# Activity of Rh<sup>x+</sup> Species in CO Oxidation and NO Reduction in a CO/NO/O<sub>2</sub> Stoichiometric Mixture over a Rh/CeO<sub>2</sub>-ZrO<sub>2</sub> Catalyst

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The catalytic activity of a 0.30 wt% Rh/CeO<sub>2</sub>-ZrO<sub>2</sub> catalyst (25%  $ZrO_2$  in weight) 188 m<sup>2</sup>g<sup>-1</sup> was studied in the oxidation of CO and reduction of NO in a CO/NO/O2 stoichiometric mixture, in the temperature range of 298-773 K. The hydrogenation of benzene, a structure insensitive reaction was used for counting surface Rh(0) atoms after either thermal treatment of the catalyst in hydrogen at 773 K, or reduction by the stoichiometric CO/O<sub>2</sub>/NO reaction mixture. The bibliography shows that the turnover rate over Rh<sup>x+</sup> is lower than that over Rh(0) by two orders of magnitude. Rhodium supported on CeO<sub>2</sub>-ZrO<sub>2</sub> submitted to the above reducing treatments was found to be totally inactive in benzene hydrogenation but active in CO/NO/O2 reaction. As a conclusion the present catalyst consisted exclusively of Rh<sup>x+</sup> surface species. The catalytic behaviour of this rhodium-supported catalyst was interpreted in terms of multiple active sites containing one Rhx+ ion grafted in the support and able to chemisorb CO and/or NO as for a rhodium homogeneous complex. This Rh<sup>x+</sup> is associated with two adjacent oxygen vacancies (and corresponding Ce<sup>3+</sup> cations) linked to the reduction of the support and permitting oxygen and NO chemisorption. A method was defined for counting surface Rh<sup>x+</sup> containing multiple sites by measuring the number of NO molecules adsorbed at low temperature and desorbing at the temperature of light-off of CO. A (NO/Rh<sup>x+</sup>) ratio of 2 was found, in agreement with a dinitrosyl species reaction intermediate. © 1998 Academic Press

## I. INTRODUCTION

During the last years, the various reactions occurring between CO, NO, and  $O_2$  over three-way metallic catalysts were the subject of numerous studies (1–4). As yet, active sites for these reactions are not well defined. Authors generally believe that zero-valent metal is responsible for the catalytic activity (1, 2) as is the case for CO/O<sub>2</sub> and CO/NO reactions over rhodium catalysts. It is known that on rhodium metal, the CO/O<sub>2</sub> reaction is structure insensitive (5) and that the rate-determining step corresponds to the reaction of adsorbed CO molecule with adsorbed oxygen atoms to produce  $CO_2$  (6). When carried out in transient conditions, the metallic surface can be considered as fully covered by CO at low temperatures, which prevents the  $O_2$  dissociation (7–9). Increasing reaction temperature can make  $O_2$  able to compete with CO for metallic adsorption sites. Once dissociatively adsorbed, oxygen oxidizes CO to  $CO_2$ , whose desorption generates new adsorption sites. When the metallic phase is dispersed on a reducible support (CeO<sub>2</sub>), CO can oxidize at lower temperatures by reacting with oxygen ions at the metal–support interface (3, 7, 10, 11). Zafiris *et al.* (9, 12) for Rh/CeO<sub>2</sub> catalysts have assumed that oxygen from reduced ceria migrate to the metallic rhodium surface where it can oxidize CO.

The CO/NO reaction occurs more easily on rhodium metal than on Pt(0) or Pd(0) (13, 14), owing to its greater ability to dissociate NO with regards to other metals, due to the position of the Fermi level in rhodium metal, localized above the  $\pi^*$  orbital of NO (15, 16). The reverse situation occurs for Pt(0) and Pd(0). When NO adsorbs on Rh(0), an enhanced charge transfer takes place from Rh(0) to the  $\pi^*_{NO}$  orbital, increasing the back donation effect and, consequently, the weakening of the N-O bond.

Contrary to the CO/O<sub>2</sub> reaction, the CO/NO reaction is structure sensitive (1, 17, 18), due to the fact that NO dissociates differently as a function of the considered metallic planes (18). For alumina supported rhodium, Kaspar *et al.* (17) have shown that at room temperature more than 60% of NO molecules dissociate on the Rh(0) particles and that the NO dissociation increases with the particle diameter; so, above 15 Å, more than 90% of the adsorbed NO dissociates over Rh(0) particles, the remaining 10% desorbing as N<sub>2</sub>O and NO at 563 K. According to Cho *et al.* (19, 20), the N<sub>2</sub>O desorption at low temperature is correlated with the beginning of the CO/NO reaction which can only start with the accessibility of the active sites initially occupied by N<sub>2</sub>O. This N<sub>2</sub>O formation clearly indicates that

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nitrogen atoms can bind, prior to NO dissociation. Thus, the formation of N<sub>2</sub>O does not necessarily involve the interaction at the metal surface of an adsorbed nitrogen atom with an adsorbed NO, as usually admitted, but can also result from the breaking of the NO bond of hyponitrite species  $(N_2O_2)^{2-}$  originating from the dimerization of two adjacent adsorbed NO (21–23):  $(NO)_{2ads.} \rightarrow N_2O_{gas} + O_{ads.}$ . N<sub>2</sub>O formation was also observed over Pt/Al<sub>2</sub>O<sub>3</sub> and Pt-CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts, especially in the case of highly dispersed metallic phase (22). Let us also note, that rhodium sites generating  $(NO)_2$  species do not exclusively consist of zerovalent rhodium atoms, since dinitrosyl complexes can be evidenced on exchangeable rhodium ions in zeolites (24).

As for  $CO/O_2$  reaction, reduced ceria can significantly improve the catalytic activity of the system in the CO/NO reaction (25, 26), by the presence of oxygen vacancies at the metal support interface favouring the NO reduction; oxygen atoms originating from the dissociation of NO at the interfacial sites could locate in the oxygen vacancies, while retaining a labile character which makes possible an additional contribution to the CO oxidation.

In the presence of the three reagents (CO, NO, O<sub>2</sub>), the two preceding reactions are competing, due to the fact that NO and  $O_2$  compete for the active sites of the samples for the CO/NO/O<sub>2</sub> reactions. Leclercq et al. (3) have observed for Pt/Al<sub>2</sub>O<sub>3</sub> low NO conversion as long as O<sub>2</sub> is present in the reagent mixture and have concluded that the NO adsorption sites could be blocked by adsorbed oxygen. Conversely, for Rh/Al<sub>2</sub>O<sub>3</sub>, Oh et al. (27) have shown that the presence of NO in the reagents could inhibit the CO/O<sub>2</sub> reaction, at low CO/NO conversion. At low temperature of reaction, these authors have found that undissociated NO molecules are present at the surface and could block the adsorption sites for the  $CO/O_2$  reaction. When the reaction temperature increases, these NO molecules dissociate on the metal, with a simultaneous formation of N<sub>ads</sub> and O<sub>ads</sub>. adsorbed species which can easily desorb from the metallic surface  $(N_{ads.} + N_{ads.} \rightarrow N_2 \text{ and } CO + O_{ads.} \rightarrow CO_2)$ , regenerating active sites for the CO/O<sub>2</sub> reaction. Even if conclusions are sometimes controversial, as it is difficult to determine which of NO and O<sub>2</sub> inhibits the active sites at low temperature, on the whole it appears that the CO/NO/O2 reactions can be considered as the succession of the CO/O<sub>2</sub> and CO/NO reactions, with closely dependent light-off temperatures (temperature for 50% conversion of reactant).

Ceric oxide additive, here again, confers to the catalysts some promoting effect on their activity in the  $CO/NO/O_2$ reactions, by generating at the metal–support interface additional bifunctional sites (3, 28); under an oxygen-deficient atmosphere, CO can migrate at the metal support interface to be oxidized by a ceria lattice oxygen with concomitant oxygen vacancy formation. The so-created oxygen vacancies at the metal–support interface can act as NO dissociation centers, or they can accomodate oxygen species originating from the dissociation of  $O_2$  on the metallic surface,

$$\begin{split} &CO^* + (O_V) \rightarrow CO_{2gas} + (_V) + (^*) \\ &NO^* + (_V) \rightarrow N^* + (O_V) \\ &(_V) + O^* \rightarrow (^*) + (O_V), \end{split}$$

where \* is the adsorption site on the metal, (<sub>V</sub>) is the oxygen vacancy on the support, (O<sub>V</sub>) is the oxygen ion located in an oxygen vacancy.

From the above bibliography data, it appears that the  $CO/NO/O_2$  reactions are complex and result from the competition between the  $CO/O_2$  and CO/NO reactions. The active sites are not yet well defined, but it is generally admitted that the reaction takes place both on the reduced metal and at the metal support interface.

High thermal stability and enhanced reducibility for the ceria-containing support are essential requirements. It has been found that incorporation of  $ZrO_2$  into a solid solution with CeO<sub>2</sub> strongly favours the reduction of the support (29, 30). These observations makes the catalytic properties of the CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts of strong interest. We have selected a CeO<sub>2</sub>-ZrO<sub>2</sub> solid solution of high specific surface area loaded with rhodium. This last metal being chosen for its ability to enhance the NO conversion (1, 2).

The present work was devoted to the characterization (identification and counting) of active sites for the CO/ $NO/O_2$  reactions present on a high surface area Ce/Zr oxides supported rhodium catalyst. Catalyst preparation, metal content, reactant mixture composition were carefully chosen to study the Rh/CeO<sub>2</sub>-ZrO<sub>2</sub> sample using experimental conditions as close as possible to those used for real postcombustion reactions.

## **EXPERIMENTAL**

## Catalyst Preparation

The CeO<sub>2</sub>-ZrO<sub>2</sub> support (25% ZrO<sub>2</sub> in weight) was a high specific surface area (188 m<sup>2</sup>g<sup>-1</sup>) solid solution supplied by Rhône Poulenc, after calcination at 623 K, they were nitrates containing support even after this calcination step. The Rh(Cl)/CeO<sub>2</sub>-ZrO<sub>2</sub> samples were prepared by anionic exchange from an acidic solution of RhCl<sub>3</sub> · 3H<sub>2</sub>O (Johnson Matthey) adjusted with HCl at pH = 1.9. The amount of RhCl<sub>3</sub> · 3H<sub>2</sub>O introduced into the solution was calculated to obtain a metal loading of 0.30 wt%. It was verified that the presence of residual nitrate ions did not perturb the anionic exchange process. After exchange the samples were filtered, washed with distilled water, and dried in air for 3 h. The anionic exchange with rhodium complexes was reproducible.

## Catalyst Characterization

Specific surface area measurements were determined by physisorption of nitrogen at 77 K using a Quantasorb Jr. dynamic system, fitted out with a catharometer detector. The specific areas were calculated using the BET method. Samples studied by high resolution electron microscopy were ground and dispersed in pure ethanol; the suspension was stirred in an ultrasonic bath and one drop was deposited on a carbon-coated grid. HRTEM images were performed with a JEOL JEM 100 CXII apparatus equipped with a top entry device and operating at 100 kV.

Infrared spectra of the various samples were recorded using a Brücker IFS 66-V interferometer. After thermal treatment at a given temperature, samples were cooled to room temperature and flushed with argon. Spectra were recorded *in situ* at 298 K and accumulated during 32 scans. The standard resolution was 4cm<sup>-1</sup>.

Temperature-programmed reductions (TPR) were performed on 50 mg of CeO<sub>2</sub>-ZrO<sub>2</sub> or Rh/CeO<sub>2</sub>-ZrO<sub>2</sub> samples placed in a conventional quartz microreactor using a gas mixture of 5 vol% H<sub>2</sub> diluted in argon. The total flow rate was controlled by mass flow meters and was set to 25 cm<sup>3</sup>min<sup>-1</sup>. Experiments were carried out from room temperature to 1173 K at a heating rate of 5 K min<sup>-1</sup>. TPR calibration was carried out by simulating the complete hydrogen consumption of the hydrogen content of the reactant mixture (5 vol%  $H_2$ /Ar). For that, a 100% Ar flow was sent in the reactor, while the reactant mixture was flowing in the reference branch. Such a calibration allows the correct evaluation of the surface area of the TPR peaks. Samples were previously submitted to an oxidative treatment at 673 K, in order to eliminate  $NO_3^-$  ions originating from the support synthesis and make reproducible TPR plots. Note that such a treatment does not significantly modify the surface area of the samples, no more than their rhodium or chloride contents. It was assumed that the rhodium phase consisted in well dispersed Rh<sub>2</sub>O<sub>3</sub> cristallites after the oxidizing treatment.

X-ray-induced photoelectron spectra of the reduced CeO<sub>2</sub>-ZrO<sub>2</sub> supports were recorded on a spectrometer equipped with a non-monochromatized X-ray source (Mg-K $\alpha_{1,2}$ ) and an electrostatic hemispherical analysis device working in a fixed analysis transmission (FAT) mode. Binding energies were corrected from charge effects by reference to the C<sub>1s</sub> peak of carbon contamination fixed at  $E(C_1) = 285$  eV. The pressure in the spectrometer chamber was approximately  $5 \times 10^{-9}$  Torr ( $6.6 \times 10^{-7}$  Pa) during data acquisitions. Prereduced samples were transferred under vacuum from the reactor into glass tubes and then placed into the spectrometer chamber under argon atmosphere using a glove box.

Benzene hydrogenation measurements were carried out in a conventional system described elsewhere (32). Reactions were performed at a total pressure of 760 Torr (101 kPa.) in a differential dynamic microreactor. The total flow rate was set to 100 ml min<sup>-1</sup>. The partial pressure of benzene was 51.8 Torr  $(6.9 \times 10^3 \text{ Pa})$  so that a zero-order relative to benzene was obtained. In a typical run the catalyst prior to run was pretreated at 773 K in flowing H<sub>2</sub> or in the postcombustion mixtures (CO/NO/O<sub>2</sub> or CO/O<sub>2</sub>). The catalyst was then cooled to temperature of reaction under helium and the C<sub>6</sub>H<sub>6</sub>/H<sub>2</sub> mixture was passed over the catalysts. Cyclohexane was the only product of the reaction.

The catalytic activities of the samples were characterized in the CO/NO/O<sub>2</sub> reaction in temperature-programmed experiments from 298 to 773 K (light-off conditions) at a constant heating rate of 453 Kh<sup>-1</sup> with a space velocity from 90 to 125,000  $h^{-1}$ . Catalytic tests were performed at atmospheric pressure in a flow reactor. The feed stream (15 Lh<sup>-1</sup>) consisted of a stoichiometric gas mixture containing 1.5 vol% CO, 0.20 vol% NO, and 0.65 vol%  $O_2$  in helium, the composition of which being monitored by mass flowmeters. The catalyst sample (200 mg) was placed into a quartz reactor in an oven whose heating rate was monitored by a West 2050 programmator. First a CO/NO/O<sub>2</sub> reaction up to 773 K was made before any catalytic run in order to get reproducible data and, more particularly, to desorb any nitrate preadsorbed ions due to the support synthesis. Continuous analysis of the gas mixture at the inlet and at the outlet of the reactor was performed by a Maihak Finor infrared detector for CO, a Thermoelectron chemiluminescent NO/NO<sub>x</sub> analyzer for NO, and by gas chromatography to control the eventual presence of  $N_2O$  in the effluents. Prior to each catalytic run, fresh samples were heated at 773 K in the reactant mixture (453 K  $h^{-1}$ ), then cooled to room temperature in helium. Experimental data were given as conversion versus temperature plots allowing the determination of the temperatures of light-off (50% conversion) of reactants and the temperature at which 98% of the total conversion has been reached  $(T_{98\%})$ .

#### **RESULTS AND DISCUSSION**

The catalytic activity of  $CeO_2$ - $ZrO_2$  or rhodium supported over  $CeO_2$ - $ZrO_2$  samples in the postcombustion reactions was characterized after a standard thermal pretreatment in the stoichiometric feed.

## 1. Reducing Character of the CO/NO/O<sub>2</sub> Reactant Mixture

It was observed after pretreatment of catalysts at 773 K, either under the stoichiometric CO/NO/O<sub>2</sub> mixture, or under pure hydrogen, that the catalytic behaviour displayed by these materials in the postcombustion reactions are similar, as shown by the temperatures of light-off of CO and NO and 98% conversion temperatures (Table 1).

It was easily demonstrated that under hydrogen at 773 K,  $Ce^{4+}$  ions of ceria after reduction reduced to  $Ce^{3+}$ , as shown first by the increase of intensity of the XP signals

TABLE 1Catalytic Characteristics of the Reduced Samples in the CO/NO/O2 Reactions (1) Prereduced at 773 K in the (CO/NO/O2) Reactant Mixture, (2) Prereduced at 773 K in H2

Catalysts	Rh (wt%)	$\tau_{\rm CO^*}$	T <sub>loco</sub> (K)	T <sub>loNO</sub> (K)	Т <sub>98%</sub> (К)
CeO <sub>2</sub> -ZrO <sub>2</sub>	0.00	83	613	736	at 773 K $\tau_{\rm CO} = 73.8$ $\tau_{\rm NO} = 96.5$
<ol> <li>(1) Rh/CeO<sub>2</sub>-ZrO<sub>2</sub></li> <li>(2) Rh/CeO<sub>2</sub>-ZrO<sub>2</sub></li> </ol>	0.30 0.30	82 80	477 456	500 480	562 553

*Note.*  $\tau = \text{conversion \%}$ ,  $T_{\text{lo}} = \text{temperature of light-off}$ ,  $T_{98\%} = \text{temperature at which the total conversion reaches 98\%}$ ,  $\tau_{\text{CO}*} = \text{CO conversion when NO just begins to be converted.}$ 

 $u'(E_B=904.7~eV)$  and  $v'(E_B=886.2~eV)$  characteristics of  $Ce^{3+}$  in the X-ray-induced photoelectron spectra of the Ce(3d) level (33) (Fig. 1).

Then by the presence of hydrogen consumption peaks in the TPR profiles (Fig. 2) which can be ascribed to surface and bulk ceria reduction occurring respectively at 673 and 785 K and at lower temperatures in the presence of rhodium (below 473 K and at 548 and 733 K). The shift of the TPR peaks towards the lower temperatures of reduc-



**FIG. 1.** XP spectra of the Ce3d signal in the CeO<sub>2</sub>-ZrO<sub>2</sub> support before (1) and after (2) reduction in hydrogen at 773 K.



FIG. 2. Thermoprogrammed reduction in a 5 vol%  $H_2/Ar$  (heating rate 5 K · min.<sup>-1</sup>, total flow 25 cm<sup>3</sup> min.<sup>-1</sup>) of the fresh Rh/CeO<sub>2</sub>-ZrO<sub>2</sub> sample (solid line) and of the corresponding unloaded support (dashed line).

tion can suggest the occurrence of an hydrogen spillover effect implying the formation of rhodium metal. In agreement with already published data (29, 31) the rhodium precursor is reduced in Rh(0) atoms at low temperatures (in the 323–523 K temperature range, probably below 373 K). At this point of the TPR process, where Rh(0) is available, a spillover effect of H<sub>2</sub> in the presence of rhodium metal occurs and favours the surface reduction of the support. Furthermore, as soon as formed, Rh(0) atoms migrate over the surface, locate into cationic vacancies of the support, and are reoxidized as Rh<sup>x+</sup> with surrounding Ce<sup>4+</sup> cations; Zr<sup>4+</sup> is considered to enhance the stabilization of rhodium at the oxidized state.

Finally by the appearance of the 2124 cm<sup>-1</sup> infrared band (above 623 K for the bare support, and as low as 423 K for the rhodium-containing catalyst), characteristic of the  ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$  transition of the Ce<sup>3+</sup> ion formed in both the ceria surface and the bulk of the oxide support according to Binet *et al.* (34) (Fig. 3).

The use of the reactant mixture (CO/NO/O<sub>2</sub>) instead of H<sub>2</sub> for the pretreatment of Rh/CeO<sub>2</sub>-ZrO<sub>2</sub> does not modify the catalytic behaviour of this sample. This implies a similar reducing effect of the stoichiometric mixture and of H<sub>2</sub> with regards to the solid. It was checked that a fresh 0.3 wt% Rh/CeO<sub>2</sub> (144  $m^2g^{-1}$ ) did not hydrogenate benzene, whereas after treatment under H<sub>2</sub> or under the stoichiometric CO/NO/O2 reactants mixture at 723 K, the  $C_6H_6/H_2$  reaction occurred. The percentages of zero-valent metal exposed reduced, using the structure-insensitive reaction concept (32), were quite similar whatever the nature of the pretreating atmosphere (20.0% under  $H_2$  and 19.0% under the reactant mixture); this unambiguouly affords evidence of the reducing character of the CO/NO/O2 feed. The catalyst reduction under the stoichiometric mixture is necessarily due to the presence of CO which can reduce ceria (35), without modifying the oxidation state of  $Zr^{4+}$ (as in the presence of  $H_2$ ). Moreover, we can state that the Rh/CeO<sub>2</sub>-ZrO<sub>2</sub> reduction takes place below 523 K, before



FIG. 3. Infrared spectra in the 2000–2300 cm<sup>-1</sup> frequency interval of the CeO<sub>2</sub>-ZrO<sub>2</sub> support as a function of the temperature of reduction in a 5 vol% H<sub>2</sub>/Ar.

the beginning of the  $CO/O_2$  reaction since the conversion versus Tplots of the not pretreated sample does not differ from that of the sample pretreated in the reactant mixture (Fig. 4, Table 1). In the presence of CO, the reduction of the metallic precursor (Rh<sup>3+</sup>) to Rh(0) can also be predicted, concomitantly with the reduction of the support. Unfortunately, for the Rh(0)/CeO<sub>2</sub>-ZrO<sub>2</sub> system, the eventual presence of zero-valent rhodium cannot be shown by



FIG. 4. CO (dashed line) and NO (solid line) conversion curves in the 298–773 K temperature range of the  $CeO_2$ - $ZrO_2$  support (a) and of the Rh/CeO\_2- $ZrO_2$  sample (b), both pretreated in the CO/NO/O<sub>2</sub> mixture at 773 K.

HRTEM or XPS, due to the lack of contrast for the electron microscopy plates and, in both cases, due to the very low rhodium content of the samples. In contrast, it was possible to show unambiguously the presence (or absence) of Rh(0) on the surface of the samples before and after pretreatment in the reactant mixture at 773 K by measuring their hydrogenous activity in hydrogenation of benzene (32).

In fact, it was verified that the considered Rh/CeO<sub>2</sub>-ZrO<sub>2</sub>  $(25 \text{ wt}\% \text{ ZrO}_2)$  samples never display any activity in the  $C_6H_6/H_2$  reaction. One can wonder about the origin of the lack of hydrogenous activity of these samples. It cannot be ascribed to some lack of accessibility of Rh(0) for three main reasons: first, there is no support sintering, as CeO<sub>2</sub>-ZrO<sub>2</sub> reduces at 773 K in H<sub>2</sub> with only 20% loss of its initial surface area (36) and there is no metal encapsulation by the reduced support at 773 K, since for lower reduction temperatures (573 K) for which the encapsulation effect cannot occur, the reduced sample is already inactive in benzene hydrogenation. Furthermore as it will be seen, hereafter, rhodium species are quite accessible for  $CO/NO/O_2$  reactions. So, assuming that everything remain the same when the reactant mixture is used as reducing agent, it appears that rhodium in Rh/CeO<sub>2</sub>-ZrO<sub>2</sub> treated at 773 K in H<sub>2</sub>, or in the CO/NO/O<sub>2</sub> mixture, is stabilized at the catalyst surface as non hydrogenant "oxidized Rh<sup>x+</sup> species," due to a strong "rhodium-support" interactions.

## Catalytic Activity of the Reduced CeO<sub>2</sub>-ZrO<sub>2</sub> Support, in the CO/NO/O<sub>2</sub> Reactions (Fig. 4a)

Let us note that the reactant mixture composition is such that the totality of  $O_2$  in this feed cannot oxidize more than 87% CO. At 523 K NO desorption occurs, suggesting that NO molecules were preadsorbed on the active sites created during the reduction step of the sample. Simultaneously, CO oxidation starts, involving exclusively oxygen of the reactant mixture and in no case oxygen originating from NO dissociation, as NO is leaving the surface. CO and NO conversions are not complete at 673 K but can reach 100% at higher temperatures. In the present case active sites must be Ce<sup>3+</sup> ions and their associated oxygen vacancies.

So, concerning the reduced CeO<sub>2</sub>-ZrO<sub>2</sub> support, the following reaction steps can be proposed:

(a) NO from the reactant mixture adsorbs at 298 K in the oxygen vacancies of the reduced support.

(b) in the 523–573 K temperature range adsorbed NO desorbs from the support surface, liberating the oxygen vacancies required for the dissociative adsorption of  $O_2$  which reacts (at the dissociated state) with CO adsorbed on the support.

(c) at higher temperature (653 K), when the totality of the reactant oxygen is consumed in the oxidation of the quasitotality of CO, a new NO adsorption can occur, leading to NO reduction and CO oxidation.

# 3. Catalytic Activity of the Reduced Rh/CeO<sub>2</sub>-ZrO<sub>2</sub> Catalyst in the CO/NO/O<sub>2</sub> Reactions (Fig. 4b)

In the presence of rhodium (Fig. 4b), the reaction steps of the postcombustion reaction are quite similar to those observed in the study of the activity of the unloaded support (Fig. 4a). However, the catalytic activity is strongly enhanced in the presence of metal, and appears at 393 K; i.e. 140 K less than that of the bare support (533 K). The CO/O<sub>2</sub> reaction is still associated with a concomitant molecular NO desorption starting at a temperature as low as 373 K, prior to the beginning of the CO/NO reactions. Furthermore, when the NO reduction occurs, low amounts of N<sub>2</sub>O are shown by chromatographic analysis of the effluents. This suggests that NO molecules adsorbed in the oxygen vacancies can form either dinitrosyl groups or dimers involved in the mechanism of reduction of NO to N<sub>2</sub>.

The strong activity enhancement of rhodium-supported samples confirms that the oxidized rhodium species are quite accessible at the support surface and are part of the active site. The occurrence of molecular NO desorption in the presence of rhodium clearly indicates that rhodium is oxidized since Rh(0) (17, 37) as well as Pt(0) (4) would have already dissociated the NO molecule at 298 K. The existence of the molecular NO desorption steps occurring simultaneously with the appearence of the CO/O<sub>2</sub> activity still suggests that NO was previously adsorbed in the oxygen vacancies belonging to the active site, so impeding the dioxygen dissociation in these vacancies and, consequently, the CO oxidation. So, it appears that the active site could present a mixed character and consists of oxidized rhodium species and oxygen vacancies associated with Ce<sup>3+</sup> cations.

A reaction pathway close to that proposed for the nude support can be considered as follows:

(a) Desorption at 373 K of the preadsorbed molecular NO in oxygen vacancies; CO adsorption on  $Rh^{x+}$  ions, and reaction with oxygen atoms originating from the dissociation of the dioxygen of the feed in free oxygen vacancies pertaining to the mixed sites accessible after the desorption at 373 K of the preadsorbed molecular NO in oxygen vacancies.

(b) As soon as dioxygen of the feed is totally consumed by CO, NO adsorbs again in free oxygen vacancies of the mixed sites. To explain the low concentrations of  $N_2O$  in the gas phase when NO begins to react, it can be assumed to be produced by the decomposition of a surface dinitrosyl or dimer (NO)<sub>2</sub> species adsorbed on the mixed sites. NO can be considered as a ligand for Rh<sup>x+</sup>, leading to a Rh<sup>x+</sup>(NO)<sub>2</sub> species which decomposes immediately to  $N_2O$  and then to  $N_2$ , releasing oxygen atoms in the vacancies. CO is another potential ligand for Rh<sup>x+</sup> which can then be oxidized by consumption of these oxygen atoms.

The presence of Rh<sup>x+</sup> leads consequently to a very important catalytic effect, since it allows the reaction to occur at a temperature of reaction lower than that on the bare support. The promoting effect of rhodium could be ascribed to an electronic tranfer from  $Rh^{x+}$  to the reduced ceria support leading to the lowering of the Ce-O bond (8) which confers some labile character to the oxygen in ceria and allows the CO/O and NO  $\rightarrow$  N<sub>2</sub>O or N<sub>2</sub> reactions to take place at low temperature.

## Titration Method of Rh<sup>x+</sup> Species Active in CO/NO/O<sub>2</sub> Reactions Present at the Surface of the Rh/CeO<sub>2</sub>-ZrO<sub>2</sub> Catalyst

(a) Principle. As found above, the surface catalytic sites of Rh/CeO<sub>2</sub>-ZrO<sub>2</sub> in CO/NO/O<sub>2</sub> reactions can be considered as a mixed site consisting of one Rhx+ ion and two oxygen vacancies associated to Ce<sup>3+</sup> ions. The NO desorption peak appearing concomitantly with the beginning of the CO/O<sub>2</sub> reaction is characteristic of these mixed sites. In fact, it seems obvious that NO molecules desorbing during this peak, desorbed from the mixed sites (one NO per oxygen vacancy, or  $Rh^{x+}$ ). Counting the number of NO molecules desorbing at the light-off temperature of CO brings information on the number of rhodium ions implied in the mixed sites. The rhodium content in the weight of the catalyst used for one run being known from chemical analysis and assuming that every Rh<sup>x+</sup> is accessible to the reaction, the stoichiometry of NO/Rh can be easily deduced from the NO/Rh ratio.

Desorption of NO preadsorbed on the catalyst surface in experimental conditions as close as possible as those selected in the postcombustion reaction must lead to a quantitative titration of the active  $Rh^{x+}$  species.

(b) Adsorption-desorption of NO on activated  $Rh/CeO_2$ - $ZrO_2$  catalysts

1. Catalyst pretreatment; formation of active sites. Mixed sites first have to be created by contacting the globally reductive reactant mixture. The composition of the feed for catalyst activation (total flow = 15 Lh<sup>-1</sup>) was 1.5 vol% CO/0.65 vol% O<sub>2</sub> in helium.

Let us note, that the temperatures and intensities of the NO desorption peaks observed at the light-off temperature of the CO/O<sub>2</sub> reaction for two samples pretreated either in the CO/NO/O<sub>2</sub> or in the CO/O<sub>2</sub> (without NO) mixtures are quite similar (Table 1, Fig. 4). This indicates that whatever the mixture used (CO/NO/O<sub>2</sub> or CO/O<sub>2</sub>), after thermal treatment at 773 K and cooling at room temperature at 298 K in helium, that the support surface is reduced, leading to the formation of oxygen vacancies partly engaged in the mixed sites. Nevertheless, in order to avoid any NO adsorption at low temperatures during the pretreatment stage of the titration, the CO/O<sub>2</sub> mixture was used as the support reducing agent.

2. Adsorption of NO on the activated material, at room temperature by flowing 0.2 vol% NO in helium (15  $Lh^{-1}$ ). NO adsorption was proceeded by flowing 0.2 Vol% NO/He



FIG. 5. Thermodesorption in the reducing  $(CO/O_2)$  mixture and the 298–773 K temperature range of NO preadsorbed at 298 K on the surface of the Rh/CeO<sub>2</sub>-ZrO<sub>2</sub> sample previously reduced in the  $(CO/O_2)$  mixture.

to the stabilization of the initial NO concentration at the outlet of the reactor.

3. Thermodesorption of NO adsorbed on the Rh/ CeO<sub>2</sub>-ZrO<sub>2</sub> surface by flowing (15 Lh<sup>-1</sup>) 1.5 vol% CO/ 0.65 vol% O<sub>2</sub>/He.

After adsorption of NO on Rh/CeO2-ZrO2 at 298 K and flushing of the reactor by helium, the sample was submitted to a thermodesorption from 298 to 773 K in flowing  $CO/O_2$ mixture with the same composition as for the CO/NO/O<sub>2</sub> reactions (Fig. 5). Two NO desorption peaks can be seen. It is possible to discriminate the contribution of NO, either adsorbed on the support or located in the mixed sites. The first one concerns NO molecules desorbing between 298 and 423 K, before the beginning of the CO/O<sub>2</sub> reaction; consequently, these molecules do not interact with the active sites, but are weakly adsorbed on the support surface. The second one corresponds to NO desorbing at the lightoff temperature of the  $CO/O_2$  reaction. The measurement of the surface area of this peak leads to the accurate number of NO molecules retained by the actives sites once the first peak has been completely eluted.

Counting the number of NO molecules desorbing between 423 and 523 K (second desorption peak) (Fig. 5) leads to a NO/Rh ratio close to 2. In order to check this stoichiometry, the NO/Rh ratio was determined for Rh/CeO<sub>2</sub>-ZrO<sub>2</sub> samples with different total rhodium contents (Table 2). It can be seen that the NO/Rh ratio remains fairly constant with a mean value of 2. This result not only confirms the ratio NO/Rh, but also confirms that all the rhodium is atomically dispersed at the surface of the support in an oxidized state accessible for the CO/NO/O<sub>2</sub> reactions. Furthermore, it shows that the intermediate reaction must be either a dinitrosyl or a dimer (NO)<sub>2</sub>.

So, it can be concluded that the active site in the  $(CO/NO/O_2)$  reactions at the surface of the activated  $Rh/CeO_2$ - $ZrO_2$  catalysts consists of dispersed  $Rh^{x+}$  ions

NO/Rh Evaluation as a Function of the Rh Content in Rh/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts

Rh (wt%)	0.30	0.24	0.18	0.16	0.11
NO/Rh*	1.97	1.82	1.92	2.20	1.96

*Note.* \* NO determined from NO adsorption–desorption measurements, and taking only into consideration the number of NO molecules desorbing at the light-off temperature of the  $CO/O_2$  reaction. Rh = total rhodium content in the sample.

surrounded by two oxygen vacancies of the reduced support and associated with  $Ce^{3+}$  cations.

Nevertheless, note that the preceding results do not give the oxidation state of rhodium in the mixed site. After Howitt *et al.* (38)  $Rh^{3+}$  can be excluded, as it is inactive in the postcombustion reactions. Elsewhere, Soria *et al.* (39) by EPR spectroscopy of rhodium ions in  $Rh/CeO_2$ systems reduced at 773 K showed the presence of  $Rh^{2+}$ ions.

In order to get further information about the value of the rhodium oxidation state in the mixed sites, we studied by infrared spectroscopy the adsorption of CO on the Rh/CeO<sub>2</sub>-ZrO<sub>2</sub> sample reduced at 773 K in H<sub>2</sub> (Fig. 6). Despite the poor resolution of the IR bands of CO adsorbed on rhodium, two couples of bands were shown at 2063–2008 cm<sup>-1</sup> and 2046–1975 cm<sup>-1</sup>. These bands could be identified as those ascribed to the vibrations of C-O at 2040–2030 cm<sup>-1</sup> and 2110–2075 cm<sup>-1</sup> in the gem carbonyl Rh<sup>1+</sup>(CO)<sub>2</sub> species, more or less shifted, depending on the degree of interaction of the oxygen atoms of the CO ligands with the reduced support. So, it is likely that the oxidation state of rhodium in the mixed sites could be Rh<sup>1+</sup> state.



**FIG. 6.** Infrared vibration bands (in the 2300–1700 cm<sup>-1</sup> frequency interval) of CO adsorbed on the Rh/CeO<sub>2</sub>-ZrO<sub>2</sub> sample reduced at 773 K in H<sub>2</sub> during 2 h as a function of the partial pressure of CO: (1) 0.4 kPa, (2) 0.8 kPa, (3) 1.6 kPa, (4) 4.6 kPa, (5) 10.2 kPa, (6) 13.5 kPa.

### CONCLUSION

The catalytic activity of Rh/CeO<sub>2</sub>-ZrO<sub>2</sub> samples with regard to the reducing stoichiometric CO/NO/O<sub>2</sub> reaction mixture was studied. It was shown that the catalytic activity of these samples was due to the presence of mixed sites consisting of oxidized Rh<sup>x+</sup> species (Rh<sup>1+</sup>) stabilized with two oxygen vacancies (and associated to Ce<sup>3+</sup> cations) of the reduced CeO<sub>2</sub>-ZrO<sub>2</sub> support.

A titration method of these active mixed sites was developed using NO adsorption-desorption measurements on the activated surface in experimental conditions as close as possible to the catalytic ones; it was deduced that the stoichiometry of the mixed site consisted of one Rh<sup>x+</sup> and two oxygen vacancies associated to  $Ce^{3+}$  ions. The promoting effect of Rh<sup>x+</sup> species on the catalytic activity in the postcombustion reactions of these samples was clearly shown by comparison with the reactivity of the unloaded CeO<sub>2</sub>-ZrO<sub>2</sub> support. This one only displayed catalytic activity for temperatures 150 K higher than that of the sample containing rhodium. Rh/CeO<sub>2</sub>-ZrO<sub>2</sub> was found to be still active in three-way catalysis, even after drastic ageing. The ageing resistant character of these samples working alternatively under oxidative and reducing conditions could be now interpreted in terms of active sites consisting of both Rh(0) and  $Rh^{x+}$  species (40).

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