the reactor after the 250°C pretreatment in H_2. The slow transient seen during catalyst stabilization following pretreatment cannot be reproduced merely by reduction with CO at 147°C. Therefore, the slow transient seen reversibly under reaction conditions is likely due to a different process than occurs during initial stabilization. Also, when the 10% CO portion of the cycle was changed to pure He, no overshoot was observed when the CO, O_2 portion of the cycle was introduced.

Using only k_4 as an adjustable parameter, simulations of the cycling data were performed with the parameters determined from steady state experiments and the value of n_s found from the step-response experiment. In these calculations, the fractional coverage of O^i was evaluated by integrating Eq. 6. The best-fit simulations resulting from minimizing an objective function based on the difference between the observed and calculated CO mole fraction response are shown in Figures 2b and 3b for periods corresponding to the experimental results in Figures 2a and 3a. A value of $k_4 = 7.5 \times 10^{-8}$ mol/s was found to yield the optimal fit. Figures 2 and 3 show the excellent agreement between model and data for two widely different periods. Using the estimated value of k_4, simulation of the step-response experiment used for evaluating n_s gave the same result as was calculated when k_4 was unknown.

A more comprehensive comparison of the experimental data and model is presented in Figure 4, where the time-average reaction rate is shown for various symmetric cycling periods and feed streams of 10% CO, 10% O_2, and 10% CO. The average experimental reaction rate was calculated using the time-average CO effluent mole fraction. In these calculations, the assumption of constant exit molar flow rate was invoked yielding the equation

$$\bar{r} = \frac{F_T(\bar{x}_1^i - \bar{x}_1)}{(1 - 0.5\bar{x}_1)} \tag{9}$$

Due to the low conversion of CO and the high concentration of inert He, the assumption of constant F_o should be reasonable. The time-average reaction rate was calculated for the simulations using

$$\bar{r} = \frac{1}{\tau}\int_0^\tau k_2 x_1 \theta_1 \, dt \tag{10}$$

where τ is the cyclic period. Both the experimental and simulated results indicate that as $\tau \rightarrow 0$, relaxed steady state operation (Bailey and Horn, 1971), the average reaction rate increases. Thullie *et al.* (1986) have shown that Eley-Rideal surface kinetics will, in general, give the largest average reaction rate as the cycling period approaches zero.

The modeled relative rates of formation and consumption of O^i on the surface can be tested with asymmetric cycled feed streams. Here, γ is the fraction of the period in which the feed is 10% CO. During the remainder of the period, $(1 - \gamma)\tau$, the feed contains 10% CO and $5/(1 - \gamma)$% O_2, so that the time-average mole fraction of O_2 in the reactant feed stream was 0.05 for all of the experiments. Figures 5 and 6 show a comparison between experiment and simulation for $\gamma = 0.25$ and $\gamma = 0.75$, respectively. The simulation of $\gamma = 0.25$ reproduces the experiment but the simulation for $\gamma = 0.75$, while agreeing with the qualitative shape of the experimental trajectories, gives a reduced reaction rate during the oxygen portion of the cycle. Summarized in Figure 7 are simulation and experimental time-average reaction rates for several values of γ. Shown are results for two different cycling periods, $\tau = 60$ and 1,800 s. As illustrated in Figure 7, the greatest disparity between model and experimental results is seen for $\gamma > 0.5$.

Discussion

In agreement with past studies of oxidation reactions on silver, the experimental data presented here indicate the presence of at least two adsorbed oxygen forms on Ag/Al_2O_3 during CO oxidation at 147°C. An apparent inactive or negligibly active oxygen species is formed and consumed on a much slower time scale than is characteristic of the CO—O_2 reaction. While the exact chemical form of this inactive species has not been precisely determined, it is clear that this species can only be removed in a reducing environment and will not desorb at the reaction temperature. The presence of a contaminant in the oxygen feed stream causing the loss of activity seems unlikely due to the purity of the oxygen source and to the ability of either CO or H_2 to restore the catalyst activity. These observations are consistent with the formation of an inert adsorbed oxygen species, as was proposed in the reaction model.

Neither of the papers postulating reaction sequences for the CO—O_2 reaction over silver, Keulks and Chang (1972) or Kobayashi (1982b), resports a comparably slow transient under their reaction conditions. There are two possible reasons for this disparity: (1) different reaction temperatures, and (2) different

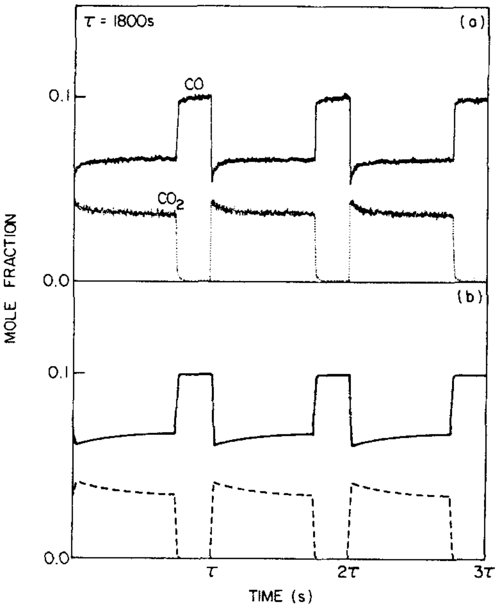

Figure 5 Trajectories for asymmetric cycling with τ = 1,800 s, γ = 0.25.
(a) experimental; (b) simulation

experimental schemes. Reaction studies at temperatures comparable to those employed in those two works could not be performed in the present experimental apparatus because the resulting reaction rate was immeasurably small. Keulks and Chang report data for CO introduced to an O_2 preexposed catalyst but not for O_2 introduction following CO reduction. An experiment similar to those presented here was reported by Kobayashi using a step change in the reactant feed from 5.5% CO, 94.5% He to 5.5% CO, 19.7% N_2O, 74.8% He. No overshoot was observed in CO_2 production at the reported reaction temperature of 20°C.

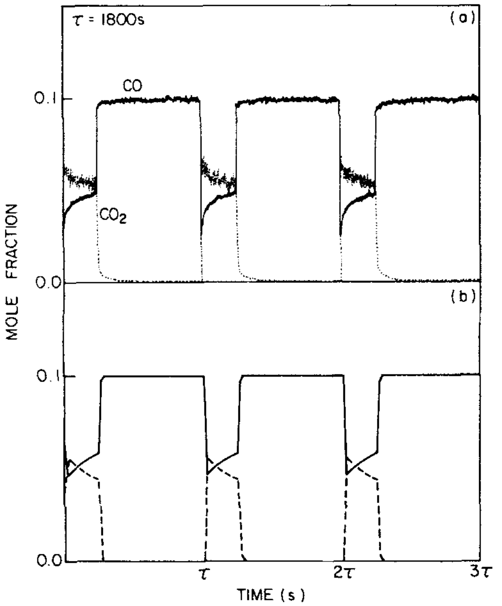

Figure 6. Trajectories for asymmetric cycling with τ = 1,800 s, γ = 0.75.
(a) experimental; (b) simulation

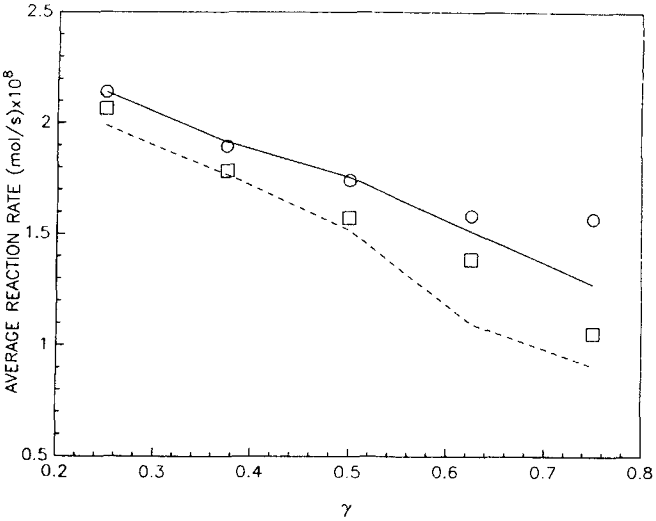

Figure 7. Effect of γ on time-average reaction rate.
τ = 60 s: ○ experimental, —— simulation
τ = 1,800 s: ☐ = experimental, – – – simulation

The model presented in steps A–D is similar to the reaction sequence proposed by Kobayashi (1982b) except that a monatomic oxygen species is taken as the active site for CO adsorption; but, as with the Kobayashi model, only one adsorbed oxygen form is assumed to be active. The vacant site in the proposed model is likely some type of silver oxide that is not reduced by CO at 147°C but can be reduced at 250°C with H_2. This is corroborated by a comparison of the number of active sites for O_2 adsorption found from the chemisorption experiment and from fitting the experimental step-response data. The uptake of oxygen in the chemisorption experiment, which was performed on the catalyst used in the experimental reactor following the completion of the transient experiments, was more than three times the fitted value. Two characteristic time scales are suggested by the proposed model, one corresponding to the total number of active sites and one associated with the kinetics of the inert oxygen step. Experimental transients exhibited both fast and slow time-scale responses attributed to the surface reaction that could be reproduced by the model.

While the postulated reaction model reproduced a wide range of experimental cycling results, it was not as quantitatively accurate for asymmetric cycling with $\gamma > 0.5$. The difference between the simulated and experimental time-average reaction rates for $\gamma > 0.5$ implies that the activity of the catalyst can be regenerated more rapidly than is given by model simulations. As shown in figure 6, though, the qualitative features of the CO and CO_2 responses for $\gamma = 0.75$ are reproduced by the simulation. For this large value of γ any discrepancy between the experimental and simulated time-average reaction rate will be magnified because the conversion of CO only occurs during 25% of the period.

Conclusions

The interaction of oxygen with silver is complex. Although oxygen adsorption experiments allow characterization of the possible forms of adsorbed oxygen species, the contribution of the various forms to oxidation kinetics is not clear. This complexity was manifested in long-time-scale dynamics observed in the CO oxidation reaction on Ag/Al_2O_3 during step-response experiments. The transients were characterized using cycled feed stream experiments where the cycle periods were varied for symmetric and asymmetric feed conditions. The overall reaction appeared to proceed on two time scales that could be attributed to reactions occurring on the surface. These experiments could be explained with blockage of the active sites occurring due to some type of adsorbed oxygen species. A model was postulated with an inert adsorbed oxygen species that was able to give excellent reproduction of the experimental data.

Acknowledgment

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Notation

F = flow rate, mol/s
k_i = rate parameter, mol/s
K_e = equilibrium parameter
n = reactor capacity, mol
n_s = active sites on catalyst, mol
r = reaction rate, mol/s
$\bar{r}$ = time-average reaction rate, mol/s
S = vacant site
t = time, s
x_i = gas phase mole fraction

Greek letters

γ = fraction of period with CO, He feed
τ = cyclic period, s
θ_i = fractional surface coverage

Subscripts

CO = carbon monoxide
o = outlet
O_2 = oxygen
T = total

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