STRUCTURAL STUDIES OF Pt-Sn CATALYSTS ON HIGH AND LOW SURFACE AREA ALUMINA SUPPORTS

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For a series of catalysts containing 1 wt.% Pt and Sn:Pt ratios ranging from ca. 1 to 8, the only crystalline alloy phase detected by XRD was SnPt (1 : 1). The XRD intensity of lines for the SnPt (1 : 1) alloy phase increase with increasing Sn:Pt ratios, indicating the presence of unalloyed Pt in the samples containing low tin loadings.

The study of alloy catalysis received impetus in 1950 with the introduction of benzene hydrogenation data for a series of Cu-Ni alloy catalysts [1–3], and again in the 1960s with the introduction of a commercial process utilizing Pt-Re naphtha reforming catalysts [4]. PtSn alloy catalysts for naphtha reforming were also introduced in the 1960s. While these catalysts have been subjected to extensive characterization studies since that time the question of the extent that alloys of the metals are formed is still a subject of debate. Likewise, the PtSn alloy catalysts were slow to gain a role in commercial processes but the introduction of continuous regenerative naphtha reforming increases the importance of PtSn catalysts.

In both of these bimetallic reforming catalysts, evidence was found to support either the formation [5–7] or the absence [8,9] of alloy following reduction. For the most part alloy formation was not directly observed but was deduced from a measurement of the average valence state of Re or Sn. XPS (X-ray photospectroscopy) data [10,11] indicated that the tin atoms were not present in the metallic state even when Pt was present in the metallic state. In-situ X-ray diffraction data [12] showed an alloy was formed but that for the PtSn composition utilized (Pt_3Sn_8), only the PtSn phase was present. Lieske and Volter [13] reported, based on the temperature programmed reduction and adsorption of oxygen and hydrogen, that the amount of alloyed tin increases with an increase in Sn content. Mössbauer studies [14–18] provided evidence for the formation of

Pt-Sn alloy, and much of the reported data indicated that the Pt-Sn-γ-Al_2O_3 catalysts are multicomponent in that they have highly dispersed products of the chemical interactions of Sn (IV), Sn (II) and Sn (O) with both Pt and the surface of the support. The present XRD studies utilize a range of PtSn compositions and both a low and high surface area alumina support.

Various compositions of Pt-Sn catalysts, with a constant Pt content and variable Sn content, were prepared on two alumina supports. These supports were Degussa alumina (surface area of about 110 m^2/g) and U.C.I. alumina (300 m^2/g surface area). The Degussa alumina differs from the U.C.I. alumina since it consists of agglomerates small non-porous spheres so that the impregnated metals should be added only to the external surface of these non-porous spheres. Platinum and tin were impregnated on these supports in the atomic ratios of 1 : 1, 1 : 2.7, 1 : 5 and 1 : 8. The supports were impregnated with a solution of the required amounts of dihydrogen hexachloroplatinate (IV) ($H_2PtCl_6.6H_2O$) and $SnCl_2.2H_2O$ in acetone, using an incipient wetness technique. The impregnated catalysts were then dried at 120 ° C in air overnight. The catalysts were calcined at 450 ° C for about 4 hours, and then reduced in flowing hydrogen for about 16 hours at 500 ° C. The samples were passivated in a nitrogen (98%)-oxygen mixture. These catalysts were analyzed in the Rigaku X-ray diffractometer, using Cu Kα radiation with a step scan of 0.02 degree and with a scan time of 10 sec/step in the 2θ range of interest.

An indexed diffraction pattern obtained from a reduced catalyst containing Pt:Sn atomic ratio = 1 : 8 on Degussa alumina support is shown in fig. 1, with h, k, l, indices for the PtSn peaks identified. For the catalyst series the amount of Pt-Sn phase increases with increase in Sn content for the catalysts prepared on 300 m^2/g alumina support. The X-ray diffraction patterns from the catalysts containing various Pt:Sn ratios are similar to those shown in fig. 1, and only the Pt-Sn (1 : 1) phase could be observed. The catalysts with the highest Pt:Sn did not contain other PtSn alloy phases, such as $PtSn_4$, Pt_2Sn_3, $PtSn_2$. This was also the case for the catalysts prepared on 110 m^2/g Degussa alumina support.

The integrated areas of the most intense PtSn (102) X-ray diffraction peaks were measured and are plotted versus Sn content in fig. 2. The crystallite size measured from the line width at half maximum intensity, using Scherrer equation for the catalysts on both alumina supports is shown in fig. 3. The PtSn (102) profile for the Pt:Sn = 1 : 1 sample was so broad and the interference of the alumina background was so great that the crystallite size for this sample could not be calculated. The amounts of Pt:Sn (1 : 1) alloy phase formed, and the crystallite size for this phase, are slightly larger for the catalysts on 300 m^2/g surface area support than on 100 m^2/g Degussa alumina support.

As Pt (111) and (200) profiles overlap with more intense alumina peaks, the observation of these peaks was rather difficult. However, Pt (311) profile at $2\theta = 81.2°$ is not overshadowed by a peak from the alumina supports. The presence of a Pt (311) peak indicates that the catalyst with Pt:Sn = 1 : 8 has, in

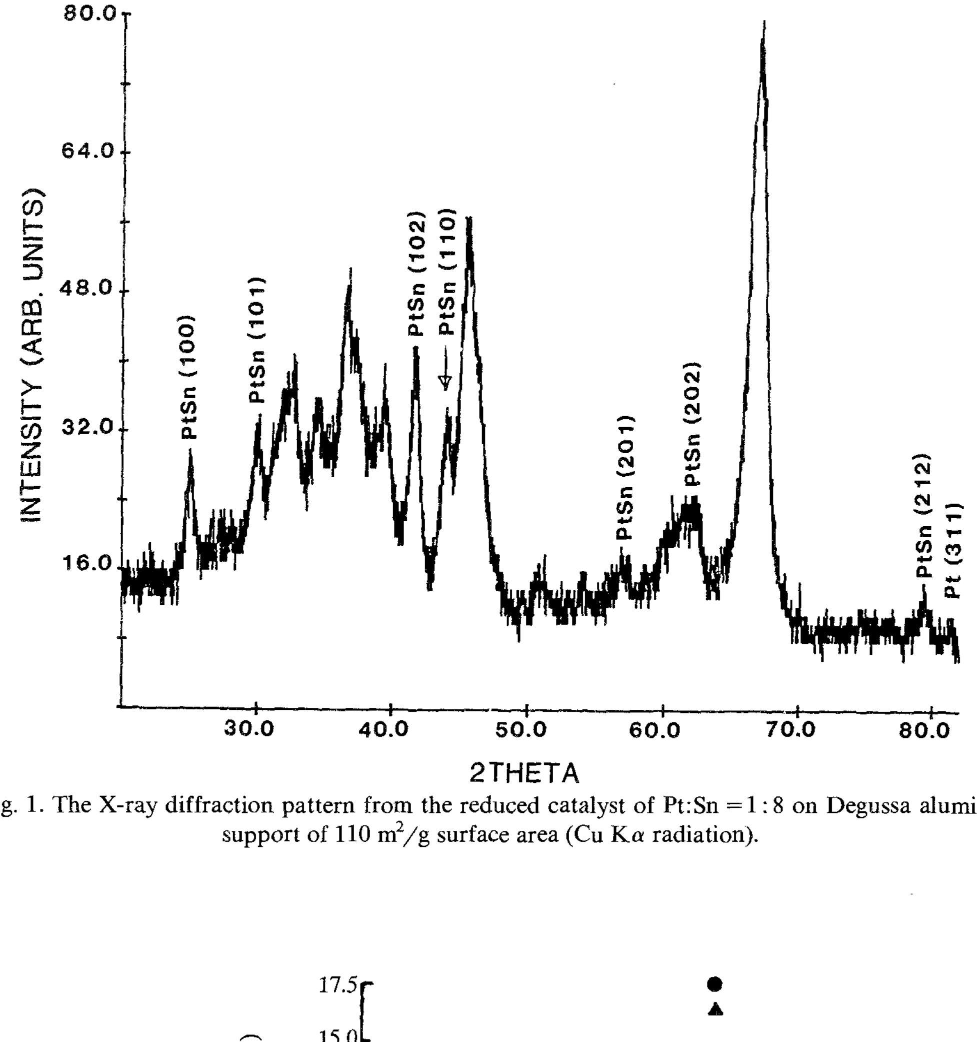

Fig. 1. The X-ray diffraction pattern from the reduced catalyst of Pt:Sn = 1:8 on Degussa alumina support of 110 m^2/g surface area (Cu Kα radiation).

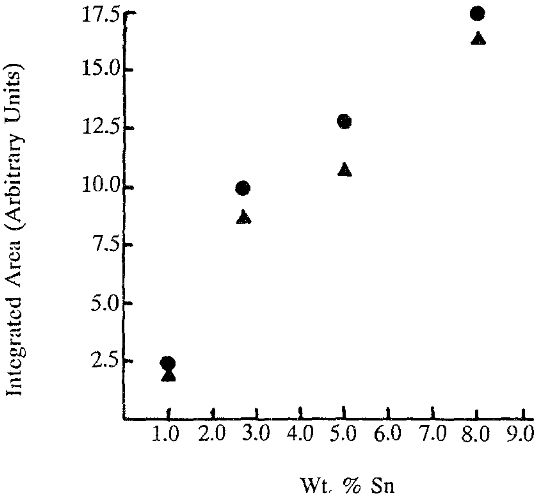

Fig. 2. The integrated intensity measured from the 100% PtSn (102) profile versus Sn content: (●) on the U.C.I. alumina support and (▲) on Degussa alumina support.

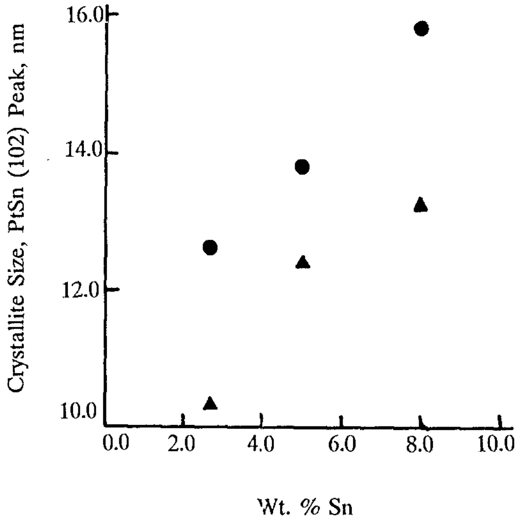

Fig. 3. The crystallite size measured from the line with of the PtSn (102) peak at half maximum intensity; (●) on U.C.I. alumina support and (▲) on Degussa alumina support.

addition to the formation of PtSn (1 : 1) phase, the fcc platinum phase. However, the catalysts with lower Sn loadings did not show the presence of a platinum phase. Thus, it appears that the presence of high Sn loadings facilitates the migration and agglomeration of Pt.

In another experiment, it was intended to observe the time factor for the formation of PtSn phase. The catalyst having Pt:Sn = 1:8 supported on U.C.I. alumina was reduced for periods of 2 to 16 hours. No PtSn phase was formed when this material was reduced for 2 hours; after 4 hours of reduction the PtSn phase attained about 75% of the intensity and after 16 hours of reduction, the sample exhibited the maximum intensity.

A material containing 10% Sn and no platinum was prepared. The X-ray diffraction pattern from the reduced sample was identical to that of the alumina support. The oxidized sample showed the formation of two small peaks which were from neither the SnO nor SnO_2 compounds. These additional peaks are believed to be due to a tin aluminate phase.

The XRD patterns indicate the presence of only one alloy phase, PtSn (1 : 1). No evidence was obtained for other PtSn alloy phases, such as Pt_3Sn, Pt_2Sn_3, $PtSn_2$ and $PtSn_4$. The XRD data are in excellent agreement with the data obtained from the known unsupported Pt-Sn alloys, both in terms of peak positions and relative intensities [19]. Thus, our data indicate that only one alloy phase is formed over a wide range of Pt:Sn compositions.

Presumably, platinum is reduced to the metallic state for each composition of the two catalyst series. This, combined with the observation of only one alloy phase, led us to anticipate that all samples of a series would exhibit similar intensities for each peak of the Pt:Sn (1 : 1) XRD pattern; this anticipated result was not realized (fig. 2). The surprising result is that as the Sn/Pt ratio becomes larger, the amount of the PtSn (1 : 1) alloy increases rather than providing a mixture of alloy phases in which the tin rich alloys dominate at the higher Sn/Pt ratios.

The passivation step introduces an undesirable complication. However, the PtSn alloy phase when passivation is used is the same as obtained in our earlier study [12] where the use of in-situ XRD equipment eliminated the need for the passivation step. In the lower Sn/Pt range a significant fraction of both Pt and Sn are present in a form that is X-ray amorphous. XPS data indicate that the Pt is present in the zero valent state but that a significant amount of tin is present in an oxidized state. Presumably the platinum not present as PtSn (1 : 1) alloy is present as atomically or highly dispersed Pt crystallites that are too small to produce detectable XRD peaks. The oxidized tin is present in an X-ray amorphous form, presumably in a surface layer of "tin-aluminate".

Tin alters the activity and aromatic selectivity of a Pt catalyst, which implies an intimate contact between some form of tin and Pt(O). Catalytic activity appears to go through a maximum near Sn/Pt ~ 3 to 4 [20]. This later observation raises the question about the identity of the catalytically active species in the PtSn alumina catalyst: is it the PtSn alloy or is it X-ray amorphous Pt that is modified to become more active by contact with a Sn species? Activity as used here must include a factor that takes into consideration the aging resistance since it may be the ability of Sn to retard aging that provides an apparent increase in activity. If the maximum in activity at a Sn-Pt ratio of 3 to 4 is valid then the implication is that it is the dispersed, X-ray-amorphous Pt, rather than the PtSn (1 : 1) alloy, that is catalytically active for hydrocarbon conversions.

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