

XAFS characterisation of Pt and PtIn catalysts supported on silica

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Introduction

In order to improve the catalytic properties (selectivity, deactivation, ...) of supported Pt catalysts, a promoter like Sn, In, Re or Ge is usually added. Indium has been scarcely studied, in spite of its interesting behaviour [1]. In this work we analyse the effect of In on the microstructure of the platinum particles and the effect of the preparation procedure of bimetallic PtIn/SiO₂ catalysts. We also take into account the effect of the support as we have previously investigated the carbon supported PtIn catalysts.

Experimental

A commercial silica (ACROS), silicagel 0.2-0.5mm, pore size 6 nm, was used as support. The catalysts were prepared by impregnation in excess volume (contact time = 36h) followed by solvent evaporation at T = 60°C. Aqueous solutions of H₂PtCl₆ and In(NO₃)₃ were used, 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. A monometallic Pt/SiO₂ sample was also prepared. Drying and reduction were carried out at 383K (overnight) and at 623K (in H₂ flow, 12 h), respectively. The Pt L_{III}-edge absorption spectra were recorded in the transmission mode at RT (E= 11300-12700 eV). A FT was performed on k³-weighted oscillations over the range of 3-12 Å⁻¹.

Results and discussion

Dried catalysts

FT-EXAFS data indicate that, in general terms, platinum atoms show a high Coordination Number (CN) with Cl atoms, only slightly lower than in H₂PtCl₆. Comparing the three catalysts, the monometallic one presents the lowest CN for Pt-Cl. The intensity of the white line is for the monometallic catalyst less intense than for bimetallic, what confirms the lower Cl coordination in the former, related to a soft interaction with the support surface. The two dried bimetallic catalysts have an electronic density similar to that of H₂PtCl₆. Because the adsorption of H₂PtCl₆ by silica is low, the catalysts consist of the metal precursors deposited on the support with a weak interaction with the support, that is slightly stronger in the case of the metallic catalyst. It seems that the presence of indium hinders the interaction of Pt species with the support.

Reduced catalysts

Fig. 1 shows the FT-EXAFS spectra obtained for the reduced catalysts Pt/SiO₂, PtIn/SiO₂ (SI) and PtIn/SiO₂ (C) and for a Pt foil. Data of Pt/C have also been included.

The monometallic sample presents a strong interaction with the support as the peak at 1.7 Å reveals (assigned to a Pt-O bond [2]) and a structure of the platinum particles (signal between 2 and 3 Å) different from the one corresponding to the platinum foil. Taking as a reference the results previously obtained with Pt/Carbon catalysts [2], where the structure of the Pt foil is clearly observed, a very important effect of the SiO₂ support in the state of supported Pt is inferred. It can be considered that in Pt/SiO₂ there are small particles of metallic platinum bonded to the support surface through Pt-O-Si bonds. In the case of the bimetallic catalysts, the previously assigned Pt-O distance is not observed. The structure of platinum resembles that found in the Pt/SiO₂ catalyst, but there are differences in the profiles found for the three catalysts in the 2-3 Å zone, that reveal an effect of the In presence and of the preparation procedure. According to the white line (Fig. 2), reduced bimetallic catalysts present an electronic density similar to that of Pt foil. It means that it is Pt⁰ although with a crystalline structure different from that of Pt foil. For Pt/SiO₂ the white line is more intense than for Pt foil. Such a result confirms a strong interaction between Pt and the support via Pt-O bonds and that In hinders the interaction of Pt with the support.

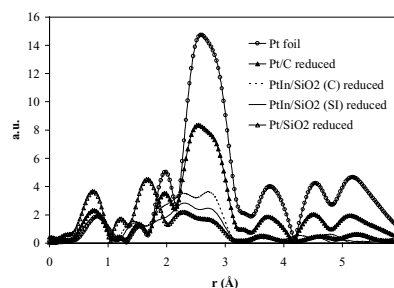


Fig. 1. FT-EXAFS of reduced catalysts.

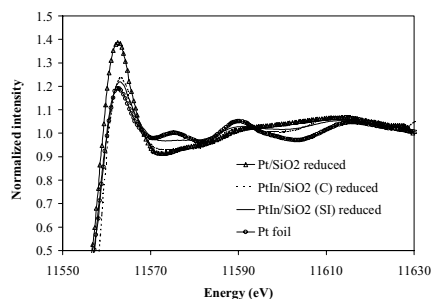


Fig. 2. White line of reduced catalysts.

References

- [1] Fabio B. Passos et al., J. Catal. 178, 478-488 (1998).
- [2] M.C. Román et al., Curr.Top.Catal., 1 17-42 (1997).

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