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INFLUENCE OF CERIUM CONTENT AND OF TRANSITION METAL ON THE CERIUM L_{III} ABSORPTION OF Pd-Ce/γAl₂O₃ CATALYSTS

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Introduction

Cerium, associated with a transition metal, has been used in two important catalytic processes:
- Cracking of heavy petroleum fractions (zeolites exchanged with a rare earth (La, Ce) and a transition metal (Pt, Pd,...))
- Purification of automobile exhaust gases (cerium and transition metal (Pt, Rh, Pd,...) salts coimpregnated on γ-Al₂O₃)

In this last reaction, cerium has proved to:
- i) enhance the catalytic activity, due to its high oxygen storage capacity;
- ii) prevent the loss of surface area during the high thermal treatment;
- iii) disperse the transition metal.

No studies have been devoted to the electronic state of cerium in these catalysts, in spite of its essential role, especially for the oxygen storage properties.

In this paper, we report absorption spectra of cerium dispersed on a γ-Al₂O₃ support and we emphasize the following parameters:
- i) cerium loading and ii) presence of a transition metal (Pd)

In another paper(2), these results will be compared with XPS 3d core level of cerium.

II Experimental

X-Ray absorption measurements

The X-Ray absorption of cerium on the L_{III} edge has been measured using the synchrotron facility of LURE on DCI ring (EXAFS III spectrometer) operating at 1.72 or 1.85 GeV. The BRAGG reflexion of Si(220) has been used to select the energies. The intensity of the beam line varied between 150 and 200mA.

Some spectra have been recorded on a laboratory EXAFS spectrometer. The beam was produced by a RIGAKU rotating anode and monochromatized by a Si(311) cristal. A proportional and a scintillation counter were used for the initial and the transmitted beam.

- Catalysts preparation:
  We report the catalysts prepared by coimpregnation of Ce(NO₃)₃ and Pd(NH₃)₄Cl₂ 10⁻¹N aqueous solutions on γ-Al₂O₃ WOELM of 165m²/g BET surface area. After wetting (2 hrs, 110°C) the catalysts are calcined 4 hours at 200°C under synthetic air (10ml/min), then reduced (2.5°C/min up to 400°C, then one hour at 300°C). Their characteristics are:

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Results and discussion:

In figure I, we report the experimental LIII edge for pure CeO₂, Pd/CeO₂ and Pd-Ce/γ-Al₂O₃ catalysts. The spectra are deconvoluted from an experimental resolution (2.5 eV). The absorption edge intensity is normalized to the transitions in the continuum states. All spectra have been analyzed according to a procedure described in ref(2).

CeO₂, in agreement with previous reported spectra (3,4,5,7,8), have been fitted with five lines (noted A, B₁, B₂, C₁ and C₂) whose two major contributions (B and C) are due to dipole allowed transitions from 2p to 5d unoccupied states (figure 2). B and C structures are attributed to cerium in respectively the 4f¹ and 4f⁰ configurations (4,5), in agreement with the position in energy for the absorption of a pure CeIII compounds such as Ce(NO₃)₃ (figure 3). Splitting of these lines into a doublet (B₁, B₂ and C₁, C₂ respectively) may be attributed to a crystal field effect (3) or to the presence of localized and delocalized f states (4). The 4f¹ configuration for CeO₂ (normally a pure 4f⁰ "tetravalent" compound) may be due to a mixing of 4f and 2p orbitals (initial state effect) or to transitions from ligand to 4f orbital caused by the screening of the 2p hole (final state effect). However final state effects are strongly suppressed for the LIII absorption, as the 5d excited photoelectron participates to the screening of the core hole. Thus, unlike 3d core level XPS where final state effects are effective, resulting in strong 4f¹ and 4f² satellites (6), LIII edge absorption is a more direct probe of the electronic configuration of cerium.

On the other hand, the LIII edge of pure CeIII compounds such as Ce(NO₃)₃ (fig.3) and Ce(OH)₃ exhibits a strong white line B₁ (3).

Thus valuable informations on the electronic configuration of cerium can be deduced from LIII edge of cerium containing catalysts. For such complex systems, it is expected that cerium belongs to phases of different electronic configuration. Thus the spectra could be intermediate between the +III and +IV references.

For Pd-Ce/γ-Al₂O₃ catalysts we note a complete reduction from +4 to +3 state when the cerium loading decreases, characterized by the enhancement of the line B₁ and the disappearance of the other lines. Beneath 3% weight, cerium is in a completely reduced state. All spectra have been fitted using a constant set of parameters, within experimental errors: energy position E₀ and an empty density of states W (figure 2). For B₁ line, the value of W is 3.0 ± 0.5 eV, in agreement with reported 2.5 ± 0.2 eV for Ce(OH)₃ (3). As for intermetallic cerium compounds, the width of 5d density of states increases notably (9), we can concluded that the ionic character of cerium remains unchanged for all catalysts. These results are in agreement with XPS cerium 3d core level spectra of the same samples, although XPS is a more sensitive surface probe than XAS(2).
Some preliminary LIII edge spectra on Ce/γ-Al₂O₃ prepared in the same conditions are also given (fig. 3). As in the case of Pd-Ce/γ-Al₂O₃, we note a pronounced reduced state of cerium for small loadings.

**IV Discussion**

For low cerium loadings, cerium atoms can occupy cationic vacant sites of the high surface area of γ-Al₂O₃. Thus they have an oxidation number of +3.

Probably some diffusion of the rare earth cations occurs within the support. These processes seem rather independent of the presence of a transition metal.

However these cationic sites will be rapidly saturated and for higher cerium loadings (>1 3%), tridimensional CeO₂ will grow up on the surface.

The addition of palladium results in a partial reduction of cerium oxide by at least two processes:
- a chemical reaction of cerium oxide occurs with chlorine from the precursor salt Pd(NH₃)₄Cl₂ to form the oxychloride CeOCl. This compound is stable under our preparation conditions and has been evidenced by XRD.
- Thermo programmed reduction (TPR) and XPS indicate an important spill over of hydrogen, dissociated on palladium atoms, to CeO₂ or Ce/γ-Al₂O₃, which results in a reduction of cerium in both cases.

The occurrence of a reduced state of cerium, far from its normal oxidation state IV, are of importance for the catalytic process:
- by occupying cationic vacant sites of γ-Al₂O₃, cerium +III cations block cracks and fissures and thus prevent loss of surface area during severe treatments occurring in a motor cycle;
- by creating an electronic interaction with palladium, cerium maintains the palladium in a dispersed state at the surface and prevents sintering;
- the presence of a non stoechiometric oxide phase CeOₓ (x<2) in the vicinity of the transition metal increases the oxygen storage capacity of the catalyst.

**Bibliography**

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3. E. Beaurepaire, F. Le Normand and G. Krill, this Conference
Figure 1: XAS cerium L\textsubscript{III} edge of Pd/Ce\textsubscript{2}O\textsubscript{3} and Pd-Ce/\gamma Al\textsubscript{2}O\textsubscript{3} catalysts in function of the cerium loading (DCI experiment, deconvoluted from experimental resolution 2.5eV)

Figure 2: Fit of pure CeO\textsubscript{2} and Pd-Ce 0.5/\gamma Al\textsubscript{2}O\textsubscript{3} catalysts.

Figure 3: XAS cerium L\textsubscript{III} edge of CeO\textsubscript{2}, Ce (12.5 and 1.5)/\gamma Al\textsubscript{2}O\textsubscript{3}, Ce(NO\textsubscript{3})\textsubscript{3}.