

Changes in the electronic structure of Pt/CeO₂ based DENOX catalysts as a function of the reduction treatment. Detection of a Pt-H anti-bonding shape resonance and Pt-H EXAFS

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Abstract

This work shows clearly that the nature of the strong metal support interaction (SMSI) on Pt/CeO₂ catalysts is twofold. At reduction temperatures of 773K the SMSI state is due to a *electronic modification* of the Pt induced by reduction of the support. At higher reduction temperatures the SMSI state originates from a decoration of the Pt particles by the partially reduced support. These conclusions are based upon results obtained from HREM and analysing the Pt-H anti-bonding state and Pt-H EXAFS which were extracted from the Pt L_{II} and L_{III} edges.

1 INTRODUCTION

The increasing care for the environment demands a great effort in the control of engine emissions. Especially the control of NO_x from vehicle exhaust is a challenge. Due to its unique redox properties CeO₂ is a major component in the currently used three way catalysts (TWC). However the chemistry involved in CeO₂ containing catalysts is complex and not fully understood yet. One of the interesting aspects of CeO₂ is its ability to have a strong interaction with the metals supported on it [1]. When Pt is supported on CeO₂ it is known that depending on the reduction treatment of the catalyst its chemical behavior and physico-chemical properties are changing [2]. Different explanations are given in literature for these phenomena. These include, (i) alloy formation between Pt en Ce [3], (ii) decoration of the Pt particles by partially reduced CeO₂ [4] and (iii) pure electronic interactions [5]. However, the exact nature of the metal-support interaction remains still unclear.

In order to clarify the change occurring in Pt/CeO₂ induced by the reduction temperature we investigated this material by different physico-chemical techniques after reduction at two

different temperatures (473K and 773K). Infrared spectroscopy (IR) of adsorbed CO and hydrogen chemisorption was applied in order to visualize the change in chemisorption properties of the material. High Resolution Electron Microscopy (HREM) was used for elucidating the particle size of the Pt particles and to investigate to what extent the metal particles are decorated by the support. Finally, with X-ray Absorption Fine Structure (XAFS), in particular the X-ray Absorption Near Edge Structure (XANES), the electronic properties of the catalyst were investigated.

2. EXPERIMENTAL

2.1 Catalyst Preparation

A 7wt% Pt/CeO₂ sample was prepared by incipient wetness impregnation with an aqueous solution of [Pt(NH₃)₄](OH)₂. The use of a chlorine free metal precursor is indispensable since chlorine has a significant influence on both the structural [6,7] and redox [8,9] properties of ceria.

The ceria support was obtained by heating a high surface area CeO₂ (130 m².g⁻¹, 99.9 % purity) in a flow of H₂ at 823 K for 4h. Subsequently it was flushed with inert gas for 1h at 823 K, and finally reoxidized with flowing O₂(5%)/He at 773 K. The resulting support, with a BET surface area of 80 m².g⁻¹, exhibited a good textural stability. The above mentioned treatment excludes that the support sinters during the reduction treatment of the sample, and hence, it prevents the metal encapsulation effect [10] as the likely origin of the changes in chemisorption capability observed in this work.

2.2 XAFS data collection

The EXAFS measurements were performed at the SRS (Daresbury, UK) at wiggler station 9.2 and at the ESRF (Grenoble, France) at beamline BM29. To suppress higher harmonics, the monochromator was detuned to 50%. The samples were then mounted in an in-situ cell equipped with Be windows [11]. The samples were reduced *in situ* at the desired temperature (473K or 773K for 1 hour, heating ramp 10K/min) and EXAFS spectra were recorded at liquid N₂ temperature (further denoted as H-Pt). Subsequently the sample was heated to 773K in a He flow to remove the adsorbed hydrogen (ramp rate 10K/min, dwell time 1hour). Next an EXAFS spectrum was measured at liquid nitrogen temperature (further denoted as Pt).

The data analysis was carried out by standard methods described elsewhere using the XDAP program [12].

2.3 Isolation of Pt-H anti-bonding shape resonance and Pt-H EXAFS

Table 1: Information from absorption edges

	L _{III}	L _{II}
H-Pt	AS+ΔVB+ΔXAFS+REF	ΔXAFS+REF
Pt	ΔVB + REF	REF

REF=XAFS of Pt without H₂; ΔXAFS=Additional EXAFS induced by H₂ adsorption, ΔVB=change in valence band; AS=Anti-bonding state

The electronic properties of the metal can be visualized by adsorbing hydrogen on the metal and determining the Pt-H anti bonding state and the Pt-H EXAFS [13]. The procedure to obtain the Pt-H anti-bonding state is described

elsewhere and only shortly summarized here. The basis for this procedure is the subtraction of the Pt L_{II} and L_{III} edges in the presence and absence of hydrogen. Moreover, a special alignment procedure is essential in order to correct for initial and final state effects [13]. The information present in the H-Pt and Pt L_{II} and L_{III} edges is summarized in Table 1. For example the Pt-H anti-bonding state can be obtained by $[L_{III}(\text{H-Pt}) - L_{III}(\text{Pt})] - [L_{II}(\text{H-Pt}) - L_{II}(\text{Pt})]$. In a similar way the Pt-H EXAFS and the change in valence band (ΔVB) can be determined.

3. RESULTS

3.1. CO and H₂ chemisorption

The chemisorption properties of Pt/CeO₂ reduced at 473K, 773K and after reduction at 773K followed by a mild oxidation and re-reduction at 473K are shown in Table 2. It can be

Table 2: Chemisorption capacities and dispersions of Pt/CeO₂ after different treatments.

Treatment	H/Pt ratio	Integrate CO area (a.u.)	Dispersion from HREM (%)
Red 473K	0.45	41	62
Red 773K	0.17	27	61
Red 773K, Oxidized 473K, Red 473K	-	42	-

clearly seen in that table that the hydrogen and CO (expressed as integrated area of the peak representing linear CO in IR (data not shown here)) chemisorption capacity of Pt/CeO₂ reduced at 773K is significantly lower than that for the sample reduced at 473K. The dispersions as calculated from HREM are also given in Table 2. The suppressed hydrogen chemisorption capacity after reduction at 773K

can be reverted by a mild oxidative treatment. The hydrogen and CO chemisorption capacity is than completely restored (see Table 2).

3.2. HREM

In order to investigate the nature of this behaviour HREM was carried out. The HREM pictures of the two Pt/CeO₂ samples are similar. Both in the structure of the support and the structure and size of the Pt particles no differences could be observed up to a reduction temperature of 777K. The images show clean and well faced metal particles, thus indicating that no metal decoration occurs. Likewise, no indication of Pt-Ce alloying phenomena could be found. All these observations are in fairly good agreement with earlier HREM studies on Pt/CeO₂ [14,15], as well as with those recently performed in our laboratory [16] on a Pt/CeO₂ sample other than that investigated here.

3.3. Analysis of the Pt L_{II} and L_{III} X-ray absorption edges

The aligned Pt L edges for the samples reduced at 473 and 773K in the presence of hydrogen and in vacuum are shown in Figure 1. The spectra are aligned according to a procedure developed in our group [13]. The L_{II} edge of the sample in vacuum is taken as a reference. Next, the H-Pt L_{II} edge was aligned to that in vacuum at 0.6 of the edge step height. The L_{III}

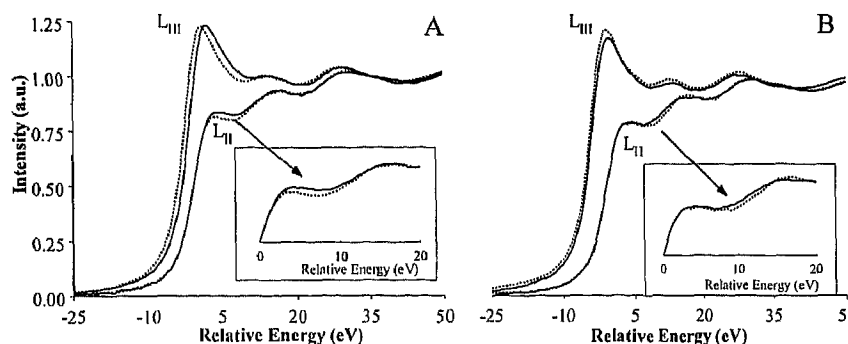


Figure 1: Pt L_{II} and L_{III} edged in vacuum (dashed line) and H₂ (solid line) after reduction at 473K (A) and 773K (B)

H-Pt and Pt edge of the sample are shifted in such a way that the EXAFS oscillation of the L_{II} and L_{III} edges overlap each other from 100-500eV over the edge. In this way all edges are aligned and can be subtracted from each other for a given temperature.

It is clear from Figure 1 that for the sample reduced at 473K the L_{III} edge is slightly shifted to lower energies when measured in vacuum compared to that measured in H₂. At the L_{II} edge it can be seen that the feature at about 8eV above the edge is less intense in vacuum compared to that in H₂. After reduction at 773K the situation is different. The difference in position between the H-Pt and Pt L_{III} edges is smaller and their intensities are different. All these changes can be related to different modes of chemisorbed hydrogen.

According to Table 1, the Pt-H anti-bonding state and Pt-H EXAFS can be isolated by subtracting the different edges. In Figure 2 the Pt-H anti-bonding state and Pt-H EXAFS are plotted for the samples reduced at the two different temperatures. From Figure 2a it is clear that the amplitude of the Pt-H anti-bonding shape resonance is less intense after reduction at 773K compared to that after reduction at 473K. This indicates clearly that less hydrogen is adsorbed after reduction at 773K. Figure 2b shows the Pt-H EXAFS is different for the two temperatures. For the sample reduced at 473K only one peak could be observed whereas two peaks are observed after reduction at 773K. This is a clear indication that at high reduction temperature the mode(s) of hydrogen chemisorption are different.

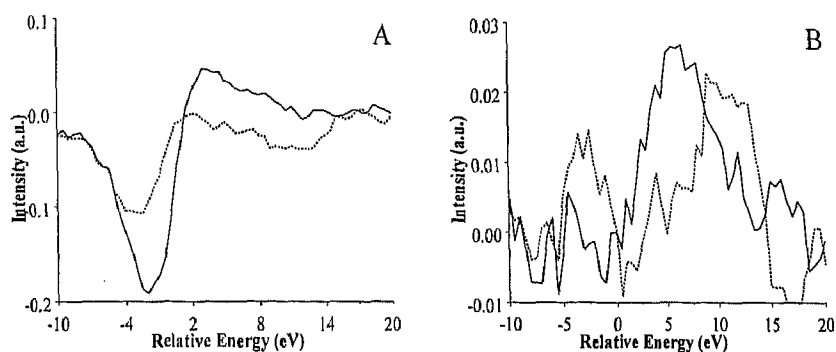


Figure 2: A) Pt-H antibonding state after reduction at 473K (solid line) and 773K (dotted line) and B) Pt-H EXAFS after reduction at 473K (solid line) and 773K (dotted line)

4. DISCUSSION

As was already shown before and reconfirmed in this study, the hydrogen chemisorption capacity of Pt/CeO₂ decreased significantly with increasing reduction temperature [1,2]. A strong indication for the occurrence of a SMSI state is the reversibility of the chemisorption properties by oxidative treatments (see Table 2) [17]. Different explanations are given in literature for these phenomena. These include, (i) alloy formation between Pt and Ce [3], (ii) decoration of the Pt particles by partially reduced CeO₂ [4] and (iii) pure electronic interactions [5]. To also exclude sintering of the metal the Pt dispersions were calculated from HREM as is shown in Table 2. It is obvious from these values that sintering does not occur by increasing the reduction temperature from 473K to 773K. The HREM results also exclude the decoration of the metal particles and alloy formation as reason for the suppression of the chemisorption capacity of Pt/CeO₂ after reduction at 773. It is important to note here that after higher reduction temperatures (>973K, i.e., well above those investigated here) metal decoration and alloying phenomena does occur [16].

From the arguments given above it must be concluded that changes in the electronic structure induced by the support up to a reduction temperature of 773K are the origin of the suppressed chemisorption capacity. Significant differences are observed in the Pt-H anti-bonding state shape resonance and the Pt-H EXAFS (see Figure 2). The integrated peak area of the Pt-H anti-bonding state (Figure 2a) for the sample reduced at 773K is about 1/3 of that of the sample reduced at 473K. This is in perfect agreement with the results obtained by hydrogen chemisorption, which is decreased by 2/3 after reducing the sample at 773.

It has been recently shown that the electronegativity of the support oxygen ions directly influences the electronic structure of the supported particles [18-21]. In this case increasing the reduction temperature increased the Ce³⁺ content in the support from 5.5 to 9.1% (as could be calculated from the Ce-XANES [22]). This increased reduction degree makes the support more electron rich and decreases the electronegativity of the support oxygen ions. It has been shown by our group that in this case the ionisation potential of the supported Pt particles decreases [18-21]. A strong indication for a change in the electronic structure is the change in shape and position of the Pt-H anti-bonding shape resonance of the Pt/CeO₂ sample after reduction at 773K. A full analysis according to the methods published previously [13] will learn whether the position of the Pt-H anti-bonding state is becoming closer to the Fermi level, which leads to a population of the Pt-H anti-bonding state and thus a suppressed hydrogen chemisorption capacity.

In addition the Pt-H EXAFS spectrum shows differences after reduction at 773K. The exact nature of the different modes of hydrogen chemisorption is currently under investigation. Preliminary theoretical calculations indicate that besides the normal Pt-H adsorption mode also a Pt-H₂ is present after reduction at 773K.

5. CONCLUSIONS

When the reduction temperature of Pt/CeO₂ was increased from 473K to 773K its ability to chemisorb hydrogen and CO was significantly suppressed. At a reduction temperature of 773K no sintering, alloy formation or decoration of Pt particles could be observed. Therefore it is concluded that under these circumstances the suppression of chemisorption is caused by a modification of the electronic properties of the metal. Due to the increased reduction degree

of the support the oxygen atoms of the support become less electron negative. This causes the ionisation potential of the Pt to decrease, which makes it more difficult for hydrogen to adsorb. The change in electronic properties of the metal was clearly visualised by a change in the position of the Pt-H anti-bonding state and Pt-H EXAFS. A full analysis of the Pt-H AS will learn whether the position of the Pt-H anti-bonding state is becoming closer to the Fermi level, which leads to a population of the Pt-H anti-bonding state and thus a suppressed hydrogen chemisorption capacity. Note that after reduction at 973K decoration of Pt particles was observed which can explain the suppressed chemisorption in that case.

LITERATURE

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