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RESEARCH NOTE

Effect of Mild Re-oxidation Treatments with CO_2 on the Chemisorption Capability of a Pt/CeO_2 Catalyst Reduced at 500°C

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By combining FTIR spectroscopy of chemisorbed CO and HRTEM, we have studied the evolution undergone by the metal chemisorption capability and nanostructural properties of a Pt/CeO_2 catalyst reduced at increasing temperatures from 200 to 500°C. As revealed by the ν_{CO} integrated absorption data on Pt, a progressive metal deactivation is observed. The analysis of the HRTEM micrographs allows us to exclude metal sintering, decoration, and Pt–Ce alloying phenomena as the likely origin of the observed effect. If the catalyst reduced at 500°C is further heated under CO_2 (300 Torr), at a very mild temperature, 200°C, its chemisorption capability is partly recovered. This regeneration effect is interpreted as due to the Pt-assisted CO_2 re-oxidation of the ceria support with inherent chemisorption of the resulting CO on the metal microcrystals. These observations are consistent with the model recently proposed by our laboratory on the nature of the strong metal–support interaction phenomena occurring in NM/CeO_2 catalysts. © 2001 Academic Press

Key Words: **Pt/CeO_2; recovery from a SMSI state; CO_2 mild re-oxidation treatment; FTIR of chemisorbed CO; HRTEM; EUROPT-1.**

The information available about strong NM (Rh, Pd, Pt)–CeO_2 interaction effects has been reviewed (1). A model accounting for the chemical and nanostructural evolution undergone by these catalysts upon increasing the reduction temperature from 200 to 900°C has also been proposed (1). In accordance with (1), the nature of the phenomena occurring in ceria-supported catalysts qualitatively agrees with that exhibited by the classic NM/TiO_2 systems (2). When the reduction temperature is increased, electronic perturbations of the supported metal would be observed first, the migration of the reduced support on top of the metal particles (decoration) taking place in a second step, at higher reduction temperatures.

A major difference has been noted between NM/CeO_2 and NM/TiO_2 catalysts (1). As evidenced by the HRTEM studies, reduction temperatures as high as 700°C are required to induce the metal decoration in ceria-based catalysts (3). This contrasts with the well-known behaviour of titania-suppported systems on which metal covering is typically observed at much lower reduction temperatures: 450–500°C (4, 5).

In the case of Pt/CeO_2 catalysts, Pt–Ce alloying phenomena have also been suggested to occur (6). However, they could only be unequivocally established on catalysts reduced at or above 900°C (7).

In this work, some new results lending further support to the model briefly outlined above are presented and discussed. The Pt(7.1 wt%)/CeO_2 sample was prepared by the incipient wetness impregnation technique from 99.9% pure ceria with 49 $m^2 g^{-1}$. The support was obtained from a high surface area (130 $m^2 g^{-1}$) kindly provided by Rhodia. It was further heated for 4 h, in a flow of pure H_2, at 550°C, then flushed with He, for 1 h, at 550°C, cooled to 25°C in a flow of He, and finally reoxidised under flowing O_2 at 500°C. By application of this pre-treatment, a texturally stabilised ceria sample could be obtained. In this way, the likely contribution of the support sintering, and inherent metal encapsulation (1), to the observed deactivation phenomena could reasonably be excluded. Likewise, to avoid the strong structural (8) and chemical (9) perturbations associated with the incorporation of chloride ions into the ceria lattice, we have used a chlorine-free metal precursor: $[Pt(NH_3)_4](OH)_2$. To summarise, the design of the preparation procedure was aimed at minimising those effects,which are known to disturb the unambiguous interpretation of the strong metal–support interaction phenomena.

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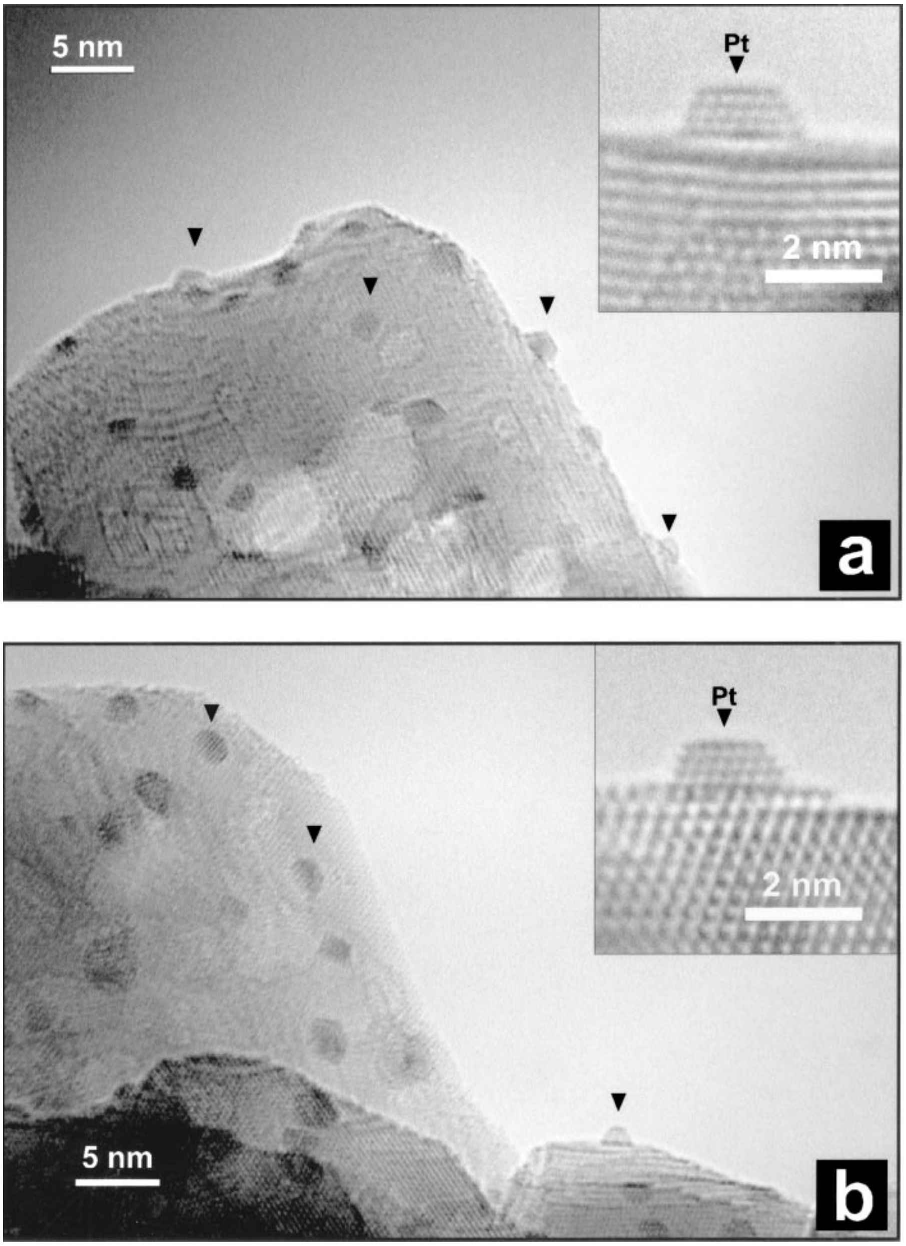

FIG. 1. Representative HRTEM images of the Pt/CeO_2 catalyst reduced in a flow of pure H_2, for 1 h, at 200°C (a) and 500°C (b).

The nanostructural characterisation of the Pt/CeO_2 catalysts was performed by using a JEOL, JEM-2000-EX, transmission electron microscope, with a point resolution of 0.21 nm. The HRTEM images were digitised on a CCD camera (COHU-4910) and processed by using the SEMPER 6+ software package according to the methodology proposed in (10). Two main conclusions could be drawn from the analysis of tens of micrographs like those reported in Fig. 1:

(1) The platinum particle size distribution was only slightly modified by the reduction treatment. When the procedures described elsewhere (3) were followed, mean metal particle sizes of 1.7 and 2.0 nm and metal dispersion of 64 and 57% could be determined for the catalysts reduced at 200 and 500°C, respectively.

(2) Within the investigated range of reduction temperatures, the HRTEM images do not provide any evidence of metal decoration, Pt–Ce alloying phenomena, or even morphological changes in the platinum microcrystals. These observations are in good agreement with some earlier HRTEM studies performed on different Pt/CeO_2 samples (4, 6, 11).

The evolution undergone by the chemisorptive properties of the Pt/CeO_2 catalyst upon increasing the reduction

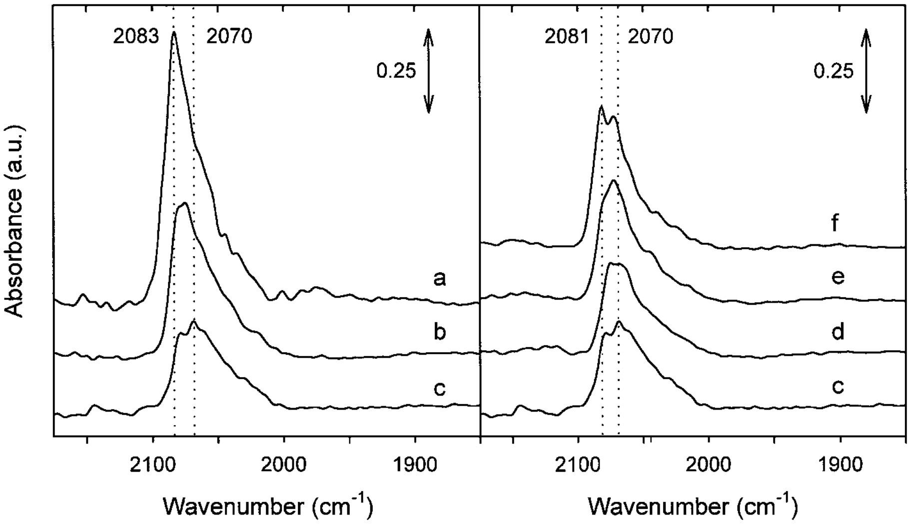

FIG. 2. FTIR spectra corresponding to CO chemisorbed on Pt/CeO_2. Catalysts reduced/evacuated, for 1 h, at 200°C/500°C (a), 350°C/500°C (b), and 500°C/500°C (c) and further treated with 300 Torr of CO, at 25°C. After experiment (c), the catalyst was evacuated at 500°C (1 h) and then treated with 300 Torr of CO_2, for 1 h, at 25°C (d), 100°C (e), and 200°C (f). Spectra d–f were always recorded after the catalyst was cooled to 25°C under CO_2 pressure.

temperature was probed by using FTIR spectroscopy of the chemisorbed CO. In this way, information specifically dealing with the chemical properties of the supported noble metal phase could easily be obtained (12).

The FTIR spectra were recorded on a Mattson-5020 instrument, at a resolution of 4 cm^{-1}. To improve the signal-to-noise ratio, 250 spectra were routinely averaged. The self-supported disks of the catalyst were reduced *in situ*, with flowing pure H_2, at 200, 350, or 500°C, for 1 h. They were further evacuated at 500°C (1 h) and finally cooled to 25°C under vacuum.

Figures 2a–2c show the spectra corresponding to the characteristic ν_{CO} region for CO chemisorbed on platinum. As expected for Pt (13, 14), the spectra are consistent with the formation of linear forms of chemisorbed CO. They were recorded under CO (P_{CO}: 300 Torr), at 25°C. As the reduction temperature is increased, the spectra undergo significant modifications. In addition to a shift toward lower wavenumbers, the band intensity drops by a factor of 2.4, thus indicating a notable inhibition of the platinum chemisorption capability. Table 1 summarises the corresponding integrated absorption data.

To check the reversibility of the observed deactivation, we have also studied the effect of a very mild re-oxidation treatment. Instead of applying the classic re-oxidation routine for recovering catalytic systems from a SMSI state, which is known to consist of heating the deactivated catalyst under oxygen at 400–500°C, followed by a re-reduction treatment at 200–350°C (15, 16), we have just heated the catalyst under CO_2 (P_{CO2}: 300 Torr) at 200°C. It is well known that reduced Pt/CeO_2 activates the CO_2 dissociation (17, 18). The process involves both the metal particles and the oxygen vacancies at the support, thus leading to reoxidised ceria with inherent formation of CO chemisorbed on the platinum microcrystals. Consequently, the regeneration treatment proposed here would allow oxidation of the support under very mild conditions, far from those required to induce significant microstructural modifications on the metal particles or destroy the support overlayer characterising the decoration phenomena (1, 3).

We have also checked the likely occurrence of side disturbing effects associated with the CO_2 treatment applied here. For this purpose, we have run a parallel experiment on the standard EUROPT-1 catalyst reduced at 500°C. This catalyst with metal loading and dispersion (19, 20) similar to those exhibited by our Pt/CeO_2 sample was used as a reference system showing, under the reduction conditions used here, conventional non-SMSI behaviour.

In accordance with the proposed re-oxidation procedure, the Pt/CeO_2 catalyst reduced at 500°C was further treated with 300 Torr of CO_2 at increasing temperatures from 25 to 200°C. Figures 2d–2f and Table 1 account for the corresponding results. As deduced from Fig. 2, the CO_2 dissociation starts to be observed at 25°C. Upon heating the catalyst at 100 and 200°C, always under CO_2 pressure, a notable increase of the CO–Pt band intensity is observed. Moreover, in accordance with Table 1, the integrated absorption recorded after the CO_2 treatment at 200°C is 30% larger than that determined for the catalyst reduced at 500°C. This indicates a recovery of the platinum chemisorption capability.

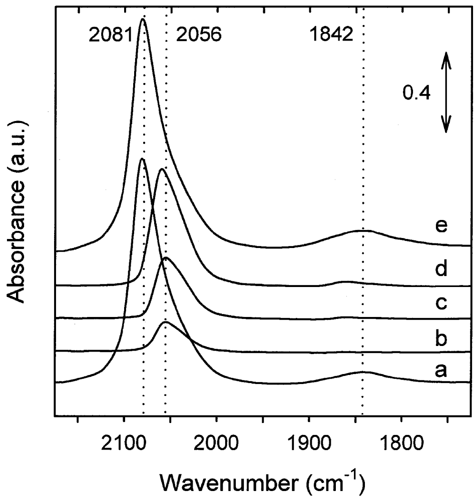

FIG. 3. Evolution of the ν_{CO} FTIR spectrum corresponding to the EUROPT-1 (Pt/SiO_2) catalyst reduced/evacuated for 1 h at 500°C/500°C and further treated with CO_2 (300 Torr) for 1 h at 25°C (b), 100°C (c), and 200°C (d). The spectra were always recorded under CO_2 pressure, at 25°C. Spectra corresponding to the catalyst reduced/evacuated at 500°C/500°C, cooled to 25°C under vacuum, and then treated with CO (300 Torr) at 25°C (a) and to the sample resulting from experiment (d), further evacuated at 500°C (1 h), and finally treated with CO (300 Torr) at 25°C (e), are also included for comparison.

Regarding the EUROPT-1 catalyst, Fig. 3 and Table 1, our results indicate that, in the absence of reduced ceria CO_2, dissociation does also occur. In relative terms, however, the effect is much less important. Thus, Table 1 shows that, for the catalyst reduced at 500°C and further heated under CO_2 at 200°C, the CO–Pt bands are 50% less intense than those recorded for the EUROPT-1 reduced at 500°C and further treated with CO at 25°C.

TABLE 1

FTIR Spectroscopy Study of CO Chemisorbed on Pt/CeO_2 and Pt/SiO_2 Catalysts; Integrated Absorption Data

Run	Treatment	Integrated Absorption (a.u.)	
		Pt/CeO_2	Pt/SiO_2
1	(Redn. 200°C/Evac. 500° C) + CO (P_{CO}: 300 Torr) at 25°C	60	—
2	Evac., 500°C + (Redn. 350°C/Evac. 500°C) + CO(P_{CO}: 300 Torr) at 25°C	43	—
3	Evac., 500°C + (Redn. 500°C/Evac. 500°C) + CO (P_{CO}: 300 Torr) at 25°C	25	68
4	Evac., 500°C + CO_2 (P_{CO2}: 300 Torr) at 25°C	24	7
5	CO_2 (P_{CO2}: 300 Torr) at 100°C + cooling to 25°C under CO_2 pressure	31	15
6	CO_2(P_{CO2}: 300 Torr) at 200°C + cooling to 25°C under CO_2 pressure	34	31

We have also checked the likely occurrence of chemical or microstructural irreversible modifications on the platinum microcrystals associated with the CO_2 treatment. For this purpose, the CO_2-treated Pt/SiO_2 sample was further evacuated at 25°C (1 h) and put in contact with 300 Torr of CO. As deduced from the results reported in Fig. 3, no significant differences are observed between the CO spectra recorded before and after the CO_2 treatment. Accordingly, we may conclude that, in spite of some CO_2 dissociation occurring, the treatment applied here has negligible side effects on the chemical properties of the supported platinum microcrystals.

To summarise, when FTIR spectroscopy and HRTEM are combined, a very mild and clean chemical procedure, allowing the effect of ceria re-oxidation on the chemisorptive properties of the metal microcrystals supported on it to be checked, has been developed. This procedure takes advantage of the specificity of the FTIR spectroscopy to probe the CO interaction with Pt as well as of the acknowledged capacity of CO_2 for re-oxidising the reduced ceria. Because of the mildness of the applied thermal treatment, and the absence of side reactions that might induce some poisoning of the catalyst, our results lend further support to the model proposed in Ref. (1). In accordance with this model, the deactivation occurred in Pt/CeO_2 catalysts reduced at a temperature not higher than 500°C may be interpreted as mainly due to electronic perturbations induced on the metal by the reduced support.

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