

XAFS characterisation of Pt and PtSn catalysts supported on carbon black

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Introduction

Supported PtSn are effective catalysts for dehydrogenation or cyclization reactions [1]. The properties and even the accessibility of the active phase are strongly influenced by the nature of the support. We have already investigated by XAFS the structure of the active phase of PtSn catalysts supported on activated carbon and on SiO₂ focusing the attention on the preparation method and the temperature of reduction [2,3]. In the present work, the support of the catalysts studied is carbon black. On this non-porous material the active phase is expected to be more accessible to reactants. However, because its surface chemistry is different from that of activated carbon, the properties of the active phase developed are, as well, probably different.

Experimental

The commercial carbon black V3G was used as support. The catalysts were prepared using solutions of H₂PtCl₆ and SnCl₂ following two procedures: i) successive impregnation (first Sn and then Pt) (sample PtSn/V3G (SI)), and ii) coimpregnation (sample PtSn/V3G (CI)). The desired Pt loading is about 1wt.% and the atomic ratio Pt/Sn 1. A monometallic Pt/V3G was also prepared. Drying and reduction were carried out at 383K (overnight) and at 623 K (in H₂ flow, 12 h), respectively. The Pt_L-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 Å⁻¹.

Results and discussion

Dried catalysts

Probably due to the non-porous structure of the carbon black, the amount of metals loaded is much lower than expected:

PtSn/V3G (SI).....0.41wt%Pt and Sn/Pt= 0.17

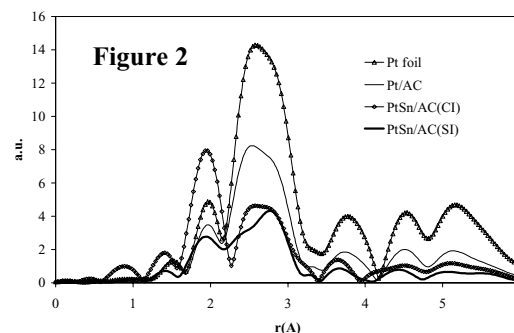
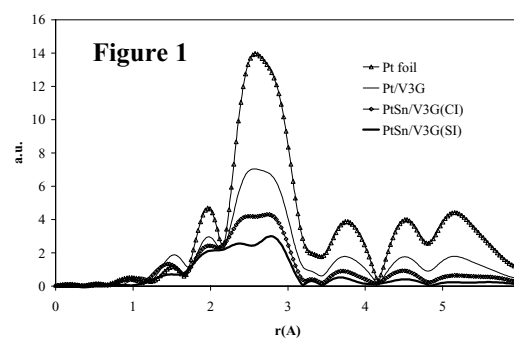
PtSn/V3G (CI)..... 0.55wt%Pt and Sn/Pt= 0.08

The FT-EXAFS spectra obtained for the dried catalysts contain a main maximum at about 2 Å, corresponding to Pt-Cl bonds. The intensity of this maximum is lower than in the precursor compound, H₂PtCl₆ according to a decrease and/or change in the coordination of Pt due to the interaction of the platinum precursor with surface oxygen groups and/or via a reduction process in which carbon acts as a reducing agent and as a coordinating ligand. A slight effect of the preparation method is observed being the modification of the coordination sphere of Pt lower for the sample prepared by successive impregnation (PtSn/V3G(SI)). However, the analysis of the white line shows that in both bimetallic PtSn and the monometallic Pt supported catalyst the electronic density of Pt is similar. In the case

of analogous samples prepared with activated carbon the effect of the preparation method was more pronounced [2], probably because the support contains more surface oxygen groups.

Reduced catalysts

Fig. 1 shows the FT-EXAFS profiles obtained for the reduced samples Pt/V3G, PtSn/V3G (SI) and PtSn/V3G (CI) and for a platinum foil. Fig. 2 shows the corresponding FT-EXAFS profiles of the analogous catalysts prepared with activated carbon (AC) [2].



For both supports the FT-EXAFS data of the bimetallic samples show three maxima although with different relative intensity. The assignment of these features to different Pt or PtSn is controversial [2]. At the moment, we are investigating this aspect by considering the presence Pt_xSn_y alloys in the fitting calculations.

What is more remarkable is that even with the noticeably low amount of Sn in catalysts prepared with V3G, PtSn species are developed. XPS of the PtSn/V3G catalysts show that even with a total Sn/Pt close to 0.1, there is a surface enrichment of tin (surface Sn/Pt about 3). In the case of samples prepared on AC with Sn/Pt=1, the surface Sn/Pt was about 20.

References

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