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CO Oxidation over Rh Dispersed on SiO_2, Al_2O_3, and TiO_2: Kinetic Study and Oscillatory Behavior

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The kinetic behavior of Rh supported on SiO_2, Al_2O_3, and TiO_2 in the CO oxidation reaction has been investigated. It was found that the maximum turnover frequency (TOF) is approximately the same over the three catalysts, although the maximum is shifted to lower CO pressures for Rh/Al_2O_3 and Rh/TiO_2 than for Rh/SiO_2 catalyst. At high CO pressures, a change from -1 to -0.4 in the reaction order with respect to CO was observed over Rh/Al_2O_3, while in the case of Rh/TiO_2 a similar change from -1 to -0.2 was observed. These changes are attributed to the contribution of the CO dissociation step to the total oxidation rate. Oscillatory behavior and hysteresis were observed on all catalysts at 393 K. However, the window of oscillation with respect to the CO pressure was much wider on Rh/SiO_2 than on the other catalysts. On-line mass spectrometry was used to follow the precise oscillatory patterns as a function of reaction temperature over the Rh/SiO_2 catalyst. The oxidation/reduction of the rhodium surface is proposed to be the dominant mechanism responsible for the observed oscillatory behavior. © 1995 Academic Press, Inc.

INTRODUCTION

The oxidation of carbon monoxide over Group VIII metals has been extensively studied due to its practical importance in the control of emissions and also due to its complex kinetic behavior (oscillatory phenomena). The CO/O_2 reaction on Rh is generally considered to be structure-insensitive. Identical rates and activation energies have been measured over two different crystal planes of Rh, namely, Rh(111) and Rh(100) (1), while very good agreement with respect to turnover frequencies also exists between single Rh crystals and supported Rh/Al_2O_3 catalysts (2, 3). No rhodium particle size effects on the intrinsic oxidation rate have been observed over Rh supported on α-Al_2O_3 (dispersion ranging from 0.017 to 1.0), although a support effect with the low-temperature activity decreasing in the order Rh/α-Al_2O_3 > Rh/SiO_2 Rh/θ-Al_2O_3 has been reported (4). The structure sensitivity of the CO/O_2 reaction over other metals has been reviewed by Che and Bennett (5).

At low temperatures, there is a negative-order dependence of the reaction rate on CO partial pressure and a positive-order dependence on O_2 partial pressure (3). This observation is in apparent contradiction with the values of heats of adsorption of CO and O_2 on clean Rh surfaces, where oxygen is known to adsorb much more strongly than CO (6, 7). Thus, a Langmuir–Hinshelwood model with values of adsorption parameters corresponding to those obtained over clean surfaces fails to describe the observed kinetic behavior. One would have to assume that the rate of oxygen adsorption is strongly inhibited by CO in order to obtain agreement with experimental data (8).

Inhibition by O_2 has been observed at high P_{O_2}/P_{CO} ratios ($P_{O_2}/P_{CO} > 30$ for Rh(111) at 500 K (1)), a result which coincides with a sudden increase in the oxygen surface coverage. The formation of a surface oxide which has low catalytic activity has been considered as a possible mechanism of catalyst deactivation at high P_{O_2}/P_{CO} ratios (1, 9). Surface oxides of Rh have been detected by imaging atom-probe mass spectrometry for O_2/CO ratios greater than 30–40 at 500 K (10), while it was also found that CO can easily reduce this rhodium oxide species at temperatures higher than 420 K (11). XPS performed on a Rh/Al_2O_3 catalyst showed that the catalyst surface consists primarily of Rh_2O_3 in a net oxidizing environment in the temperature range of 473–773 K (12). Facile oxidation of Rh supported on Al_2O_3 at 300 K in 0.1 atm O_2 was also observed by EXAFS (13). In addition, similar inhibition effects under oxidizing conditions have been observed for Pd and Ir single-crystal catalysts (14).

The oxidation of CO is the most typical example of a reaction that can exhibit oscillatory behavior. Comprehensive reviews discussing oscillatory behavior in catalytic reactions and its theoretical modeling have appeared in the literature (15–18). As far as oscillations in the CO/O_2 reaction are concerned, most of the experimental studies have concentrated on Pt catalysts. In the low pressure region, oscillations of the reaction rate on Pt(100) have been attributed to the periodic surface phase transformation hex ↔ (1 × 1) (19–21). In the atmospheric pressure

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region the onset of oscillations has been attributed to periodic oxidation/reduction of the Pt surface (22). Similar reasoning (oxidation or formation of subsurface oxygen) has also been applied in the case of Pd(110) (23) as well as polycrystalline Pd and Ir catalysts (24, 25). Oscillations on supported Pt and Pd catalysts have also been reported (26–34). In some cases, the appearance of oscillations was accompanied by a breakdown of surface uniformity, and it was proposed that the oscillations are of a spatiotemporal nature (27, 28). Infrared thermography has been used to study the spatially nonuniform character of oscillatory behavior over Rh/SiO_2 catalysts (33). Oscillations over Rh/Al_2O_3 catalysts in the form of wafers or pellets have been studied using transmission infrared spectroscopy (35, 36). It was found that oscillations in the CO_2 production rate were accompanied by oscillations of the surface coverage of linear CO species, while the coverage of the Rh dicarbonyl species did not exhibit any oscillatory pattern. The low rate regime corresponded to a high coverage of linear CO, while the period and amplitude of the oscillations were affected by the O_2 concentration in the feed.

The present work reports results on the kinetic behavior of the CO oxidation reaction over Rh supported on SiO_2, Al_2O_3, and TiO_2. On-line mass spectrometry was employed to study the oscillatory behavior of this reaction over the Rh/SiO_2 catalyst, a phenomenon not observed over Rh/Al_2O_3 and Rh/TiO_2 catalysts under the same experimental conditions. To our knowledge, this is the first time that oscillatory phenomena of this reaction have been measured through the gas phase responses of CO_2 and CO over the Rh/SiO_2 catalyst. This information allows better modeling of the oscillatory behavior than is possible with information only on the surface coverage changes of adsorbed CO, as measured by FTIR techniques. Significant carrier effects have previously been reported for CO adsorption and CO hydrogenation (37) over the present Rh-supported catalysts.

EXPERIMENTAL

Catalysts

Details of the preparation and characterization of the Rh/SiO_2, Rh/Al_2O_3, and Rh/TiO_2 catalysts employed in the present study have been reported previously (37). All catalysts were prepared using $RhCl_3 \cdot 3H_2O$ as a precursor compound and contained 0.5 wt.% Rh. The dispersion of the Rh metal in the fresh supported Rh catalysts was found to be 1.0, 1.0, and 0.7 for Rh/SiO_2, Rh/Al_2O_3, and Rh/TiO_2, respectively (37).

Apparatus

The apparatus employed for kinetic studies has been described previously (37). The CO/O_2 reaction was investigated in the temperature range 363 to 413 K. The feed (50–350 cm^3 STP/min) consisted of 0.04–4% CO and 6% O_2, with N_2 as a diluent gas. The catalyst bed (catalyst weight of approximately 15 mg, and particles within the size range of 0.063–0.125 mm) was diluted with γ-Al_2O_3 particles of the same size as the catalyst so as to give a ratio of 5 parts Al_2O_3 to 1 part catalyst. This dilution was found necessary in order to obtain isothermal conditions along the length of the catalyst bed. It was determined that γ-Al_2O_3 was not catalytically active in this temperature range. After each set of measurements, the catalyst was exposed to air followed by H_2 flow for 30 min at 473 K to clean the surface of any contamination.

The oscillatory behavior of the reaction was studied in a different reactor system, which was coupled to a mass spectrometer for continuous measurement of CO and CO_2 effluent concentrations. This system is described in detail elsewhere (38). Measurements were performed in the temperature range 381–403 K using a reactant mixture of 0.5% CO/6% O_2/balance He at a flow rate of 30 cm^3/min (ambient). The catalyst weight employed was 0.5 g.

Infrared spectra were obtained using a Nicolet 740 FTIR spectrometer equipped with a DRIFT cell. Details concerning the procedure of IR experiments are given elsewhere (39). Infrared spectra of adsorbed CO on Rh/SiO_2 were recorded under a flow of the reaction mixture consisting of 0.5% CO, 6% O_2, balance He at 393 K. An infrared spectrum obtained under He flow at the reaction temperature was used as the background, which was subtracted from the spectra obtained under reaction conditions.

RESULTS

Steady-State Kinetic Studies

Steady-state kinetic measurements were conducted in order to determine the influence of the carrier on kinetic parameters of the CO oxidation reaction over Rh crystallites. The influence of CO partial pressure on the reaction rate is shown in Fig. 1 for the Rh/SiO_2 catalyst. The experiments were conducted at 393 K at a constant oxygen partial pressure of 6 kPa. Prior to the measurements, the catalyst was reduced under H_2 flow at 473 K and then cooled under N_2 to 393 K. Therefore, Rh can be considered to be in a fully reduced state upon initiation of the reaction. Curve a in Fig. 1 was obtained starting from a high CO partial pressure and decreasing it stepwise. CO inhibition in the reaction rate was observed at P_{O_2}/P_{CO} ratios smaller than 12, while at low CO pressures the reaction order was found to be positive with respect to CO. Oscillations in the CO and CO_2 effluent concentrations were observed for CO partial pressures between 0.1 and 1 kPa. Because a gas chromatograph was used for the analysis of the reaction mixtures, the effluent CO_2 and CO concentrations could

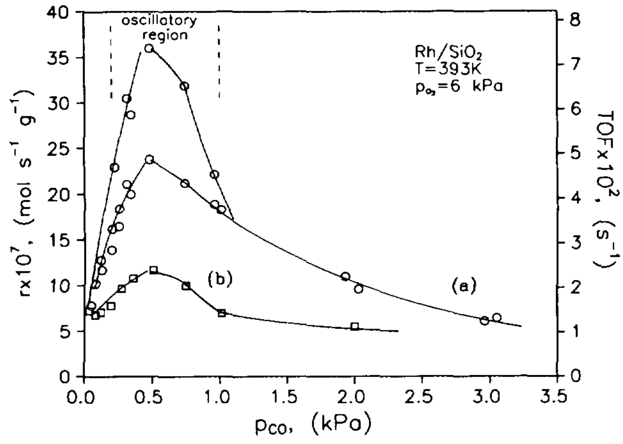

FIG. 1. Effect of CO partial pressure on turnover frequency (TOF) of CO oxidation reaction over the Rh/SiO_2 catalyst. T = 393 K, P_{O_2} = 6 kPa. (a) Results obtained by decreasing CO pressure. (b) Results obtained by increasing CO pressure. Symbols, experimental points; line, fitting curve.

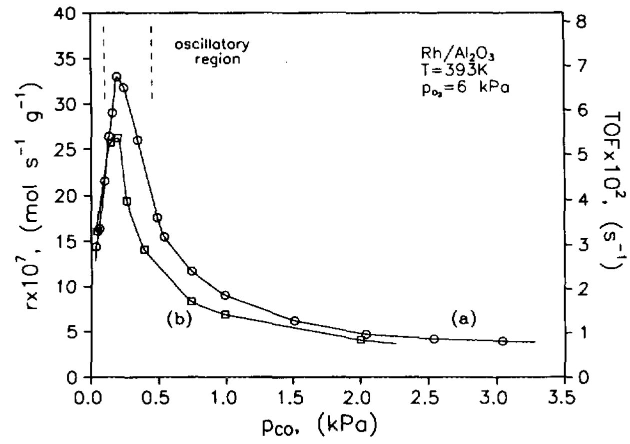

FIG. 2. Effect of CO partial pressure on turnover frequency (TOF) of CO oxidation reaction over the Rh/Al_2O_3 catalyst. T = 393 K, P_{O_2} = 6 kPa. (a) Results obtained by decreasing CO pressure. (b) Results obtained by increasing CO pressure. Symbols, experimental points; line, fitting curve.

not be measured continuously. Nevertheless, oscillations of the CO_2 and CO concentrations were readily observable and the minima and maxima of the CO oxidation rate are shown in Fig. 1. Curve b in Fig. 1 was obtained starting from a low CO pressure (0.05 kPa) and in this case substantially lower (by a factor of 2 to 3) reaction rates were observed. This hysteresis phenomenon was found to be reversible. Exposure of the catalyst to high CO pressures for a sufficient time, or reduction by H_2 at 473 K, completely restored the initial activity (Curve a). Oscillations were not observed when starting from low CO pressures (Curve b).

Corresponding results for the Rh/Al_2O_3 catalyst are shown in Fig. 2. Negative-order dependence of the rate with respect to CO partial pressure is observed for P_{O_2}/P_{CO} ratios smaller than 30; i.e., CO inhibition persists at even lower CO pressures than for the Rh/SiO_2 catalyst. A hysteresis effect is also observed in this case. The difference between Curves a and b in Fig. 2, however, is much less pronounced. Oscillatory behavior was found in the region of the maximum rate, at CO pressures between 0.1 and 0.4 kPa, and on decreasing and increasing CO pressure.

The effect of CO partial pressure on the oxidation rate over the Rh/TiO_2 catalyst is presented in Fig. 3. CO inhibition was observed for P_{O_2}/P_{CO} ratios lower than 60, compared to 30 for Rh/Al_2O_3 and 12 for Rh/SiO_2 catalysts. Oscillatory behavior was readily observed only in the CO pressure region where the maximum rate appears. The oscillatory region is, therefore, confined to a narrow region in the pressure range of 0.1 kPa CO under these experimental conditions. The hysteresis behavior that was observed over all three Rh catalysts when they were exposed to oxygen-rich reaction mixtures is similar to that observed over Pd/zeolite catalysts (34). As discussed in a later section, the most plausible explanation for this behavior is the oxidation of the rhodium surface. This leads to deactivation of the catalyst, because oxidized rhodium is less active in CO oxidation than rhodium metal (40).

The reaction order with respect to CO partial pressure, in the CO inhibiting region, was determined by plotting on a log–log graph the TOF as a function of P_{CO}, as shown in Fig. 4. The reaction orders as obtained from the slopes of Fig. 4 are reported in the second column of Table 1. A reaction order of −1 is predicted by a Langmuir–Hinshelwood mechanism with CO being more strongly

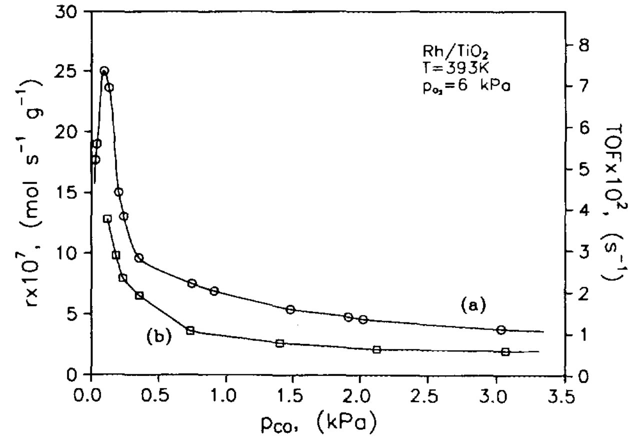

FIG. 3. Effect of CO partial pressure on turnover frequency (TOF) of CO oxidation reaction over the Rh/TiO_2 catalyst. T = 393 K, P_{O_2} = 6 kPa. (a) Results obtained by decreasing CO pressure. (b) Results obtained by increasing CO pressure. Symbols, experimental points; line, fitting curve.

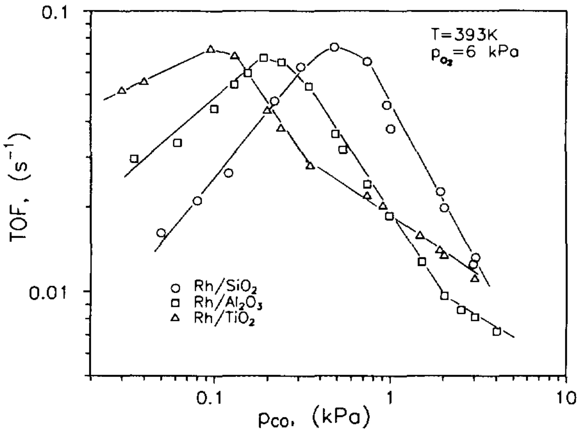

FIG. 4. Determination of the reaction order with respect to CO partial pressure in the CO inhibiting region from the slope of log(TOF) vs log(P_{CO}) plots. T = 393 K, P_{O_2} = 6 kPa.

adsorbed than oxygen (8). This is indeed observed over the Rh/SiO$_2$ catalyst in the range of CO pressures examined. For Rh/TiO$_2$ and, to a lesser extent, for Rh/Al$_2$O$_3$, a change in the reaction order at high CO pressures is observed, while a reaction order of −1.0 is observed only at intermediate CO pressures. At higher CO pressures the reaction order becomes −0.4 for Rh/Al$_2$O$_3$ and −0.2 for Rh/TiO$_2$. This implies that, over these catalysts, changes in the reaction mechanism may occur when the CO pressure is increased beyond a certain value. The CO pressure at which the transition occurs seems to also be affected by the carrier (see Fig. 4). Thus, over Rh/TiO$_2$ the transition occurs at a CO pressure of approximately 0.4 kPa, while over Rh/Al$_2$O$_3$ it occurs at approximately 2 kPa.

The maximum turnover frequency observed, as well as the turnover frequency at a P_{CO} of 2 kPa, which is in the CO inhibiting region, is also reported in Table 1. At a P_{CO} of 2 kPa, TOFs differ at most by a factor of 2 and are in the range $1 - 2 \times 10^{-2}$ s^{-1}. Based on literature data for Rh(111), Rh(100), Rh/Al$_2$O$_3$, and Rh/SiO$_2$ (1–4), and after extrapolation to the experimental conditions employed in the present work, values in the range $1.0 - 2.5 \times 10^{-2}$ s^{-1} are obtained, which are in very good agreement with the results of the present work. The maximum TOF values does not seem to depend on the kind of support used to disperse Rh. Values around 7×10^{-2} s^{-1} were obtained in all cases. However, as already shown in Figs. 1–3, the maximum TOF appears at a different P_{O_2}/P_{CO} ratio for each catalyst.

TABLE 1

Kinetic Parameters of Supported Rh Catalysts in the CO/O$_2$ Reaction (T = 393 K, P_{O_2} = 6 kPa)

Catalyst	n_{CO}	(TOF)$_{max}$ (s^{-1})	(TOF)^a (s^{-1})	E_{act} (kJ/mol)
Rh/SiO$_2$	−1.01	0.074	0.020	104 ± 4
Rh/Al$_2$O$_3$	−0.96, −0.43	0.067	0.010	95 ± 3
Rh/TiO$_2$	−0.95, −0.21	0.076	0.014	72 ± 2

[a] P_{CO} = 2 kPa.

The apparent activation energy of the reaction was determined in the temperature range 363–413 K at a CO partial pressure of 2 kPa and an oxygen partial pressure of 6 kPa. These results are also shown in Table 1. The activation energy was found to decrease in the order SiO$_2$ > Al$_2$O$_3$ > TiO$_2$. The values obtained over Rh/SiO$_2$ and Rh/Al$_2$O$_3$ (about 100 kJ/mol) are comparable to those reported in the literature (1–4). The value obtained over the Rh/TiO$_2$ catalyst, however, is significantly lower.

Oscillatory Behavior

The oscillatory behavior of the CO oxidation reaction was investigated in detail in a reactor system which was connected to a mass spectrometer, thus making possible the continuous measurement of effluent CO and CO$_2$ concentrations. Using a catalyst weight of 0.5 g, a flow rate of 30 cm^3/min (ambient), and a mixture containing 0.5% CO/6% O$_2$/He, oscillations were observed only in the case of the Rh/SiO$_2$ catalyst. The temperature range in which oscillations appeared was 381–403 K. Typical oscillations of CO$_2$ and CO effluent concentrations as a function of time on stream are shown in Figs. 5a and 5b for reaction temperatures of 383 and 388 K, respectively, and for a given period of 28 min, where oscillations appear to have quite a regular periodic pattern. The period of the oscillations at 383 K was found to vary between 135 and 195 s. At 388 K the period varied between 50 and 103 s. At 393 and 401 K the oscillations exhibit a more complex pattern, while the amplitude becomes smaller. These results are shown in Figs. 6a and 6b, respectively. In Fig. 6b the time zero is that corresponding to the switch from He to CO/O$_2$/He mixture. No oscillations were observed at temperatures higher than 402–403 K.

An important observation is that the CO$_2$ concentration at the peaks has values which exceed the feed concentration of CO (0.5 mol%). This implies that CO accumulates on the catalyst surface prior to the occurrence of the maximum in the CO$_2$ rate. This is illustrated in Fig. 7, where the sum of the CO and CO$_2$ concentrations in the reactor effluent stream is plotted as a function of reaction time. It can be observed that in a given time the (CO$_2$ + CO)$_{exit}$ concentration is smaller than the feed CO concentration (horizontal line at 0.5% CO). During this time, part of the CO adsorbs and accumulates on the Rh surface. When the CO surface concentration reaches a critical value, CO is rapidly oxidized toward CO$_2$, giving rise to CO$_2$ concentrations which are higher than the one corresponding to 100% conversion of CO. The amount of CO which accumulates on the surface at 383 K over a period of oscillation was

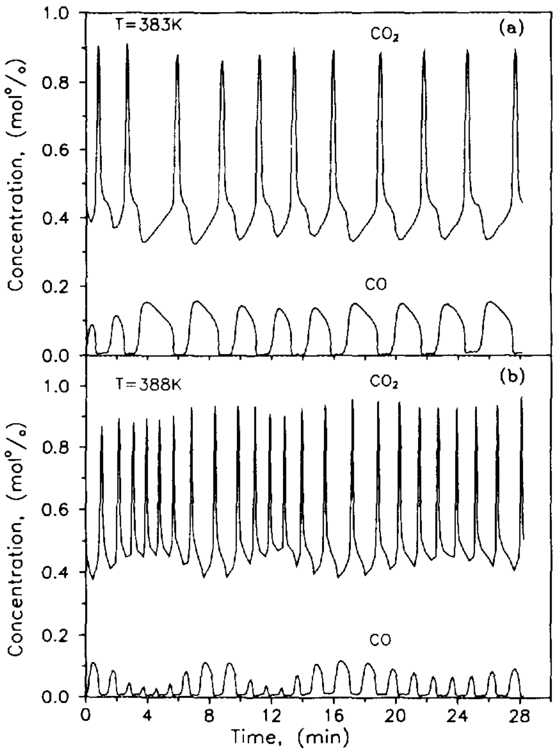

FIG. 5. Oscillatory behavior of the CO/O_2 reaction over the Rh/SiO_2 catalyst. Feed composition 0.5% CO/6% O_2/93.5% He. (a) T = 383 K and (b) 388 K.

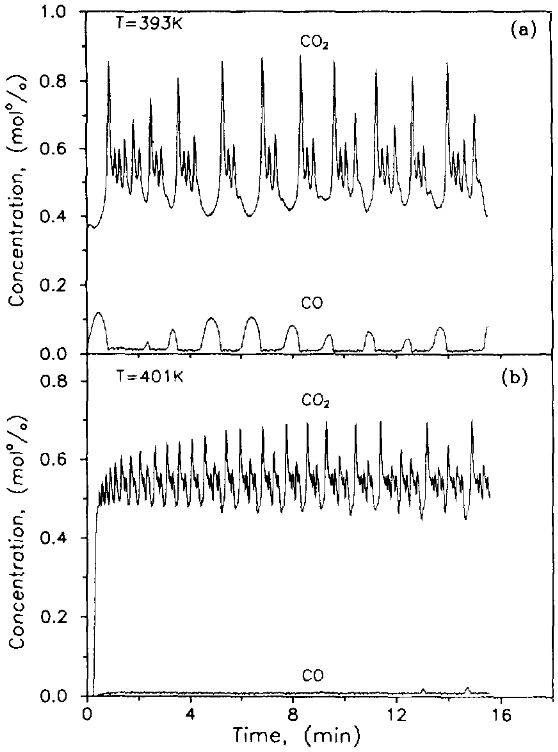

FIG. 6. Oscillatory behavior of the CO/O_2 reaction over the Rh/SiO_2 catalyst. Feed composition 0.5% CO/6% O_2/93.5% He. (a) T = 393 K and (b) 401 K.

estimated to be approximately 2.2 μmol, which corresponds to a change in the surface coverage of CO, $\Delta\theta$, of 0.046 of a monolayer. At 388 K, the corresponding quantities were found to be 1.1 μmol and $\Delta\theta$ = 0.023. At 393 and 401 K, the CO coverage changes were found to be smaller than 0.02.

The surface coverages of CO and oxygen under reaction conditions at 393 K over the Rh/SiO_2 catalyst were determined as follows: The 0.5%CO/6%O_2/He mixture was passed over the catalyst for 10 min at 393 K, followed by purging with He for 5 min at the same temperature. The amount of surface oxygen was determined by titration with a CO/He mixture based on the amount of CO_2 produced. The amount of surface CO was determined from the amount of CH_4 produced during TPSR with hydrogen. The oxygen coverage was found to be significantly larger than the CO coverage (θ_O was approximately 0.4 compared to the θ_{CO} of 0.15). This is not unexpected, taking into account that the reaction mixture employed is net oxidizing.

FTIR Spectra of Adsorbed CO on Rh/SiO_2 under Reaction Conditions

Surface species accumulating on the Rh/SiO_2 catalyst during CO oxidation, as a function of time-on-stream, were monitored by FTIR spectroscopy. Selected spectra recorded under reaction conditions (T = 393 K, 0.5%CO/6%O_2/He reaction mixture) are shown in Fig. 8, Curves a–c, for 2, 10, and 120 min on stream. For comparison, the spectrum obtained after exposure of the Rh/SiO_2 catalyst

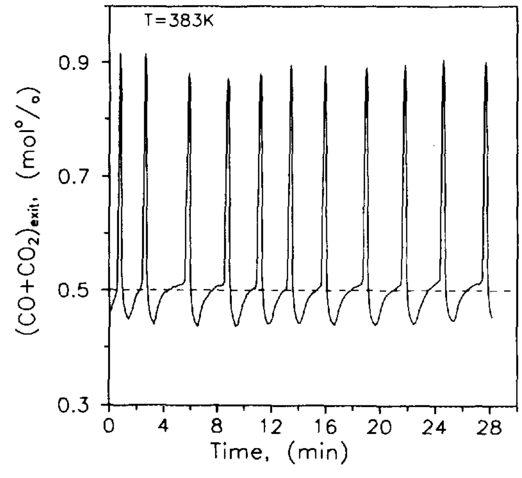

FIG. 7. Carbon mass balance as a function of reaction time during oscillatory behavior over the Rh/SiO_2 catalyst. T = 383 K. Feed composition 0.5% CO/6% O_2/93.5% He.

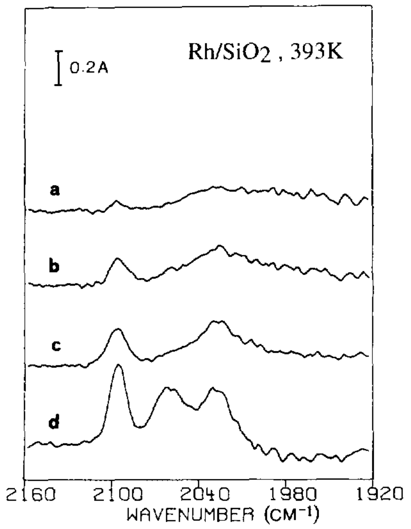

FIG. 8. Infrared spectra of adsorbed CO on Rh/SiO$_2$ under reaction conditions. Reaction mixture 0.5% CO, 6% O$_2$, 93.5% He. Exposure time at 393 K: (a) 2 min, (b) 10 min, and (c) 2 h. (d) 76 Torr CO at 298 K for 2 h.

to CO (76 Torr) for 120 min at room temperature is also presented in Fig. 8, Curve d. The bands of adsorbed CO are found to develop gradually with time-on-stream and reach a stable level after 60–120 min of reaction. In addition to a weak band of bridged CO at ca. 1860 cm^{-1} (not shown), three bands at 2096, 2055, and 2029 cm^{-1} can be distinguished. The twin bands at 2096 and 2029 cm^{-1} are attributed to the symmetric and asymmetric carbonyl stretching frequencies of gem dicarbonyl on isolated Rh$^{\mathrm{I}}$ sites (41). The shoulder band at 2055 cm^{-1} is assigned to linearly bound CO on Rh crystallites (42). Compared with the spectrum of CO adsorbed at room temperature (Fig. 8, Curve d) the concentration of linear CO (2055 cm^{-1}) under reaction conditions is much smaller. The adsorbed CO at the working catalyst surface is mainly in the gem-dicarbonyl form. The formation of the gem-dicarbonyl species is due to the oxidative disruption of Rh–Rh bonds in the Rh crystallites, induced by CO. The high proportion of these species under reaction conditions might be related to the presence of oxygen, which favors the conversion of Rh^0 sites to Rh$^{\mathrm{I}}$ sites. It was not possible to observe any periodic changes in the intensity of adsorbed CO bands, which could be correlated with the oscillatory behavior of the Rh/SiO$_2$ catalyst.

DISCUSSION

Steady-State CO Oxidation Kinetics

Kinetic parameters of CO oxidation over Rh catalysts were determined as a function of the carrier employed for the dispersion of the metal. Maximum observable turnover frequencies over the three catalysts were found to be approximately equal. Thus, it could be argued that the reaction rate constant of the rate-determining step is not sensitive to the carrier of the catalysts. A support effect is, however, evident in the P_{O_2}/P_{CO} ratio at which the maximum rate appears. As Fig. 4 indicates, the kinetic curve and the maximum in turnover frequency are shifted to lower CO pressures on Rh/Al$_2$O$_3$ and Rh/TiO$_2$ than on Rh/SiO$_2$. Based on a Langmuir–Hinshelwood mechanism, with CO inhibiting the reaction more than oxygen, the position of the maximum rate relates to the relative adsorption strength of CO and oxygen on the catalyst surface, or equivalently to the relative ratio of CO and oxygen surface coverages. The lower the CO pressure at which the rate maximum appears, the higher the adsorption strength of CO relative to that of oxygen. However, such a correlation is not straightforward because although oxygen is known to adsorb more strongly than CO on clean Rh surfaces (6, 7), CO appears to be the most strongly bound species on the working catalyst surface under reaction conditions. CO TPD experiments employing the same catalysts as those used in the present work did not show increased adsorption strength of CO (36). It was found, however, that the tendency of CO toward dissociation increases in the order Rh/SiO$_2$ $\ll$ Al$_2$O$_3$ $<$ TiO$_2$. The high activity of Rh/TiO$_2$ in CO dissociation was attributed to creation of new sites at the Rh–TiO$_2$ interface, which provides another pathway toward dissociation, assuming that CO can be tilted with the O atom toward TiO$_2$ (36). Cho and Stock (43) have observed that oxidation of CO proceeds via dissociative as well as direct oxidation on Rh/Al$_2$O$_3$ at 473–573 K. Kiss and Gonzalez (40) have also postulated the presence of surface carbon originating from CO dissociation during CO oxidation over a Rh/SiO$_2$ catalyst at temperatures in the region of 373 K. At temperature 393 K, employed in the present work, there are indications that dissociation of CO on Rh/TiO$_2$ and Rh/Al$_2$O$_3$ catalysts might be important at low P_{O_2}/P_{CO} ratios (Fig. 4). It has been found by TPD that these catalysts, especially Rh/TiO$_2$, are active in CO dissociation (37). The observed change in the reaction order at high CO pressures (from -1.0 to -0.2 for Rh/TiO$_2$ or -0.4 for Rh/Al$_2$O$_3$) implies that over these catalysts there is less CO inhibition at high CO pressures, which can be explained by assuming that CO$_2$ is produced both by direct oxidation and through CO dissociation. The change in the reaction order takes place at lower CO pressures on Rh/TiO$_2$ than on Rh/Al$_2$O$_3$, an observation which is in accordance with the larger tendency of CO toward dissociation over Rh/TiO$_2$. The reduced activation energy of the reaction which was observed over Rh/TiO$_2$ (Table 1) may imply a change in either the reaction mechanism or the rate constant, k, compared to the case of the other two catalysts. Therefore, it appears that the support effects observed under CO oxidation conditions are a consequence of the different behavior of Rh toward CO adsorption and dissociation when it is supported on SiO_2, Al_2O_3, or TiO_2 carriers.

The deactivation which was observed (Figs. 1–3) when the catalysts were exposed to an oxygen-rich reaction mixture (O_2/CO ratio of approximately 100) deserves attention. This phenomenon can be attributed to oxidation of the Rh surface under these conditions. It has been reported by Kellogg (10) that surface rhodium oxides are formed at P_{O_2}/P_{CO} ratios of about 40 at 500 K, which lead to deactivation of Rh. XPS results of Oh and Carpenter (12) also show that the deactivation observed at high P_{O_2}/P_{CO} ratios is due to the formation of Rh_2O_3 on the catalyst surface. Similar deactivation phenomena have been reported for Pd and Pt catalysts (23, 24, 34), although it appears that Rh can be oxidized more easily than Pd or Pt. It was found in the present work that the support influences the degree of deactivation. The most severe deactivation was observed over the Rh/SiO_2 catalyst. It has also been found that CO can reduce the rhodium oxides formed (11). Reduction by 1 Torr CO was appreciable at temperatures around 418–430 K (time required for reduction ca. 5 min) but very slow at 400 K. At 393 K, the temperature used in the present study, reduction by CO might not be a very fast process, especially in the presence of oxygen. The observed deactivation shown in Figs. 1–3 suggests that the oxidation potential of Rh is higher when it is supported on SiO_2 than when it is supported on Al_2O_3 or TiO_2 carriers.

Oscillatory Behavior

Observations of oscillatory behavior during CO oxidation on Rh surfaces are rather few. To our knowledge, no oscillations have been reported for Rh single crystals under UHV conditions. Oscillations have been observed only for polycrystalline or supported Rh under atmospheric conditions (35, 36, 44, 45). In the present work it was found that the range of CO pressures where oscillations are possible is much wider on Rh/SiO_2 than on Rh/Al_2O_3 or Rh/TiO_2 catalysts. The shape and period of oscillations observed in this work over Rh/SiO_2 at 383 and 388 K are similar to those reported by Shanks and Bailey over Rh/Al_2O_3 at 428 K (36). The observed oscillatory behavior can be correlated with the observed deactivation of the catalysts, which was attributed to oxidation of Rh. A model of cyclic oxidation/reduction of the metal surface has frequently been employed in the literature to explain oscillatory behavior over Pt, Pd, and Ir catalyst surfaces (25). Similar oscillatory and deactivation phenomena observed in the case of Pd/zeolite catalysts have also been attributed to oxidation/reduction of Pd (34). The ability of the Rh surface to become oxidized is a well-documented phenomenon (10–12). The hysteresis observed in the present work (Figs. 1–3) also shows that oxidation of Rh can take place at 393 K under highly oxidizing conditions (O_2/CO ratio of approximately 100). It should also be noted that a hysteresis behavior for the CO oxidation reaction has been theoretically predicted without taking into account any transformation (such as oxidation) of the catalytic surface (46). The titration experiments showed that the Rh surface under reaction conditions, in a lean reaction mixture, is mainly covered by oxygen, which in turn leads to the oxidation of the Rh surface. An oxidation/reduction mechanism is also supported by the observation that oscillations appear for lean CO/O_2 mixtures (36, 44).

According to the oxidation/reduction mechanism, at the high conversion state of oscillations the low concentration of CO and the possible increase of temperature of the Rh crystallites favor the formation of rhodium oxides. This leads to a decrease of Rh activity followed by cooling of the crystallites. CO adsorbs and accumulates on the oxidized Rh surface during this low conversion state. When the CO coverage reaches a critical value, reduction of Rh becomes fast and the CO_2 production rate increases. CO accumulation during the low-activity stage was indeed observed experimentally in the present work and provides a strong evidence in favor of this mechanism. With increasing temperature, less CO accumulation is required for the onset of oxide reduction. This is explained by the strong temperature dependence of the kinetics of oxide reduction by CO, as observed by Kellogg (11). The same argument can be employed to explain the observed decrease in the period of the oscillations as the reaction temperature increases. The development of more complex oscillatory patterns at higher temperatures (Figs. 6a and 6b) might be related to desynchronization of the oxidation/reduction cycles at different parts of the catalyst bed, due to the increase in the rate of oxide reduction or formation as the temperature increases. Similar complex patterns have been observed by Shanks and Bailey (36) in the case of a Rh/Al_2O_3 catalyst at 437 K.

FTIR experiments failed to show oscillatory behavior of any of the adsorbed CO IR bands. The observation of gradual buildup of the gem-dicarbonyl band implies that this form of adsorbed CO is a spectator species and does not participate in the mechanism of oscillations. This result, as well as the finding that the linear CO band is of very low intensity under reaction conditions, is in accordance with results of other investigators (36, 40) and suggests that the linear CO is the reactive CO species.

CONCLUSIONS

The following conclusions regarding the influence of the support on the kinetic behavior of Rh in the CO oxidation reaction can be derived from the results of the present study:

1. The maximum turnover frequency is independent of

the support used to disperse Rh. A support effect is, however, evident in the sense that this maximum appears at a different P_{O_2}/P_{CO} ratio on each catalyst.

2. The reaction order with respect to CO becomes less negative than -1 at high CO pressures on Rh/Al_2O_3 and especially on Rh/TiO_2. This is attributed to the contribution of the CO dissociation step in the CO oxidation rate.

3. Oscillatory behavior and hysteresis have been observed over all three catalysts examined. The driving mechanism responsible for these phenomena appears to be the oxidation/reduction of the rhodium surface.

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