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Chemical and microstructural investigation of Pt/CeO_2 catalysts reduced at temperatures ranging from 473 to 973 K.

S. Bernal *, M.A. Cauqui, G.A. Cifredo, J.M. Gatica, C. Larese, J.A. Pérez Omil

Departamento de Ciencia de Materiales, Ingeniería Metalúrgica y Química Inorgánica, Facultad de Ciencias, Universidad de Cádiz, Apartado 40, Puerto Real, 11510 Cádiz, Spain

Abstract

The combined application of chemical techniques and HREM shows that platinum deactivation in Pt/CeO_2 catalysts steadily increases with the reduction temperature (T_r: 473–1173 K). Though no suppression of the H_2 adsorption was observed, the TPD-H_2 traces indicate the occurrence of significant chemical changes with T_r. As revealed by HREM, the metal decoration starts at T_r: 973 K, a temperature well above those at which the chemical effects can be observed.

Keywords: Pt/CeO_2 catalysts

1. Introduction

In spite of the research efforts devoted to the investigation of the ceria supported noble metal catalysts, the actual nature of the metal–support interaction phenomena occurring in these catalysts is still far from being well understood [1–3]. For the last few years, our laboratory has been working on the Rh/CeO_2 system [1,4–11]. From this study, in which a battery of experimental techniques, including volumetric adsorption [5], TPD [6], FTIR of chemisorbed hydrogen [5], XPS [7], magnetic balance [4,6–8] and high resolution electron microscopy [1,4,5,9–11], was applied in a combined manner, a number of interesting conclusions could be drawn. As is discussed in Refs. [5–8], the chemistry of the H_2-(Rh/CeO_2) is rather complex, being sensitive to many different factors like, the metal precursor, the reduction/evacuation conditions, the metal dispersion or the ceria surface area. However, no dramatic inhibition of the metal chemisorptive properties was found in our case [11]. This contrasts with the behaviour observed on catalysts exhibiting the so-called SMSI effect [11,12]. Also worth noting, on Rh/CeO_2 catalysts, the metal decoration effects, as revealed by HREM [1], could only be observed on samples reduced at 973 K or higher temperatures. On Rh/TiO_2, a catalyst which shows the classic SMSI effect, the metal decoration phenomena do occur at 773 K or even lower reduction temperatures [11,13].

Here, we report on the Pt/CeO_2 system. From this work, the influence of the noble metal on the nature of the metal–support interactions occurring in ceria containing catalysts could be checked. Likewise, some valuable information about the deactivation mechanisms operating in

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* Corresponding author. Fax. (+34-56) 834924.

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M/CeO_2 catalysts and by extent in TWC's, could be gained.

2. Experimental

The series of Pt/CeO_2 catalysts investigated here was prepared by the incipient wetness impregnation technique, from a low surface area (3.5 m^2 g^{-1}) 99.9% pure cerium dioxide. $[Pt(NH_3)_4](OH)_2$ was used as metal precursor. The metal loading was 2.5% by weight. The impregnated ceria sample was dried in air, at 383 K, for 10 h, and further stored in a desiccator until its reduction 'in situ'. The reduction treatment consisted of heating the precursor–support system with flowing H_2 (60 cm^3 min^{-1}) at 473, 623, 773 or 973 K, for 1 h. The heating rate was 10 K min^{-1}.

Hydrogen volumetric adsorption measurements were performed at 295 K in a high vacuum system equipped with a capacitance gauge MKS Baratron, model 220 BHS. The time elapsed between successive adsorption measurements was 20 min. The final hydrogen pressure was 300 Torr.

The TPD and D_2/H_2 exchange studies were carried out in an experimental device coupled to a quadrupole mass spectrometer, VG, model SENSORLAB-200-D. The standard experimental conditions used to run the TPD experiments were: Ar flow rate: 60 cm^3 min^{-1}, heating rate: 10 K min^{-1}. The sample weight was typically 200 mg.

The HREM (high resolution electron microscopy) images were recorded on a JEOL, JEM-2000-EX instrument, equipped with a top entry specimen holder and an ion pump. The structural resolution was 0.21 nm. The samples to be investigated were prepared as reported in Ref. [1].

3. Results and discussion

Hydrogen volumetric adsorption experiments were carried out on the whole series of catalysts investigated here. From this study, H/Pt ratio values of 0.20 (T_r: 473 K), 0.15 (T_r: 623 K), 0.14 (T_r: 773 K), and 0.10 (T_r: 973 K) could be estimated. In accordance with these results, the hydrogen adsorption capability of our catalysts steadily decreases with the reduction temperature. It would be noted, however, that no sharp drop of such a capability could be found. This observation is in good agreement with some earlier H_2 [14,15] and CO [16,17] chemisorption studies reported for Pt/CeO_2 catalysts reduced at different temperatures including 773 [14–16] and even 973 K [17].

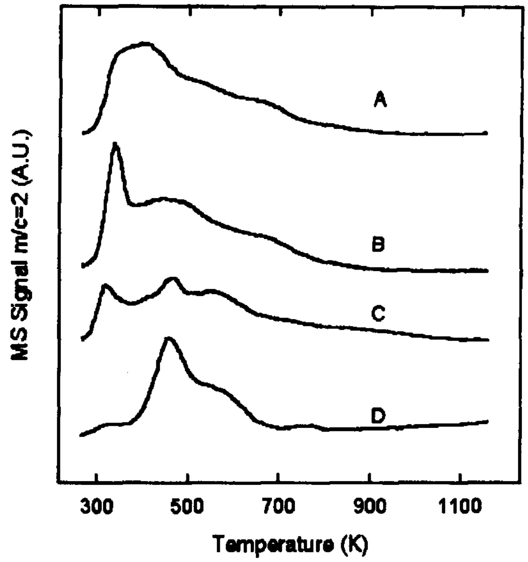

Fig. 1. TPD–MS study of the H_2 (m/c: 2) evolution from a series of Pt (2.5%)/CeO_2 catalysts reduced at: (A) 473 K; (B) 623 K; (C) 773 K; and (D) 973 K and further cooled under flowing H_2.

The interaction of H_2 with the whole series of Pt/CeO_2 catalysts was also investigated by using TPD–MS. After reduction at each of the temperatures mentioned above, the catalysts were cooled under flowing H_2 up to 191 K, then the sample was flushed for 30 min with Ar, at 191 K, and finally the TPD experiment was run. Fig. 1 accounts for the diagrams recorded from 295 to 1200 K. As can be deduced from Fig. 1, the TPD traces notably change with the reduction temperature. In particular, the intensity of the features peaking below 400 K diminish very significantly. This contrasts with the behaviour observed for the so-called EUROPT-1 (Pt/SiO_2) catalyst, which was used as a reference sample. In effect, parallel TPD experiments carried out on the EUROPT-1 sample did not show any significant influence of the reduction temperature on the shape of the desorption traces, Fig. 2.

The observations above suggest that, in the case of the Pt/CeO_2 catalysts, the reduction temperature plays an important role in determining their chemical properties against the hydrogen adsorption.

The behaviour of our Pt/CeO_2 catalysts was also investigated with the help of H_2/D_2 exchange experiments. The reduced samples were cooled in a flow of H_2 to 295 K, then they were treated with flowing D_2, for 1 h, at 295 K, and further cooled to 191 K, always in a flow of D_2. Following this treatment, the TPD experiments were run as described above. Fig. 3 reports on the TPD diagrams for D_2 (*m/c*: 4), HD (*m/c*: 3) and H_2 (*m/c*: 2) recorded for the Pt/CeO_2 catalysts reduced at 623, 773 and 973 K. After correcting the D_2 and HD signals by the corresponding sensitivity factor relative to H_2, 0.8 and 0.9, respectively, the global desorption traces, also included in Fig. 3, could be obtained.

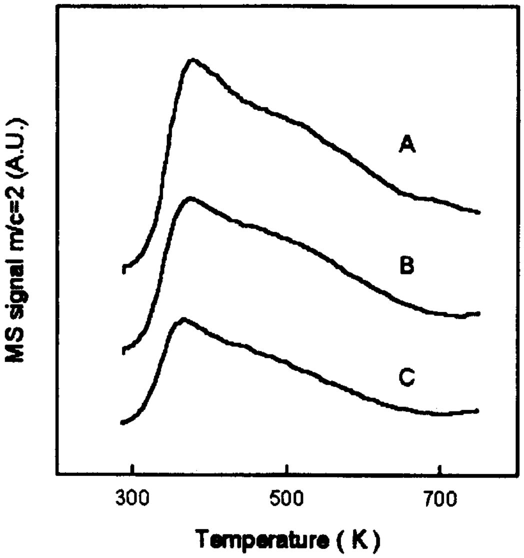

Fig. 2. TPD–MS study of the H_2 evolution from the EUROPT-1 (Pt/SiO_2) catalyst reduced at: (A) 623 K, (B) 773 K and (C) 973 K, and further cooled under flowing hydrogen. The experiments were carried out in the same way as those reported in Fig. 1.

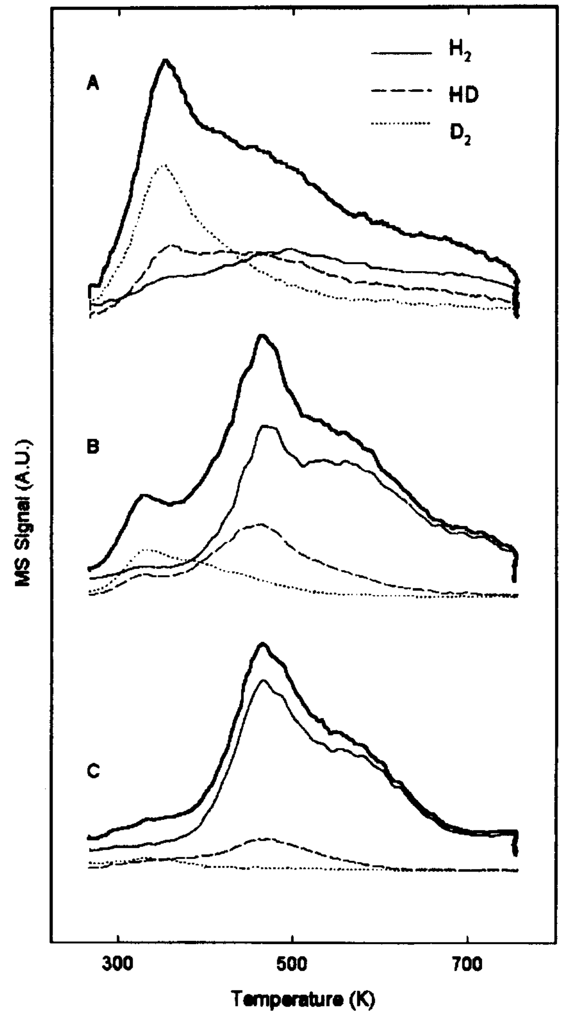

Fig. 3. TPD–MS study of the Pt/CeO_2 catalysts reduced with flowing H_2 at 623 K (A), 773 K (B) and 973 K (C), further cooled under H_2 to 295 K and finally treated with flowing D_2 for 1 h, at 295 K. Traces corresponding to D_2 (*m/c*: 4); HD (*m/c*: 3); and H_2 (*m/c*: 2); as well as the global desorption curves, $H_2 + HD + D_2$, are included.

The diagrams reported in Fig. 3 provide some further details about the chemistry of the H_2-(Pt/CeO_2) system. In effect, the traces recorded for D_2 and HD clearly show that the amount of exchanged deuterium steadily decreases with the reduction temperature, thus, confirming the

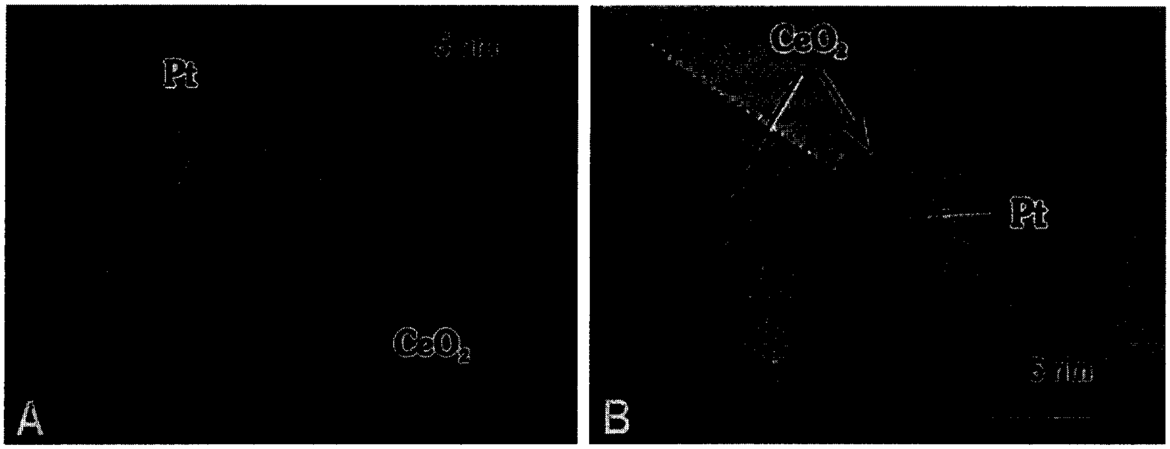

Fig. 4. HREM images corresponding to our Pt/CeO_2 catalyst reduced at 773 K (A) and 973 K (B).

occurrence of significant changes in the chemical behaviour of platinum.

In parallel with the chemical experiments, the microstructure of our Pt/CeO_2 catalysts could also be investigated by means of HREM. Fig. 4 shows representative HREM images of the samples reduced at 773 and 973 K. From the analysis of some tenths of micrographs like those shown in Fig. 4, a number of observations can be outlined. First, an estimate of the mean platinum microcrystal size could be made. They were found to be 2.9 and 4.4 nm for the catalysts reduced respectively at 773 and 973 K. If these data are compared to the H/Pt values determined from H_2 volumetric adsorption, we may note a relative depression of the chemisorptive capability of our samples. Second, no indication of metal decoration effects could be obtained from the images recorded for catalysts reduced at 773 K or lower temperatures. This fully agrees with earlier HREM studies carried out on Pt/CeO_2 catalysts [18,19], as well as with the results reported by us for Rh/CeO_2 catalysts [1,5,10]. Also in agreement with the results reported for Rh/CeO_2 [1], metal decoration effects (covering by the reduced support) could only be observed on the catalyst reduced at 973 K.

To summarize, the results obtained for the series of Pt/CeO_2 catalysts investigated here suggest that, upon increasing the reduction temperature from 473 to 973 K, their chemical properties are disturbed in a rather progressive way. This is also suggested by the disagreement found between the metal dispersion data determined from chemisorption and HREM measurements. Since metal decoration effects could only be observed on the catalyst reduced at 973 K, electronic effects are probably involved in the modification of chemical behaviour noted here. To arrive at a finer understanding of the processes involved, some further chemical and microstructural investigations are in progress.

Acknowledgements

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