

XAFS characterisation of PtIn catalysts supported on activated carbon

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Introduction

Supported PtSn and PtIn are effective catalysts for dehydrogenation or cyclization reactions[1]. However, although the literature about PtSn is well documented, this is not the case for PtIn catalysts. The purpose of the present study is to elucidate the effect of the preparation method and the support surface chemistry in the state of Pt in dried PtIn/carbon samples, and the structure of the metallic particles in reduced catalysts.

Experimental

The catalysts were prepared using solutions of H_2PtCl_6 and $In(NO_3)_3$ following two procedures: i) successive impregnation (first In and then Pt), denoted by SI, and ii) coimpregnation, denoted by C. The Pt loading is about 1wt.% and the atomic ratio Pt/In is 1. Two activated carbons with different surface oxidation (C and C-HP (treated with H_2O_2)) were used as support. Drying and reduction were carried out at 383K (overnight) and at 623 K (in H_2 flow, 12 h), respectively. The Pt_{III} -edge absorption spectra were recorded in the transmission mode at RT ($E=11300-12700$ eV). A FT was performed on k^3 -weighted oscillations over the range of $3-12 \text{ \AA}^{-1}$.

Results and discussion

Dried catalysts

Fig. 1a shows the FT-EXAFS spectra obtained for the samples Pt/C, PtIn/C (SI) and PtIn/C (C) and H_2PtCl_6 .

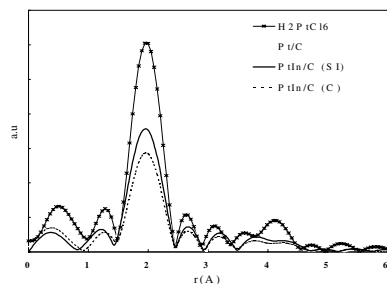


Fig 1. FT-EXAFS of dried catalysts (support C)

These results show an important decrease and/or change in the coordination of Pt upon impregnation. Differences between the three catalysts should be related to the different interaction of the platinum precursor with the carbon support. Such an interaction can take place via coordination with surface oxygen groups and/or via a reduction process in which carbon acts as a reducing agent and as a coordinating ligand [2,3]. For the two bimetallic catalysts, an effect of the preparation method is observed. It can be interpreted as follows: in the SI procedure, surface oxygen groups are occupied by In when the impregnation with the H_2PtCl_6 solution takes place; in the C procedure, however, there is a competition between In and Pt, and more platinum can be coordinated to oxygen.

The interaction with oxygen groups can be, as well, conditioned by the chemical state of such groups, that depends on the pH. The analysis of the white line shows that in the supported catalysts, platinum is less electrodeficient than in H_2PtCl_6 , what proves the partial reduction of Pt. The presence of indium conduces to a less electrodeficient state of platinum, that can be related either to a different interaction with carbon or to some interaction with In.

In comparison, with the oxidised C-HP support, almost no differences have been found in the structure of Pt in Pt/C-HP and PtIn/C-HP(C) catalysts, but the effect of the surface chemistry is noticeable in sample PtIn/C-HP(SI). As interpreted above, in an extensively oxidised support, competence for the oxygen surface groups is less relevant. The white line intensity for the three samples is close.

Reduced catalysts

Fig. 2 shows the FT-EXAFS profiles obtained for the reduced samples Pt/C, PtIn/C (SI) and PtIn/C (C) and for a platinum foil (reference). The profiles in Fig. 2 reveal that in the monometallic catalyst, Pt has a structure similar to that of platinum foil (calculated CN is 9).

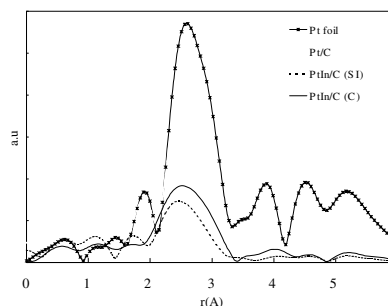


Fig. 2. FT-EXAFS of reduced catalysts (support C).

However, in the bimetallic catalysts, the structure is quite different (the fitting was not possible with Pt foil as a reference). This suggests that some alloying between Pt and In has occurred. The results obtained show some effect of both, the preparation method and, the support surface oxidation in the metallic or bimetallic particles. A deeper investigation of these effects requires the availability of suitable reference, subject of the next work. The XANES region shows that all the reduced bimetallic catalysts give a similar intensity of the white line and of the edge position, that is, after reduction the electronic state of platinum can be considered to be quite similar.

References

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