CO Oxidation over a Pt/CoO$_x$/SiO$_2$ Catalyst: A Study Using Temporal Analysis of Products

Y. J. Mergler,1 J. Hoebink,2 and B. E. Nieuwenhuys$^3$

Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

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Pt/CoO$_x$/SiO$_2$ catalysts consisting of 5 wt% Pt and 3 wt% Co$_3$O$_4$ are highly active for CO oxidation below 100°C. In the present study the technique of temporal analysis of products was used to obtain information on the mechanism of the high activity. The behaviour of a 3 wt% CoO$_x$/SiO$_2$ and a 5 wt% Pt/SiO$_2$ catalyst was compared with that of a Pt/CoO$_x$/SiO$_2$ catalyst. Several models proposed to explain the high activity of the Pt/CoO$_x$/SiO$_2$ catalyst are discussed.

INTRODUCTION

In previous papers (1–3) it was reported that a Pt/CoO$_x$/SiO$_2$ catalyst with 5 wt% Pt and 3 wt% Co$_3$O$_4$ has an excellent activity in CO oxidation at low temperatures and a good selectivity to N$_2$ in NO reduction by H$_2$. The performance of this catalyst in CO oxidation is particularly interesting, since CO is already converted at room temperature. One of the present problems in automotive catalysis is the low activity of the current three-way catalyst (TWC) in CO and hydrocarbon oxidation at low temperatures following the so-called cold-start (below 400°C) (4). Hence, a catalyst with a higher intrinsic activity at low temperatures is desired.

Our earlier studies (1, 2) have shown that a Pt/CoO$_x$/SiO$_2$ catalyst has a much lower onset temperature for CO oxidation with O$_2$ than Pt/SiO$_2$, both under CO-rich and O$_2$-rich conditions and after both reductive and oxidative pretreatment. Preliminary studies (3) indicated that the optimum percentage of Co$_3$O$_4$ was 3 wt% for a 5 wt% Pt catalyst. X-ray diffraction, CO chemisorption, and Fourier transform infrared spectroscopy were used to characterise the catalyst (5). On the basis of the data obtained three possible models that may account for the excellent activity observed were presented (1). These models are summarised below.

EXPERIMENTAL

(a) Preparation of the Catalysts

A 5 wt% Pt/SiO$_2$ catalyst was made by the urea decomposition method (12). H$_2$Pt(OH)$_6$ was dissolved in hot nitric acid and added to an acidic silica suspension of pH 2. Urea is known to inhibit sites required for the dissociative adsorption of O$_2$ on Pt (6, 7). The high activity of the Pt/CoO$_x$/SiO$_2$ catalyst may suggest that by the addition of cobalt oxide, the CO inhibition becomes smaller. The beneficial effect of CoO$_x$ was sought for mainly in the role of oxygen. Model 1 is based on the assumption that cobalt cations promote the dissociative adsorption of O$_2$ on Pt by an increased back-donation of electrons into the antibonding orbitals of O$_2$ adsorbed on Pt. The second and third models account for the improved activity by a reaction between weakly bound O on the cobalt oxide and CO on Pt at the Pt–CoO$_x$ interface (model 2) or on Pt (model 3). In the latter case, O should spill over from the cobalt oxide to the Pt (8), in the presence of the reactant CO/O$_2$ flow. In addition to these models, based on a beneficial effect of the oxide on the availability of oxygen, there are other possible mechanisms. For example, it might be that the CO inhibition is diminished because of a lower heat of adsorption of CO on Pt in the presence of CoO$_x$. This might be caused by a “promoting” effect of CoO$_x$ (model 4) or by Pt–Co alloy formation (model 5). If cobalt oxide is completely reduced, Pt–Co alloys may be formed. It has been reported that PtCo(111) alloys have a Pt-rich surface layer and a second layer that is enriched in Co (9–11). It was found that CO is more weakly bound on this Pt-Co alloy surface compared to pure Pt (11).

On account of the previously found results (1, 2, 5) we proposed that the most likely models are models 2 and 3. By using the temporal analysis of products (TAP) technique the CO oxidation over Pt/CoO$_x$/SiO$_2$ was investigated in more detail. The models that may account for the excellent CO oxidation activity of this Pt/CoO$_x$/SiO$_2$ catalyst are discussed on the basis of the new results.
was added and the suspension was heated to about 85 °C under vigorously stirring. After 48 h the suspension was filtered and dried overnight at 100 °C. Prior to the impregnation of cobalt, the Pt/SiO2 catalyst was reduced in flowing H2 for 3 h at 400 °C. Cobalt nitrate was used to impregnate the Pt/SiO2 catalyst, resulting in a Pt/CoOx/SiO2 catalyst with 5 wt% Pt and 3 wt% CoOx and an atomic ratio of Pt:Co = 1:1.5. A 3 wt% Co3O4/SiO2 catalyst was made for comparison. The catalysts were dried overnight at 100 °C after the impregnation and subsequently reduced in H2 for 3 h at 400 °C.

(b) Characterisation of the Catalysts

The catalysts were characterised by X-ray diffraction (XRD) and CO chemisorption. CO chemisorption measurements were carried out at room temperature in an atmospheric flow apparatus with H2 as a carrier gas. Prior to the CO chemisorption, the catalyst was reduced in situ for 1 h at 400 °C under a H2 flow. CO was injected until the saturation level was reached. XRD measurements were performed after reduction in H2 and oxidation in air for 1 h at 400 °C.

The main characteristics of the catalysts are shown in Table 1. Apparent Pt dispersions were estimated to be 18% for Pt/SiO2 and maximum 7% for Pt/CoOx/SiO2 assuming that one CO molecule adsorbs per surface Pt atom. The real Pt dispersion of Pt/CoOx/SiO2 could not be calculated because CoOx also adsorbed CO at room temperature. This was confirmed by FTIR spectroscopy measurements (5). By assuming that only Pt adsorbed CO, the Pt dispersion would be 7%.

Pt particles, with an average particle size of 60 Å, were observed by XRD after a reductive pretreatment. As can be seen in Table 1, the mean Pt particle diameter for Pt/SiO2 is larger than for the Co-containing Pt catalyst with the lower dispersion. Apparentley, the Pt/SiO2 catalyst contains a large amount of very small Pt particles, which are invisible in XRD.

(c) TAP Measurements

The CO oxidation reaction over the Pt/SiO2, CoOx/SiO2, and Pt/CoOx/SiO2 catalysts were studied using a TAP reactor. Both the TAP apparatus and the technique have been described in detail by the inventors (13, 14), and only those aspects most relevant to this study will be included here. A catalytic microreactor, filled with 0.07 g catalyst, is used with a quadrupole mass spectrometer as gas-phase analysis device. A valve assembly permits the introduction of either a very narrow gas pulse or a continuous flow. The gas pulses may contain 10^12 to 10^20 molecules, depending on the time the valves are set open. The two fast-acting valves can be used either singly or in tandem. The continuous gas flow mode of operation allows one to evaluate the steady-state performance of the catalyst and to pretreat the catalyst prior to the pulsing experiments. Three types of experiments were used in this study. In single-pulse experiments CO and O2 are pulsed at the same time. During pump probe experiments, one of the reactants is pulsed first, and the other reactant is pulsed after a controlled time interval. This interval may range from 0.01 to 10 s. The third experiment consisted of multipulse experiments. Unless stated otherwise in the text, the catalysts were precoated with O2 before pulses of CO were given to deplete the surface of oxygen and to cover it with CO.

The gases used were CO (99.997%), H2 (99.999%), and Ar (99.9999%), supplied by Hoekloos. O2 (99.995%) was supplied by Air Products. Gas mixtures of CO/Ar and O2/Ar were made in such a way that the gas ratio was stoichiometric for the single-pulse, pump probe, and multipulse experiments. With the CoOx/SiO2 catalyst in single-pulse and pump probe experiments a CO/O2 ratio of unity, oxidising mixture, was also used. For the multipulse experiments the CO and O2 pulses were calibrated. The pulses of CO contained 4.4 × 10^16 molecules of CO and the O2 pulses contained 2.2 × 10^16 molecules of O2.

Description and sequence of the performed TAP measurements. Before the catalysts were inserted into the TAP reactor, they were reduced in flowing H2 for 3 h at 400 °C. The catalysts were reduced again in situ with a H2/Ar gas mixture at 400 °C for 1 h. After the in situ reduction the catalyst was cooled to the required reaction temperature. The TAP measurements always started at the lowest temperature indicated in Tables 2 to 5. Single-pulse experiments were performed before the pump probe experiments. After the pump probe experiments the temperature was increased. A freshly in situ reduced catalyst was used in the multipulse experiments. Multiple experiments over the Pt/SiO2 catalysts were performed from high to low temperatures, while for the Pt/CoOx/SiO2 catalyst the temperature was raised during the course of the multipulse experiments. Since CO inhibition occurs on Pt at low temperatures, the temperature was decreased for the Pt/SiO2 catalysts to keep as many Pt surface atoms available for the reaction as possible. To prevent as much as possible (re)oxidation of the CoOx during the experiments, the temperature was increased.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>wt% Pt</th>
<th>wt% CoOx</th>
<th>mol CO/g catalyst</th>
<th>Dispersion (%)</th>
<th>XRD analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoOx/SiO2</td>
<td>—</td>
<td>3</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Pt/SiO2</td>
<td>5</td>
<td>—</td>
<td>4.7 × 10^-5</td>
<td>18</td>
<td>Pt, 160 Å</td>
</tr>
<tr>
<td>Pt/CoOx/SiO2</td>
<td>5</td>
<td>3</td>
<td>1.8 × 10^-5</td>
<td>7°</td>
<td>Pt, 60 Å</td>
</tr>
</tbody>
</table>

* By assuming that only Pt adsorbed CO (see text).
increased for the Pt/CoO$_x$/SiO$_2$ catalyst. The temperatures were chosen such that for all three catalysts, they include the temperature where 50% CO conversion was reached (1).

In single-pulse and pump probe experiments a number of pulses is averaged to improve the signal-to-noise ratio. Care was taken to ensure that the pulse shapes did not change from pulse to pulse. Usually the minimum number of pulses was 10.

The results of the single-pulse and pump probe experiments were used for a qualitative comparison of the catalysts under various conditions. For these experiments only the areas under the reactant and product curves will be given, which provide us with enough information to indicate certain trends in the behavior of the catalysts. For the multipulse experiments the amounts of CO$_2$ molecules produced have been calculated and these values are displayed in the tables.

The TAP measurements are presented in three types of figures. In multipulse experiments the intensity of the reactants CO or O$_2$ or the product CO$_2$ at every pulse of CO or O$_2$ are displayed as a function of time. For single-pulse and pump probe experiments the intensity or the normalised intensity of the reactants and product are displayed as a function of time. Normalised intensity means that the intensities are given relative to the intensity of the mass with the highest maximum. By using normalised intensities, accurate peak positions can be determined (14) and information about the contribution of the fragments of mass 44 (CO$_2$) to mass 28 (CO) is obtained. For example, if all the CO is converted into CO$_2$, the mass 28 curve can be entirely ascribed to the mass 28 fragment of CO$_2$. In that case, when intensities of the mass 28 and mass 44 (CO$_2$) curves are normalised, the variations of the mass 44 and mass 28 intensities in time coincide, with the peak area of mass 28 amounting to 10% of the peak area of mass 44.

The width and peak time (peak maximum) are influenced by several factors, such as desorption kinetics, number of adsorption sites, reaction rate, and occurrence of intraparticle diffusion. For the case of a nonreactive gas, which adsorbs at one type of sites, adsorption and desorption of the gas molecules causes the peak to be widened with a concomitant shift in peak time to a higher value. Peak broadening is also observed when intraparticle diffusion is occurring. When the number of adsorption sites decreases, the curve narrows and shifts to shorter peak times, reflecting less adsorption broadening. In the case of a reaction between gas molecules, when the reaction rate increases, both reactant and product curves shift to shorter times and narrow. The product curve shifts because the product is formed earlier. The reactant curve shifts because reaction selectively depletes the tail of the curve. The molecules in the tail spend more time in the reactor and, therefore, have more chance to react. When a reactant is much more strongly adsorbed than a product, the product curve can peak before the reactant (14).

**RESULTS**

CoO$_x$/SiO$_2$

Single-pulse and pump probe experiments were performed over the prereduced CoO$_x$/SiO$_2$ catalyst, using a CO/O$_2$ ratio of unity. The areas under the CO, O$_2$, and CO$_2$ curves are presented in Table 2. Figure 1 shows an example of the results. At higher temperatures, the separation between the peaks of CO and O$_2$ became more pronounced due to higher CO and O$_2$ conversion, an effect which dominates over the different Knudsen diffusion coefficients. The experiments were carried out from 190 to 260°C.

The results summarised in Table 2 show that upon increasing the temperature, more CO and O$_2$ disappear, while less CO$_2$ is formed. Such a trend was also observed when a CO/O$_2$ ratio of 2 was used. Somehow, CO and O$_2$ remain on the catalyst as inactive species. It is likely that some O$_2$ is used in oxidising a part of the prereduced CoO$_x$ catalyst. CO might form carbonate-type species. As can be seen in Fig. 1, CO reacts with oxygen to CO$_2$. Since argon is not adsorbed on the catalyst, it can be used as a reference point on the time scale. In general, if the reaction between CO and O$_2$ is fast, the change in the fluxes of CO and O$_2$ with time should show a maximum earlier than that of Ar. The product CO$_2$ must be formed and must desorb first before it can leave the reactor. This leads, in general, to a maximum in the CO$_2$ flux appearing later in time than that of Ar. Figure 1 illustrates the above described general features for the CoO$_x$/SiO$_2$ catalyst.

Pump probe experiments at 190°C, in which CO was pulsed at $t=0$ and the time interval between CO and O$_2$ pulse was varied, showed that variations of the time intervals at low temperatures (T < 190°C) did not affect the amounts of CO$_2$ formed (Table 3). However, at 260°C, a

**TABLE 2**

Summary of the Areas, A, (a.u.) under the CO, O$_2$ and CO$_2$ Curves during Single Pulse Experiments over CoO$_x$/SiO$_2$, Pt/CoO$_x$/SiO$_2$ and Pt/SiO$_2$, Respectively. The Area under the CO Curve is Corrected for the Contribution of the Mass 28 Fragment of CO$_2$

<table>
<thead>
<tr>
<th>Catalyst: CoO$_x$/SiO$_2$</th>
<th>Pt/CoO$_x$/SiO$_2$</th>
<th>Pt/SiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>$A_{CO_2}$</td>
<td>$A_{O_2}$</td>
</tr>
<tr>
<td>25</td>
<td>10.0</td>
<td>1.0</td>
</tr>
<tr>
<td>40</td>
<td>9.0</td>
<td>12.8</td>
</tr>
</tbody>
</table>
FIG. 1. Normalised intensities of CO, O₂, CO₂, and Ar as a function of time after a CO/O₂ pulse at \( t = 0 \) over a CoOₓ/SiO₂ catalyst at 190°C.

A significant increase in the CO₂ formation was found, when a longer time interval was used between the CO and O₂ pulses. When O₂ was pulsed at \( t = 0 \), a longer time interval before CO was pulsed led to a decrease in the CO₂ production, as can be seen in Table 3.

Pt/CoOₓ/SiO₂

Single-pulse and pump probe experiments. The data obtained for CO₂ formation using single-pulse experiments are summarised in Table 2. The same trend, as seen for CoOₓ/SiO₂, is observed here above 100°C. Upon increasing the temperature from 25 to 100°C, more CO reacted with O₂ leading to an increase in the CO₂ formation. However, above 100°C, more CO and O₂ were used, while the formation of CO₂ decreased.

When the single-pulses at room temperature are considered, shown in Fig. 2a, one sees that the flux of CO is decreasing slowly with time, as indicated by a rather long tail. Some of the CO desorbs slowly from the catalyst at room temperature. This is better illustrated in Fig. 2b where the single pulses were given at 190°C. At this temperature the reaction between CO and O₂ should be complete (3). This means that upon normalisation of the data, the curves of mass 28 and 44 should coincide as the signal of mass 28 must be caused by the fragmentation of CO₂. However, a tail in the signal of mass 28 was detected, which cannot originate from CO₂.

Pump probe experiments at room temperature over Pt/CoOₓ/SiO₂ showed that a longer time interval between the CO pulse at \( t = 0 \) and the O₂ pulse causes an increase in the amount of CO₂ formed. This is illustrated in Table 4, in which the area under the CO₂ curve is larger when the time interval between the CO pulse at \( t = 0 \) and O₂ is longer.

When the area under the CO₂ curve formed at room temperature was compared with the curve formed at 40°C under the same conditions, it was found that more CO₂ was produced at the higher temperature of 40°C (Table 4).

Multipulse experiments. Figure 3a shows the measured flux of oxygen for Pt/CoOₓ/SiO₂ at 40°C when O₂ was pulsed directly after a reductive pretreatment. All the oxygen of the first 20 O₂ pulses was used. Oxygen saturation of the catalyst was reached after about 25 O₂ pulses. CO₂ production, shown in Fig. 3b, was accomplished by pulses of CO

![Graph](https://example.com/graph.png)

Figure 3a shows the measured flux of oxygen for Pt/CoOₓ/SiO₂ at 40°C when O₂ was pulsed directly after a reductive pretreatment. All the oxygen of the first 20 O₂ pulses was used. Oxygen saturation of the catalyst was reached after about 25 O₂ pulses. CO₂ production, shown in Fig. 3b, was accomplished by pulses of CO

![Graph](https://example.com/graph.png)

Figure 3b shows the measured flux of oxygen for Pt/CoOₓ/SiO₂ at 40°C when O₂ was pulsed directly after a reductive pretreatment. All the oxygen of the first 20 O₂ pulses was used. Oxygen saturation of the catalyst was reached after about 25 O₂ pulses. CO₂ production, shown in Fig. 3b, was accomplished by pulses of CO

**TABLE 3**

<table>
<thead>
<tr>
<th>CO pulse at ( t = 0 ), O₂ pulse at time (s)</th>
<th>Area ( T = 190°C ), Area ( T = 260°C )</th>
<th>O₂ pulse at ( t = 0 ), CO pulse at time (s)</th>
<th>Area ( T = 260°C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>41.8</td>
<td>—</td>
<td>32.0</td>
</tr>
<tr>
<td>0.5</td>
<td>41.8</td>
<td>24.2</td>
<td>0.5</td>
</tr>
<tr>
<td>1.0</td>
<td>41.6</td>
<td>—</td>
<td>27.2</td>
</tr>
<tr>
<td>2.0</td>
<td>24.2</td>
<td>31.2</td>
<td>2.0</td>
</tr>
<tr>
<td>4.0</td>
<td>40.7</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>
TABLE 4

Areas (a.u.) under the CO2 Curve during Pump Probe Experiments over Pt/CoOx/SiO2 at 25 and 40 °C

| CO pulse at t = 0,  
<table>
<thead>
<tr>
<th>O2 pulse at time (s)</th>
<th>T = 25 °C</th>
<th>T = 40 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>10.0</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>11.7</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>12.9</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>15.0</td>
</tr>
</tbody>
</table>

at 40 °C over the fully oxygen-covered catalyst. Hereafter, a series of experiments with O2 pulses were performed with a CO-precovered catalyst. The results are shown in Fig. 3c. One can see that the oxygen of the first O2 pulses is not used completely for the reaction with CO and for covering the catalyst. The CO2 production at 40 °C, obtained after O2 pulses over a CO precovered catalyst is also shown in Fig. 3d. Figures 4a and 4b show the CO2 production when O2 and CO was pulsed at 190 °C over, respectively, CO-covered and oxygen-covered Pt/CoOx/SiO2. Figure 4b shows that the CO2 production is continuing, even after depleting the catalyst of oxygen and covering it with CO.

Pt/SiO2

Single-pulse and pump probe experiments. Single-pulse experiments, performed at 100 and 190 °C, showed that more CO2 was formed at the higher temperature with a concomitant higher consumption of CO and O2 than at the lower temperature. Figure 5 shows that the flux of CO decreased very slowly with time during single-pulses at 100 °C. CO desorption from the catalyst is very slow at this temperature of 100 °C. Table 2 shows the areas under the CO2, CO, and O2 curves for single-pulse experiments over Pt/SiO2 at 100 and 190 °C.

Pump probe experiments at 190 °C showed that a longer time interval between a CO pulse at t = 0 and O2 resulted in a decrease in the CO2 formation. The area under the CO2 curve after an oxygen pulse at 0.25 s was $14.1 \times 10^{-3}$ and after an oxygen pulse at 1 s it was $13.7 \times 10^{-3}$.

Multipulse experiments. Figures 6a–6d show the result of the multipulse experiments over Pt/SiO2. Figures 6a...
was covered with oxygen, prior to a CO multipulse experiment.

**DISCUSSION**

(a) **CO Inhibition**

Figure 6 illustrates some interesting features characteristic of Pt in CO oxidation (15). CO is known to inhibit CO oxidation on Pt at lower temperatures (7, 16). The CO inhibition effect is well demonstrated in Fig. 6a where O\textsubscript{2} was pulsed to a CO-precovered Pt/SiO\textsubscript{2} catalyst. O\textsubscript{2} needs a free site to adsorb molecularly and an ensemble of adjacent free sites to dissociate. Due to slow CO desorption at 54\textdegree C, some free sites were generated and the reaction could start. CO\textsubscript{2} will desorb immediately from the Pt surface after its formation (7) leading to more free sites for O\textsubscript{2} to dissociate. The CO\textsubscript{2} production increased until a certain value of the CO coverage was reached. From that point the CO\textsubscript{2} formation decreased. On the other hand, when CO was pulsed at 54\textdegree C to an oxygen-precovered Pt/SiO\textsubscript{2} catalyst, the reaction started immediately, as is shown in Fig. 6b. The oxygen layer leaves enough free sites for CO to adsorb and CO\textsubscript{a} reacts with O\textsubscript{a} to CO\textsubscript{2}.

At higher temperatures, when CO desorption is fast, the CO inhibition is diminished. This is illustrated by Fig. 6c, where O\textsubscript{2} pulses at 190\textdegree C to a CO-precovered Pt/SiO\textsubscript{2} catalyst led directly to the production of CO\textsubscript{2}. CO pulses at 190\textdegree C to an oxygen-precovered Pt/SiO\textsubscript{2} catalyst led to an initially high CO\textsubscript{2} production, which diminished with time due to the fast CO\textsubscript{2} desorption (15).

The amount of CO\textsubscript{2} molecules formed during the multipulse experiments can be calculated from the areas under the CO\textsubscript{2} peaks. Table 5 shows the amount of CO\textsubscript{2} molecules formed when CO was pulsed over an oxygen-precovered Pt/SiO\textsubscript{2} at several temperatures.

It is shown in Table 5 that with increasing temperature the CO\textsubscript{2} production decreases, due to the increase of CO desorption. The same conclusion was drawn on the basis of the single-pulse experiments described in the preceding paragraph. We stress here that this behaviour is totally

### Table 5

| CO\textsubscript{2} Formed over Pt/SiO\textsubscript{2} and Pt/CoO\textsubscript{x}/SiO\textsubscript{2} during CO Multipulse Experiments at Various Temperatures |
|---|---|
| Temperature (\textdegree C) | CO\textsubscript{2} Molecules ($\times 10^{-17}$) |
| | Over Pt/SiO\textsubscript{2} | Over Pt/CoO\textsubscript{x}/SiO\textsubscript{2} |
| 40 | — | 3.0 |
| 54 | 12.9 | — |
| 100 | 13.0 | 3.9 |
| 190 | 9.1 | 5.1 |
| 260 | 7.4 | — |
different from the results on Pt/CoOₓ/SiO₂ and CoOₓ/SiO₂. On these two catalysts CO seems to be held at the surface at higher temperatures.

A striking difference is observed between the freshly reduced and the CO precovered Pt/CoOₓ/SiO₂ catalyst upon comparison of the consumption of the first 10 to 20 oxygen pulses at 40°C in O₂ multipulse experiments (see Figs. 3a and 3c). After a reductive pretreatment, all the oxygen is adsorbed, while for a CO-precovered catalyst oxygen is already detected in the first O₂ pulses. Since not all the oxygen reacted with preadsorbed CO or covered the free sites present or generated on the catalyst, it is likely that the reaction between COₐ and Oₐ is somehow inhibited on some parts of the catalyst surface. The total amount of oxygen consumed is the same within experimental error for both experiments, namely 3 × 10¹⁷ molecules. It would be expected that, in the case of O₂ multipulses applied at room temperature after reduction of the Pt/CoOₓ/SiO₂ catalyst, partial reoxidation of the partially reduced CoOₓ would take place.

Figures 3b and 3d show that over a Pt/CoOₓ/SiO₂ catalyst CO₂ production started directly after the first pulse of, respectively, CO and O₂ at 40°C. If there is any CO inhibition of the rate of CO₂ formation it must be very small, since CO₂ is already produced at 40°C.

When the amount of CO₂ molecules, measured over an oxygen-precovered Pt/CoOₓ/SiO₂ catalyst at several temperatures was calculated, it was found that the CO₂ production increased with increasing temperature (Table 5). CO₂ production during multipulse experiments with O₂ pulses over a CO-precovered Pt/CoOₓ/SiO₂ catalyst, or with CO pulses over an oxygen-precovered catalyst, resulted in similar numbers of CO₂ molecules produced. In contrast to Pt/SiO₂, the CO₂ production increased with increasing temperature, while CO desorption is expected at higher temperatures.

Comparison of the multipulse experiments over Pt/SiO₂ and Pt/CoOₓ/SiO₂ revealed a strong CO inhibition of oxygen adsorption and CO₂ formation on Pt for the Pt/SiO₂ catalyst, whereas CO inhibition is absent or small on the Pt/CoOₓ/SiO₂ catalyst. In contrast to Pt/SiO₂, the Pt/CoOₓ/SiO₂ catalyst showed an increase in the CO₂ formation with increasing temperature. This is rather unusual, since with an increasing temperature an increasing desorption rate of CO with a concomitant decrease of CO₂ formation is to be expected.
In order to determine if lattice oxygen of cobalt oxide is used for the CO oxidation (17), a pump probe experiment in which O₂ was pulsed at t=0 and CO after different time intervals was carried out. A longer time interval between the O₂ and CO pulse led, in the case of a prerduced CoOₓ/SiO₂ catalyst, to a decrease in the CO₂ formation, as can be seen in Table 3. If CO uses lattice oxygen to form CO₂, one might expect that an increase in the time interval does not strongly influence the amount of CO₂ formed. However, a large effect of the time interval is observed. This result seems to indicate that oxygen provided by the oxygen pulse is used for the reaction with CO over CoOₓ/SiO₂. Since it is known that Pt may decrease the reduction temperature of metal oxides, it is possible that some lattice oxygen is used during multipulse experiments over Pt/CoOₓ/SiO₂ catalysts. A qualitative multipulse experiment at 190°C, with CO pulses over a oxygen-precovered CoOₓ/SiO₂ catalyst (not shown), showed the very same continuing CO₂ production as was seen here. Co₃O₄ is known to reduce around 200°C (18).

When, in multipulse experiments, oxygen pulses are supplied at 40°C to a CO-precovered Pt/CoOₓ/SiO₂ catalyst (Fig. 3c), not all the oxygen per pulse is used. A parently, the adsorption of oxygen is hindered by the presence of CO. It is possible that some CO is adsorbed in an inactive state or has formed carbonate-type species.

One must be aware of the fact that at room temperature the Pt/CoOₓ/SiO₂ catalyst is very active in CO/O₂ oxidation and no significant CO inhibition is found (1). However, the CO desorption rate on pure Pt is almost zero at room temperature (7, 15). This means that the addition of CoOₓ to Pt either decreases the adsorption energy of CO (19, 20) on Pt or provides sites for O₂ dissociation, in this way positively influencing the catalytic activity.

It became clear from multipulse and single-pulse experiments that CO desorbs rather slowly from Pt/SiO₂ compared to Pt/CoOₓ/SiO₂. If the adsorption energy of CO on Pt is strongly lowered upon the addition of CoOₓ, one would expect a decrease in the CO₂ formation with an increasing time interval between the CO and O₂ pulses. Since more CO₂ is found with an increasing time interval and the fact that single-pulse experiments indicate that the Pt/CoOₓ/SiO₂ catalyst does have some strongly bound CO, the explanation that CO is much more weakly bound on all the available Pt surface atoms seems unlikely. It may be argued that the adsorption energy of CO is only weakened on Pt atoms at the interface of Pt-CoOₓ. In this way oxygen may dissociate on free Pt sites generated by CO desorption. A new argument against weakly bound CO on Pt is provided by FTIR measurements (5). A addition of 5 mbar CO to a prerduced Pt/CoOₓ/SiO₂ catalyst showed neither shifts in wavenumbers of adsorbed CO on Pt nor additional absorption bands that could be described to weakly bound CO on Pt (20). The Pt-CO band was found at 2070 cm⁻¹ for both the Pt/CoOₓ/SiO₂ and the Pt/SiO₂ catalyst. In the opinion of the authors, the above presented results are completely in line with the model that Pt/CoOₓ/SiO₂ is particularly active due to the presence of sites for O₂ dissociation located on the CoOₓ. From FTIR measurements, we learned that CO is also bound to CoOₓ at lower temperatures (5). The increase in CO₂ with an increasing time interval between the CO and O₂ pulse may very well be caused by CO desorption from CoOₓ leading to more O₂ dissociation sites and thus to more CO₂ production. The reaction between CO and O₂ may take place at the interface of the Pt-CoOₓ particles, leading to free sites on the Pt and on the partially reduced cobalt oxide. The pump probe experiments lead to the conclusion that the CO molecule is less strongly bound on CoOₓ of Pt/CoOₓ/SiO₂.

Longer time intervals in pump probe experiments between the CO and O₂ pulse led to an increased CO desorption and more free sites on CoOₓ to dissociate oxygen. It was also observed that some of the CO remained strongly bound to the catalyst, indicated by the tail in mass 28 in Figs. 2a and 2b. This must be strongly bound CO on Pt or carbonate on CoOₓ or both. These observations indicate that the improved activity of the Pt/CoOₓ/SiO₂ catalyst in CO oxidation is caused by an improved oxygen supply. Most of the Pt sites are still inhibited by CO at low temperatures due to the presence of O₂ on CoOₓ and CO on adjacent Pt sites, the reaction can proceed at room temperature. These results indicate that in the case of the CO/O₂ reaction over Pt/CoOₓ/SiO₂ catalysts, model 2 is the most likely one. This model is supported by the results of Campman (21) and Oh and Eickel (22) in studies of the CO oxidation over noble metal/ceria/alumina catalysts. It was found that high partial pressures of CO, the reaction order in CO changed from −1 to zero. This phenomenon cannot be explained by spillover effects. When CO and O₂ are competing for free sites on the noble metal, a CO reaction order of zero is rather unlikely. Oh and Eickel explain their results by assuming that (lattice) oxygen at the noble metal/ceria interface is responsible for the formation of CO₂.

(c) Inactive CO, CO Islands, or Carbonate-Type Intermediates

When in single-pulse experiments for CoOₓ/SiO₂ the areas under the CO, O₂, and CO₂ curves are considered in relation to the catalyst temperature (Table 2) it appears that the areas under the CO and O₂ curves decreased with increasing temperature. Interestingly, the area under the CO₂ curve also decreased. With increasing temperature more CO and O₂ are held on the catalyst. O₂ is presumably used to reoxidise the CoOₓ. CO may be adsorbed in an inactive state, for example, in a dissociative state on metallic Co, or may form carbonate-type species (23). The same effect was
found for the Pt/CoO$_x$/SiO$_2$ catalyst above 100°C. Below this temperature the CO$_2$ formation increased with a decreasing area under the CO and O$_2$ curve (Table 4). Above 100°C the CO$_2$ formation decreased with an increasing CO and O$_2$ uptake.

The pump probe experiments carried out over Pt/SiO$_2$ at 190°C showed that longer time intervals between the CO pulse at t = 0 and the O$_2$ pulse led to a decrease in the CO$_2$ formation. A longer time interval between the CO and O$_2$ pulse led to an increase of CO desorption and a concomitant decrease in CO$_2$ formation. However, the pump probe experiments with CO pulsed at t = 0 showed for Pt/CoO$_x$/SiO$_2$ that, even at room temperature, more CO$_2$ was produced as the time interval between the CO and O$_2$ pulse was increased.

The results obtained by single-pulse and pump probe experiments indicate that part of the CO and O$_2$ is held on the Pt/CoO$_x$/SiO$_2$ catalyst. CO can be released with time as was shown in pump probe experiments where the CO$_2$ production increased as the time interval between the CO and O$_2$ pulse was increased. It could be that part of the inactively held CO on the catalyst is held in the form of carbonates. Bielanski and Haber (23), in their review of CO oxidation over transition metal oxides, consider that, around room temperature, the CO$_2$ production may proceed by carbonate-type intermediates. Carbonate-type intermediates might explain the above-described observations. However, no distinct features of the formation or existence of carbonates on the surface of CoO$_x$/SiO$_2$ or Pt/CoO$_x$/SiO$_2$ catalysts were seen with FTIR (5). It is possible that the carbonate concentration or extinction coefficient is very low, which would result in no definite carbonate IR bands.

It has become clear that part of the CO is held in an inactive form on the Pt/CoO$_x$/SiO$_2$ catalyst at lower temperatures. CO might have formed densely packed islands on Pt or might have formed carbonates. With an increasing time interval between CO and O$_2$ pulses or with an increasing temperature, more CO becomes available and can react with O$_2$.

CONCLUSIONS

It was found that with an increasing CO and O$_2$ uptake a decrease in the CO$_2$ formation took place over CoO$_x$/SiO$_2$ in the temperature range 190 to 260°C. This effect also occurred above 100°C for Pt/CoO$_x$/SiO$_2$. These effects can be attributed to oxidation of CoO$_x$ and formation of carbonate-type species or both.

At lower temperatures it is also possible that CO is held inactively on the Pt/CoO$_x$/SiO$_2$ catalyst in the form of Pt-CO islands, which are inaccessible to oxygen.

CO desorbs rather slowly from Pt/SiO$_2$ compared to Pt/CoO$_x$/SiO$_2$. Single-pulse and pump probe experiments support the idea that some of the CO molecules are less strongly bound to the Pt/CoO$_x$/SiO$_2$ catalyst. Presumably, CO is less strongly bound to CoO$_x$ of the Pt/CoO$_x$/SiO$_2$ catalyst. It seems that there is some strongly bound CO present on Pt of the Pt/CoO$_x$/SiO$_2$ catalyst at low temperatures.

The results obtained with the TA technique are consistent with a model in which the reaction between CO and O$_2$ takes place at the interface of the platinum and cobalt particles.

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