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Ionic Redox Behaviour of La(Sr)MnO$_3$ Catalyst during Transient CO Oxidation

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The technique of solid electrolyte potentiometry (SEP) was employed to monitor *in situ* the oxygen activity (the oxidation state) of La(Sr)MnO$_3$ catalyst during CO oxidation under steady-state and transient conditions. The reaction at 550°C was found to proceed through an ionic redox mechanism; the reoxidation and the reduction reactions occur at different sites on the catalyst surface and oxygen diffuses through the oxide lattice from the ox-sites, where it is adsorbed, to the r-sites, where it reacts with CO. Under reaction conditions it cannot be assumed that oxygen adsorbed at the r-sites is in equilibrium with oxygen adsorbed at the ox-sites. The rate was accordingly found to be a function of the catalyst oxygen activity and the gas-phase oxygen (reoxidation determined reaction) or carbon monoxide (reduction-determined reaction) partial pressure. Transient data can also be interpreted within the framework of the ionic redox model.

INTRODUCTION

Catalyst oxygen activity can be measured *in situ* by means of solid electrolyte potentiometry (SEP). The technique has been applied to a number of reactions on metals (1, 2) and, only recently, on oxide catalysts (3, 4). The SEP oxygen activity has proved to be very useful in explaining the dynamic behaviour of the rate of reaction (3–9).

It has been shown previously (4) that the oxidation of CO on La(Sr)MnO$_{3-\delta}$ catalyst at 550°C could exhibit multiple steady-state rates and hysteresis even when phase transformations of the oxide catalyst did not take place. The results were explained by means of an ionic redox model (4), where the reoxidation of the reduced sites occurs by lattice diffusion of oxygen rather than by gas-phase oxygen. The multiple steady states were attributed to a lack of equilibrium between reoxidation and reduction sites due to finite diffusional rates in the catalyst. The reaction kinetics were accordingly quantitatively described by means of the thermodynamic oxygen activity of the catalyst.

The reaction mechanism consists of the following steps.

1. Reoxidation of ox-sites by gas-phase oxygen

$$O_2(g) + S_{ox} \rightarrow O_2S_{ox} \qquad [1]$$

$$O_2S_{ox} + S_{ox} \rightarrow 2\,OS_{ox}, \qquad [2]$$

where S_{ox} represents a vacant site responsible for catalyst oxidation;

2. diffusion of oxygen species from the ox-sites to the bulk

$$OS_{ox} + V_b = S_{ox} + O_b, \qquad [3]$$

where O_b represents lattice oxygen and V_b represents an oxygen vacancy;

3. diffusion of oxygen species from the bulk to the r-sites (S_r)

$$O_b + S_r = V_b + OS_r; \qquad [4]$$

4. reduction reaction of oxygen with CO at the r-sites

$$CO(g) + OS_r \rightarrow CO_2(g) + S_r. \qquad [5]$$

The scheme can be considered to consist of two overall processes, the reoxidation and the reduction of the solid catalyst, which contain the steps [1]–[3] and [4]–[5], respectively. The rates of the reoxidation (assuming molecular oxygen adsorption is the rate-limiting step), r_{ox}, and reduction, r_r, reactions will be given by

$$r_{ox} = k_{ox}P_{O_2}(1 - \theta_{ox}) \qquad [6]$$

$$r_r = k_r P_{CO}\theta_r, \qquad [7]$$

where θ_{ox} and θ_r stand for the coverages of oxygen species at the ox- and r-sites, respectively. The SEP oxygen activity, α_O, has been shown to reflect the thermodynamic activity of the lattice oxygen in the oxide bulk (4),

$$K_b\alpha_O = \frac{[O_b]}{[V_b]}, \qquad [8]$$

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where K_b is an "absorption" equilibrium constant which describes the incorporation of oxygen into the oxide lattice.

If equilibrium is established between the ox-sites, the r-sites, and the bulk (the lattice diffusion is infinitely fast compared to the surface reactions), then the concentration of oxygen at the r-sites will be equal to the concentration of oxygen at the ox-sites (4),

$$\theta_{ox} = \theta_r = K_O\alpha_O/(1 + K\alpha_O), \qquad [9]$$

where K_O is the oxygen adsorption equilibrium constant. The overall reaction rate, r, will then be given by

$$r = \frac{k_{ox}k_r P_{O_2} P_{CO}}{k_{ox}P_{O_2} + k_r P_{CO}}. \qquad [10]$$

The ionic redox model then results in a Mars–van Krevelen redox model where the reoxidation of the reduced sites occurs via gas-phase oxygen (single-site mechanism).

However, if the bulk is in equilibrium with the ox-sites but not with the r-sites (the reoxidation of the r-sites [4] is not fast compared to reduction of these sites by CO), then

$$r_{ox} = k_{ox}P_{O_2}(1 - \theta_{ox}) = \frac{k_{ox}P_{O_2}}{1 + K\alpha_O} \qquad [11]$$

$$r_r = k_r P_{CO}\theta_r \neq \frac{k_r P_{CO} K\alpha_O}{1 + K\alpha_O}. \qquad [12]$$

The rate of reaction can be determined by the kinetics of reoxidation as a function of the oxygen partial pressure and the catalyst oxygen activity. Accordingly, a reoxidation-determined reaction is then said to be taking place. If the bulk is in equilibrium with the r-sites but not with the ox-sites (the reoxidation of the bulk [3] is not fast compared to oxygen adsorption), then

$$r_r = k_r P_{CO}\theta_r = \frac{k_r P_{CO} K\alpha_O}{1 + K\alpha_O} \qquad [13]$$

$$r_{ox} = k_{ox}P_{O_2}(1 - \theta_{ox}) \neq \frac{k_{ox}P_{O_2}}{1 + K\alpha_O}. \qquad [14]$$

In this case, a reduction-determined reaction is said to be taking place. Such a model predicts multiple steady states at any given gas-phase composition dependent upon the catalyst state, α_O.

The purpose of this paper is to discuss further the ionic redox model in light of transient results.

EXPERIMENTAL METHODS

The solid-state electrochemical cell used in this study,

$$\text{air, Pt}|\text{ZrO}_2\text{, 8\%Y}_2\text{O}_3|\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3\text{, O}_2\text{, CO, CO}_2\text{, N}_2\text{,} \qquad [15]$$

has been described in detail elsewhere (4, 10). The working oxide electrode was simultaneously the catalyst for the reaction under study. The platinum electrode served as the reference.

The experiments were performed over two $La_{0.5}Sr_{0.5}MnO_3$ electrodes prepared from the same oxide powder. The surface areas of the oxide electrodes were measured (after reaction) by krypton BET to be 98 ± 3 cm^2 (electrode A) and 232 + 3 cm^2 (electrode B), respectively. The projected areas of both electrodes were 3.0–3.3 cm^2. A Binos 100 nondispersive infrared photometer (Roseount) was placed in the reactor outlet stream to analyse carbon monoxide and carbon dioxide continuously (the time response of the IR analyser was of the order of a few seconds). The steady-state kinetic and emf measurements during CO oxidation were performed at 550°C and 1.65 bar. In most cases, the time necessary for the rate to reach a steady value was of the order of a few minutes. Some 24 h were allowed between successive experiments at 550°C for the emf to reach a constant value (±2 mV). (Steady states were defined as states where the emf and rate remained constant over a period of 168 h, much longer than the time constants of the associated transients.) The steady-state experiments have been reported and discussed elsewhere (4).

The activity of the La(Sr)MnO$_3$ catalyst electrode was investigated under dynamic conditions. The steady state was perturbed by reducing treatments. Initially, the catalyst was at steady state in a certain CO/O$_2$/N$_2$ gas-phase atmosphere. The reacting mixture was then suddenly replaced with a CO/N$_2$ mixture by switching the gaseous oxygen supply to nitrogen. In this way the partial pressure of carbon monoxide remained the same. The catalyst was reduced up to a certain degree (until the emf would reach a value of, e.g., −400 mV) and the catalyst was reexposed to the original CO/O$_2$/N$_2$ gas mixture. The emf and the CO$_2$ concentration in the outlet stream were simultaneously recorded at all times. Such reduction–reaction experiments were performed on oxygen-rich and oxygen-lean reacting mixtures at 550°C.

RESULTS AND DISCUSSION

An example of the reduction–reaction transients at 550°C is presented in Fig. 1; the outlet percentage CO$_2$ and the emf are plotted against time. The catalyst was initially at steady state in an oxygen-rich mixture of 15.5% O$_2$ and 6% CO. Four runs (Figs. 1a–1d) were performed; in each case the catalyst was reduced to a different extent, as indicated by the different minimum emf values obtained. In all cases, the rate under transient conditions exceeded

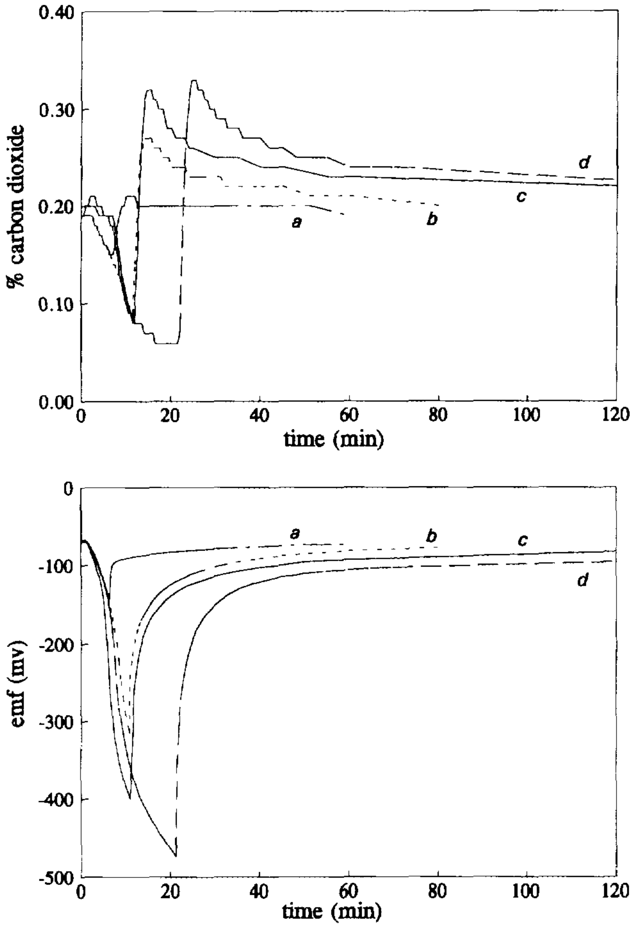

FIG. 1. Reduction–reaction transients on La(Sr)MnO$_3$ catalyst (electrode A) at 550°C. Reaction mixture 6% CO, 15.5% O_2. Reducing gas 6% CO; reduction time (a) 6, (b) 11, (c) 11, (d) 21 min.

the steady-state rate. The more reduced the catalyst (i.e., the lower the oxygen activity), the higher the transient rate. The transient rate eventually approaches the steady-state rate, as the emf approaches its steady-state value, i.e., as the catalyst returns to its original state. Similar observations were made for a CO-rich reacting mixture.

The reduction–reaction transients (Fig. 1) in the vicinity of a reoxidation-determined steady state can be explained as follows. Oxygen vacancies are created during the reduction treatment. The adsorption of gas-phase oxygen and the supply of lattice oxygen from the bulk to the r-sites are enhanced by the presence of the extra vacancies. When the reaction mixture replaces the reducing mixture, the rate exceeds the steady-state value. The rate decreases to its steady-state value as the catalyst is reoxidized. The time constant of the reduction–reaction transients should be associated with the dynamics of the solid catalyst, i.e., oxygen-diffusional phenomena.

However, gas-phase dynamic phenomena will occur at the initial stage of the transient, a period of 4–5 min. This can be seen during the oxidation–reaction transient at 550°C, presented in Fig. 2. At t = 0, the steady-state reacting mixture 15% O_2, 6% CO/N_2 was switched to a 15.5% O_2/N_2 gas mixture. The outlet percentage CO_2 decreased rapidly and disappeared within 4–5 min. The reaction mixture was then reintroduced; the rate of reaction returned to the original value again within 4–5 min. Although the state of the catalyst is perturbed during the experiments, changes in catalyst oxygen activity are much more modest than in the reduction experiments. Consequently, catalyst-diffusional phenomena do not appear to play a significant role in the transient oxidation–reaction behaviour.

The solid lines in Fig. 3a show all possible steady-state rates predicted by the ionic redox model at 15.5% O_2 and 6% CO as a function of the oxygen activity of the catalyst. The reoxidation kinetics expression (Eq. [11], line 1) predicts only one of the experimentally observed steady states (square), while the other one (triangle) is estimated by the

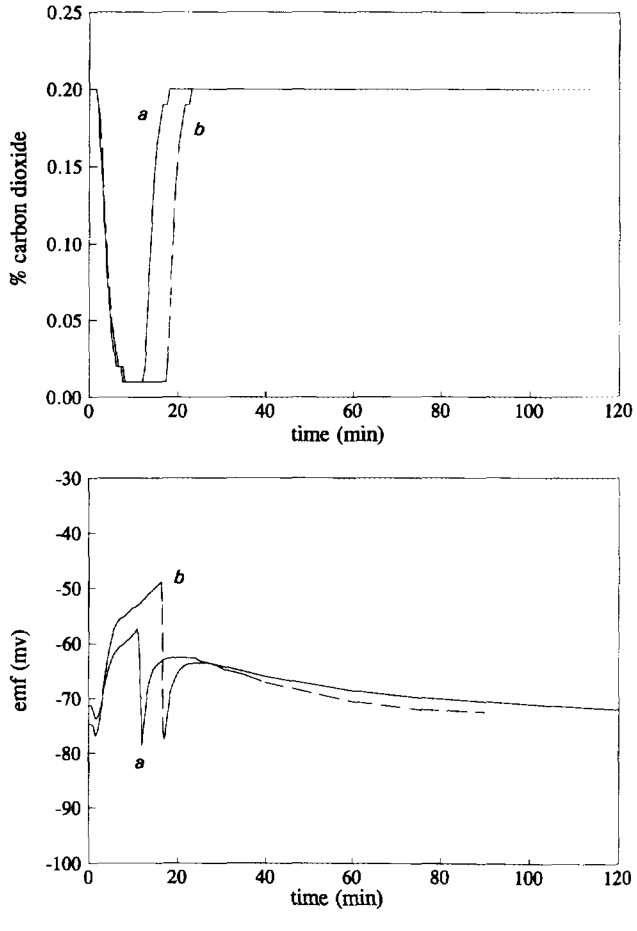

FIG. 2. Oxidation–reaction transients on La(Sr)MnO$_3$ catalyst (electrode A at 550°C. Reaction mixture 6% CO, 15.5% O_2. Oxidizing gas 15.5% O_2; oxidation time (a) 11, (b) 16 min.

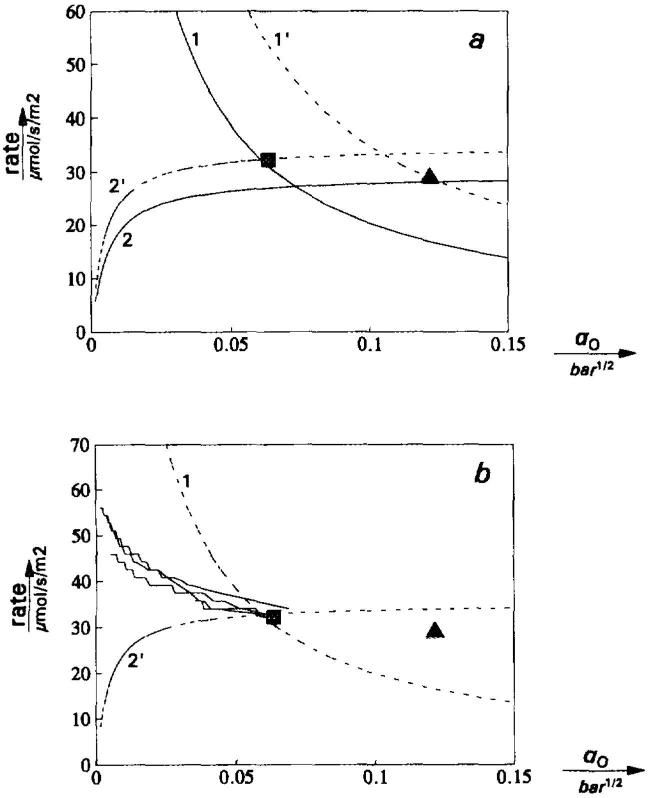

FIG. 3. La(Sr)MnO$_3$ catalyst (electrode A) at 550°C and 6% CO, 15.5% O$_2$. (a) Reoxidation (1) and reduction (2) rates predicted by the steady-state model. (b) Transient rate (solid lines). Squares and triangles denote steady states that obey reoxidation and reduction-determined kinetics, respectively.

reduction kinetics (Eq. [13], line 2). (Note that the steady state corresponding to the square was the steady state used in the transient experiments of Figs. 1 and 2.)

In Fig. 4a data for electrode B under the same gas-phase conditions of 15.5% O$_2$ and 6% CO are presented. The reoxidation kinetics, shown by the solid line 1, describe three steady-state data (squares) while reduction kinetics describe the behaviour of the other point (triangle). The behaviour is similar to electrode A except that more steady states were observed in the case of electrode B and that k_{ox} and k_r were slightly different for the two electrodes,

$$(\mathrm{A})\; k_{ox} = 1.8 \times 10^3 \frac{\mu\mathrm{mol}}{\mathrm{s\,bar\,m^2}}, \quad k_r = 3.0 \times 10^2 \frac{\mu\mathrm{mol}}{\mathrm{s\,bar\,m^2}} \quad [16]$$

$$(\mathrm{B})\; k_{ox} = 2.3 \times 10^3 \frac{\mu\mathrm{mol}}{\mathrm{s\,bar\,m^2}}, \quad k_r = 4.5 \times 10^2 \frac{\mu\mathrm{mol}}{\mathrm{s\,bar\,m^2}}. \quad [17]$$

In Fig. 5a, one can observe that the steady state obtained at 5% O$_2$ and 15.5% CO (asterisk) is described by both the reoxidation (line 1) and reduction (line 2) kinetics.

In Figs. 3 and 4, line 1′ shows the rate of catalyst reoxidation assuming that $\theta_{ox}/\theta_{ox}^e$ (where θ_{ox}^e is the oxygen coverage at the ox-sites that would be in equilibrium with the catalyst oxygen) is constant. Likewise, lines 2′, 2″, 2‴ show the rates of catalyst reduction for the reoxidation-determined steady states assuming that θ_r/θ_r^e is constant.

In Figs. 3b, 4b, and 5b, the transients (solid lines) at 15.5% O$_2$, 6% CO for electrodes A and B and 5% O$_2$, 15.5% CO, are presented. (It should be noted that the period of the reducing treatment did not allow for modifications of the steady state; the rate of reaction and the oxygen activity returned to their initial values when the catalyst was reexposed to the reaction mixture.) It can be seen that the trajectories are similar for different initial degrees of reduction (each line corresponds to a different initial degree of catalyst reduction).

After reexposure of the reduced catalyst to reactant gas, the oxygen activity of the catalyst surface would be expected to be higher than the measured oxygen activity of the catalyst (this is the driving force for catalyst reoxidation). Hence the surface reoxidation rates are suppressed during a transient and the surface reduction rates are en-

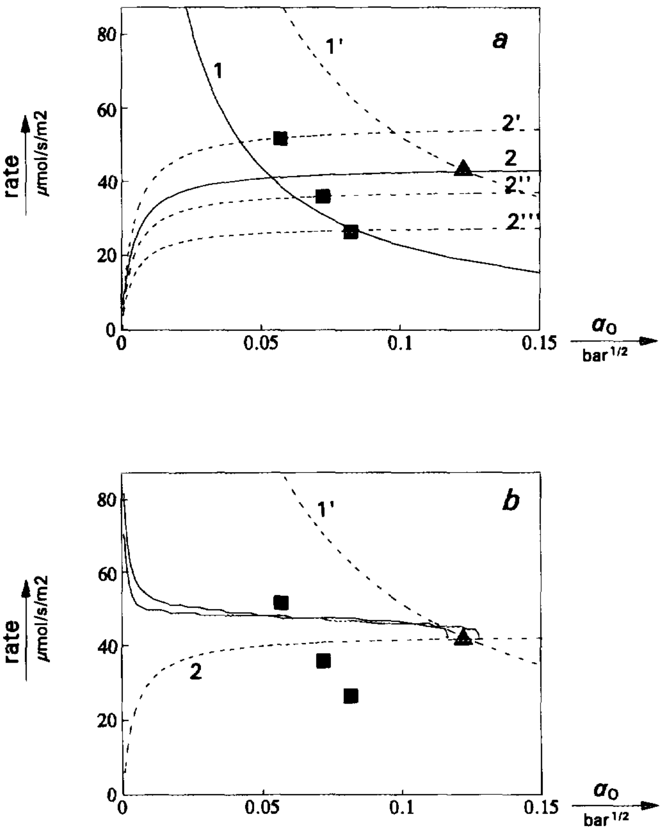

FIG. 4. La(Sr)MnO$_3$ catalyst (electrode B) at 550°C and 6% CO, 15.5% O$_2$. (a) Reoxidation (1) and reduction (2) rates predicted by the steady-state model. (b) Transient rate (solid lines). Squares and triangles denote steady states that obey reoxidation and reduction-determined kinetics, respectively.

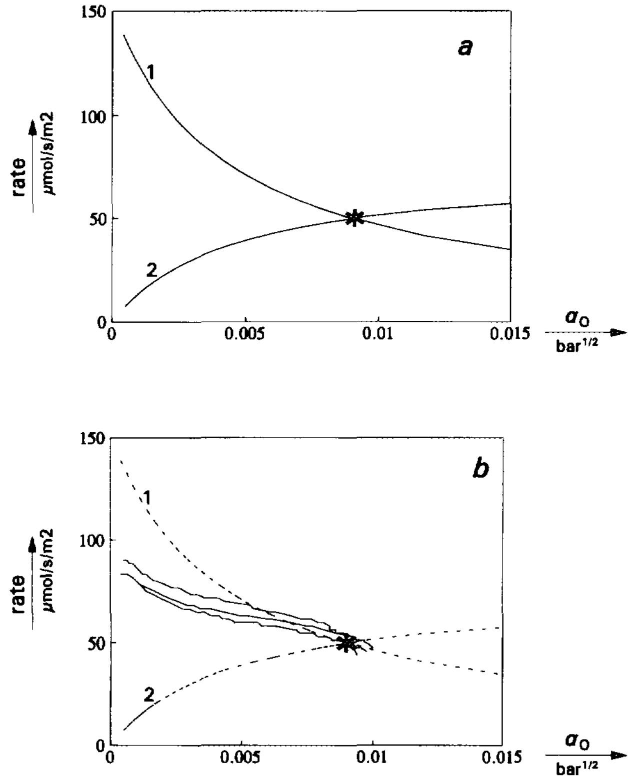

FIG. 5. La(Sr)MnO$_3$ (electrode A) catalyst at 550°C and 15.5% CO, 5%O$_2$. (a) Reoxidation (1) and reduction (2) rates predicted by the steady-state model. (b) Transient rate (solid lines). The asterisk denotes the steady state that obeys Mars–van Krevelen behaviour.

hanced. Reoxidation kinetics would determine the maximum possible reaction rate while reduction kinetics would determine the minimum possible reaction rate. Therefore, all transient rates for a reduced catalyst should lie between the oxidation and reduction lines.

Initially the surface ox- and r-oxygen species are not in equilibrium with the bulk. In the oxygen-rich mixture (e.g., Fig. 4b) the equilibrium between the bulk and the r-sites (line 2) seems to be approached earlier than the equilibrium between the bulk and the ox-sites. Conversely, in the CO-rich gas-phase mixture (Fig. 5b), the equilibrium between the bulk and the ox-sites (line 1) is established earlier than the equilibrium between the bulk and the r-oxygen; the transient rate approaches the steady state through the reoxidation curve.

In general it appears that oxygen-lean and oxygen-rich mixtures favour reoxidation- and reduction-determined reactions, respectively, as the catalyst state approaches its final steady state. Oxygen-lean mixtures and/or a reduced catalyst may result in a more reduced surface with higher rates of catalyst reoxidation. The rate of catalyst reduction rises to accommodate the higher rate of reoxidation. This results in an approach to steady state via reoxidation kinetics (Fig. 5). For oxygen-rich mixtures and an oxidised catalyst, the rate of reoxidation and rate of reaction might not be expected to be significantly different from the final steady-state rate (Fig. 4) due to the lack of extra vacant oxygen sites and steady state is approached via reduction kinetics.

CONCLUSIONS

The ionic redox mechanism assumes that the reoxidation and the reduction reactions occur at different sites on the catalyst surface and that oxygen diffuses through the oxide lattice from the ox-sites, where it is adsorbed, to the r-sites, where it reacts with CO. A reoxidation-determined reaction, where molecular oxygen adsorption is a rate-limiting step, takes place when the exchange of oxygen between the r-sites and the bulk deviates from equilibrium. A reduction-determined reaction occurs when the exchange of oxygen between the ox-sites and the bulk deviates from equilibrium. The ionic redox model also provides a framework within which transient behaviour can begin to be interpreted. Furthermore, additional kinetic information related to both catalyst reduction and reoxidation can be obtained during gas-phase perturbations.

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