JOURNAL OF CATALYSIS **172,** 446–452 (1997)
ARTICLE NO. CA971886

The Kinetics of Carbon Monoxide Oxidation on Tin(IV) Oxide Supported Platinum Catalysts

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Received May 6, 1997; revised August 12, 1997; accepted August 12, 1997

The kinetics of the oxidation of carbon monoxide by oxygen have been studied in the temperature range $0 < \vartheta < 80^\circ C$ on alumina-supported Pt/SnO_2 catalysts, the respective areas of the two active compounds being varied independently of each other. Rate measurements have been performed as well as titration experiments. The results indicate that the chemisorption of CO is restricted to platinum, whereas oxygen is adsorbed on both Pt and SnO_2. The rate pattern may be described by a mechanism where the migration of adsorbed species is added to the classical elementary reaction sequence of CO oxidation on platinum. Monte Carlo simulations show that the proposed mechanism can explain the experimental results. Under conditions where the rate is zero order with respect to both CO and O_2, simulation indicates that the migration rate of oxygen could be the determining step. Oxygen spillover from SnO_2 to Pt cannot be excluded but is not necessary to describe the experimental results. © 1997 Academic Press

INTRODUCTION

Carbon monoxide is oxidized on platinum–tin dioxide catalysts under conditions where neither platinum nor tin dioxide alone is catalytically active. In fact, at temperatures as low as 20°C and at sufficiently high partial pressures of carbon monoxide and oxygen the oxidation rate on Pt/SnO_2 is zero order with respect to both reactants. Under the same conditions the reaction is inhibited on pure platinum by a monolayer of adsorbed carbon monoxide and on pure tin dioxide, where a generally agreed redox mechanism is effective (1, 2), no catalytic activity can be measured. The observed synergism is well documented but there is no general agreement concerning its origin. There are various studies of CO oxidation on Pd/SnO_2 and Pt/SnO_2 catalysts. Both catalysts behave similarly and therefore we do not differentiate between them in the following. The catalysts investigated are quite diverse. The BET surface areas vary between 6–9 m^2/g (3) and 135 m^2/g (4), the noble metal content ranging from 0.2 (5) to 15.8 wt% (6). Thus a quantitative comparison of the results seems difficult.

Several explanations of the observed synergism are given in the literature. Bond *et al.* propose a bifunctional mechanism based on the spillover of both carbon monoxide and oxygen from the noble metal to tin dioxide (5, 7). Sheintuch *et al.* (8) also consider a bifunctional mechanism but restrict the spillover to CO. The explanation of Schryer *et al.* (9) is based on the existence of a new phase—a platinum–tin alloy. Finally, Gangal *et al.* (4) introduce the hypothesis that the adsorption of the reactants leads to a local temperature increase of the platinum particles, promoting the reaction on adjacent SnO_2 sites.

As we had based our explanation on a fifth assumption, namely the spillover of oxygen from tin dioxide to the noble metal (10, 11), we decided to perform a detailed kinetic study of the reaction in order to discriminate between the different hypotheses.

EXPERIMENTAL

The catalyst preparation is mainly based on the patent literature (12); it is described in detail elsewhere (13, 14). Briefly, a porous inert support was loaded by use of a tin oxide sol up to 25 wt% SnO_2 and subsequently impregnated with platinum. During the preparation the drying temperature was always 80°C and the calcination temperature 350°C.

The results presented in the following were obtained with catalysts supported on α-Al_2O_3. The supports are formed by extrusion to leaflets of dimensions $30 \times 10 \times 1\ mm^3$. The tin(IV) oxide loading of the catalyst is quantified gravimetrically. The platinum content is obtained by a spectrophotometric method which has been described elsewhere (15). Transmission electron microscopy (TEM) measurements have shown that the support is completely covered by a thin SnO_2 layer, a result confirmed by LEIS measurements. The surface areas of tin dioxide and platinum could be varied independently of each other by either varying the concentration of the impregnation solution (Pt) or by increasing the calcination time (SnO_2). The influence of the latter is represented in Fig. 1. The results equally show that the reduction of the surface area is not influenced by the presence of platinum.

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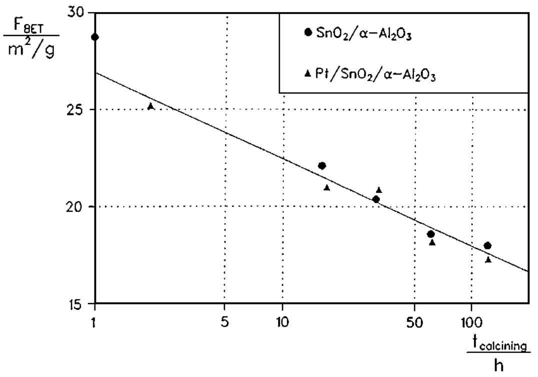

FIG. 1. BET surface area of the catalysts as a function of the calcination time.

The rate measurements are carried out in a gradientless recirculation system operated at a flow rate of 180 ml/min (STP) and a recirculation ratio of 25. The catalyst sheet is supported by a frit in a tubular glass reactor the temperature of which is controlled via a water passed jacket. Using the stoichiometry

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2, \qquad [1]$$

the reaction rate, which is related to the total catalyst mass, is defined as

$$r_m = \frac{1}{m_{\mathrm{cat}}} \cdot \frac{d\xi}{dt}; \qquad [r_m] = \frac{\mathrm{mol}}{\mathrm{g \cdot s}}. \qquad [2]$$

The extent of reaction ξ is determined by mass balancing the open system in steady state. The concentrations of carbon monoxide and carbon dioxide are measured by nondispersive infrared spectroscopy; oxygen is determined by use of a magnetomechanical device (MAGNOS 3, Hartmann & Braun) based on the paramagnetism of O_2.

The sorption capacities of the catalysts for carbon monoxide and oxygen are determined by a titration method. For this purpose the reactor is operated as a simple flow-through reactor without recirculation. It is first flushed with a nitrogen stream containing one of the reacting species (1 vol% CO or 6 vol% O_2), then swept with pure nitrogen, and finally passed by the other of the two reactants in nitrogen. In the last step the preadsorbed compound reacts with the added one to form carbon dioxide. The quantity of the preadsorbed species is obtained by the measurement of the total amount of carbon dioxide evolved,

$$n_{\mathrm{i,ads}} = \dot{V} \int C_{\mathrm{CO_2,ex}} \cdot dt; \qquad [n_{\mathrm{i,ads}}] = \mathrm{mol}, \qquad [3]$$

where $\dot{V}$ designs the volume flow and $C_{\mathrm{CO_2,ex}}$ the time-dependent CO_2 concentration at the reactor outlet. The sorption capacity is defined as the adsorbed quantity relative to catalyst mass,

$$\Gamma_{\mathrm{i}} = \frac{n_{\mathrm{i,ads}}}{m_{\mathrm{cat}}}; \qquad [\Gamma_{\mathrm{i}}] = \frac{\mathrm{mol}}{\mathrm{g}}. \qquad [4]$$

All tin-dioxide-containing catalysts used in the present study had 25 wt% SnO_2. The rate measurements were carried out in the temperature range $0 < \vartheta < 80°C$. The concentrations of the reactants are varied from 0 to 0.6 mol/m^3 in the case of CO and from 0 to 3.7 mol/m^3 in the case of oxygen. Up to 0.6 mol/m^3 water vapor can be added to the mixture of the reactants. During the measurements the rate is determined as a function of one reactant; all other concentrations are kept constant.

The titration measurements are made at 60°C. The sweeping time between preadsorption and reactions is varied from 15 min to 1 h in steps of 15 min.

RESULTS

Typical results of titration experiments are shown in Figs. 2 and 3. The variation of the CO_2 concentrations is shown simultaneously with the concentration of the titrating gas (deshed lines) in the presence (strong dashes) and absence (fine dashes) of the catalyst. The difference between the two curves in Fig. 3 indicates the adsorption of CO. In the case of O_2 the precision of the measurement is not sufficient to show this effect. In the case of the titration of sorbed CO by O_2 (Fig. 2), carbon dioxide is formed somewhat later than the arrival of oxygen in the reactor, but it is completely removed after a few minutes. In the opposite case (Fig. 3), carbon dioxide is evolved as soon as CO enters the reactor, but it may be 2 or 3 h until the adsorbed oxygen completely disappears.

The hatched areas under the CO_2 curve are used to calculate the sorption capacities. In the case of CO this capacity is independent of the sweeping time between adsorption and titration. In the case of oxygen the amount of CO_2 evolved decreases with increasing sweeping time. The

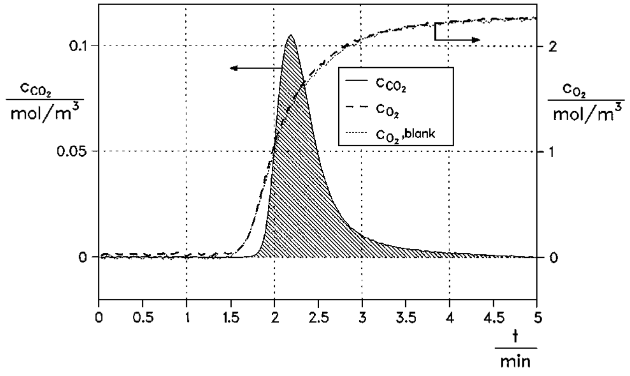

FIG. 2. Time dependent concentrations in the titration of adsorbed CO by O_2.

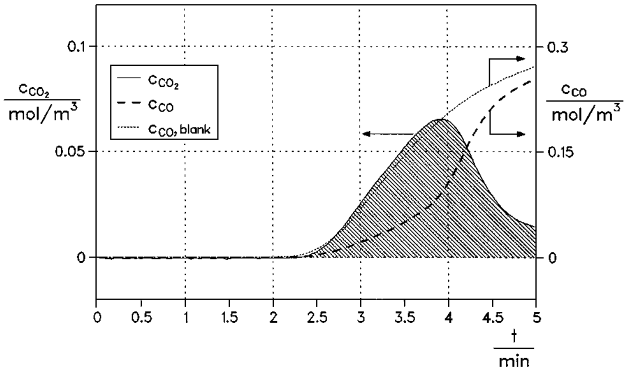

FIG. 3. Time dependent concentrations in the titration of adsorbed oxygen by CO.

desorption of oxygen is roughly second order with respect to its sorption capacity. The latter is therefore determined after extrapolation to a sweeping time of 0 of the results obtained at different intervals. The order of magnitude of the sorption capacities Γ_i is 10^{-5} mol/g in the case of CO and 10^{-4} mol/g for oxygen.

Γ_{CO} is proportional to the platinum content of the catalyst. The dependence is nearly linear up to values of 1 wt% Pt as shown on Fig. 4. It is independent of the tin dioxide surface area F_{SnO_2} in the experimentally studied range from 70 to 110 m²/g SnO_2 (17.5 to 27.5 m²/g catalyst). Γ_O increases with X_{Pt}, the slope being steeper than in the case of Γ_{CO}, as well as with F_{SnO_2}. Both capacities remain unchanged in the presence of water vapor.

If we admit that CO adsorbs exclusively on platinum, we can use the values of Γ_{CO} to calculate the partial surface area of platinum together with the platinum dispersion D (16) on the different catalysts. The results are summarized in Table 1, where sample 1, a catalyst without any SnO_2, is included. The results indicate that the platinum dispersion of the SnO_2-containing catalysts is nearly independent of the platinum loading and of the SnO_2 surface area (see samples 3, 5, 6).

TABLE 1

Platinum Surface Area and Dispersion of Different Catalysts (Catalyst 1 Does Not Contain Tin Dioxide)

Catalyst	X_{Pt} (wt%)	F_{Pt} (m²/g)	D
1	0.9	0.2	0.1
2	1.7	2.0	0.4
3	0.98	1.6	0.6
4	0.42	0.7	0.5
5	0.89	1.4	0.6
6	0.93	1.4	0.6

The measurements of the reaction rate show the typical pattern reported before (13) (examples are given in Figs. 5 and 6):

- At low carbon monoxide concentration the reaction is first order with respect to carbon monoxide and practically temperature-independent.
- At higher carbon monoxide concentration and sufficiently high oxygen concentration the rate is zero order with respect to both carbon monoxide and oxygen. Its temperature dependence is described by an exponential expression.
- The sharp decrease between the two domains is typical for platinum containing catalysts at low temperatures and is normally explained by the transition from an oxygen covered surface to a carbon monoxide covered one.

In the zero order domain the values are about one order of magnitude higher than in the case of supports based on cordierite or silica. A quantitative comparison with the values reported in preceding studies is therefore not possible (10, 11). At the moment we cannot explain this effect of the inert support.

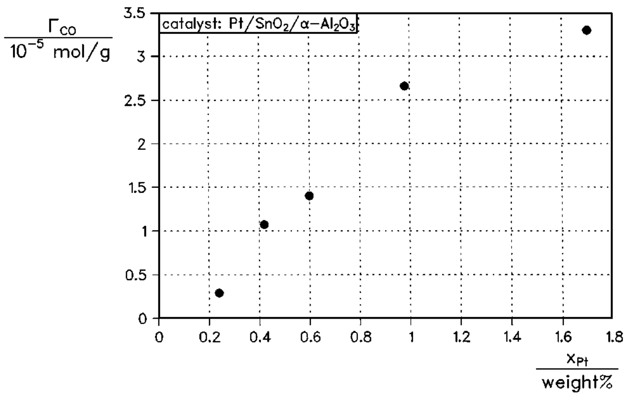

FIG. 4. The sorption capacity for carbon monoxide, Γ_{CO}, as function of the platinum content of the catalyst.

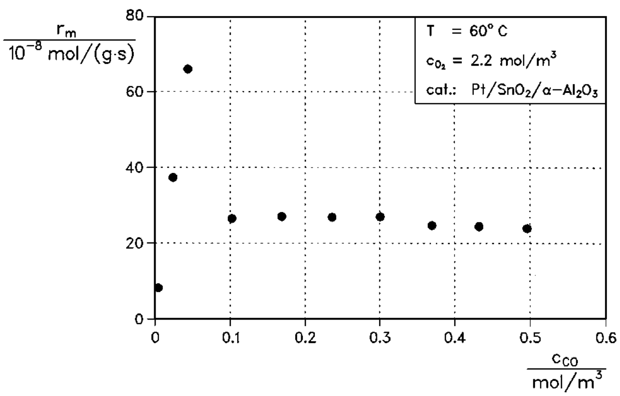

FIG. 5. Dependence of the reaction rate on the carbon monoxide concentration.

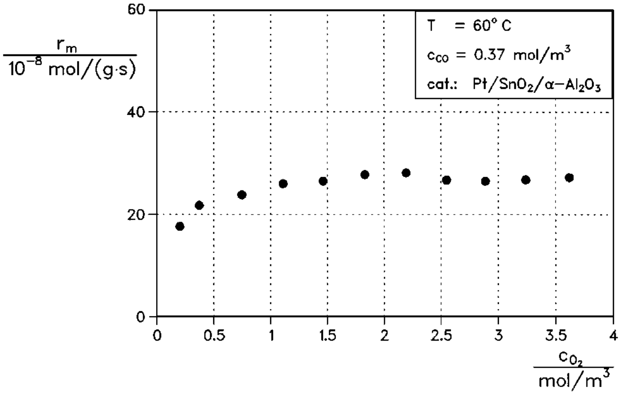

FIG. 6. Oxidation rate as a function of the oxygen concentration.

In the present study we therefore restricted ourselves to Al_2O_3 supported catalysts. In all cases—independently of platinum loading and SnO_2 surface area—we observe the same rate pattern as a function of CO partial pressure as shown on Fig. 5. Looking at the influence of the platinum content of the catalysts at constant SnO_2 surface area we see that in the first order region the mass-related rate is independent of X_{Pt}, whereas it increases linearly with the platinum loading in the zero order domain. In the case of constant platinum loading but different SnO_2 surface areas the rate is also uninfluenced in the first order range but increasing in the region of zero order.

Finally, we can remark that in the zero order domain the rate increases with the water content of the gas phase, as has been reported earlier (11).

DISCUSSION

The rate pattern as a function of the CO partial pressure showed two different domains (Fig. 5). The first order regime is known from various platinum-containing catalysts. It is obtained at low values of the partial pressure ratio p_{CO}/p_{O_2} where the platinum surface is mainly covered by a loosely packed layer of chemisorbed oxygen and the reaction proceeds via a Langmuir–Hinshelwood reaction between adsorbed species (17, 18). At atmospheric pressure the global rate is first order with respect to carbon monoxide as it is limited by the CO mass transport to the active surface (19). Therefore the values of the reaction rate, even if they seem independent of SnO_2 surface area, do not allow any conclusions as to basic reaction kinetics.

In the zero order domain, however, the extension of the tin dioxide surface area is an essential factor in the observed rate values as shown in Table 2. There is clearly a strong synergism between platinum and tin dioxide. How can this effect be explained?

For this let us first consider the titration experiments. We explain the results by the hypothesis that carbon monoxide adsorbs only on platinum but that oxygen adsorbs on both platinum and tin dioxide. This is based on the following:

- the quantity of oxygen adsorbed on tin dioxide containing catalysts, Γ_O, is one order of magnitude higher than the corresponding quantity of carbon monoxide, Γ_{CO}, whereas on SnO_2 free platinum catalysts it is even lower than the latter (17, 20);
- Γ_{CO} is independent of the SnO_2 surface area but increases nearly linearly with the platinum content X_{Pt};
- Γ_O is increasing with both X_{Pt} and F_{SnO_2};
- oxygen desorbs from the catalysts at low temperatures, whereas it is well known that oxygen and carbon monoxide do not desorb from platinum at these temperatures to a measurable extent.

This explanation is consistent with the shape of the titration curves.

In the case of preadsorbed carbon monoxide the time lag between O_2 admission and CO_2 evolution is due to the fact that oxygen cannot adsorb on CO covered platinum (17, 18). Thus it has to be sorbed near the platinum particles and react at the phase boundary Pt–SnO_2. After small parts of the CO on Pt have reacted, oxygen can adsorb equally on the noble metal, the reaction rate increases, and the CO_2 evolution peaks rapidly so that the titration is finished within several minutes. In the opposite case, CO_2 is formed immediately, but as CO can adsorb only on platinum, oxygen adsorbed on SnO_2 has to migrate to the Pt particles and therefore the titration experiment lasts much longer.

Thus Γ_{CO} is a measure of the platinum surface area, a hypothesis already used in the calculation of the noble metal dispersion reported in Table 1. As it is equally admitted that the oxidation involves CO adsorbed on platinum, the reaction rate should be directly proportional to Γ_{CO}, which is confirmed by the results shown on Fig. 7. In the zero order domain the rate is equally increasing with growing oxygen sorption capacity. The values nearly follow a parabolic law but there is some scattering which cannot be related to the carbon monoxide sorption capacity.

TABLE 2

Tin Dioxide Surface Area and Oxidation Rate at 60°C in the Domain of Zero Order in the Case of Different Catalysts Related to Total Catalyst Weight

Catalyst	F_{SnO_2}(m^2/g)	$r_m \times 10^8$ mol/(g·s)
1	—	0.14
2	25.2	36.4
3	25.2	25.6
4	25.2	7.4
5	21.0	4.9
6	18.2	2.1

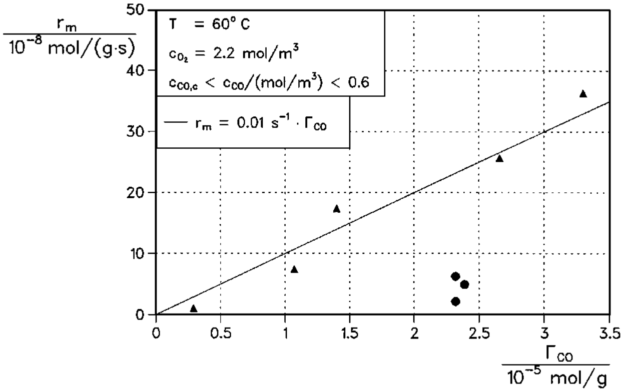

FIG. 7. Reaction rate in the domain of zero order as a function of the carbon monoxide sorption capacity (▲, $F_{SnO_2} = 25.2\ m^2/g$; ●, additionally calcined catalysts).

The combined rate and titration experiments lead us to conclude that in the zero order domain, where on pure platinum catalysts the oxidation is inhibited by the coverage of the noble metal by adsorbed CO, the reaction is sustained in the case of SnO_2-containing catalysts due to the adsorption of oxygen on SnO_2. This oxygen subsequentially diffuses to the noble metal particles to react with adsorbed CO via the normal Langmuir–Hinshelwood step. We therefore propose the following tentative mechanism. We start with the generally accepted elementary reaction sequence in the CO oxidation on platinum (17, 18), that is, molecular adsorption and desorption of carbon monoxide,

$$CO + S_{Pt} \leftrightarrow CO\text{–}S_{Pt}, \qquad [5]$$

dissociative adsorption and molecular desorption of oxygen,

$$O_2 + 2\,S_{Pt} \leftrightarrow 2\,O\text{–}S_{Pt}, \qquad [6]$$

and the reaction of both adsorbed species,

$$CO\text{–}S_R + O\text{–}S_R \rightarrow CO_2 + 2\,S_R, \qquad [7]$$

where S_{Pt} designates an adsorption site on platinum and S_R means a site where the reaction takes place.

As the measurements have shown that oxygen equally adsorbs on and desorbs from tin dioxide, the following corresponding step is included:

$$O_2 + 2\,S_{SnO_2} \leftrightarrow 2\,O\text{–}S_{SnO_2}. \qquad [8]$$

The Langmuir–Hinshelwood reaction is possible only if the reacting species can migrate toward each other. As carbon monoxide cannot adsorb on SnO_2, its mobility is limited to the platinum surface:

$$CO\text{–}S_{Pt} + S_R \rightarrow CO\text{–}S_R + S_{Pt}. \qquad [9]$$

Finally, oxygen can migrate on both surfaces; we do not need the differentiation between SnO_2 or Pt sites and may write

$$O\text{–}S + S_R \rightarrow O\text{–}S_R + S. \qquad [10]$$

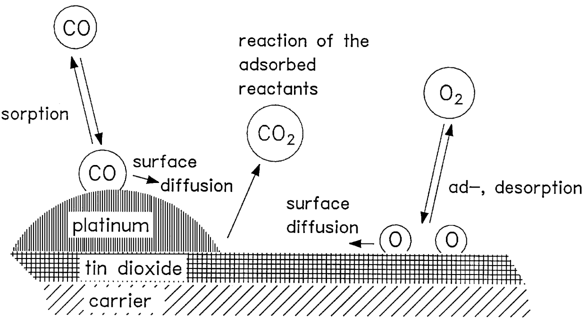

FIG. 8. Schematic representation of the elementary reaction steps.

The elementary reaction sequence is schematically shown in Fig. 8, where the interaction of oxygen with a platinum particle is omitted for simplification.

SIMULATION

In order to obtain a deeper insight into the relative importance of the different steps in the elementary reaction sequence, the oxidation was simulated by Monte Carlo methods. The calculations are based on the model introduced by Ziff *et al.* (21), which was considerably extended with respect to the catalyst representation and the elementary reaction sequence, especially concerning the possibility of migration of adsorbed species. Surface diffusion of carbon monoxide (22) and oxygen (23) has already been considered in the literature. In the following only the main features will be reported; details are given elsewhere (14).

The catalyst is considered as a field of 100 × 100 elements, identified as sites of platinum or tin dioxide, respectively. It is created by a random process but the surface is "smoothed" by excluding isolated sites of either platinum or tin dioxide. Figure 9 shows a typical model catalyst with about 4% platinum.

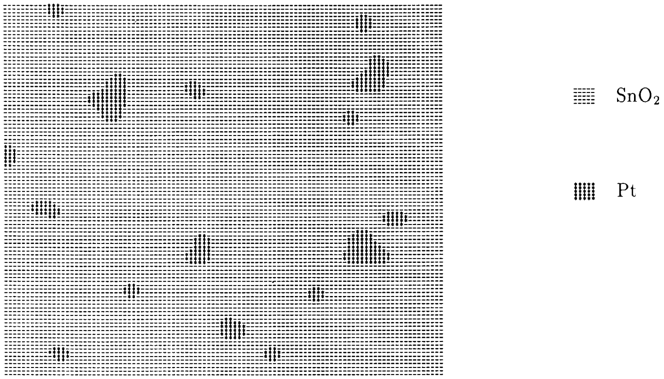

FIG. 9. Schematic representation of a typical model catalyst used in simulation.

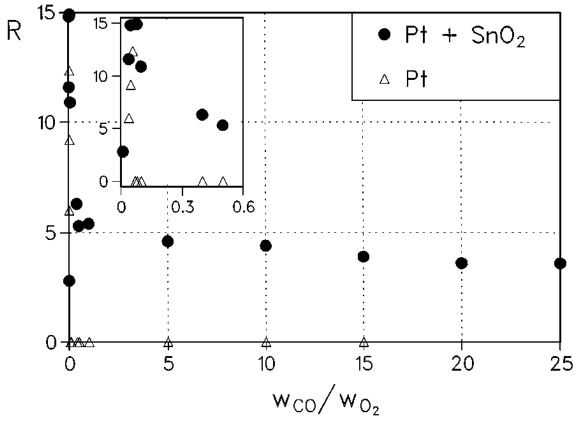

FIG. 10. Reaction rate in arbitrary units as a function of the ratio of the molar fractions w_{CO}/w_{O_2} (simulation).

The composition of the gas phase, constituted merely of CO and O_2, is characterized by the ratio of the molar fractions, w_{CO}/w_{O_2}. During the calculations different probabilities are prefixed for adsorption, migration, and desorption. All other processes occur at random:

- the choice of the element of the surface to be considered
- adsorption of either CO or O_2 if the element is vacant
- migration (neighboring site vacant) or desorption if the element is covered.

The reaction probability is taken to be equal to one if two neighboring sites are covered simultaneously by CO and O. Typical results obtained on a model catalyst with 6% platinum are shown in Figs. 10 and 11, where the rate is given in arbitrary units. The results obtained by simulation compare favorably with the experiments represented in Figs. 5 and 6: we observe the same rate patterns. In the domain where the rate is independent of the gas phase composition, that is, zero order with respect to both reactants, the simulation indicates that the reaction rate is determined by the migration rate of oxygen on the surface. Additionally, the rate increases with the number of tin dioxide elements adjacent to platinum elements, that is, the extension of the three-phase borderline gas–noble metal–oxide.

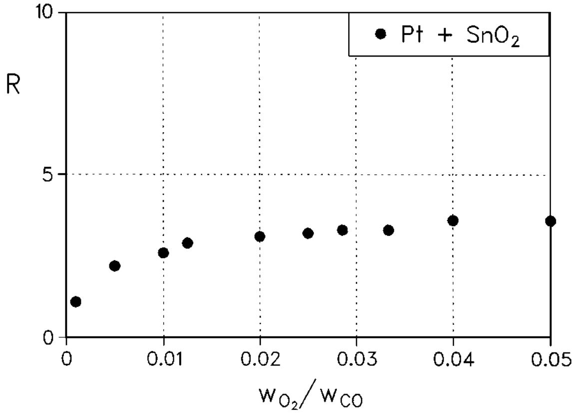

FIG. 11. Reaction rate in arbitrary units as a function of the ratio of the molar fractions w_{O_2}/w_{CO} (simulation).

Thus the experimental observations are reproduced by the simulation. This shows that the mechanistic model and the supposed catalyst are appropriate for describing the CO oxidation on platinum–tin dioxide catalysts. The proposed elementary reaction sequence seems able to reproduce the real process. Even if the simulation does not really produce new information, it leads to an illustration of the elementary sequence and allows us—within the framework of the proposed model—to determine the influence of various process parameters upon quantities such as surface coverage or the rate-determining step in a simple way.

CONCLUSIONS

A detailed kinetic study has shown that the synergism in the oxidation of carbon monoxide on platinum–tin dioxide catalysts is mainly due to the adsorption of oxygen on the oxide surface. Subsequently, it migrates to the reaction sites situated at the border between oxide and noble metal particles. However, neither the experimental results nor the model calculations allow the localization of the reactive sites. We cannot distinguish between the three-phase boundary line platinum–oxide–gas and the adjacent sites. Thus the possibility of oxygen spillover from tin dioxide onto platinum cannot be excluded but is not necessary to explain the observed results.

ACKNOWLEDGMENT

We are grateful to Dr. R. G. van Welzenis, University of Technology Eindhoven, for kindly performing the LEIS measurements.

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