

LOW TEMPERATURE CO OXIDATION OVER Pt-Sn CATALYSTS SUPPORTED ON ACTIVATED CARBON CLOTH

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Introduction

The catalytic oxidation of CO at low temperatures is an interesting reaction from the environmental point of view and also concerning to long-life CO₂ lasers and sensor applications. Hence, a number of studies have been carried out with different systems. Among them, good results have been obtained with Pt/SnO_x catalysts [1,2] in terms of high activities at low temperatures. A synergism between the tin oxide and the platinum phases has been reported, which results in the weakening of the carbon-oxygen bond in carbon monoxide, thus activating the molecule and enhancing the reactivity [3]. Some other models have also been suggested. Thus, a bifunctional mechanism based on the spillover of both carbon monoxide and oxygen from the noble metal to tin dioxide has been proposed. Also, a different bifunctional mechanism restricts the spillover phenomena to CO or to O₂. On the other hand, it has been proposed that the adsorption of reactants leads to a local temperature increase of the platinum particles, which promotes the reaction on adjacent SnO_x sites. Finally, other explanations [4] are based on the existence of a new phase: a platinum-tin alloy.

The aim of this work is to add some light to this topic by studying the CO oxidation reaction over platinum-tin catalysts supported on activated carbon cloth with different surface properties. In this way, catalysts with several tin contents (from 1 wt.% to 12 wt.%) and subjected to different reduction treatments have been studied. Thus, a range of surface compositions (platinum-tin surface atomic ratio, oxidised and reduced species, and possibility of formation of alloy phases) have been analysed. The support chosen for these bimetallic catalysts has been an activated carbon cloth. This material adds to the well-known properties of carbonaceous materials as supports for this kind of systems (inertness, high surface area, etc.) a higher contact efficiency, a lower pressure drop under reaction conditions and an optimal physical shape for its practical application.

Experimental

The support used (ACC) has been an activated carbon cloth (RS 1301, from Actitex[®]) with a BET surface area of 1200 m²g⁻¹, a mean pore diameter of 0.6-0.8 nm and an ash

content of 0.48 wt.%. Tin oxide was deposited on the support at different loading (1, 6 and 12 wt.%) by impregnation with aqueous solutions prepared by dissolving the proper amounts of tin (II) oxalate in diluted HNO₃. The excess of solvent was removed by flowing nitrogen, and the resulting samples were dried at 393 K in air and subsequently heat-treated at 623 K under flowing helium. Platinum (1 wt.%) was introduced by impregnation of the SnO₂/ACC samples with aqueous solutions of H₂PtCl₆. After removing the excess of solvent, the solids were dried overnight at 393 K. A monometallic Pt/ACC catalyst was also prepared for the sake of comparison.

After reduction at different temperatures, the catalysts have been characterised by temperature programmed reduction (TPR) under diluted hydrogen, and X-ray photoelectron spectroscopy (XPS).

The CO oxidation reaction was carried out in a quartz reactor with CO:O₂:He ratios of 10:10:80 in the feed, with a total flow rate of 50 ml/min. The analysis of reactants and products was performed by on-line mass spectrometry.

Results and Discussion

Temperature-programmed reduction (TPR) studies reveal a strong interaction between platinum and tin dioxide, in such a way that the reduction of the latter is favoured by platinum. Thus, whereas the maximum reduction peak (H₂ consumption) for SnO₂/ACC is obtained at about 915 K, two peaks are obtained in the presence of the noble metal. The high-temperature peak matches that obtained on SnO₂/ACC, and it is thus assigned to the reduction of tin oxide not interacting (or with a low interaction) with platinum. However, a low-temperature reduction peak appears in the platinum containing catalysts, which is centred at about 710 K. This one is assigned to the reduction of tin oxide in close contact with platinum particles, through a mechanism involving hydrogen atoms generated on the platinum surface and spilt over tin oxide. The analysis of the reduction behaviour of these catalysts by X-ray photoelectron spectroscopy (XPS) reveals that the complete reduction of oxidised platinum in the precursor salt to metallic platinum is hindered in the presence of tin oxide.

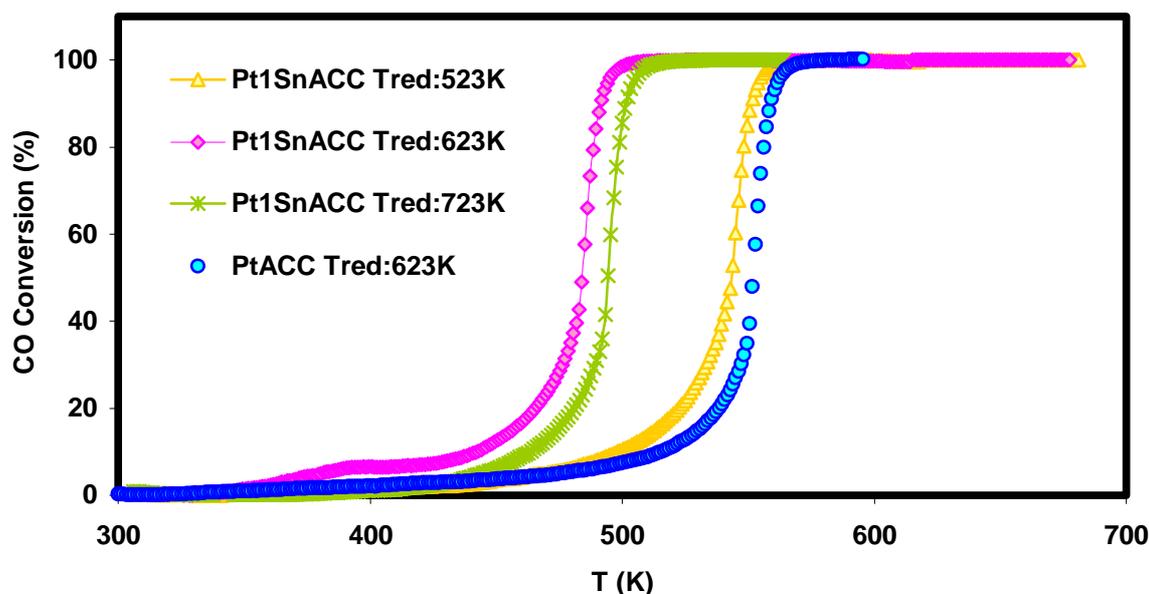


Fig. 1 Oxidation of CO on bimetallic Pt1Sn/ACC catalysts reduced at different temperatures, and monometallic Pt/ACC reduced at 623 K. Light-off curves (0.1 g catalyst; flow rate, 50 ml/min; CO:O₂:He = 10:10:80).

The Pt $4f_{7/2}$ band appears close to 72.0 eV whatever the reduction temperature used, and this binding energy is somewhat higher than the obtained for the monometallic Pt/ACC catalysts (71.4 eV). On the other hand, a given amount of tin oxide is reduced to metallic tin after reduction at 623 and 723 K, this leading to the possibility of formation of Pt-Sn alloy phases. The existence of these phases could also explain the relatively high binding energy obtained for platinum in the catalysts reduced at high temperatures. It can be then concluded that catalysts reduced at 523 K contain metallic platinum in an electron deficient state and oxidised tin species. The reduction treatment at 623 K or 723 K favours the partial reduction of tin oxide, with the subsequent formation of Pt-Sn alloy phases.

The catalytic behaviour of the different catalysts after reduction treatment at 523, 623 and 723 K has been analysed by determining the light-off curves obtained with 0.1g of catalyst.

Figure 1 plots the light-off curves obtained with the bimetallic Pt1Sn/ACC catalyst, after reduction at different temperatures, as well as the curve obtained with the monometallic Pt/ACC catalyst reduced at 623 K. The curves show the beneficial effect of tin in this reaction. The light-off temperature (50% conversion) decreases from 553K for Pt/ACC to 485 K for Pt1Sn/ACC, both reduced at 623K. It is also evident from Figure 1 that 623 K is the optimal reduction temperature, as the light-off temperature for the catalyst reduced at 723 K increases to 495 K and that for the catalyst reduced at only 523 K is as high as 545 K. XPS studies reveal that at 523 K platinum is in a metallic state (although in an electron deficient state), whereas tin remains oxidised. But, after reduction at 623 K, a given amount of tin is reduced, and is able to form an alloy phase with platinum. Furthermore, the

surface atomic Pt/Sn ratio is the highest after reduction at 623 K. When the reduction temperature is increased up to 723 K the formation of Pt-Sn is even more favoured, but now the Pt/Sn atomic ratio at the catalyst surface is lower, thus explaining the somewhat higher light-off temperature of this catalyst.

These data reveal that the formation of Pt-Sn alloy phases is beneficial for CO oxidation. The less active bimetallic catalyst, with an activity close (although somewhat higher) to the monometallic Pt/ACC, is obtained after reduction at 523K, when tin remains in an oxidised state which makes impossible the formation of alloy phases.

The effect of tin content has been analysed in samples reduced at 623 K. It has been found that the light-off curves are displaced towards higher temperatures as the tin loading increases, the best results being obtained with catalyst Pt1Sn/ACC.

References

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