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Role of metallic tin in PtSn reforming catalysts

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Metallic tin was detected using X-ray photoelectron spectroscopy (XPS) after H_2 reduction of 5%Pt/SnO_2, 5%Pt-5%Sn/SiO_2, and 5%Pt-29%Sn/Al_2O_3. However, no metallic tin could be detected in PtSn/Al_2O_3 catalysts with tin loadings up to 5 wt%. These findings indicate that tin reducibility depends on the extent of interaction between SnO_x and the substrate. Hexane reaction studies indicate that metallic tin poisons all reforming reaction channels regardless of the support.

Keywords: PtSn bimetallic catalysts; metallic tin; XPS; TEM; oxygen chemisorption; hexane reforming reaction

1. Introduction

The role of tin in PtSn catalysts has been the subject of many studies [1–8], although few have provided a direct correlation of surface composition and catalytic behavior for reforming reactions [1–3]. While most work using low tin loading PtSn/Al_2O_3 catalysts has demonstrated that tin persists in an oxidic state after hydrogen reduction [1–5], other studies suggested that PtSn-alloy formation occurs and that this alloy formation is an important contributor to improved reforming selectivity and activity maintenance [6,7]. It is of great fundamental and practical interest to gain some insight into the conditions for PtSn-alloy formation and its consequences in reforming catalysis. In this communication, we have used XPS, O_2-chemisorption, TEM and hexane reaction studies to explore the catalytic role of metallic tin in Pt/SnO_2, PtSn/SiO_2 and PtSn/Al_2O_3. It is shown that tin reducibility varies with the substrate, and in the case of alumina supported catalysts, initial tin oxide loadings and dispersion. Metallic tin poisons platinum catalytic activity for all hydrocarbon reaction channels.

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2. Experimental

Combined XPS and hexane reaction studies were carried out using a Leybold apparatus equipped with a microreactor that has been described previously [9]. Fresh ($\approx$ 100 mg) catalyst samples mounted on a copper holder were activated with flowing hydrogen at 708 K and atmospheric pressure. XPS data were collected using Mg K_α radiation and an analyzer pass energy of 50 eV; binding energies for insulated samples (SiO_2 and Al_2O_3 supported catalysts) were referenced to Si(2p) or Al(2p) lines of the supports at 103.4 and 74.7 eV, respectively. After XPS measurements, hexane reaction was investigated under differential flow conditions at low conversion ($< 4\%$), atmospheric pressure, and 708 K with a molar H_2/C_6 feed ratio of 6.0. Products were monitored on-line with a gas chromatograph calibrated with certified CH_4/N_2 mixtures. Dynamic O_2-uptake studies were carried out using similar activation conditions in a different apparatus using a 100–200 mg sample charge, a TCD detector and 2% O_2/He. TEM and microelemental analysis results were obtained with a JOEL 2000 CX instrument using samples from the XPS/reaction studies.

SnO_2 was produced by hydrolyzing aqueous $SnCl_2$ with NH_4OH followed by filtration, drying, and air calcination at 923 K for 4 h. Supported catalysts were prepared by impregnating Cabosil or high purity Cyanamid alumina 60/150 mesh powders with aqueous $SnCl_2$ to the point of incipient wetness followed by drying and calcination at 923 K. Platinum was then added by impregnation of H_2PtCl_6 followed by drying and calcination at 673 K for 4 h. Elemental compositions were determined by X-ray fluorescence. Residual chloride was less than about 0.3 wt%, and no Cl was detected by XPS after reduction.

3. Results and discussion

It is well established that Sn^{2+} and Sn^{4+} are not distinguishable by XPS [10]. Sn(3d) spectra for SnO_2 and SnO display two peaks at 486.4 and 494.9 eV. After H_2 activation at 708 K, two additional peaks at 1.9 eV lower binding energy which are associated with metallic tin were observed in Sn(3d) spectra for 5%Pt/SnO_2, 5%Pt-5%Sn/SiO_2 and 5%Pt-29%Sn/Al_2O_3 (fig. 1). The percentage conversions to metallic tin in these materials are roughly 30–40% for Pt/SnO_2, 70% for PtSn/SiO_2, and 15% for 5%Pt-29%Sn/Al_2O_3. By contrast, earlier studies of PtSn/Al_2O_3 catalysts with tin loadings of 0.3–5 wt% showed no evidence for metallic tin even under more severe activation conditions [1–3].

Our new results indicate that the interaction between SnO_x and alumina is loading dependent. While pure SnO_2 is partially reducible to metallic tin in the absence of Pt, interactions between SnO_x and SiO_2 prevent reduction to metallic tin in the absence of platinum, although this interaction is not strong

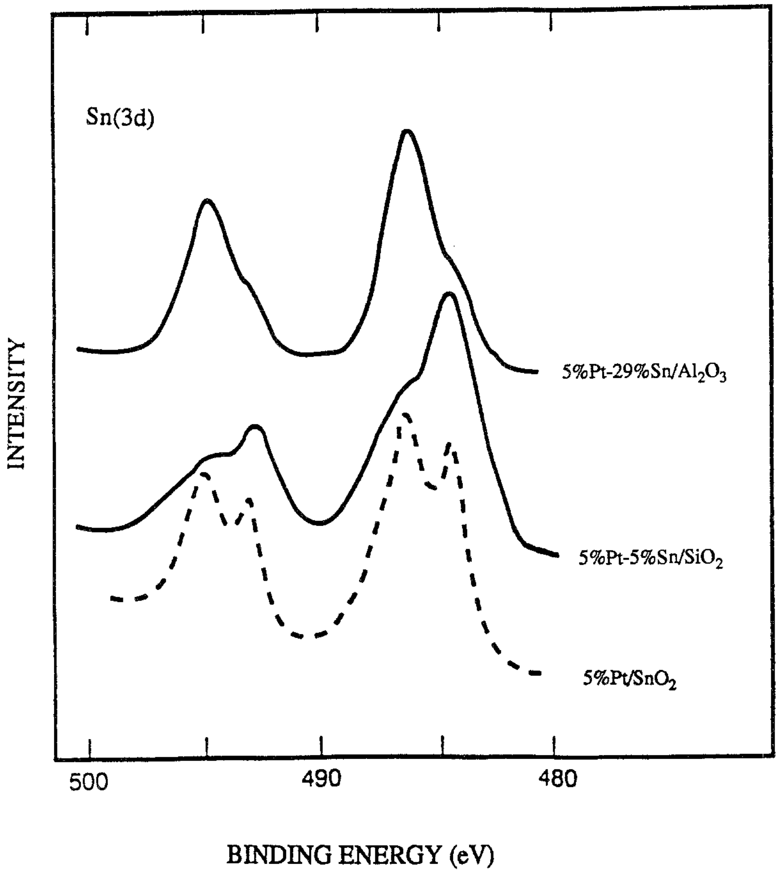

Fig. 1. Sn(3d) spectra of 5%Pt/SnO_2, 5%Pt-5%Sn/SiO_2 and 5%Pt-29%Sn/Al_2O_3 after hydrogen reduction at 708 K.

enough to stabilize SnO_x in the presence of Pt. Stronger interactions between "highly dispersed" SnO_x and alumina stabilize SnO_x for tin loadings up to at least 5 wt% even when platinum is present. However, at very high loadings (e.g., 29%), a significant fraction of the tin becomes reducible to metallic state. This reduction appears to be facilitated by the presence of large, more weakly interaction SnO_x clusters. This conclusion is supported by TEM and microelemental analysis results which revealed a high density of tin-rich 50–300 Å particles in both the 5%Pt-5%Sn/SiO_2 and 5%Pt-29%Sn/Al_2O_3 catalysts, whereas in PtSn/Al_2O_3 catalysts with tin loadings up to 5 wt%, only small particles with size less than 25 Å were detectable.

Platinum (4f) binding energy shifts in catalysts containing metallic tin also suggested direct Pt–Sn interactions in these materials. Specifically, in Pt/SnO_2 and PtSn/SiO_2, Pt($4f_{7/2}$) binding energies were detected at 71.4–71.8 eV which are 0.4–0.8 eV higher than that for bulk platinum (71.0 eV). These binding energy values compare favorably with that for Pt_3Sn (71.9) [11] although we do

Table 1
Properties of PtSn catalysts

Catalyst	O_2 uptake [a] (μmol/g)	Reaction rate (mol/g s)	Turnover rate [b] (molec/Pt_s s)	Selectivity (wt%) [c]		
				C_5	2-MP+MCP	B
Pt black		2.1×10^{-7}		37	trace	63
Pt black : SnO_2 (2:1) [d]		3.7×10^{-8}		61	trace	39
5%Pt-SnO_2		not active				
5%Pt-SiO_2	29	3.6×10^{-7}	6.2×10^{-3}	33	25	42
5%Pt-5%Sn/SiO_2	20	2.2×10^{-8}	5.5×10^{-4}	35	trace	65
5%Pt-Al_2O_3	141	9.0×10^{-6}	3.2×10^{-2}	54	21	25
5%Pt-1.9%Sn/Al_2O_3	119	3.9×10^{-6}	1.6×10^{-2}	25	60	15
5%Pt-29%Sn/Al_2O_3	14	1.8×10^{-7}	6.4×10^{-3}	49	40	11

[a] Second cycle oxygen uptake (see text).
[b] Based on surface Pt-site density from second cycle oxygen uptake.
[c] C_5: hydrogenolysis products; 2-MP: 2-methylpentane; MCP: methylcyclopentane; B: benzene.
[d] Physical mixture (reaction rate on this catalyst is calibrated based on the weight of Pt black).

not know the stoichiometry of PtSn alloys formed in these systems. Furthermore, in the case of Pt/SnO_2, the Pt/Sn XPS intensity ratio decreased by an order of magnitude after reduction indicating that platinum becomes largely covered by tin (or partially reduced tin oxide). Evidence for similar strong Sn–Pt interactions in the PtSn/SiO_2 and 5%Pt-29%Sn/Al_2O_3 catalysts was obtained from oxygen adsorption measurements that are summarized in table 1. In these studies, the catalysts were initially H_2-activated at 708 K, O_2-uptake experiment was carried out in the dynamic pulse mode at 295 K, chemisorbed oxygen was then titrated with H_2 at 295 K, and finally, a second oxygen uptake cycle was carried out at 295 K. While the first cycle O_2-uptake includes adsorption on both platinum and partially reduced tin sites, the second cycle is largely specific to exposed Pt sites [1]. The amount of oxygen adsorbed in this second cycle on catalysts containing metallic tin was much smaller than that for tin free catalysts and PtSn/Al_2O_3 catalysts with low tin content supported the view that platinum may become covered by tin in the former materials or at least is rendered inactive for O_2-uptake.

Striking changes in Pt-reactivity are reflected in the results of hexane reaction studies (table 1). While Pt/Al_2O_3, Pt/SiO_2 and PtSn/Al_2O_3 catalysts with tin contents below 5 wt% (no metallic tin) all showed high activity for hexane isomerization, hydrogenolysis and cyclization, all of the catalysts which displayed metallic tin in XPS studies (e.g., Pt/SnO_2, PtSn/SiO_2, 5%Pt-29%Sn/Al_2O_3, as well as Pt-black /SnO_2 physical mixtures) showed significantly lower catalytic activity for hexane reforming. Moreover, the selectivities exhibited by these metallic tin containing catalysts showed no significant improvements in isomerization and cyclization versus hydrogenolysis. As such, metallic tin appears to operate as a non-selective poison, and the nature of this poison does not appear to be very support dependent. This behavior contrasts sharply with that for PtSn/Al_2O_3 catalysts with lower tin content which showed improved selectivity for isomerization. In this case, the interaction between Pt and non-metallic SnO_x appears to selectively poison hydrogenolysis activity and also improves activity maintenance [1–3].

These findings appear to be in good agreement with early studies of unsupported PtSn-intermetallic compound by Dautzenberg and Sachtler [8] which showed much lower hexane reforming activities as compared to platinum only. Activity decreased with increasing tin content in the sequence $Pt > Pt_3Sn > PtSn$ with Pt_2Sn_3 and $PtSn_2$ completely inactive. While the supported materials investigated here could contain a distribution of clusters with variable Sn/Pt ratios, it is notable that the average metallic-Sn/Pt atomic ratio estimated from XPS results for PtSn/SiO_2 and 5%Pt-29%Sn/Al_2O_3 was slightly greater than 1. In summary, the reducibility of tin in PtSn/Al_2O_3 catalysts varies with initial tin oxide loading, and metallic tin in PtSn/Al_2O_3 and PtSn/SiO_2 acts as potent poison for hydrocarbon skeletal rearrangement.

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References

[1] Y. Zhou and S.M. Davis, ACS Adv. Chem., in press.
[2] B.A. Sexton, A.F. Hughes and K. Foger, J. Catal. 88 (1984) 466.
[3] K. Balakrishan and J. Schwank, J. Catal. 127 (1991) 287.
[4] G. Meitzener, G.H. Via, F.W. Lytle, S.C. Fung and J.H. Sinfelt, J. Phys. Chem. 92 (1988) 2925.
[5] R. Burch, J. Catal. 71 (1981) 348;
R. Burch and L.C. Garla, J. Catal. 71 (1981) 360.
[6] H. Lieske and J. Volter, J. Catal. 90 (1984) 96.
[7] R. Srinivisan, R.J. DeAngelis and B.H. Davis, J. Catal. 106 (1987) 449.
[8] F.M. Dautzenberg, J.N. Helle, P. Biloen and W.M.H. Sachtler, J. Catal. 63 (1980) 119.
[9] S.M. Davis and G.A. Somorjai, Bull. Chem. Soc. France (1985) 271.
[10] C.L. Lau and G.K. Wertheim, J. Vac. Sci. Technol. 15 (1978) 622.
[11] S.D. Gardner, G.B. Hoflund and D.R. Schryer, J. Catal. 119 (1989) 179.