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Low-Temperature CO Oxidation over Platinum and Cobalt Oxide Catalysts

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The low-temperature CO oxidation activity of three monolith catalysts (Pt/Al_2O_3, CoO_x/Al_2O_3, and $Pt/CoO_x/Al_2O_3$) has been studied. The catalytic properties of the catalysts were investigated by using different temperature-programmed methods: CO-TPD (desorption), TPO (oxidation), TPR (reduction), TPReaction, and CO light-off. Preoxidized cobalt-oxide-containing catalysts were found to be highly active for CO oxidation at temperatures as low as 200 K, and at these low temperatures the activity is independent of the presence of platinum. The catalytic properties and how they relate to the surface reaction kinetics are discussed. © 1999 Academic Press

Key Words: **catalytic oxidation of carbon monoxide; low temperature activity; platinum; cobalt oxide; catalyst pretreatment; temperature programmed desorption; temperature programmed oxidation; temperature programmed reduction; temperature programmed reaction.**

INTRODUCTION

Background

A large amount of the emissions from cars is released during the first minutes after a "coldstart," before the catalyst becomes hot enough to convert the harmful emissions (1, 2). Also, new and fuel-efficient engines generate colder exhaust gases than current engines, resulting in slower heating of the catalyst. This places new demands on the low-temperature activity for the catalytic converters used in future emission abatement systems.

A series of papers have been published concerning low-temperature oxidation of carbon monoxide and hydrocarbons over various transition metal oxides (3–5), but very few of these materials seem to work under realistic conditions, i.e., in the presence of H_2O, SO_2, etc. However, by gaining a fundamental understanding of the catalytic properties of such materials, it might be possible to indicate how commercial catalytic converters should be modified to improve their low-temperature activity.

In a previous paper (6), where the low-temperature activity of cobalt oxide- and ceria-promoted Pt and Pd catalysts was studied, the cobalt-containing catalysts seemed to be the most active ones even in the absence of noble metals. They showed light-off temperatures of 440–470 K for carbon monoxide and propene, while the unpromoted Pt and Pd catalysts had their light-off at 520–580 K. It is therefore of interest to find out why cobalt-containing catalysts are so active.

Cobalt oxide catalysts have been studied several times over the years. Cobalt oxide is studied not only for its activity for CO and hydrocarbon oxidation (3, 5, 7, 8), but also for its use in the Fischer–Tropsch synthesis (9, 10). The most interesting results, with respect to the present work, are, however, the studies of cobalt oxide because of its unique low-temperature activity for CO oxidation. Under dry conditions, it has been found that cobalt oxide is active for CO oxidation below 220 K (11). This low-temperature activity is, however, found to be sensitive to the presence of water in the gas feed. The catalytic activity of cobalt oxide combined with noble metals has also been extensively studied. Most of these studies were made by traditional CO oxidation activity measurements (12–14), but recently a study was made using a temporal analysis of products (TAP) reactor system (15). The main results from the TAP measurements are that CO does not block the surface for O_2 adsorption on cobalt oxide (as it does on platinum) and that there is evidence of carbonate formation on the cobalt oxide.

Problem Analysis and Experimental Approach

At low temperatures, when the catalytic reactions are slow, the conversion of reactants over the catalyst is determined mainly by the reaction kinetics. This study will therefore put surface reaction kinetics into focus. The effects of mass and heat transfer do, however, play an important role when the reactions become faster, which has to

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be kept in mind when designing the experiments. The low oxidation rates of carbon monoxide and hydrocarbons at low temperatures do not involve any limitations caused by the thermodynamics: It is in principle possible to reach total conversion even below room temperature. The reason for the low catalytic activity at low temperatures is therefore kinetic barriers on the catalyst surface.

This study has been performed to identify the surface reaction mechanism responsible for the improved low-temperature activity noted on cobalt-containing catalysts compared with the noble metal-only catalysts, mentioned earlier. Three model catalysts containing platinum and/or cobalt oxide were selected for this study, having the following washcoat formulation: Pt/Al_2O_3, CoO_x/Al_2O_3, $Pt/CoO_x/Al_2O_3$. The first two samples were chosen to study the active components separately and the last one to study possible spillover and promoting effects.

To simplify the comparison of the different catalysts, it is important that they have the same total active surface area, i.e., the same number of active sites. The catalysts were therefore prepared to have the same active surface area, as measured by temperature-programmed desorption of carbon monoxide (CO-TPD), after a stabilizing thermal pretreatment. To study the catalytic properties of the catalysts, several temperature-programmed methods were chosen. To make the interpretation as easy as possible, the oxidation of carbon monoxide by oxygen was chosen as a model reaction in this study.

The activation energy for CO desorption was studied by CO-TPD. The oxidation states of platinum and cobalt oxide were explored by temperature-programmed oxidation (TPO) and temperature-programmed reduction (TPR). CO light-off measurements showed the activity of the different catalysts after different pretreatments (preoxidation or prereduction). Finally, TPReaction (one reactant preadsorbed on the surface and the other one present in the gas phase) under different conditions revealed information about activation barriers and blocking effects.

EXPERIMENTAL

Preparation of Catalysts

The preparation of the monolith catalysts has been described in detail in a previous paper (6) and, therefore, is only briefly described here. Any deviations from the previously described preparation method are pointed out in detail. The monolith samples of cordierite, 15 mm long and 15 mm in diameter, were cut out from a commercial honeycomb structure with 64 square channels per square centimeter. The monoliths were then repeatedly impregnated with γ-Al_2O_3 as the support material and then with cobalt ($Co(NO_3)_2$) and/or platinum (H_2PtCl_6) as the active material. The monolith samples were calcined after each impregnation step. The bimetallic Pt–Co catalyst was prepared by successive impregnation of first cobalt and then platinum. Nominal compositions of the three catalysts used in this study are listed in Table 1.

TABLE 1

Characteristic Data of the Three Catalysts[a]

	Pt/Al_2O_3	CoO_x/Al_2O_3	$Pt/CoO_x/Al_2O_3$
Al_2O_3 content (mg)	200	160	160
CoO_x content[b] (mg)	—	40	40
Pt content (mg)	20	—	2
BET surface area (m^2)	27.5	24.9	22.7
Amount of adsorbed CO from CO-TPD (μmol)	7.8	6.3	6.5
Amount of adsorbed O_2 from TPO (μmol)	29	183	158
Amount of adsorbed H_2 from TPR (μmol)	54	353	289

[a] Amounts are given per monolith sample.
[b] Calculated as Co_3O_4.

To ensure a stable structure of the catalysts during the measurements, the cobalt-containing catalysts were calcined in air at 1100 K for 60 min, after the three first impregnations with cobalt (out of ten), to form a stabilizing $CoAl_2O_4$ spinel layer before the remaining amount of cobalt was added (7). The formation of the spinel is identified by its characteristic light blue color, compared with the almost black cobalt oxide (Co_3O_4). All catalysts were finally calcined in air at 825 K for 60 min, reduced in 4 mol% H_2 at 725 K for 60 min [this treatment also removes chlorides from the Pt impregnation (16)], and then exposed to a slightly net-oxidizing gas mixture of 1.00 mol% CO, 0.15 mol% C_3H_6, and 1.38 mol% O_2 at 825 K for 90 min at a flow rate of 3000 ml/min, to stabilize them.

Specific Surface Area

The specific surface areas of the three catalysts were determined by nitrogen adsorption in accordance with the BET method (17). The measurements were made on a Digisorb 2600 instrument from Micrometrics and were based on five measurements at relative pressures of nitrogen in the range 0.05–0.21.

Flow Reactor Measurements

The flow reactor measurements were all made in a quartz tube (15-mm-i.d.) flow reactor, which has been described in detail elsewhere (18, 19). The gas flow into the reactor was controlled by separate mass flow controllers and the gas composition after the monolith catalyst was continuously analyzed by a quadropole mass spectrometer

TABLE 2

Experimental Procedures during the Flow Reactor Measurements

- CO-TPD
    - Oxidation in 2% O_2 at 900 K for 10 min
    - Reduction in 4% H_2 at 900 K for 10 min
    - Adsorption in 4% CO at 270 K for 5 min
    - Heating ramp in Ar from 270 to 900 K
- TPO (TPR)
    - Reduction (oxidation) in 4% H_2 (2% O_2) at 900 K for 10 min
    - Heating ramp in 2% O_2 (4% H_2) from 150 to 900 K
- CO light-off
    - Reduction in 4% H_2 at 900 K for 10 min
    - Heating ramp in 1% CO and 0.6% O_2 from 150 to 500 K
    - Oxidation in 2% O_2 at 500 K for 10 min
    - Heating ramp in 1% CO and 0.6% O_2 from 150 to 500 K
- TPReaction
    - Reduction in 4% H_2 at 900 K for 10 min
    - Oxidation in 2% O_2 at 270 K for 5 min
    - Heating ramp in 4% H_2 from 150 to 900 K
    - Oxidation in 2% O_2 at 270 K for 5 min
    - Heating ramp in 4% CO from 150 to 900 K
    - Oxidation in 2% O_2 at 900 K for 10 min
    - Reduction in 4% H_2 at 900 K for 10 min
    - Adsorption in 4% CO at 270 K for 5 min
    - Heating ramp in 2% O_2 from 150 to 900 K

(Balzer QMA 120). Heating of the reactor was achieved by an electrical heating coil around the quartz tube, which was thermally insulated with quartz wool. Cooling of the reactor was performed by injecting liquid nitrogen, inside the insulating quartz wool, onto the quartz tube. The temperature was measured in the middle of one of the center channels inside the monolith by a 0.5-mm chromel–alumel thermocouple, and was controlled by a programmable temperature controller generating linear ramps. The mass spectrometer was calibrated using known gas mixtures. The gases used in this study were 4 mol% CO, 4 mol% H_2, and 2 mol% O_2, all in Ar, and pure Ar, all of 99.9997% purity and supplied by Air Liquide, France. A detailed description of the experimental procedures during the flow reactor measurements is given below and summarized in Table 2.

During CO-TPD measurements, the catalysts were first oxidized in 2 mol% O_2 at 900 K for 10 min (to clean the catalyst surface) and then reduced in 4 mol% H_2 at 900 K for 10 min. The reactor was flushed with Ar and cooled down to 270 K. The catalysts were then exposed to 4 mol% CO at 270 K for 5 min and the reactor was again flushed with Ar. At temperatures below 270 K, CO starts to adsorb on the Al_2O_3 support (20), causing errors when calculating the active catalytic area. (This was noted by making CO-TPD measurements on a monolith sample containing γ-Al_2O_3 only, where CO was adsorbed at different temperatures.) The TPD measurement were then performed in a 50 ml/min Ar flow, while the reactor was heated from 270 to 900 K at the rate of 40 K/min.

During TPO and TPR measurements, the catalysts were first reduced in 4 mol% H_2 or oxidized in 2 mol% O_2, respectively, at 900 K for 10 min. The reactor was then cooled down to room temperature in the respective mixture and the gas flow was switched to Ar before the reactor was further cooled down to ca. 150 K (Ar starts to condense if it is cooled below 100 K). TPO and TPR measurements were then performed in 2 mol% O_2 or 4 mol% H_2, respectively, at the flow rate of 100 ml/min, while the reactor was heated from 150 to 900 K at the rate of 40 K/min.

During the CO light-off measurements, the catalysts were first reduced in 4 mol% H_2 at 900 K for 10 min. The reactor was then flushed with Ar and cooled down to ca. 150 K. The gas feed was switched to the reaction mixture containing 1.0 mol% CO and 0.6 mol% O_2, at the flow rate of 200 ml/min, where the CO always was turned on first to have the same starting conditions. The reactor was then heated from 150 to 500 K at the rate of 20 K/min after which the CO was turned off to oxidize the catalyst for 10 min, and then it was cooled down again in Ar to ca. 150 K. A new heating ramp in the reaction mixture was performed in the same way as the previous one.

During the TPReaction measurements, three different types of measurements were made in series for each catalyst: (i) The catalysts were first exposed to O_2 and then heated in H_2. (ii) The catalysts were first exposed to O_2 and then heated in CO. (iii) The catalysts were first exposed to CO and then heated in O_2. At the first type of measurement (i), the catalysts were initially reduced in 4 mol% H_2 at 900 K for 10 min. The reactor was then flushed with Ar and cooled down to 270 K. The catalysts were then exposed to 2 mol% O_2 at 270 K for 5 min, and the reactor was again flushed with Ar and cooled down to ca. 150 K. The measurements were performed in 4 mol% H_2, at the flow rate of 100 ml/min, while the reactor was heated from 150 to 900 K at the rate of 40 K/min. At the second type of measurement (ii), the reactor was flushed with Ar at 900 K and cooled down to 270 K. Again, the catalysts were exposed to 2 mol% O_2 at 270 K for 5 min, and the reactor was flushed with Ar and cooled down to ca. 150 K. The measurements were performed in 4 mol% CO, at the flow rate of 100 ml/min, while the reactor was heated from 150 to 900 K at the rate of 40 K/min. Finally, at the third type of measurement (iii), the catalysts were first oxidized in 2 mol% O_2 at 900 K for 10 min (to remove carbon from the catalyst surface) and then reduced in 4 mol% H_2 at 900 K for 10 min. The reactor was flushed with Ar at 900 K and cooled down to 270 K. The catalysts were exposed to 4 mol% CO at 270 K for 5 min and the reactor was flushed with Ar and cooled down to ca. 150 K. The measurements were then performed in 2 mol% O_2, at the flow rate of 100 ml/min, while the reactor was heated from 150 to 900 K at the rate of 40 K/min.

RESULTS

Specific Surface Area

The results from the BET measurements are presented in Table 1. The BET surface areas of the three catalysts are between 22.7 and 27.5 m^2, indicating that they have a similar microscopic structure. This means that the surface areas are on the order of 110–140 m^2 per gram of washcoat.

CO-TPD

The results from the CO-TPD measurements are given in Table 1 and the CO-TPD spectra are presented in Fig. 1. The active areas of the three samples are fairly similar, since the amounts of CO adsorbed on the catalysts differ by about 20%. The amount of CO adsorbed on the Pt/Al_2O_3 catalyst corresponds to a platinum dispersion of 11%, with the assumption that 0.7 CO molecules are adsorbed per surface noble metal atom (21). With the same assumption the cobalt dispersion of the CoO_x/Al_2O_3 catalyst (here x is likely to be zero after the reducing pretreatment, at least on the cobalt surface) becomes 2%, but all of the initial cobalt is not available due to spinel formation during the preparation procedure.

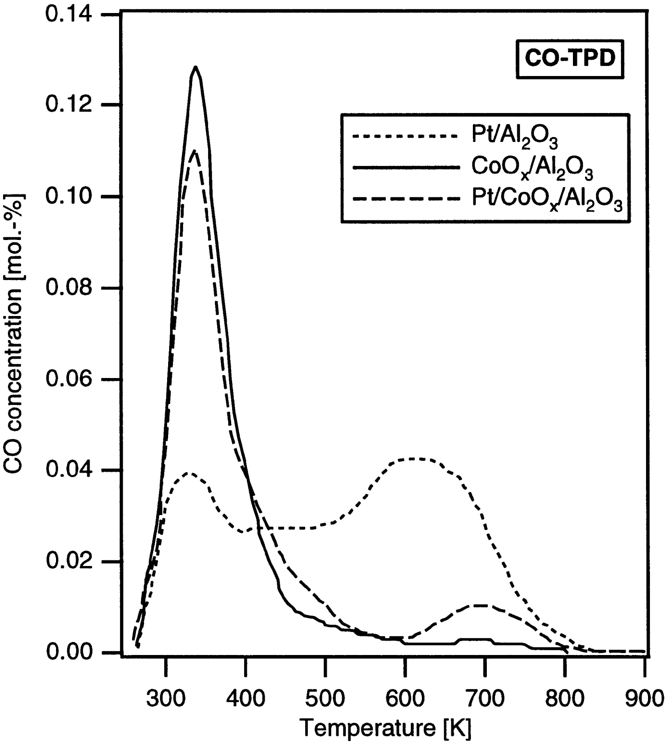

FIG. 1. CO-TPD spectra for the three catalysts. The catalysts were first oxidized in 2 mol% O_2 and then reduced in 4 mol% H_2 at 900 K. CO was adsorbed at 270 K and the catalysts were then heated at 40 K/min from 270 to 900 K in an argon flow of 50 ml/min.

The CO-TPD spectrum for the Pt/Al_2O_3 catalyst shows a wide peak between 300 and 800 K, with two maxima at 330 and 620 K, respectively. The CoO_x/Al_2O_3 catalyst shows a large sharp peak between 300 and 450 K, with its maximum at 330 K, and a smaller peak around 690 K. The spectrum for the $Pt/CoO_x/Al_2O_3$ catalyst is similar to the corresponding spectrum for the CoO_x/Al_2O_3 catalyst, but the first peak has a shoulder on the high-temperature side and the second peak is larger.

The wide peak shown in the CO-TPD spectrum of the Pt/Al_2O_3 catalyst indicates that the activation energy for desorption varies as a function of the surface coverage of CO on the platinum surface and depends on the size distribution of the platinum particles, which is normally seen for dispersed platinum (22). The first narrow desorption peaks in the CO-TPD spectra of the CoO_x/Al_2O_3 and $Pt/CoO_x/Al_2O_3$ catalysts indicate a much smaller variation of the activation energy for desorption as a function of surface coverage (23). The second smaller peak at 690 K has been noted before in vacuum CO-TPD measurements on polycrystalline metallic cobalt (23) and was attributed to oxygen contamination of the surface. This is an indication that the cobalt oxide can be reduced in hydrogen at 900 K to metallic cobalt with only some minor oxygen contamination due to, e.g., trace amounts of oxygen present in the high-purity gases used. The CO-TPD spectrum of the $Pt/CoO_x/Al_2O_3$ catalyst, with only a small amount of platinum present, seems to be a superposition of the two other spectra, indicating that platinum and cobalt do not interact under these conditions.

TPO and TPR

The results of the TPO and TPR measurements are summarized in Table 1 and the corresponding spectra are presented in Fig. 2. The oxidation for all of the catalyst samples starts at about 160 K. On the Pt/Al_2O_3 catalyst there is first an oxygen consumption peak at 200 K, corresponding to a monolayer on the platinum (as measured by CO-TPD), and then a slower uptake follows during the rest of the temperature ramp. The TPO spectra for the CoO_x/Al_2O_3 and $Pt/CoO_x/Al_2O_3$ catalysts also start with consumption peaks at 200 K, but then there are large consumption peaks reaching their maxima at 590 and 500 K, respectively (8). The presence of platinum seems to increase the reoxidation rate of the cobalt when the temperature exceeds 400 K. The total oxygen uptake is somewhat lower for the $Pt/CoO_x/Al_2O_3$ catalyst compared with the CoO_x/Al_2O_3 catalyst.

The TPR spectrum for the Pt/Al_2O_3 catalyst shows a small peak at 170 K (corresponding to a monolayer of oxygen on the platinum) and then a larger sharp peak at 210 K, which agrees with earlier reports (24). The TPR spectra for the CoO_x/Al_2O_3 and $Pt/CoO_x/Al_2O_3$ catalysts also start with some small consumption peaks at 170 K and the $Pt/CoO_x/Al_2O_3$ catalyst also shows a small peak at 210 K.

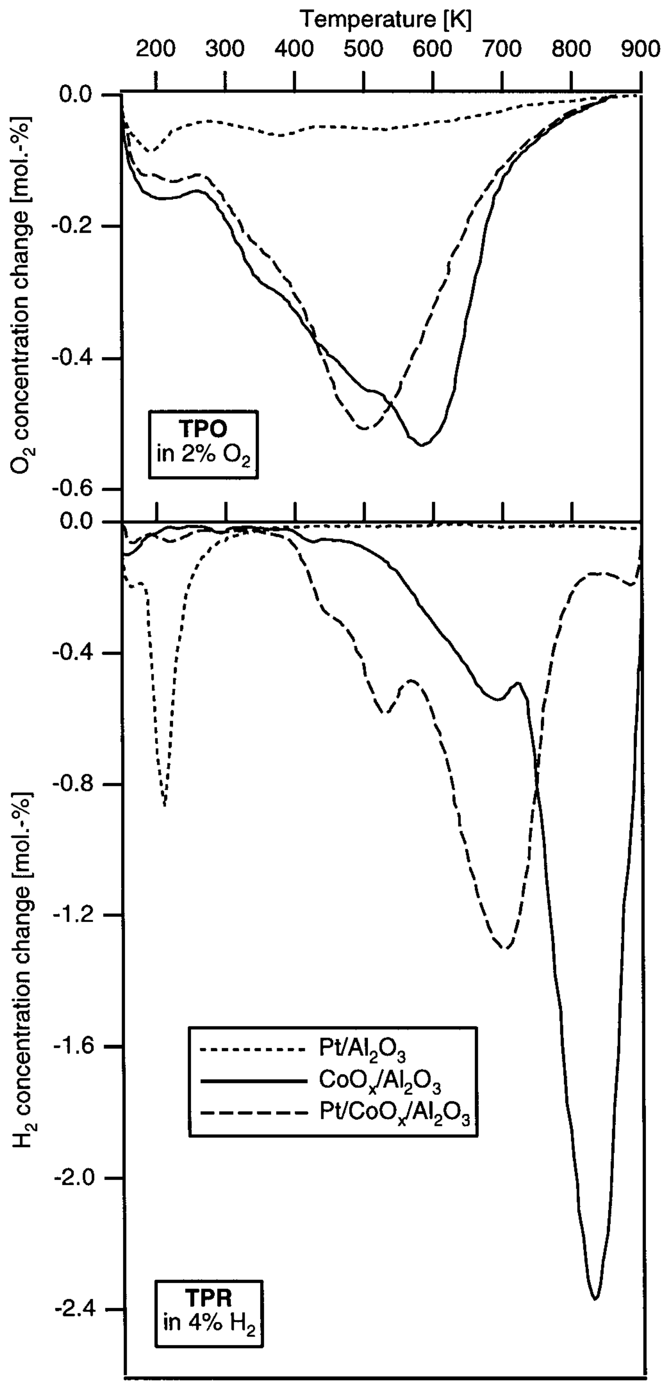

FIG. 2. TPO and TPR spectra for the three catalysts. The catalysts were first reduced in 4 mol% H_2 or oxidized in 2 mol% O_2 at 900 K. The catalysts were then heated at 40 K/min from 150 to 900 K in 2 mol% O_2 or 4 mol% H_2 at a flow rate of 100 ml/min.

At higher temperatures, the reduction then continues in a two-step process with consumption peaks at 680 and 830 K for the CoO_x/Al_2O_3 catalyst and at 530 and 690 K for the $Pt/CoO_x/Al_2O_3$ catalyst (8). The presence of platinum seems also, as in the TPO measurement, to increase the reduction rate of the cobalt oxide when the temperature exceeds 400 K. The total oxygen removal (= half of the hydrogen consumption) is almost equal to the oxygen consumption in the TPO measurements for all three samples. If one assumes that the cobalt can be reduced from Co_3O_4 to metallic Co and reversibly reoxidized back to Co_3O_4, then approximately 50% of the initial cobalt is available and the rest should have formed the inert spinel (about 30% of the cobalt formed the spinel during the initial preparation of the catalysts).

CO Light-off

The results of the CO light-off measurements are summarized in Table 3 in the form of light-off temperatures and the corresponding spectra are presented in Fig. 3. The light-off temperature, denoted T_{50}, is here defined as the temperature where the conversion of CO reaches 50%. All light-off measurements show an initial net desorption of CO from the Al_2O_3 support below 200 K.

For the prereduced Pt/Al_2O_3 catalyst, no activity is shown until the temperature exceeds 300 K and then the reaction slowly accelerates to 50% CO conversion (T_{50}) at 450 K. However, when the Pt/Al_2O_3 catalyst is preoxidized, CO_2 production starts at 200 K, but no consumption of CO is detected at this point. CO conversion starts around 225 K and then fluctuates around 40% conversion until it accelerates, reaching T_{50} at 460 K, similar to the case when prereduced. The complex structure of the light-off spectrum for the preoxidized Pt/Al_2O_3 catalyst can probably be explained by a series of reaction events during the temperature ramp, caused by the complex reaction kinetics of CO oxidation on platinum.

For the prereduced CoO_x/Al_2O_3 catalyst, CO_2 production starts at 200 K, peaking with 20% CO conversion at 230 K and then levels out to an almost constant level of 15% until the temperature reaches 370 K. Above that temperature the CO conversion increases rapidly and reaches T_{50} at 420 K. When the light-off ramp is repeated after the preoxidation, the CO_2 production again starts at 200 K, but in this case it is matched by a corresponding CO conversion, reaching T_{50} already at 210 K. CO conversion then becomes total at 230 K and is maintained during the rest of the temperature ramp. There is also an overshoot in the CO_2 concentration at this temperature, indicating some storage on the surface.

TABLE 3

Light-off Temperatures (T_{50}) for the Three Catalysts

	Pt/Al_2O_3	CoO_x/Al_2O_3	$Pt/CoO_x/Al_2O_3$
T_{50} after prereduction (K)	450	430	420
T_{50} after preoxidation (K)	460	210	210

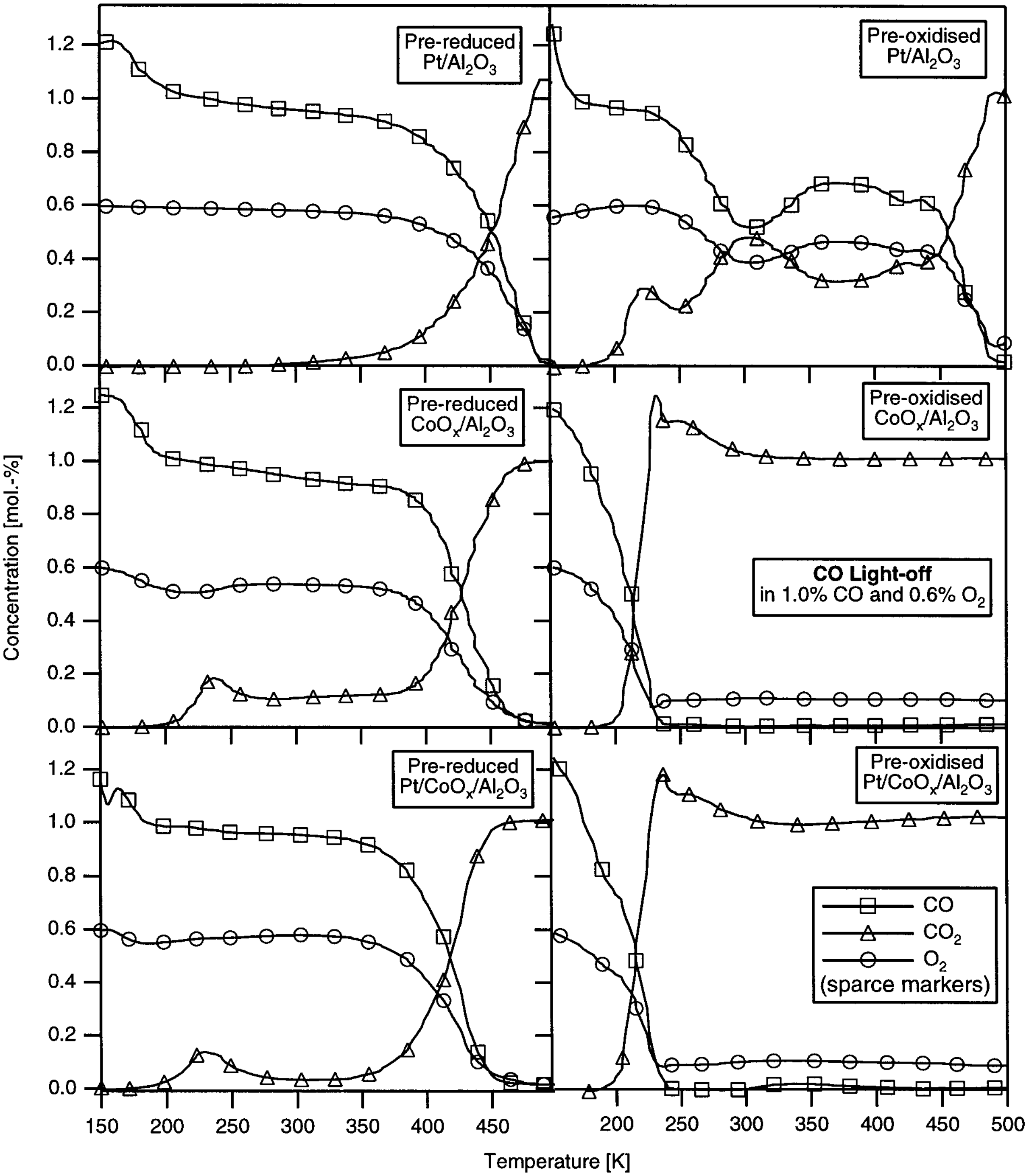

FIG. 3. CO light-off spectra for the three catalysts. The catalysts were first reduced in 4 mol% H_2 at 900 K. The catalysts were then heated at 20 K/min from 150 to 500 K in a gas mixture of 1 mol% CO and 0.6 mol% O_2 at a flow rate of 200 ml/min. At 500 K the CO was turned off for 10 min to oxidize the catalysts and then a new temperature ramp was made from 150 to 500 K in the same CO and O_2 gas mixture.

The behavior of the prereduced Pt/CoO_x/Al_2O_3 catalyst is similar to the behavior of the CoO_x/Al_2O_3 catalyst, but T_{50} is lowered by 10 K to 410 K. The spectrum after preoxidation is almost identical to that of the CoO_x/Al_2O_3 catalyst with T_{50} at 210 K.

TPReaction

The spectra of the TPReaction measurements, in which only one of the reactants (CO, O_2, or H_2) is present in the gas phase and the other (CO or O_2) is preadsorbed on the

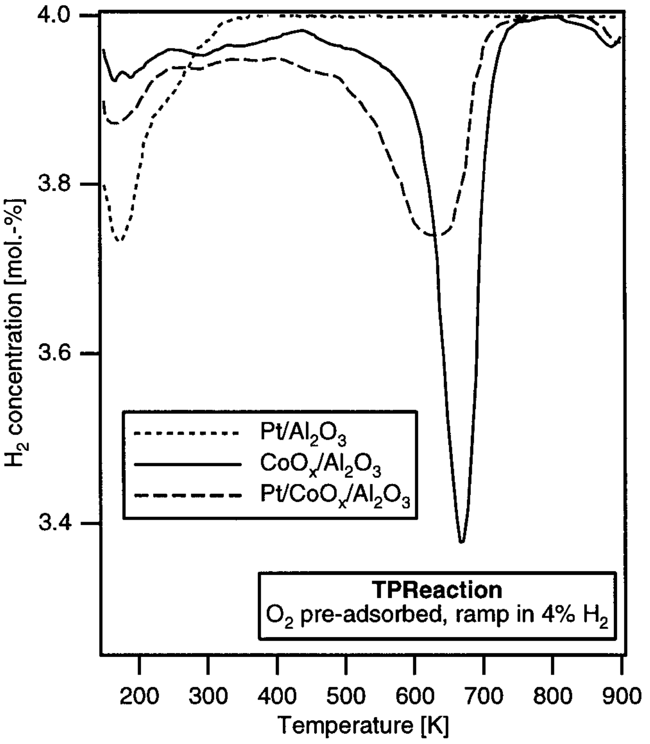

FIG. 4. TPReaction spectra for the three catalysts. The catalysts were first reduced in 4 mol% H_2 at 900 K. O_2 was adsorbed at 270 K and the catalysts were then heated at 40 K/min from 150 to 900 K in 4 mol% H_2 at the flow rate of 100 ml/min.

catalyst prior to the temperature ramp, are presented in Figs. 4, 5, and 6.

In the first type of measurement (Fig. 4), when O_2 was preadsorbed at 270 K and H_2 was present in the gas phase during the temperature ramp, all three catalysts had a peak of hydrogen consumption below 200 K. The CoO_x/Al_2O_3 and $Pt/CoO_x/Al_2O_3$ catalysts additionally had consumption peaks at 670 and 630 K, respectively.

In the second type of measurement (Fig. 5), when O_2 was preadsorbed at 270 K and CO was present in the gas phase during the temperature ramp, the results became more complex. In the beginning of the temperature ramp there is a net desorption of CO from the Al_2O_3 support on all catalysts. For the Pt/Al_2O_3 catalyst there is then a small peak of CO_2 production at 250 K, which corresponds to a monolayer of oxygen on the platinum (as measured by CO-TPD). When the temperature reaches 540 K CO_2 production starts again with a corresponding CO consumption. For the CoO_x/Al_2O_3 and $Pt/CoO_x/Al_2O_3$ catalysts no reaction can be seen until the temperature reaches 400 K when the CO_2 production slowly starts with a related CO consumption. CO_2 production then increases at 540 K as it does on the Pt/Al_2O_3 catalyst, but the peak shapes differ between the different catalysts at higher temperatures.

In the third type of measurement (Fig. 6), when CO was preadsorbed at 270 K and O_2 was present in the gas phase during the temperature ramp, the results also became complex. For the Pt/Al_2O_3 catalyst there is a peak of CO_2 production at 310 K, corresponding to the preadsorbed monolayer of CO on the platinum, and at the same time oxygen is consumed from the gas phase. O_2 consumption

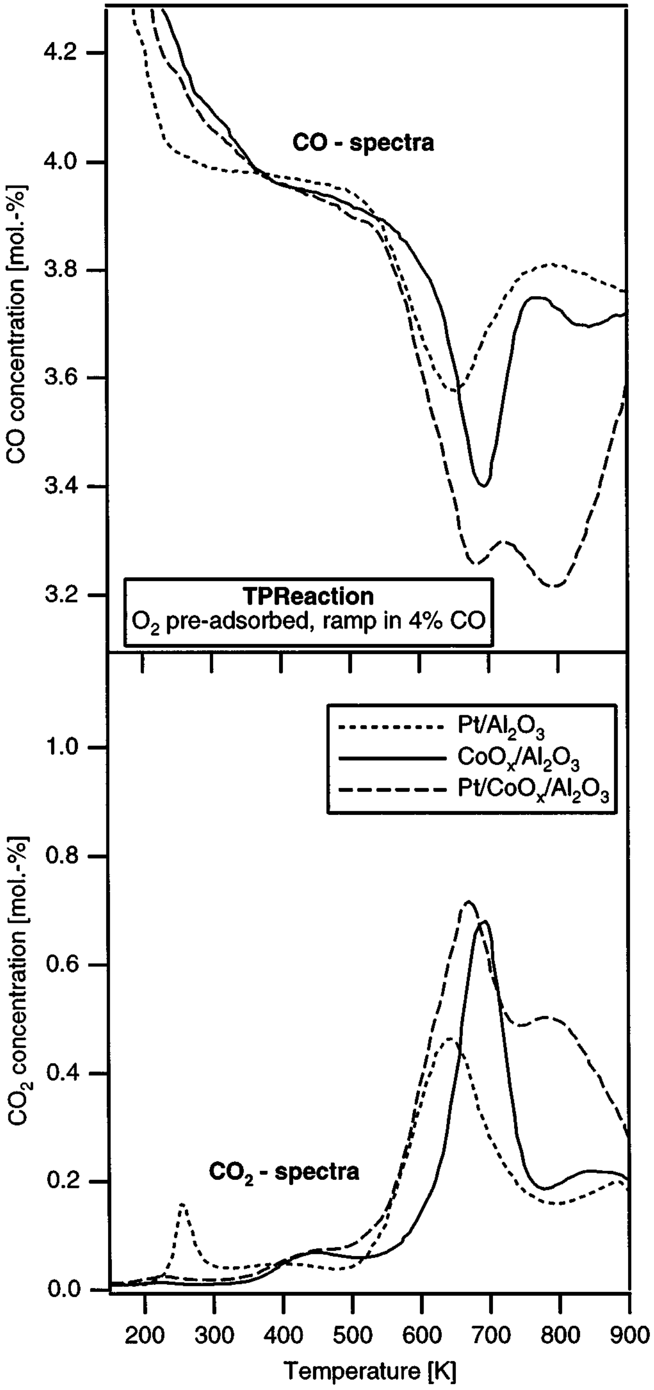

FIG. 5. TPReaction spectra for the three catalysts. The catalysts were first reduced in 4 mol% H_2 at 900 K. O_2 was adsorbed at 270 K and the catalysts were then heated at 40 K/min from 150 to 900 K in 4 mol% CO at the flow rate of 100 ml/min.

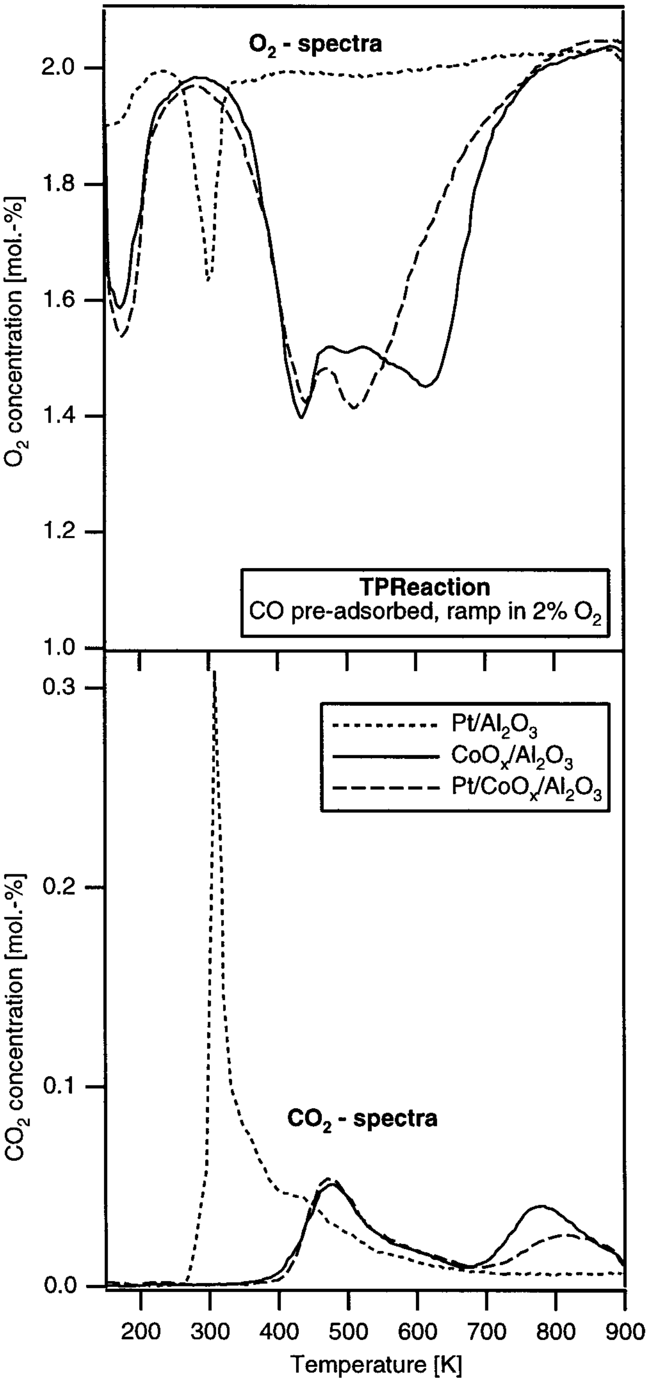

FIG. 6. TPReaction spectra for the three catalysts. The catalysts were first reduced in 4 mol% H_2 at 900 K. CO was adsorbed at 270 K and the catalysts were then heated at 40 K/min from 150 to 900 K in 2 mol% O_2 at the flow rate of 100 ml/min.

is twice as large as what would be required for CO_2 production, because it is at the same time used to form an oxygen monolayer on the platinum. For the CoO_x/Al_2O_3 and $Pt/CoO_x/Al_2O_3$ catalysts there is first some oxygen consumption below 200 K (the amount is of the same order as for the 310 K peak on the Pt/Al_2O_3 catalyst) and then again above 300 K, similar to the TPO measurements. The amounts of oxygen consumed above 300 K reveal that it is used to reoxidize the prereduced catalysts. CO_2 starts to desorb from the catalyst surface at 400 K in two peaks, the first at 470 K and the second at about 800 K. The amount of CO_2 corresponds to the amount of preadsorbed CO on the cobalt (as measured by CO-TPD).

DISCUSSION

Origin of the Low-Temperature CO Oxidation Activity

The most interesting result in this study is that the preoxidized cobalt-containing catalysts show very low light-off temperatures (Fig. 3), independent of the presence of platinum. As mentioned in the Introduction, the catalytic activity under these conditions is determined mainly by the surface reaction kinetics. One can therefore now discuss how the following five elementary properties, governing overall surface reaction kinetics, are related to the differences in low-temperature activity observed in this work:

(i) total active surface area,
(ii) surface coverage-dependent sticking coefficients for the reactants,
(iii) activation barriers for the surface reaction steps,
(iv) activation energies for desorption of surface species,
(v) possibility of spillover processes.

The first point, concerning the total active surface area of the catalysts, cannot explain the differences in activity between the three catalysts seen in this study. CO-TPD measurements showed that all catalysts have similar active surface areas (Table 1) and that the least active one (the Pt/Al_2O_3 catalyst) actually had the largest active surface area.

The second point, concerning the surface coverage-dependent sticking coefficients for the reactants, seems to be the most likely explanation for the differences in activity at low temperatures. The blocking effect of CO with regard to oxygen adsorption on platinum (15) is seen in the light-off measurements (Fig. 3) where the prereduced Pt/Al_2O_3 catalyst shows no activity below 300 K, while it is somewhat active at 200 K when preoxidized. The preoxidized platinum catalyst does not, however, adsorb any oxygen at these temperatures, indicating that CO_2 formation starts by consuming the oxygen already present on the surface. This blocking effect is seen even clearer in the TPReaction measurements, where the CO_2 peak appears at 260 K when oxygen is preadsorbed (Fig. 5) compared with 310 K when CO is preadsorbed (Fig. 6). On the prereduced cobalt-containing catalysts a similar blocking effect by CO is observed. The light-off on these catalysts does not occur until the same temperature is reached as for the prereduced Pt/Al_2O_3 catalyst (Fig. 3), indicating that reduced cobalt has catalytic properties similar to those of reduced platinum in this respect: The CO-TPD measurements (Fig. 1) show that reduced cobalt adsorbs CO with similar strength as platinum. The TPReaction measurements (the case when CO is preadsorbed and O_2 is present in the gas phase, Fig. 6), however, indicate that there is an important difference in the capacity to adsorb oxygen under these conditions. The presence of CO does not seem to block O_2 adsorption on reduced cobalt, but since no CO_2 is released into the gas phase it indicates that some kind of carbonate is formed that blocks the surface (15). When the cobalt instead is preoxidized, the situation is dramatically different. In this case the light-off measurements show that the cobalt-containing catalysts start to adsorb CO and O_2 already below 200 K (Fig. 3). In this case, one has to remember that the cobalt now has formed a bulk metal oxide, in contrast to the platinum which remains mainly as a metal with a chemisorbed layer of oxygen (25). When cobalt is present as a metal oxide it seems as if CO no longer blocks the surface, but instead it reacts to CO_2 and leaves the surface.

The third point, concerning the activation barriers for the surface reaction steps, does not seem to inhibit CO oxidation in this study. For all catalysts, the surface reaction between adsorbed carbon monoxide and oxygen occurs far below room temperature as long as both reactants are simultaneously present on the active surface.

The fourth point, concerning the activation energies for desorption of reactants and products, is an indirect cause of the blocking effect by CO on O_2 adsorption on platinum. CO conversion on the prereduced Pt/Al_2O_3 catalyst, during the light-off measurements (Fig. 3), starts at 300 K which corresponds to the start of CO desorption as seen in the CO-TPD spectrum (Fig. 1), leaving empty sites for oxygen to adsorb. A high activation energy for desorption of the reaction product formed, here CO_2, could be another reason for the low activity. In the present case it seems, however, unlikely since CO_2 starts to appear in the gas flow from 200 K during the CO light-off measurements on the preoxidized Pt/Al_2O_3 catalyst. For the cobalt-containing catalysts, the situation seems to be more complicated. As mentioned before, there are indications that prereduced cobalt might be blocked by carbonates formed on the cobalt surface and that they do not seem to decompose until the temperature exceeds 400 K, as can be seen in the TPReaction measurements (Fig. 6). The overshoots in the CO_2 concentration at 230 K, during the CO light-off measurements on the preoxidized cobalt catalysts (Fig. 3), indicate some storage of CO_2 also on oxidized cobalt. This suggests that the CO oxidation rate on cobalt in an oxidized state might be limited by the desorption rate of CO_2 (26) and thereby sensitive to high concentrations of CO_2 in the reactant mixture.

The fifth point, concerning the possibility of spillover processes, does not seem to be important in the reaction process below room temperature on the $Pt/CoO_x/Al_2O_3$ catalyst. The light-off process is identical to that on the CoO_x/Al_2O_3 catalyst, which means that the presence of platinum does not promote the reaction occurring on the cobalt oxide. At higher temperatures, however, there are strong indications of spillover processes. In the TPO and TPR spectra one can clearly see that the presence of platinum is beneficial above 400 K for activating the O_2 and H_2 used to oxidize or reduce the cobalt, respectively. The presence of a spillover process above 400 K is for instance also indicated in the previous light-off measurements (6) in a rich reactant gas mixture on a preoxidized $Pt/CoO_x/Al_2O_3$ catalyst.

The present results concerning the high activity of the preoxidized cobalt-containing catalysts at low temperatures at first seems to be inconsistent with the results in the previous paper (6). The latter showed that the prereduced cobalt-containing catalysts were the most active ones, showing light-off temperatures for CO at 450–460 K, i.e., similar to the light-off measurements on the prereduced cobalt-containing catalysts seen in this study (light-off between 420 and 430 K). Thus the results from the two studies are consistent for the prereduced catalysts, taking into account the 15 times larger flow rate in the previous measurements. However, for the preoxidized catalysts there is a large difference between the two studies. A possible explanation is that in the previous paper, propene was also present in the gas feed and might have blocked the preoxidized cobalt surface at low temperatures. This is, however, an unlikely explanation at higher temperatures (above 500 K) since the propene would then have desorbed, resulting in a high activity, while full conversion was not even reached at 825 K on the CoO_x/Al_2O_3 catalyst. Another likely explanation is that water adsorbed on the cobalt surface forms OH groups, which make the preoxidized cobalt catalysts lose most of their activity. The presence of OH groups had earlier been detected on Co_3O_4 by XPS (27). Since propene was present in the previous study (6), water was formed during conversion of the propene. Furthermore, the gases used might also have contributed, not being of as high purity as those used in this study, by containing trace amounts (a few ppm) of water. The idea that the presence of water should be one of the explanations for the large difference in activity at low temperatures is supported by earlier results (11) showing that the presence of less than 10 ppm of water has a large effect on the catalytic CO oxidation activity of cobalt catalysts. This could not, however, explain the differences at high temperatures since the effects of water, in that study, seem to be negligible above 400 K. The only reasonable explanation left for the differences in activity at high temperatures is that the reaction rate for CO oxidation on preoxidized cobalt is actually relatively slow compared with the rate on prereduced cobalt (remember the differences in flow rate). A complementary investigation of the inhibiting effects of water and propene on the oxidation of CO on preoxidized cobalt oxide will be presented in a forthcoming paper (28).

Oxidation and Reduction of the Catalytic Materials

The oxidation and reduction of catalytic materials seem to play an important role with respect to their catalytic activity, and therefore some of the experimental results are further discussed and pointed out in this section.

Oxygen consumption during TPO measurements (Fig. 2) starts at about 160 K for all catalysts, which is just above the temperature at which oxygen is known to start to dissociate on the platinum surface (29). The total amount of oxygen adsorbed by the Pt/Al_2O_3 catalyst corresponds to more than one surface monolayer and is most probably an effect of the dispersion of the platinum, which forms only a few subsurface oxide layers under these conditions (25).

Both oxidation and reduction seem to be two-stage processes on the cobalt-containing catalysts, where a first oxide layer is formed or removed and then the cobalt bulk starts to become oxidized or reduced. Earlier XPS measurements showed that Co is oxidized to CoO at 300 K (30) which corresponds to the beginning of the main oxygen consumption peak starting at 270 K in the TPO spectra. On the $Pt/CoO_x/Al_2O_3$ catalyst both TPO and TPR measurements show that less cobalt is available (for oxidation or reduction) compared with the CoO_x/Al_2O_3 catalyst, probably due to the higher degree of $CoAl_2O_4$ spinel formation. CO-TPD measurements also show that the $Pt/CoO_x/Al_2O_3$ catalyst seems to have a somewhat lower CO adsorption capacity on the cobalt sites (excluding the platinum), since the first sharp peak in the CO-TPD spectra (Fig. 1) is smaller for this catalyst.

In the first type of TPReaction measurements, when O_2 was preadsorbed and H_2 was present in the gas phase (Fig. 4), the first consumption peaks located below 200 K agreed to a large extent with the 170 K peaks seen in the TPR spectra (Fig. 2). It is the only peak observed for the Pt/Al_2O_3 catalyst, which means that oxidation of platinum at 270 K results in only a surface monolayer of oxygen. Furthermore, the CoO_x/Al_2O_3 catalyst has a sharp consumption peak at 680 K which agrees well both in size and in location with the corresponding 680 K peak in the TPR spectrum. This is another indication that the oxidation and reduction of cobalt under these conditions are two-step processes. The main consumption peak for the $Pt/CoO_x/Al_2O_3$ catalyst is, however, located at 630 K, which is closer to the second peak at 690 K than the first peak at 530 K in the TPR spectrum. Furthermore, the peak is also much smaller than the peaks in the TPR spectrum. It is therefore difficult to explain this result, but it is clear that platinum plays an important role in the oxidation and reduction processes of cobalt.

Carbonate Formation on Cobalt Oxide

There are in several experiments indications of carbonate formation on the cobalt oxide surface, especially on prereduced samples. The formation of these carbonates and how they affect catalytic activity are therefore further discussed in this section.

For the prereduced cobalt-containing catalysts one can see a small amount of CO_2 production at 230 K before the light-off occurs at about 420 K. As can be seen, the catalysts start to adsorb oxygen below 200 K even though the surface is covered by CO, a phenomenon also observed in the TPReaction spectra (Fig. 6). This oxygen is then used before light-off occurs, but as discussed before, it is probably also used to form blocking carbonates on the cobalt surface. These carbonates do not desorb from the surface until the temperature exceeds 400 K, which corresponds to the light-off occurring at 420–430 K.

In the second type of TPReaction measurement, when O_2 was preadsorbed and CO was present in the gas phase (Fig. 5), only one low-temperature peak (at 250 K) of CO_2 was observed on the Pt/Al_2O_3 catalyst. On the cobalt-containing catalysts, CO_2 peaks do not appear until the temperature reaches 450 K, which is another indication that reduced cobalt, exposed only to oxygen at low temperatures (270 K), is able to store CO_2 as some kind of carbonate. Since no oxygen is available in the gas phase and the preadsorbed oxygen is consumed at low temperatures, most of the CO_2 produced above 500 K on all the catalysts is most likely produced from CO itself via CO disproportionation (9), $CO + CO \rightarrow C + CO_2$. The storage of CO_2 on the cobalt-containing catalysts is also clearly observed in the third type of TPReaction measurement (Fig. 6), as mentioned before, but these measurements also indicate that these carbonates block the cobalt surface from oxygen adsorption up to 350 K, if compared with TPO measurements (Fig. 2). It is also clearer in this case, again compared with TPO measurements, that the reoxidation process of cobalt is a two-step process.

Since the formation of carbonates on the cobalt surface seems to play an important role in the low-temperature oxidation process of carbon monoxide, there is a need for further studies of this topic. To gain a better understanding of these processes, one should probably use surface sensitive experimental techniques, such as *in situ* FTIR.

CONCLUSIONS

Three different catalysts—Pt/Al_2O_3, CoO_x/Al_2O_3, $Pt/CoO_x/Al_2O_3$—were prepared to investigate their low-temperature activity for CO oxidation. The preoxidized cobalt-containing catalysts were found to be very active at low temperatures and showed light-off temperatures of 210 K. This low-temperature activity of the cobalt-containing catalysts was found to be independent of the presence of platinum.

Five points governing surface reaction kinetics were discussed to relate them to the differences noted in low-temperature activity of the catalysts. The surface coverage-dependent sticking coefficients for CO and O_2 are believed to be the main reason for the higher activity shown by the cobalt-containing catalysts, compared with the platinum-only catalyst. Carbon monoxide seems unable to block the cobalt surface from oxygen adsorption as it does on platinum. The activation energies for desorption of reactants and products are considered to be an indirect reason for the blocking effect of CO on platinum at low temperatures and for the blocking by CO_2 (probably in the form of surface carbonates) in the case of prereduced cobalt below 400 K.

At temperatures above 400 K the presence of platinum in the $Pt/CoO_x/Al_2O_3$ catalyst seems to increase the reduction and oxidation rates of the cobalt oxide (in the TPR and TPO experiments) by activating the H_2 and O_2 molecules, which could then be involved in spillover processes. The prereduced cobalt catalysts showed CO oxidation activity similar to that of the platinum-only catalyst. Compared with earlier results, the presence of water and/or hydrocarbons seems to poison the high activity seen on the preoxidized cobalt catalysts at low temperatures. The prereduced cobalt catalysts seem, on the other hand, to be much more resistant in this sense.

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