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Reactivity of Pt/Al_2O_3 and $Pt-CeO_2/Al_2O_3$ Catalysts for the Oxidation of Carbon Monoxide by Oxygen

II. Influence of the Pretreatment Step on the Oxidation Mechanism

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The reactivity of CeO_2/Al_2O_3, Pt/Al_2O_3, and $Pt-CeO_2/Al_2O_3$ catalysts has been studied as a function of temperature for the oxidation of carbon monoxide by oxygen. It is found that the O_2 percentage used during the pretreatment step does not change the subsequent reactivity of Pt/Al_2O_3 catalyst, while it induces a drastic modification of the $Pt-CeO_2/Al_2O_3$ reactivity. It is shown that, after a reductive pretreatment, the $Pt-CeO_2$ interaction leads to a great enhancement of the reactivity when compared to that of platinum alone, but this enhancement disappears after an oxidative pretreatment. The behaviour in each case has been tentatively correlated with catalytic sites and reaction mechanisms able to explain all of these phenomena.

INTRODUCTION

In Part I (*1*), γ-alumina-supported CeO_2, Pt, and $Pt-CeO_2$ catalysts have been characterized by temperature programmed reduction performed with CO as reducing agent. This technique consists of an oxidation of gaseous CO into CO_2 with the oxygen atoms stored on the catalyst, predominantly as oxides, but also as hydroxyl groups. This second part is devoted to the study of the influence of ceria on the reactivity of Pt/Al_2O_3 catalysts for the oxidation of carbon monoxide by gaseous oxygen.

Many investigations have already been published about the various effects of cerium dioxide on the reactivity of noble metals for the reactions involved in automotive pollution control. For simple reactions, such as CO + NO (*2–4*), CO + NO + O_2 (*2*), and CO + O_2 (*3, 5, 6*), which are performed under synthetic gas mixtures, authors generally observe a promoter effect of CeO_2 on the catalytic activity. When the catalysts are tested under a "complete" mixture of gases (e.g., N_2, CO, CO_2, H_2O, C_3H_8, C_3H_6, NO, H_2), the situation is much more complex and there is no longer agreement about the effects.

On the one hand, Kim (*7*) observed a beneficial effect of ceria for both stationary and oscillatory conditions of composition. In the first case, the effect of ceria is attributed by Kim to an enhancement of the water–gas shift (WGS) reaction, whereas an additional enhancement is obtained in the second case and is attributed to oxygen storage on ceria. These conclusions are also confirmed by the results of Weibel *et al.* (*8*) and Engler *et al.* (*9*).

On the other hand, on catalysts containing ceria, Harrison *et al.* (*10*) do not detect any enhancement of reactivity by adding ceria when the tests are performed with dry gases and conclude that the benefit of CeO_2 is only due to WGS reaction. The same observation was given by Schlatter and Mitchell (*11*), who mentioned that the benefit of ceria disappears in absence of water.

Contrary to the preceding results, Silver *et al.* (*12*) and Summers and Ausen (*13*) see

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a negative effect of ceria on the reactivity of fresh catalysts. After catalyst aging, Silver *et al.* do observe a beneficial effect of ceria, whereas Summers and Ausen find that the platinum catalysts are still deactivated by ceria because of strong Pt–CeO_2 interaction.

Besides the reactivity studies, other publications have been devoted to the study of some characteristics of the interaction between noble metals and ceria. These studies propose various interpretations regarding the modification of the noble metal catalytic properties by adding ceria: (i) presence of particular sites at the Pt–CeO_2 interface (*7, 10*), (ii) modification of the redox properties of ceria by metal and of metal by ceria (*9, 14*), (iii) a mechanical effect in which ceria stabilizes the metal dispersion (*14–16*), and (iv) spillover phenomena (*17*).

Nevertheless, the studies of all the phenomena previously cited are very complex because of the nonstationary state of the operating conditions (gas-phase composition, temperature, pressure, . . .) which induce continuous changes in the catalyst surface: modification of (i) the adsorbed species, (ii) oxidation state of the catalyst (which is of prime importance for precious metals and ceria), and (iii) restructuring of the precious metal particles.

In this context, our goal was to clarify the nature of the platinum-ceria interaction for "model" catalysts supported on γ-alumina, and to point out the possible states of the interface, as a function of the gas-phase composition (rich or lean), temperature, and pretreatment.

With this aim, the catalysts have been characterized by temperature-programmed reduction (TPR) performed under diluted CO (see Part I (*1*)). Then, they have been tested for their reactivity as a function of temperature ("light-off" tests) for the oxidation of CO by O_2, by using two sets of operating conditions so as to obtain very different space velocities from one test to the other. In each case particular care has been focussed on the pretreatment procedure in order (i) to study its importance for the reactivity of the final catalyst and (ii) to obtain a reproducible state of the catalyst surface in terms of oxidation state, stability, dispersion and water content.

EXPERIMENTAL

Preparation of the catalysts. The catalysts are prepared on a γ-alumina support, either as pellets of 2-mm diameter or as powder (250 μm < ∅ < 425 μm), for the light-off tests performed respectively at low and high space velocity (VVH) defined as the volume of feed flowing per volume of catalyst and per hour. The impregnation technique and the properties of the final catalysts have already been described in Part I (*1*).

Light-off CO + O_2 at low VVH. This test is performed within the procedure given in Fig. 1 of Part I (*1*), which also includes the TPR and TPO tests previously discussed. The operating conditions and the apparatus are the same than those used for the TPR (*1*), that is to say: 4.72 g of pelleted catalyst, a constant flow rate of 100 cm^3/min, a heating rate of 10 K/min from room temperature up to 973 K, and the gas compositions indicated in Fig. 1 of Part I (*1*).

Taking into account these operating conditions (mass of catalyst and gas flow rate), the VVH is of the order of magnitude of 2000 h^{-1}, which is quite low compared to the VVH encountered in real exhaust pipes (around 100,000 h^{-1}). The main advantage of using such a low VVH is that any adsorption of gaseous species, like CO, for example, will alter the instantaneous composition of the gas phase, and in the same way, any desorption, of CO_2 for example, will be detectable by a noticeable increase of CO_2 content in the gas phase at the outlet of the reactor. As we shall see, this means that this technique enables the following, as a function of temperature, of both the reactivity of the catalyst and the adsorption–desorption phenomena.

The light-off test by itself is performed under a gas mixture composed of 1.5% CO + 1.5% O_2/He. The outlet gas composi-

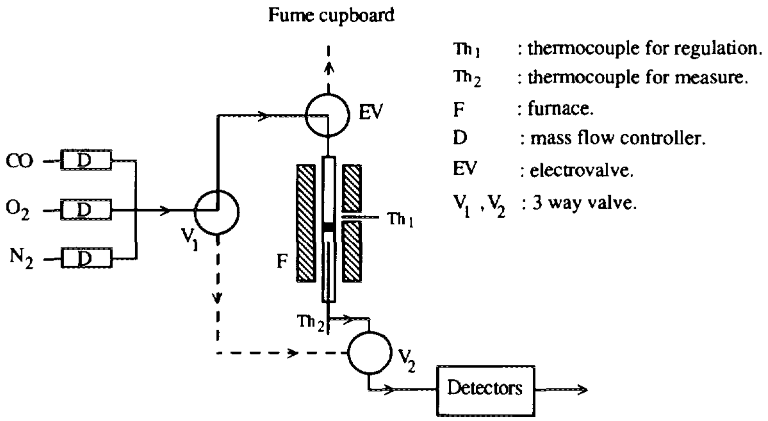


FIG. 1. Schematic drawing of the apparatus used for the light-off tests at high VVH.

tion is analysed as a function of the catalyst temperature, by infrared detectors for CO and CO_2 and with a thermal conductivity detector which measures the sum: CO% + CO_2% + O_2%.

Note that for these light-off tests performed at low VVH, the O_2 curve is not directly obtained from an oxygen analyser, but is deduced from experimental data by subtracting the CO_2 and CO contributions to the TCD curve.

Light-off CO + O_2 at high VVH. This test is performed with 100 mg of catalyst powder and a relatively high flow rate (250 cm^3/min), which leads to a VVH of about 375,000 h^{-1}. This space velocity is high enough for the adsorption–desorption phenomena to be negligible in relation to the total number of molecules passing through the catalyst per unit of time. This means that this test will enable us to obtain selectively the reactivity of the catalyst for the desired reaction test (i.e., CO + O_2 in the present case).

The apparatus used for this test is described in Fig. 1. It includes three independent gas inlets (connected with 4.5% CO/N_2, 4.5% O_2/N_2 and pure N_2 to be closer to realistic gas composition) in order to obtain various CO/O_2 ratios. The gas flow passes through the reactor and is then analysed by the detectors of CO and CO_2 (by infrared) and O_2 (by paramagnetism). The catalyst temperature is monitored by a regulator related to the furnace and is measured by a second thermocouple placed inside the reactor, just after the catalyst bed.

The pretreatment procedure of the catalyst is as follows. The sample is first stabilized for one hour at 763 K under the "*activating* gas mixture", then cooled to room temperature (RT) under the same gas composition, purged by the "*test* gas mixture" for 10 min at 298 K, and then heated again from RT to 763 K with a heating slope of 4 K/min. The data concerning temperature, CO%, CO_2% and O_2% in the gas outlet are recorded on a computer every 15 s in such a way as to follow the reactivity of the catalyst as a function of its temperature.

RESULTS

CO + O_2 LIGHT-OFF USING HIGH VVH CONDITIONS

The two platinum catalysts (with or without ceria) have been tested for their reactivity in CO + O_2 in different ways depending on the O/CO ratio used, both for the "*activation* gas mixture" and for the "*test* gas mixture". For the sake of clarity, the mixture of 0.5% CO + 0.5% O_2/N_2 will be called "lean" (O/CO = 2) and the mixture of 1% CO + 0.25% O_2/N_2 will be called "rich" (O/CO = 0.5).

The light-off curves (CO% and CO_2% as a

TABLE 1

$CO + O_2$ Light-off Results Obtained with a High Space Velocity, as a Function of the Gas Composition Used (i) for the Activation Period and (ii) for the Test Itself

Catalyst	Activation	Test	Starting T (K)	$T_{1/2}$ (K)	E_a (kJ/mol)
2% Pt/Al_2O_3	Lean	Lean	443	483	94
	Rich	Rich	433	500	58.5
2% Pt–14.7% CeO_2/Al_2O_3	Lean	Lean	453	499	79.5
		Rich	428	487	56.5
	Rich	Lean	373	426	48
		Rich	378	434	54.5

function of temperature) all exhibit classical forms, which is why we preferred to gather the results in Table 1, where the main important points related to the reactivity are given:

—*Starting* T: temperature at which a noticeable amount (250 ppm) of CO_2 is detected in the outlet gas. This temperature corresponds to 5 and 2.5% conversions for the tests performed under lean and rich gas mixture, respectively.

—$T_{1/2}$: temperature at which 2500 ppm of the initial CO are converted to CO_2. This concentration corresponds to half conversion for the lean mixture and to a quarter conversion for the rich mixture.

—E_a: Apparent activation energy calculated at conversion lower than 20%.

2% Pt/Al_2O_3

On this catalyst, only two tests have been performed using the same gas composition for both the activation period and the light-off test by itself. Table 1 (lines 1 and 2) shows that both CO/O ratios (lean and rich) used lead to starting temperatures and $T_{1/2}$ of the same order of magnitude, indicating that the activity of the catalyst is quite independent either of the activation or the test gas composition.

Nevertheless, we note that the calculated apparent activation energy differs from one test to the other, but this result cannot be taken into account since the gas compositions (or more precisely the concentrations in O_{ads} and CO_{ads}) are not identical for both tests and interfere in the evaluation of the *apparent* activation energy. Thus, the comparison of E_a is only valid between two tests performed under the same gas mixture.

2% Pt–14.5% CeO_2/Al_2O_3

The presence of ceria together with platinum significantly modifies the situation. Indeed, as seen in Table 1 (lines 3 to 6) both the starting temperature and $T_{1/2}$ seem to depend exclusively on the composition of the *activating* mixture, the Pt–CeO_2/Al_2O_3 being much more active after a reducing (rich) pretreatment than after an oxidative (lean) one.

The comparison of the E_a indicates further that when the activation is performed under an oxidative mixture, the reactivity is similar to that of Pt/Al_2O_3, but that the presence of ceria leads to a great synergistic effect when the catalyst is activated under a reducing mixture: the E_a decreases from 94 kJ mol^{-1} on Pt/Al_2O_3 (Table 1, line 1) to 48 kJ mol^{-1} on Pt–CeO_2/Al_2O_3 (Table 1, line 5).

As a first conclusion from these tests, ceria does not seem to play any role in the reactivity of preoxidized platinum catalysts but it does enhance the reactivity of platinum when prereduced. In this last case, the presence of ceria together with platinum seems to lead to new very reactive sites, on which the reaction mechanism differs from that observed on simple Pt/Al$_2$O$_3$ samples (seen by the drastic modification of E_a).

CO + O$_2$ LIGHT-OFF USING LOW VVH CONDITIONS

In this section, we discuss the reactivity of the catalysts during a light-off performed at low VVH, either after a pure reducing pretreatment (step 3 of Fig. 1 in Part I (*1*)) or after a pure oxidative pretreatment (step 6). Taking into account the low value of the VVH, there might be a gap between the temperature at which 50% of the entering CO disappears and the temperature at which 50% of the entering CO goes out as CO$_2$. In order to be sure to measure a real half-conversion temperature, and not only a simple adsorption phenomenon, this characteristic temperature is taken on the CO$_2$ curve.

Prereduced Catalysts

Before performing the light-off tests by themselves, the catalysts were submitted to the reacting mixture (1.5% CO + 1.5% O$_2$/He) at room temperature until the outlet concentrations were constant and equal to the entering ones. Figure 2 shows the variation of the gaseous components at the outlet side of the reactor during this equilibration period.

When CO and O$_2$ are introduced together at the entrance of the apparatus, it is clear from Fig. 2a that the CeO$_2$/Al$_3$O$_3$ prereduced at 973 K under 1.5% CO/He consumes oxygen at RT, since only CO comes out during the first stage of the equilibration period. This phenomenon is tentatively attributed to the reoxidation of some non-stoichiometric oxides between CeO$_2$ and Ce$_2$O$_3$.

In contrast, the catalysts based on platinum (Pt/Al$_2$O$_3$: Fig. 2b and Pt-CeO$_2$/Al$_2$O$_3$: Fig. 2c) seem to consume more CO than O$_2$ (this does not mean that no oxygen at all is stored on these catalysts). This important CO consumption at RT is attributed to CO adsorption on the metallic platinum phase.

At the end of the equilibration period at RT, the temperature is increased (10 K/min) up to 973 K under the same reactive mixture (1.5% CO + 1.5% O$_2$/He): this is the light-off test itself whose resulting curves are given in Fig. 3. The temperature at which 50% of the initial CO goes out as CO$_2$ are gathered in Table 2.

For prereduced catalysts, we note a very significant increase of reactivity in the order CeO$_2$/Al$_2$O$_3$, Pt/Al$_2$O$_3$ and Pt-CeO$_2$/Al$_2$O$_3$ which was already observed in the light-off tests performed at high VVH.

14.5% CeO$_2$/Al$_2$O$_3$. Observation of the oxygen curve of Fig. 3a shows that part of the oxygen in excess in relation to the CO oxidation stoichiometry is consumed by the sample itself. This result is more clearly visualized in Fig. 4a, which shows that between 393 and 673 K a large part of the entering O$_2$ is stored by the sample. We saw previously that the prereduced CeO$_2$/Al$_2$O$_3$ was reoxidized at RT (Fig. 2a). This new observation shows that this reoxidation was only partial and probably proceeds further when the temperature is increased.

2% Pt/Al$_2$O$_3$. This catalyst exhibits an average activity, the starting temperature for CO$_2$ formation being around 423 K and the half-conversion temperature being 476 K.

2% Pt–14.5% CeO$_2$/Al$_2$O$_3$. The catalyst containing both platinum and ceria is much more reactive than the equivalent catalyst without ceria, since it leads to CO$_2$ even at very low temperature.

The amount of CO$_2$ detected between 393 and 623 K is greater than the expected one if 100% of the entering CO (1.5%, i.e., 15,000 ppm) were converted to CO$_2$. This excess of CO$_2$ correlates well with (and is then attributed to) the important amount of CO stored at RT (Fig. 2c).

Figure 4b shows that contrary to CeO$_2$/Al$_2$O$_3$, the Pt-CeO$_2$/Al$_2$O$_3$ catalyst does not consume a noticeable amount of oxygen for its own oxidation. From this result, it can be concluded that whereas CeO$_2$/Al$_2$O$_3$ does not reoxidize totally at RT, the catalyst containing platinum does so.

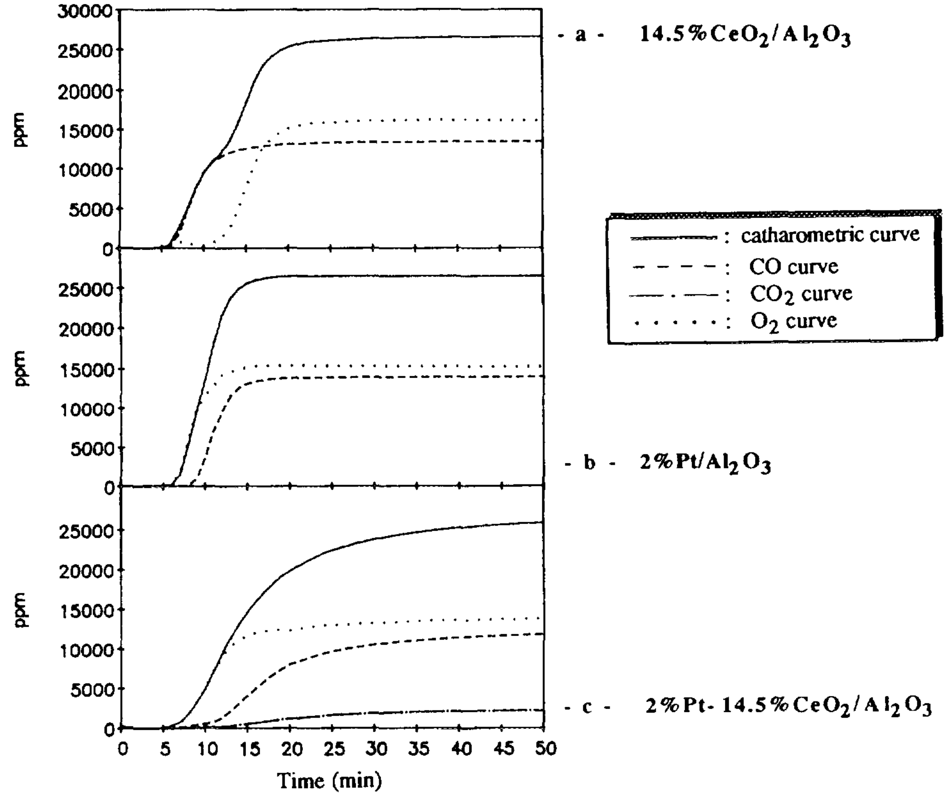


FIG. 2. Equilibration curves obtained just after the introduction of the 1.5% CO + 1.5% O_2/He mixture on prereduced catalysts: room temperature part of the light-off test performed at low VVH.

Preoxidized Catalysts

These tests are performed successively after the preceding light-off and a reoxidation treatment at 973 K under a *purely* oxidative atmosphere (5% O_2/He, see step 6 of Fig. 1 in Part I (*1*)).

2% Pt/Al_2O_3. This catalyst does not seem to be altered by the nature of the activating gas mixture. Indeed, the RT equilibration curves (Fig. 2a compared to Fig. 5a) or the light-off curves (Fig. 3a compared to Fig. 6a) are almost identical for both pretreatments. The difference in the $T_{1/2}$ is very small (see Table 2) and might be due to the fact that the platinum phase is less dispersed in the preoxidized catalyst because it has been subjected to six successive high-temperature treatments instead of only two for the prereduced Pt/Al_2O_3 sample.

2% Pt–14.5% CeO_2/Al_2O_3. Contrary to Pt/Al_2O_3 catalyst, the reactivity of Pt–CeO_2/Al_2O_3 catalyst seems to be determined by the pretreatment step. Indeed, although the prereduced Pt–CeO_2/Al_2O_3 sample is much more reactive than Pt/Al_2O_3, the preoxidized one exhibits exactly the same characteristics as the simple Pt/Al_2O_3 without ceria, either for the equilibration curves at RT or for the starting temperature and $T_{1/2}$.

As a conclusion of these low VVH light-off tests, we saw that for the equilibration curves at RT, the CeO_2/Al_2O_3 sample stored more oxygen than carbon monoxide, but that the reverse effect was observed for all catalysts containing platinum. The second point to be noted is that prereduced ceria seems to be reoxidized at RT: totally in the

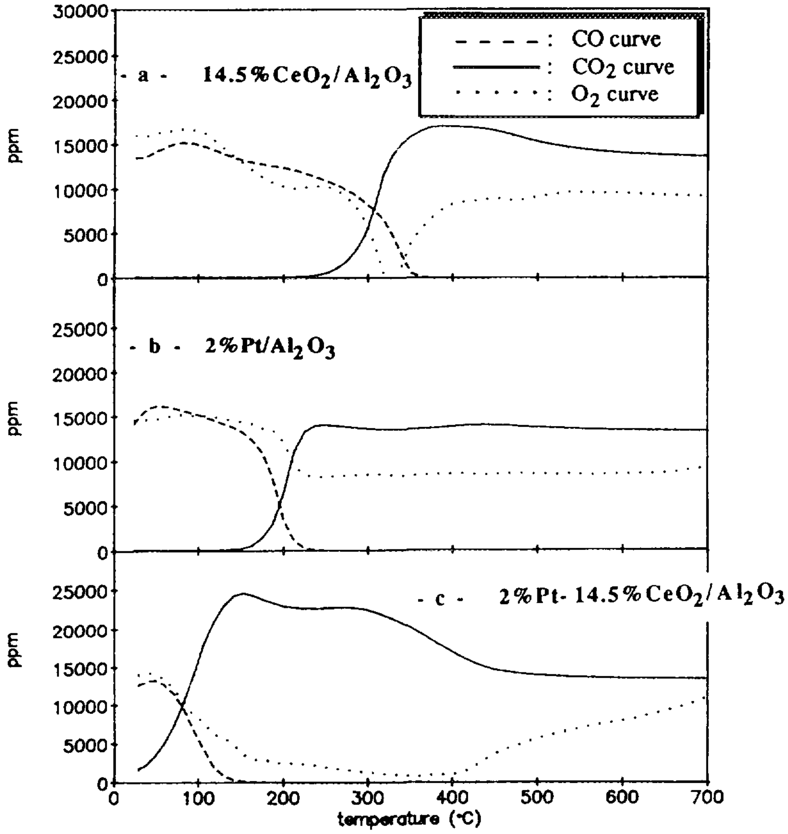


FIG. 3. Light-off tests performed at low VVH on prereduced catalysts.

presence of platinum and only partially in the absence of precious metal. In this last case, the ceria reoxidation goes further under an oxidative atmosphere when the temperature is increased. Moreover, these light-off tests at low VVH confirm the result, already obtained at high VVH, that the reactivity of Pt/Al$_2$O$_3$ is quite independent of the pretreatment gas composition and that for Pt–CeO$_2$/Al$_2$O$_3$, ceria participates in the catalyst reactivity if pretreated in a reducing atmosphere.

DISCUSSION

On the basis of the data at hand, we may try to deduce (i) the nature of the catalytic

TABLE 2

CO + O$_2$ Light-off Results Obtained with a Low Space Velocity: Temperature at Which 50% of the Entering CO Is Converted to CO$_2$

Catalyst	$T_{1/2}$ (K) on prereduced cata.	$T_{1/2}$ (K) on preoxidized cata.
2% Pt/Al$_2$O$_3$	476	499
2% Pt–14.5% CeO$_2$/Al$_2$O$_3$	357	477

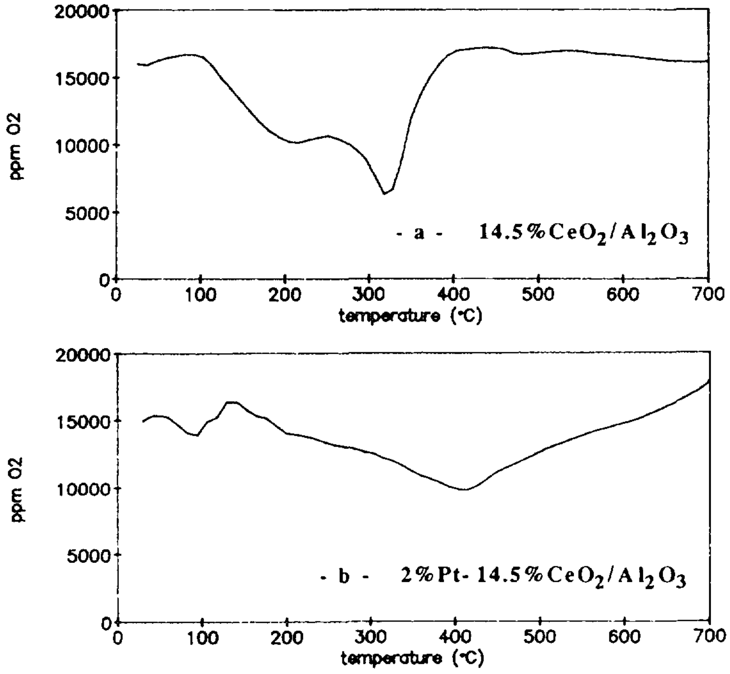


FIG. 4. Excess oxygen consumption in relation to the CO oxidation stoichiometry during the light-off tests at low VVH on prereduced catalysts. The excess O_2 curves are calculated from those of Fig. 3, by the following relation: Excess O_2 = "measured" O_2 + 1/2 measured CO_2.

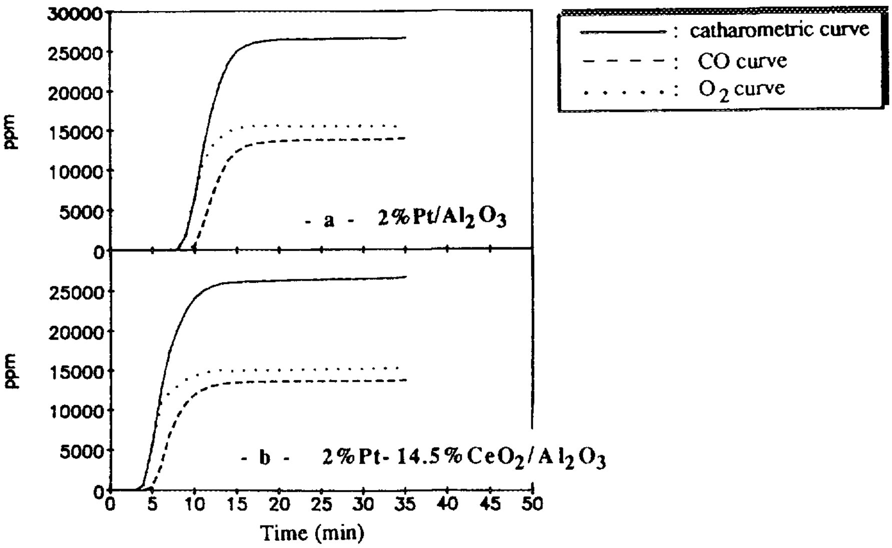


FIG. 5. Equilibration curves obtained just after the introduction of the 1.5% CO + 1.5% O_2/He mixture on preoxidized catalysts: room temperature part of the light-off test performed at low VVH.

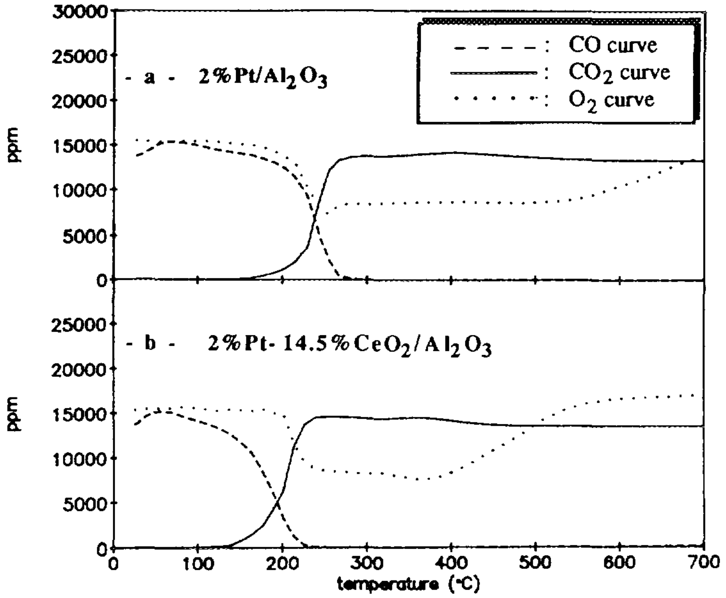
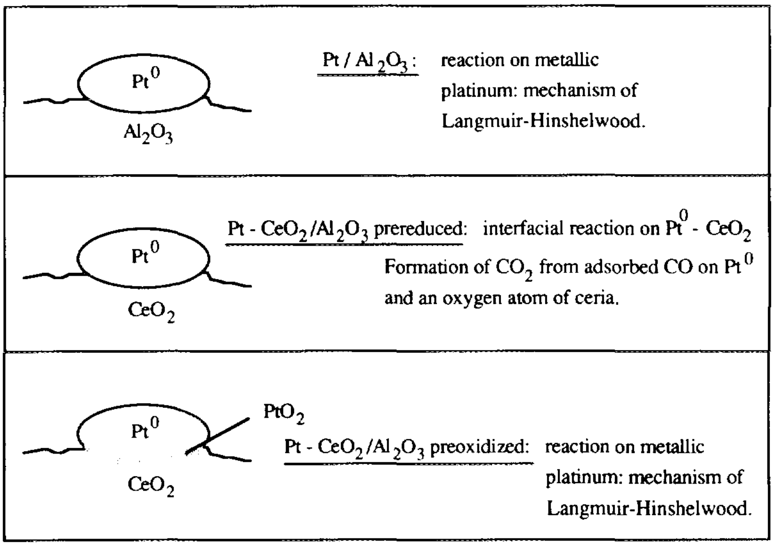


FIG. 6. Light-off tests performed at low VVH on preoxidized catalysts.

sites involved and (ii) the reaction mechanism by which CO is oxidized by O$_2$.

In order to know the oxidation state of the platinum phase at the beginning of each light-off test, one must examine the different pretreatment procedures for the low-VVH conditions and for the high-VVH conditions.

When the catalyst is prereduced, the platinum phase is clearly in its metallic state at



Pt / Al$_2$O$_3$: reaction on metallic platinum: mechanism of Langmuir-Hinshelwood.

Pt - CeO$_2$/Al$_2$O$_3$ prereduced: interfacial reaction on Pt^0 - CeO$_2$ Formation of CO$_2$ from adsorbed CO on Pt^0 and an oxygen atom of ceria.

Pt - CeO$_2$/Al$_2$O$_3$ preoxidized: reaction on metallic platinum: mechanism of Langmuir-Hinshelwood.

FIG. 7. Schematic representation of the different possible catalytic sites and reaction mechanisms for the oxidation of carbon monoxide by oxygen on Pt/Al$_2$O$_3$ and Pt-CeO$_2$/Al$_2$O$_3$ catalysts.

the end of the pretreatment. The situation is less evident in the case of preoxidized samples. For the low-VVH conditions, the preoxidation is performed at 973 K, where the PtO_2 oxide is not stable (*18*), and is then cooled to room temperature under pure helium: at this point, the platinum phase is therefore in the metallic state. For the high-VVH conditions, the preoxidation is performed at 763 K (under 0.5% CO + 0.5% O_2/N_2), that is to say, inside the temperature range where the PtO_2 is stable (*18*), and is then cooled under the same feedstream. When the temperature becomes lower than ca. 673 K, the platinum oxide is reduced by the gaseous CO but cannot be reoxidized by oxygen. This means that at the end of the "oxidative" pretreatment, the platinum phase is also reduced.

As a conclusion, we note that after each type of pretreatment (reducive or oxidative), the platinum phase should be in the metallic state.

2% Pt/Al_2O_3

On the Pt/Al_2O_3 catalyst it has been shown that the reactivity is independent of the CO/O ratio in the feedstream used for either the activation period or the test period. The catalytic activity is then attributed in all cases to metallic platinum sites, Pt^0.

Moreover, the light-off tests performed at low VVH on this catalyst have shown that at room temperature under the CO + O_2 gas mixture, the platinum phase is predominantly covered by adsorbed CO. This result is in agreement with an infrared study of competitive adsorption of gaseous CO and O_2 on a platinum phase (*19*) which led to the conclusion that oxygen could hardly dissociate on the surface because of strong CO adsorption.

We think that the light-off activity of Pt/Al_2O_3 is very well explained by the classical mechanism of Langmuir–Hinshelwood: at low temperature the platinum particles are mostly covered by CO which inhibits the dissociative adsorption of gaseous oxygen. When the temperature is increased (373–423 K in Fig. 3b) the competitive adsorption of CO and O_2 enables a small oxygen adsorption to occur. Eventually, at temperatures higher than 423 K (Fig. 3b and 6a) the desorption of some CO_2 molecules restores adsorption sites on the surface which become vacant for O_2 dissociation, and enable the reaction rate to increase.

2% Pt–14.5% CeO_2/Al_2O_3 Prereduced

For both experimental conditions the prereduced $Pt–CeO_2/Al_2O_3$ catalyst appears to be much more active than the simple Pt/Al_2O_3. Taking into account the fact that at the beginning of the light-off tests the platinum phase is reduced and the cerium phase is oxidized to CeO_2, the very high activity is attributed to catalytic sites localized at the interface between metallic platinum and ceria, the $Pt^0–CeO_2$ interface.

As seen in Fig. 2c this catalyst also adsorbs predominantly CO on its surface during the stabilisation period at room temperature under the CO + O_2 gaseous mixture. This means that, as already mentioned for the Pt/Al_2O_3 catalyst, the platinum phase is mostly covered by CO and exhibits only very few vacant sites for the dissociative adsorption of oxygen. Nevertheless, this strong CO adsorption does not affect the low-temperature activity of the catalyst. This observation indicates that the dissociative adsorption of O_2, which was the rate determining step on Pt/Al_2O_3, does not limit the reaction on prereduced $Pt–CeO_2/Al_2O_3$.

These points can be explained by the following reaction mechanism. At room temperature the platinum atoms of the $Pt–CeO_2$ interface are mostly covered by CO_{ads}. These CO_{ads} do not dispose of any atomic oxygen on platinum but they are able to pick up the "oxide" oxygen atoms provided by the interfacial ceria as already demonstrated in Part I of this work (*1*). Thus, we think that the first stage of the reaction consists of the formation of CO_2 via the reduction of the interfacial ceria by carbon monoxide adsorbed on platinum. The CO_2 desorption leads to vacant sites on the interfacial Pt and makes possible the dissociative adsorption of gaseous oxygen. Ceria is then regenerated by a spill-over phenomenon of O$_{ads}$ (on the Pt sites of the Pt–CeO$_2$ interface) toward Ce$_2$O$_3$ and reoxidation of the interface into CeO$_2$. This interpretation is described by the three following steps:

$$CO_{ads} + 2\,CeO_2 \rightarrow CO_2 + * + Ce_2O_3 \quad (1)$$

$$1/2\,O_2 + * \rightarrow O_{ads} \quad (2)$$

$$O_{ads} + Ce_2O_3 \rightarrow 2\,CeO_2 + * \quad (3)$$

where "*" stands for an adsorption site on platinum and "ads" for an adsorbed species.

From this mechanism, the key point of the very high activity observed on the prereduced Pt–CeO$_2$ catalyst would be the possibility of initiating the CO oxidation without any vacant sites for the dissociation of oxygen.

2% Pt–14.5% CeO$_2$/Al$_2$O$_3$ Preoxidized

The Pt–CeO$_2$/Al$_2$O$_3$ catalyst pretreated in an oxidative atmosphere does not exhibit the very high activity observed on the prereduced sample. In fact, its behaviour is almost identical to that of the less reactive Pt/Al$_2$O$_3$ catalyst (see Fig. 6 and Table 1), and is then attributed to the same type of sites, i.e., Pt^0 sites.

Therefore, it appears that the Pt^0–CeO$_2$ sites which were responsible for the very high activity of the prereduced sample are deactivated by an oxidative pretreatment. Since ceria is present as CeO$_2$ after both pretreatments, the only explanation of the Pt^0–CeO$_2$ interface deactivation is a partial oxidation of the platinum atoms next to ceria.

At the beginning of this discussion we arrived at the conclusion that in each case, platinum was reduced at the initial stage of the light-off test, but this result was obtained by assuming that as in Ref. (*18*), the platinum oxide was only stable in the range 673–823 K approximately. In fact, numerous authors (*20–22*) have shown that the presence of ceria could stabilise the oxidized state of platinum at higher temperature than 823 K. For this reason we believe that after an oxidative treatment of Pt–CeO$_2$/Al$_2$O$_3$ catalyst, the "bulk" platinum should be reduced when the interfacial platinum should be oxidized because of its interaction with ceria.

The very reactive Pt^0–CeO$_2$ interface being oxidized into PtO$_2$–CeO$_2$ which is inactive, the reaction takes place only on the remaining Pt^0 sites of the "bulk" platinum. Therefore, it exhibits the same behaviour as the simple Pt/Al$_2$O$_3$ catalyst via a Langmuir–Hinshelwood mechanism.

CONCLUSIONS

The activities of Pt/Al$_2$O$_3$ and Pt–CeO$_2$/Al$_2$O$_3$ catalysts have been tested for the oxidation of carbon monoxide by oxygen, using two sets of complementary experimental conditions (high and low space velocity), and different percentage CO/O$_2$ ratios either for the activation period or for the light-off test itself. As a result of these tests we have pointed out the drastic influence of the pretreatment step on the subsequent reactivity of Pt–CeO$_2$/Al$_2$O$_3$ catalyst. Indeed, this sample is much more active than Pt/Al$_2$O$_3$ if prereduced, but it exhibits the same behaviour as the sample Pt/Al$_2$O$_3$ catalyst if preoxidized.

As indicated in Fig. 7, catalytic sites and reaction mechanisms have been proposed in order to explain these effects:

—The activity of the Pt/Al$_2$O$_3$ catalyst has been ascribed to a classical Langmuir–Hinshelwood mechanism on Pt^0 sites, assuming that at low temperature carbon monoxide is strongly adsorbed on the metallic phase and inhibits the dissociative adsorption of oxygen.

—The very high activity of the prereduced Pt–CeO$_2$/Al$_2$O$_3$ sample has been attributed to Pt^0–CeO$_2$ sites localized at the platinum–ceria interface: the key point of the low-temperature reactivity would be the opportunity to initiate the reaction by the oxidation of CO adsorbed on platinum due to "oxide" oxygen from ceria.

—When the $Pt-CeO_2/Al_2O_3$ catalyst is preoxidized, we believe that the Pt^0-CeO_2 active sites of the interface are deactivated into PtO_2-CeO_2 when the "bulk" platinum keeps a metallic state. In this situation, the reaction only occurs on Pt^0 sites, exactly as for the Pt/Al_2O_3 catalyst and the promoter effect of ceria disappears.

These mechanisms are similar to those proposed by Oh and Eikel (5) on Rh/Al_2O_3 and $Rh-CeO_2/Al_2O_3$, and by Diwell *et al.* (*23*) on alumina-supported Pt and Rh catalysts with and without ceria.

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