

EXAFS Characterization of New Types of Sn-Pt/SiO₂ Catalysts

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Introduction

There is a great need for selective oxidation catalysts that will oxidize CO in the presence of hydrogen. CO is known to be a poison for fuel cells at parts-per-million (ppm) concentrations. These catalysts would have utility in removing CO without removing the hydrogen.

Pt/SiO₂ catalysts are relatively inactive for the low-temperature oxidation of CO. However both Pt/SnO₂ and Pd/SnO₂ catalysts are highly active and selective [1-3]. In SnO₂-supported catalysts, a synergism between the oxide and the metal phases has been suggested [1, 2]. A role for the formed SnPt alloy phase has also been proposed [3]. Recently, an alternative reaction mechanism has been put forward [4]; it suggests the involvement of the Pt-SnO₂ interface in the activation of CO.

The current study is aimed at elucidating the state of the active catalyst under both oxidizing and reducing conditions in order to shed light on the mechanism for selective oxidation.

Methods and Materials

In this study, two-step tin anchoring has been applied, which consists of tin anchoring from a tin alkyl complex, followed by decomposition of surface organometallic complexes by calcination in the presence of oxygen. Details on preparation can be found elsewhere [5-7]. The general scheme is shown in Fig. 1. For this study, the support studied was a high-surface-area SiO₂.

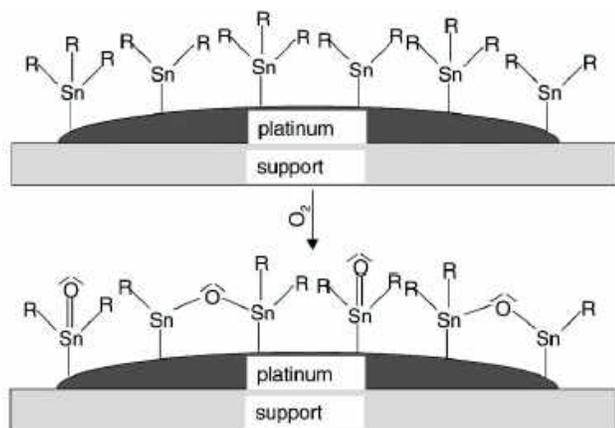


FIG. 1. Two-step tin anchoring.

The extended x-ray absorption fine structure (EXAFS) measurements were made at the Materials Research Collaborative Access Team (MR-CAT) insertion device beamline at the APS. Measurements were made in transmission mode. A cryogenic double-crystal Si(111) monochromator was used in conjunction with an Rh- or Pt-coated mirror to minimize the presence of harmonics for the Pt and Sn edges, respectively.

The sample thickness was chosen to give an absorbance of about 1.0 in the Sn and Pt edge regions: approximately 0.1 g of catalyst. The sample was centered in a 45 × 2-cm, continuous-flow, *in situ* EXAFS cell fitted with Kapton™ windows. Prior to the EXAFS measurements, the catalysts were heated to various temperatures in a gas mixture conducive to either oxidation or reduction (see Table 1). The EXAFS data were collected at room temperature in the presence of the pretreatment gas.

Table 1. Gases used during catalyst pretreatment.

Method	Pretreatment
H ₂ reduction	4% H ₂ /He
O ₂ oxidation	5% O ₂ /He

Results

The results are shown in both table and schematic form in Fig. 2. The Sn XANES data indicate that under oxidizing conditions, the Sn oxidizes completely to Sn(IV). Under reducing conditions, Sn reduces completely to Sn(0). However, the XANES spectra for reduced Sn are different than a tin foil reference, indicating that we do not have bulk tin metal.

The Pt XANES show that Pt is easily reduced to Pt(0) in the presence of hydrogen. This Pt has a similar XANES spectrum to that of a Pt metal foil. Under oxidizing conditions, however, there is incomplete oxidation of the Pt.

The Sn EXAFS spectra of the catalyst under oxidizing conditions show that Sn oxidized at 300°C is nearly all SnO₂. There is little evidence of Sn-Sn or Sn-Pt interactions. Under reducing conditions, the Sn is completely reduced at 500°C, showing no sign of oxide. There is evidence for both Sn-Sn and Sn-Pt interactions.

Oxidized (300 °C)			
Scatterer	d (Å)	C.N.	Potential CN
Sn-O	2.06	6.0	6
Sn-Pt	Decreases w/ increasing Temperature		
Sn-Sn	3.29	2.0	2 (linear)
Pt-O	2.04	1.8	4
Pt-Pt	2.79	3.7	12
Pt-Sn	2.78	0.6	
Reduced			
Scatterer	d (Å)	C.N.	Potential CN
Sn-Sn (300 °C)	2.82	0.5	12
Sn-Pt (300 °C)	2.82	5.6	12
Pt-Sn (500 °C)	2.80	2.0	
Pt-Pt (500 °C)	2.78	6.1	

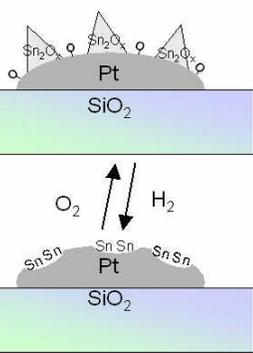


FIG. 2. Results under oxidizing and reducing conditions.

The Pt EXAFS spectra under oxidizing conditions show that the oxidation of Pt remains incomplete at 300°C and that strong interactions of Pt-Sn and Pt-Pt are still present under these conditions. Pt, which is only partially reduced at 250°C, is completely reduced by 500°C.

Discussion

The results indicate that the active component on the catalyst is a nearly isolated Sn atom (<4 atoms per cluster) interacting strongly with the fairly large Pt cluster. No evidence for alloy formation was observed in the experiments studied. From this study, the following mechanism has been proposed (Fig. 3): At low temperature (<200°C) under oxidizing conditions, a bond between the Sn and platinum still remains. The Sn has been oxidized to Sn(IV) [there is little evidence for Sn(II)], with the Sn-Sn bond being replaced by a Sn-O-Sn link. The Pt is believed to be only partially oxidized, with strong indications that the bulk of the Pt remains Pt(0). The Pt is believed to break the O-O bond to form a surface Pt-O structure. This oxygen can then be transferred to the Sn, which oxidizes the CO.

At higher temperatures (>300°C), the Sn-Pt bond is lost and replaced by a Sn-O-Pt bond. In this higher oxidation

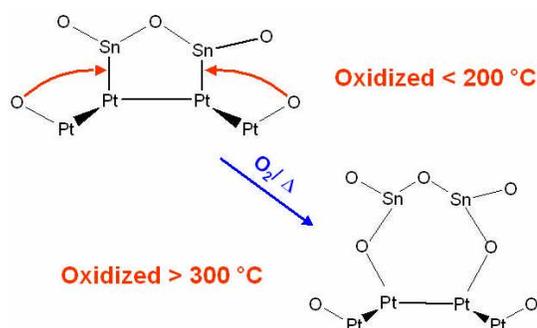


FIG. 3. Proposed selective oxidation mechanism.

state, the SnO₂ is now less selective and can oxidize H₂ as well as CO, resulting in loss in selectivity.

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