

CO Oxidation over a Pt/CoO_x/SiO₂ Catalyst: A Study Using Temporal Analysis of Products

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Pt/CoO_x/SiO₂ catalysts consisting of 5 wt% Pt and 3 wt% Co₃O₄ 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/SiO₂ and a 5 wt% Pt/SiO₂ catalyst was compared with that of a Pt/CoO_x/SiO₂ catalyst. Several models proposed to explain the high activity of the Pt/CoO_x/SiO₂ catalyst are discussed.

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INTRODUCTION

In previous papers (1–3) it was reported that a Pt/CoO_x/SiO₂ catalyst with 5 wt% Pt and 3 wt% Co₃O₄ has an excellent activity in CO oxidation at low temperatures and a good selectivity to N₂ in NO reduction by H₂. 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/SiO₂ catalyst has a much lower onset temperature for CO oxidation with O₂ than Pt/SiO₂, both under CO-rich and O₂-rich conditions and after both reductive and oxidative pretreatment. Preliminary studies (3) indicated that the optimum percentage of Co₃O₄ 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.

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CO is known to inhibit sites required for the dissociative adsorption of O₂ on Pt (6, 7). The high activity of the Pt/CoO_x/SiO₂ 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 O₂ on Pt by an increased back-donation of electrons into the antibonding orbitals of O₂ 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/O₂ 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/SiO₂ was investigated in more detail. The models that may account for the excellent CO oxidation activity of this Pt/CoO_x/SiO₂ catalyst are discussed on the basis of the new results.

EXPERIMENTAL

(a) Preparation of the Catalysts

A 5 wt% Pt/SiO₂ catalyst was made by the urea decomposition method (12). H₂Pt(OH)₆ was dissolved in hot nitric acid and added to an acidic silica suspension of pH 2. Urea

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/CoO_x/SiO₂ catalyst with 5 wt% Pt and 3 wt% Co₃O₄ 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/CoO_x/SiO₂ assuming that one CO molecule adsorbs per surface Pt atom. The real Pt dispersion of Pt/CoO_x/SiO₂ could not be calculated because CoO_x 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. Apparently, 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, CoO_x/SiO₂, and Pt/CoO_x/SiO₂ catalysts were studied using a TAP reac-

tor. 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 10¹³ to 10²⁰ 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 precovered 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 CoO_x/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 × 10¹⁶ molecules of CO and the O₂ pulses contained 2.2 × 10¹⁶ 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/CoO_x/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 CoO_x during the experiments, the temperature was

TABLE 1
Characteristics of the Catalysts

| Catalyst | wt% Pt | wt% Co ₃ O ₄ | mol CO/g catalyst | Dispersion (%) | XRD analysis |
|---------------------------------------|--------|------------------------------------|------------------------|----------------|--------------|
| CoO _x /SiO ₂ | — | 3 | — | — | — |
| Pt/SiO ₂ | 5 | — | 4.7 × 10 ⁻⁵ | 18 | Pt, 160 Å |
| Pt/CoO _x /SiO ₂ | 5 | 3 | 1.8 × 10 ⁻⁵ | 7 ^a | Pt, 60 Å |

^a By assuming that only Pt adsorbed CO (see text).

increased for the Pt/CoO_x/SiO₂ 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 behaviour of the catalysts. For the multipulse experiments the amounts of CO₂ 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 O₂ or the product CO₂ at every pulse of CO or O₂ 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 fragment of mass 44 (CO₂) to mass 28 (CO) is obtained. For example, if all the CO is converted into CO₂, the mass 28 curve can be entirely ascribed to the mass 28 fragment of CO₂. In that case, when intensities of the mass 28 and mass 44 (CO₂) 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/SiO₂

Single-pulse and pump probe experiments. Single-pulse experiments were performed over the prerduced CoO_x/SiO₂ catalyst, using a CO/O₂ ratio of unity. The areas under the CO, O₂, and CO₂ 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 O₂ became more pronounced due to higher CO and O₂ 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 O₂ disappear, while less CO₂ is formed. Such a trend was also observed when a CO/O₂ ratio of 2 was used. Somehow, CO and O₂ remain on the catalyst as inactive species. It is likely that some O₂ is used in oxidising a part of the prerduced CoO_x catalyst. CO might form carbonate-type species. As can be seen in Fig. 1, CO reacts with oxygen to CO₂. 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 O₂ is fast, the change in the fluxes of CO and O₂ with time should show a maximum earlier than that of Ar. The product CO₂ must be formed and must desorb first before it can leave the reactor. This leads, in general, to a maximum in the CO₂ flux appearing later in time than that of Ar. Figure 1 illustrates the above described general features for the CoO_x/SiO₂ catalyst.

Pump probe experiments at 190°C, in which CO was pulsed at $t=0$ and the time interval between CO and O₂ pulse was varied, showed that variations of the time intervals at low temperatures ($T < 190^\circ\text{C}$) did not affect the amounts of CO₂ formed (Table 3). However, at 260°C, a

TABLE 2

Summary of the Areas, A, (a.u.) under the CO, O₂ and CO₂ Curves during Single Pulse Experiments over CoO_x/SiO₂, Pt/CoO_x/SiO₂ and Pt/SiO₂, Respectively. The Area under the CO Curve is Corrected for the Contribution of the Mass 28 Fragment of CO₂

| Catalyst: Temperature (°C) | CoO _x /SiO ₂ | | | Pt/CoO _x /SiO ₂ | | | Pt/SiO ₂ | | |
|-------------------------------|------------------------------------|----------------------------|-----------------|---------------------------------------|----------------------------|-----------------|-----------------------------|----------------------------|-----------------|
| | A _{CO₂} | A _{O₂} | A _{CO} | A _{CO₂} | A _{O₂} | A _{CO} | A _{CO₂} | A _{O₂} | A _{CO} |
| 25 | | | | 10.0 | 1.0 | 6.2 | | | |
| 40 | | | | 14.0 | 0.7 | 6.3 | | | |
| 100 | | | | 15.0 | 0.3 | 4.9 | 10.3 | 48.4 | 19.0 |
| 190 | 19.0 | 12.8 | 23.1 | 7.9 | 0.0 | 4.1 | 13.4 | 0.0 | 1.9 |
| 230 | 13.5 | 3.5 | 8.6 | | | | | | |
| 260 | 9.4 | 1.0 | 5.2 | | | | | | |

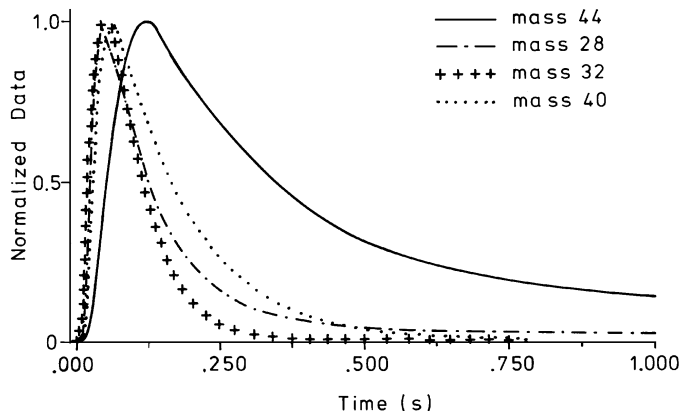


FIG. 1. Normalised intensities of CO, O₂, CO₂, and Ar as a function of time after a CO/O₂ pulse at $t=0$ over a CoO_x/SiO₂ catalyst at 190°C.

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/CoO_x/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 CoO_x/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

TABLE 3

Areas (a.u.) under the CO₂ Curve during Pump Probe Experiments over CoO_x/SiO₂ at 190 and 260°C

| CO pulse at $t=0$, O ₂ pulse at time (s) | Area | | O ₂ pulse at $t=0$, CO pulse at time (s) | Area $T=260^\circ\text{C}$ |
|--|-----------------------|-----------------------|--|-------------------------------|
| | $T=190^\circ\text{C}$ | $T=260^\circ\text{C}$ | | |
| 0.25 | 41.8 | — | — | — |
| 0.5 | 41.8 | 24.2 | 0.5 | 32.0 |
| 1.0 | 41.6 | — | — | — |
| 2.0 | — | 31.2 | 2.0 | 27.2 |
| 4.0 | 40.7 | — | — | — |

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/CoO_x/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/CoO_x/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

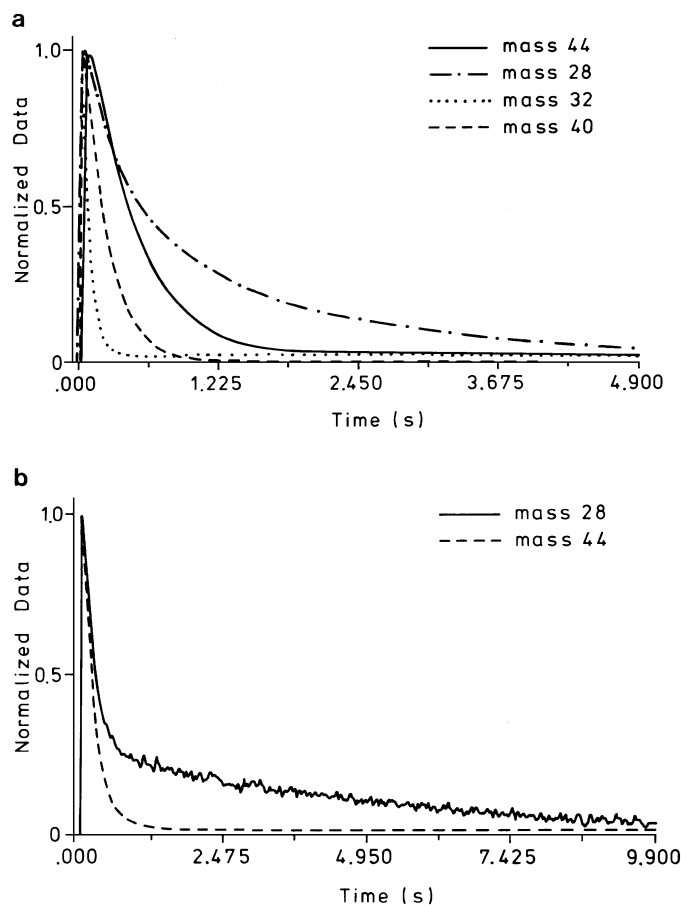


FIG. 2. (a) Normalised intensities of CO, O₂, CO₂, and Ar with time after a CO/O₂ pulse at $t=0$ over a Pt/CoO_x/SiO₂ catalyst at room temperature. (b) Normalised intensities of CO and CO₂ with time after a CO/O₂ pulse at $t=0$ over a Pt/CoO_x/SiO₂ catalyst at 190°C.

TABLE 4

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

| CO pulse at $t=0$, O ₂ pulse at time (s) | $T=25^{\circ}\text{C}$ | $T=40^{\circ}\text{C}$ |
|---|------------------------|------------------------|
| 0 | 10.0 | 14.0 |
| 0.5 | 11.7 | — |
| 4.0 | 12.9 | — |
| 5.0 | 15.0 | 16.0 |

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_a 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/CoO_x/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 14.1×10^{-3} and after an oxygen pulse at 1 s it was 13.7×10^{-3} .

Multipulse experiments. Figures 6a–6d show the result of the multipulse experiments over Pt/SiO₂. Figures 6a

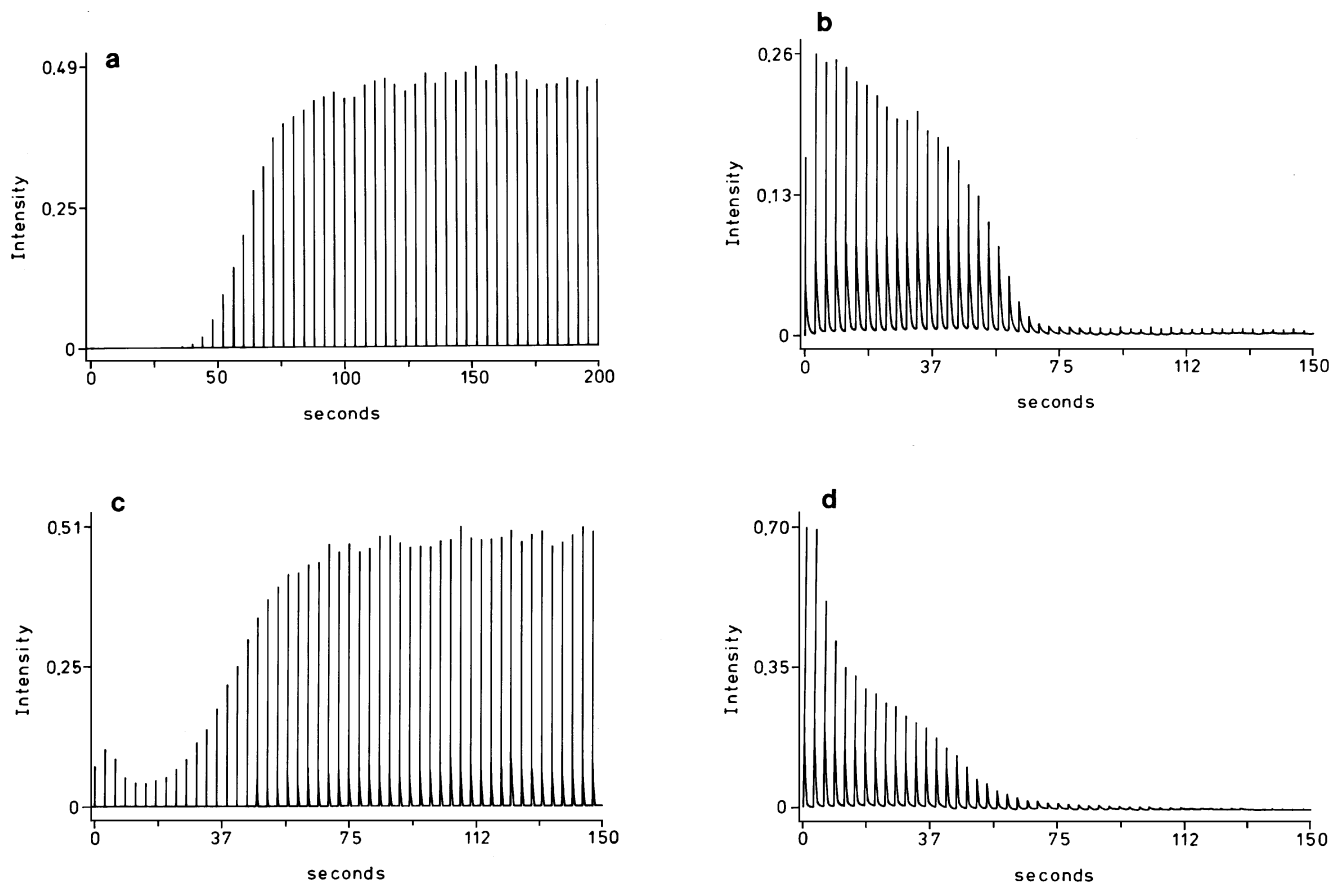


FIG. 3. Multipulse experiments at 40°C over Pt/CoO_x/SiO₂. (a) O₂ signal, measured during O₂ pulses directly after a reductive pretreatment of the catalyst; (b) CO₂ formation, measured during CO pulses over an oxygen-precovered catalyst; (c) O₂ signal, measured during O₂ pulses over a CO-precovered catalyst; (d) CO₂ signal, measured during O₂ pulses over a CO-precovered catalyst.

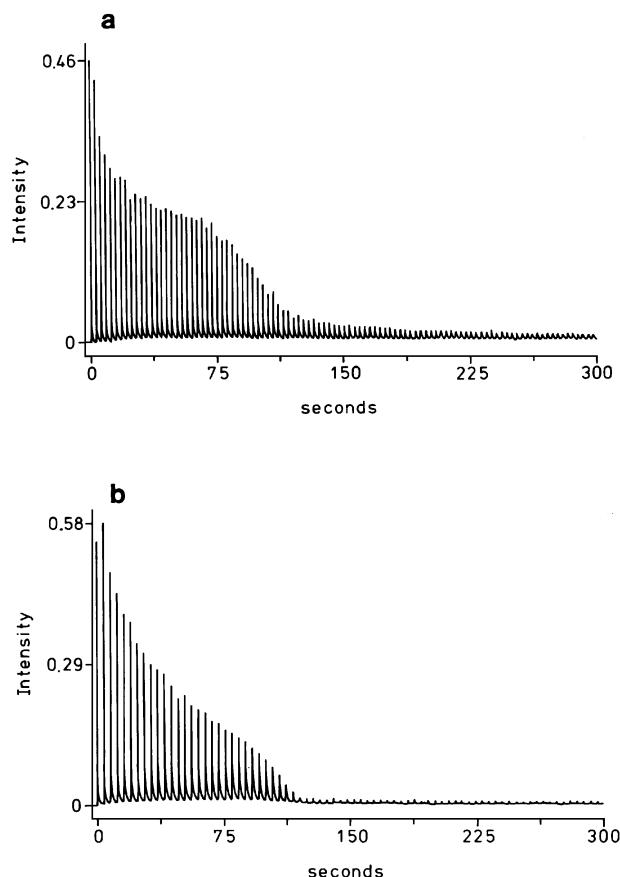


FIG. 4. Multipulse experiments at 190°C over Pt/CoO_x/SiO₂. (a) CO₂ signal, measured during O₂ pulses over a CO-precovered catalyst; (b) CO₂ signal, measured during CO pulses over an oxygen-precovered catalyst.

and 6b show the CO₂ production at 54°C for a surface precovered with CO and precovered with oxygen, respectively. Figure 6c shows the CO₂ production at 190°C when the surface was precovered with CO, prior to O₂ pulses. Figure 6d shows the production of CO₂ at 190°C when the Pt catalyst

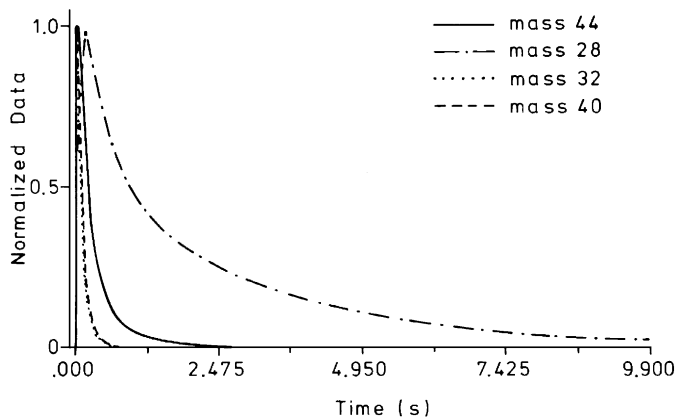


FIG. 5. Normalised intensities of CO, O₂, CO₂, and Ar with time after a CO/O₂ pulse at $t=0$ over a Pt/SiO₂ catalyst at 100°C.

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 O₂ was pulsed to a CO-precovered Pt/SiO₂ catalyst. O₂ needs a free site to adsorb molecularly and an ensemble of adjacent free sites to dissociate. Due to slow CO desorption at 54°C, some free sites were generated and the reaction could start. CO₂ will desorb immediately from the Pt surface after its formation (7) leading to more free sites for O₂ to dissociate. The CO₂ production increased until a certain value of the CO coverage was reached. From that point the CO₂ formation decreased. On the other hand, when CO was pulsed at 54°C to an oxygen-precovered Pt/SiO₂ catalyst, the reaction started immediately, as is shown in Fig. 6b. The oxygen layer leaves enough free sites for CO to adsorb and CO_a reacts with O_a to CO₂.

At higher temperatures, when CO desorption is fast, the CO inhibition is diminished. This is illustrated by Fig. 6c, where O₂ pulses at 190°C to a CO-precovered Pt/SiO₂ catalyst led directly to the production of CO₂. CO pulses at 190°C to an oxygen-precovered Pt/SiO₂ catalyst led to an initially high CO₂ production, which diminished with time due to the fast CO desorption (15).

The amount of CO₂ molecules formed during the multipulse experiments can be calculated from the areas under the CO₂ peaks. Table 5 shows the amount of CO₂ molecules formed when CO was pulsed over an oxygen-precovered Pt/SiO₂ at several temperatures.

It is shown in Table 5 that with increasing temperature the CO₂ 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

CO₂ Formed over Pt/SiO₂ and Pt/CoO_x/SiO₂ during CO Multipulse Experiments at Various Temperatures

| Temperature (°C) | CO (molecules × 10 ⁻¹⁷) | |
|------------------|-------------------------------------|--|
| | Over Pt/SiO ₂ | Over Pt/CoO _x /SiO ₂ |
| 40 | — | 3.0 |
| 54 | 12.9 | — |
| 100 | 13.0 | 3.9 |
| 190 | 9.1 | 5.1 |
| 260 | 7.4 | — |

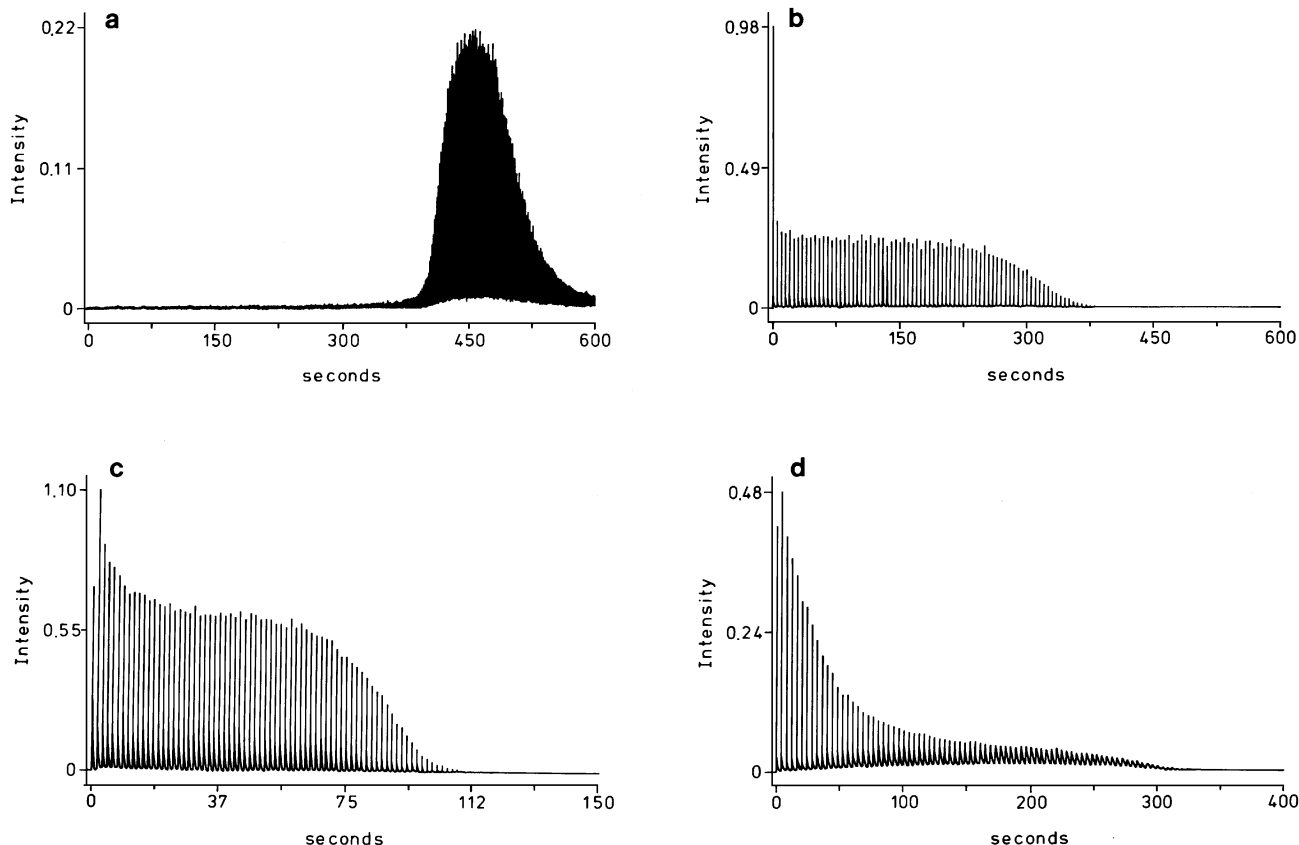


FIG. 6. Multipulse experiments over Pt/SiO₂. (a) CO₂ signal, measured at 54°C during O₂ pulses over a CO-precovered catalyst; (b) CO₂ signal, measured at 54°C during CO pulses over an oxygen-precovered catalyst; (c) CO₂ signal, measured at 190°C during O₂ pulses over the CO-precovered Pt catalyst; (d) CO₂ signal, measured at 190°C during CO pulses over an oxygen-precovered Pt/SiO₂ catalyst.

different from the results on Pt/CoO_x/SiO₂ and CoO_x/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/CoO_x/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 CO_a and O_a 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 3×10^{17} molecules. It would be expected that, in the case of O₂ multipulses applied at room temperature after reduction of the Pt/CoO_x/SiO₂ catalyst, partial reoxidation of the partially reduced CoO_x would take place.

Figures 3b and 3d show that over a Pt/CoO_x/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/CoO_x/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/CoO_x/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/CoO_x/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/CoO_x/SiO₂ catalyst. In contrast to Pt/SiO₂, the Pt/CoO_x/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.

(b) *CO and O₂ Desorption Rate and Models for the CO Oxidation over Pt/CoO_x/SiO₂*

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 CoO_x/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 CoO_x/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/CoO_x/SiO₂ catalysts. A qualitative multipulse experiment at 190°C, with CO pulses over a oxygen-precovered CoO_x/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/CoO_x/SiO₂ catalyst (Fig. 3c), not all the oxygen per pulse is used. Apparently, the adsorption of oxygen is hindered by the presence of CO_a. 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/CoO_x/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 CoO_x 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/CoO_x/SiO₂. If the adsorption energy of CO on Pt is strongly lowered upon the addition of CoO_x, 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/CoO_x/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-CoO_x. In this way oxygen may dissociate on free Pt sites generated by CO desorption. An argument against weakly bound CO on Pt is provided by FTIR measurements (5). Addition of 5 mbar CO to a prerduced Pt/CoO_x/SiO₂ catalyst showed neither shifts in wavenumbers of adsorbed CO on Pt nor additional absorp-

tion 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/CoO_x/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/CoO_x/SiO₂ is particularly active due to the presence of sites for O₂ dissociation located on the CoO_x. From FTIR measurements, we learned that CO is also bound to CoO_x 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 CoO_x leading to more O₂ dissociation sites and thus to more CO₂ production. The reaction between CO_a and O_a may take place at the interface of the Pt-CoO_x 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 CoO_x of Pt/CoO_x/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 CoO_x 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 CoO_x or both. These observations indicate that the improved activity of the Pt/CoO_x/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 O_a on CoO_x and CO_a 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/CoO_x/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 at 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 CoO_x/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 CoO_x. 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/SiO₂ catalyst above 100°C. Below this temperature the CO₂ formation increased with a decreasing area under the CO and O₂ curve (Table 4). Above 100°C the CO₂ formation decreased with an increasing CO and O₂ uptake.

The pump probe experiments carried out over Pt/SiO₂ at 190°C showed that longer time intervals between the CO pulse at $t=0$ and the O₂ pulse led to a decrease in the CO₂ formation. A longer time interval between the CO and O₂ pulse led to an increase of CO desorption and a concomitant decrease in CO₂ formation. However, the pump probe experiments with CO pulsed at $t=0$ showed for Pt/CoO_x/SiO₂ that, even at room temperature, more CO₂ was produced as the time interval between the CO and O₂ pulse was increased.

The results obtained by single-pulse and pump probe experiments indicate that part of the CO and O₂ is held on the Pt/CoO_x/SiO₂ catalyst. CO can be released with time as was shown in pump probe experiments where the CO₂ production increased as the time interval between the CO and O₂ 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, considered that around room temperature the reaction 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/SiO₂ or Pt/CoO_x/SiO₂ 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/SiO₂ 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 O₂ pulses or with an increasing temperature, more CO becomes available and can react with O_a.

CONCLUSIONS

It was found that with an increasing CO and O₂ uptake a decrease in the CO₂ formation took place over CoO_x/SiO₂ in the temperature range 190 to 260°C. This effect also occurred above 100°C for Pt/CoO_x/SiO₂. 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/SiO₂ catalyst in the form of Pt-CO islands, which are inaccessible to oxygen.

CO desorbs rather slowly from Pt/SiO₂ compared to Pt/CoO_x/SiO₂. Single-pulse and pump probe experiments support the idea that some of the CO molecules are less strongly bound to the Pt/CoO_x/SiO₂ catalyst. Presumably, CO is less strongly bound to CoO_x of the Pt/CoO_x/SiO₂ catalyst. It seems that there is some strongly bound CO present on Pt of the Pt/CoO_x/SiO₂ catalyst at low temperatures.

The results obtained with the TAP technique are consistent with a model in which the reaction between CO_a and O_a takes place at the interface of the platinum and cobalt particles.

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