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ENVIRONMENT OF PLATINUM ATOMS IN A H₂PtCl₆/Al₂O₃ CATALYST: INFLUENCE OF METAL LOADING AND CHLORINE CONTENT

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Abstract: EXAFS studies of the preparation of catalysts with different metal and chlorine contents have allowed detailed observation of platinum-support interactions. The influence of chlorine on the obtention of high dispersions is primordial. Influence of metal loading is seen essentially at the reduced stage. Mononuclear PtCl₄(O₂) support complexes formed by drying in air are transformed by calcination into PtO species. On reduction, we observe two dimensional metal particles at low platinum content, whereas at high loadings the particles become three dimensional.

INTRODUCTION

In industrial supported metal catalysts, there is a general trend towards very high dispersions. The dispersion is determined essentially by the metal loading and the role of chlorine (1). Classical characterization techniques (XPS, X-ray diffraction, electron microscopy...) are however limited to loadings of several percent or are not element specific (2). EXAFS enables us to follow the evolution of the platinum environment (3,4) as a function of these two parameters at various stages of preparation at loadings typical of industrial catalysts to achieve a better understanding of the preparation process and to determine whether high metal loading models are representative of real systems.

We have studied the main preparation steps for Pt/Al₂O₃ catalysts prepared by competitive co-impregnation of hexachloroplatinic (H₂PtCl₆) and hydrochloric acids. Using different metal loadings (from 0.3 % to 1.8 % by weight) and chlorine contents (1.11 % to 2.20 %) allows a study of the importance of support interactions. Experimental and data reduction techniques are detailed in these proceedings (6) and the results are summarized in the table. Phases and backscattering amplitudes were derived from Pt metal, H₂PtCl₆ and PtO₂ references (Fig. 1).
DISCUSSION

a) The dried stage

For a typical industrial preparation (0.6 % Pt, 2.2 % Cl) dried at 110°C, strong interactions of the complex with support oxygens are seen leading to formation of isolated mononuclear groups close to PtCl₄(0₂)₂ support (Fig. 2). This shows greater modification of the complex than suggested by the work of Lagarde and al. (3) but it is in agreement with results of other methods (5) (6). For these low metal loadings, metal loading has only a small influence on the platinum environment: there is a trend towards more oxygen and, more significantly, less chlorine surrounding the platinum atom. Although the precision of this type of result is of the order of the observed effect, the idea of a range of fixation sites being progressively filled cannot be excluded. On the other hand, chlorine plays an important role with oxygen content of the platinum coordination shell increasing as the initial chlorine decreases.

b) The calcination stage

During calcination in dry air, chlorine is progressively replaced by oxygen. It results a complex bounded to the alumina support close to Pt with 5,5 oxygen and 1,6 Chlorine as first neighbours (Fig. 3). No significant quantitative dependance on metal loading is seen but an observation of the Fourier transforms indicates that the distance may be more well defined at 0.3 %. It is indeed possible that higher loadings introduce a heterogeneous distribution at this stage. Once again, the chlorine has an important role here in preventing particle sintering in air. Even at low chlorine content, sintering does not occur at high temperatures in air showing the strong influence of the chlorine on the electronic state of the platinum.

c) Reduction

Complete reduction under hydrogen of samples calcined at 530°C leads to formation of small metal particles (4 to 6 first neighbours), two remarks are immediate (fig. 4):

- oxygen support bonds are visible at low loadings and absent at 1.5 % loading;
- dispersion decreases slightly with increasing metal content but not enough to explain the disappearance of Pt-O support bonds on a simple spherical particle on a flat oxide support model.

Two hypotheses may be put forward at this stage. Either the morphology of the particles is modified (the visibility of support bonds for low loading suggests a flatter shape whereas for high loadings the results suggest three dimensional crystallites) or the nature of the fixation site changes (edge and kink sites would give higher Pt-O coordination but may be present in limited numbers and saturated by the first particles to be formed). Analysis of higher coordination shells is necessary to clarify this point. At high loadings an increased heterogeneity of Pt-O distances may lead to a smearing out of oxygen bond lengths preventing their detection. It is to be noted however that whenever Pt-O bonds are detected in this work the distance is well defined at 2.02 + 0.04 A. We again observe a stabilising role of chlorine (5), the dispersion decreasing with lowering of chlorine content.
CONCLUSIONS

At the dried stage the precursor interacts strongly with the support to produce mononuclear, isolated PtCl$_4$(O$_2$) species. After calcination one observes isolated complexes close to a chlorided PtO$_2$ structure. Mobility of these species under hydrogen gives rise to the creation of particles during reduction.

An influence of metal loading in the dried and calcined states may be seen but, at least up to 1.5 % Pt, remains within errors. On reduction, however, the detection of support oxygen bonds for low loadings and a slightly higher dispersion suggest that two dimensional particles may here be more abundant, or that different fixation sites are available on the alumina. Very high loading catalysts (several percent) may not be representative of the industrial product, at least at the dried and reduced stages.

Chlorine content has a large influence at all preparation steps, preventing a large incursion of oxygen into the platinum coordination shell at the dried stage and serving to stabilize or redisperse the metal during calcination and reduction.

(1) J.P. Bournonville. Thesis IFP, 1979
(2) J. Berdala, Thesis IFP, 1986
(5) A.A. Castro and al. Scientific bases for the preparation of heterogeneous catalysts. Third international symposium, sept. 6-9, 1982 BELGIUM, p. A3.1

<table>
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<tr>
<th></th>
<th>Pt 0.1 %</th>
<th>Cl 2.5 %</th>
<th>Pt 0.6 %</th>
<th>Cl 2.5 %</th>
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<td></td>
<td>Pt-Pt</td>
<td>Pt-O</td>
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<tr>
<td>Dried 110°C</td>
<td>2.03 ± 0.02</td>
<td>3.38 ± 0.08</td>
<td>2.91 ± 0.02</td>
<td>3.38 ± 0.08</td>
<td>2.6 ± 0.5</td>
<td>4.5 ± 0.6</td>
<td>2.63 ± 0.05</td>
<td>4.1 ± 0.5</td>
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<td>Calcinated 550°C</td>
<td>2.04 ± 0.05</td>
<td>2.34 ± 0.08</td>
<td>2.05 ± 0.07</td>
<td>2.38 ± 0.08</td>
<td>2.5 ± 0.5</td>
<td>4.1 ± 0.5</td>
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<td>3.5 ± 0.7</td>
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<tr>
<td>Reduced 450°C</td>
<td>2.7 ± 0.04</td>
<td>2.04 ± 0.06</td>
<td>2.7 ± 0.05</td>
<td>2.04 ± 0.06</td>
<td>2.7 ± 0.05</td>
<td>2.04 ± 0.06</td>
<td>2.7 ± 0.05</td>
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Nearest neighbour distances (upper value, Å) and coordination numbers
Fig. 1: Magnitudes of the Fourier Transform of reference:
- Pt metal R=2.37 Å N=12
- H₂PtCl₆ R=2.12 Å N=6
- PtO₂ R=2.06 Å N=5

Fig. 2: F.T. of Pt ex H₂ PtCl₆/Al₂O₃
Dried 110°C
- 1.5% Pt 2.1% Cl
- 0.6% Pt 2.2% Cl
- 0.3% Pt 2.2% Cl

Fig. 3: F.T. of Pt ex H₂ PtCl₆/Al₂O₃
Calcined 530°C
- 2.2% Cl 1% Pt
- 1.1% Cl 1% Pt
- 0.3% Pt 2.2% Cl

Fig. 4: F.T. of Pt ex H₂ PtCl₆/Al₂O₃
Reduced 650°C
- 1.5% Pt 2.2% Cl
- 0.3% Pt 2.2% Cl