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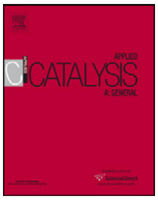

Preferential CO oxidation in hydrogen (PROX) on unsupported PtSn catalyst

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ABSTRACT

PROX reaction was studied over an unsupported PtSn catalyst. CO_2 and H_2O were produced from a H_2 flow containing 1% CO, and 0.4–2% O_2. PtSn pretreated with O_2 and H_2 contained more Pt in the near-surface region and was more active towards CO oxidation than a sample pretreated in H_2 only. In situ XPS was also carried out during PROX reaction. Sn 3d indicated the presence of Sn-oxides, near to the surface region, along with Pt_3Sn. Pt 4f peak showed metallic Pt under all conditions. Water and OH enrichment was observed in the O 1s spectrum, taken during PROX reaction.

1. Introduction

Preferential oxidation of CO in excess hydrogen (PROX) is becoming a more and more important process, providing CO-free H_2 for fuel cell application [1]. Various catalysts, including supported noble metals, have been tested for this process, as summarized in Ref. [1]. Pt was a frequently used component of the active phase [2,3]. Catalysts containing Pt and Sn as the active component have been used successfully for PROX reaction [4,5]. Pt_3Sn single crystal surfaces exhibited a much higher activity for both CO oxidation [6] and PROX [7]. Various explanations were suggested to explain the advantageous effect of – catalytically inactive – Sn to Pt catalysts [8]. The geometric concept of catalysis ("ensemble" effect) emphasizes the effect of Sn to produce single Pt sites, where special co-ordination of CO_2 (and also CO) to Pt atoms could take place [9]. The surface of Pt_3Sn single crystals contained pure sites made of Pt only and mixed sites containing Pt and Sn atoms [7]. CO adsorption was found to be possible on both types of surface sites [10]. The "electronic" concept of catalysis points to the different electronic structures of PtSn alloys. Llorca et al. [9] regarded this effect less important in Pt_3Sn. The majority of studies agree, however, that it is difficult and in fact, meaningless to separate these two effects, as they are so closely interwoven.

Unsupported metal blacks with high dispersion represent another model catalyst system comparable with supported metal catalysts in various hydrocarbon reactions [11]. Its characterization with surface electron spectroscopy is simpler, due to the absence of signals from support materials [12,13]. We studied recently an unsupported PtSn system by various physical methods (electron microscopy, X-ray diffraction, XPS depth profiling, Mössbauer spectroscopy) and tested it also in hydrocarbon reactions [14]. Different phases could be identified: Pt, Pt_3Sn, Pt_2Sn_3 and SnO_2, depending on the treatment of the catalyst in various atmospheres and at various temperatures. XRD of the stabilized particles of this PtSn system after O_2 and H_2 treatments at 673 K indicates the presence of mainly Pt_3Sn phase and some metallic Pt. Mössbauer spectroscopy detected about 90% Pt_3Sn plus 10% Pt. SnO_2 phase was not identified, but patches may be present on the surfaces. This PtSn sample was inactive in hydrocarbon reactions (C_5 ring opening and closure, aromatization, skeletal isomerization) requiring more than one Pt atom as active site [15], but it was active in hydrogenation of cyclohexene to cyclohexane and its dehydrogenation to benzene [14], requiring single-atom Pt sites. We report here results obtained in PROX reaction over unsupported PtSn catalyst, characterized also by in situ high-pressure XPS [1]. As stated in the literature [4,7,19], the presence of Sn increased the activity of Pt in CO oxidation under PROX conditions, i.e., in the presence of hydrogen. This was attributed to a much lower activation barrier on PtSn surfaces than on Pt(1 1 1) [16], confirmed also by first principle studies [17]. Dupont et al. [6,7] discussed in detail the structure of possible active sites on Pt_3Sn single crystal surfaces.

2. Experimental

2.1. Catalyst

The unsupported PtSn catalyst was prepared by reducing the salts of H_2PtCl_6 and $SnCl_4$ with a nominal atomic ratio of Pt:Sn = 3:1,

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