

The Active Site in Supported Pt Oxidation Catalysts

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Introduction

Auto exhaust cleanup is one of the largest industrial catalytic applications and is responsible for the low hydrocarbon and NO_x tailpipe emissions from modern automobiles. Pt, Pd, and Rh, the active metals, are supported on a honeycomb ceramic support. Under oxygen-rich conditions, Pt and Pd oxidize CO and hydrocarbons to CO₂; under lean conditions, Rh reduces NO_x to N₂. Over time, operation at high reaction temperatures leads to sintering, which lowers the activity and effective life of the auto exhaust catalyst.

Oxidation catalysts are generally prepared by the deposition of metal salts onto an inorganic support like alumina or silica. They are thermally activated by being heated in air at high temperature (typically greater than 600°C), giving, for example, a complex mixture of both metallic and oxidized Pt. It is well known that the activity of Pt oxidation catalysts increases with increasing particle size. Thus, although the metal oxide surface area decreases, the activity increases. The reason for this unusual behavior is not known, but it is speculated that large oxide particles are required to activate both the oxygen and the hydrocarbons.

Methods and Materials

A series of Pt-on-silica oxidation catalysts were prepared with identical metal loading but different particle sizes (from about 10 to 100 Å). Two-percent Pt was adsorbed onto silica from a solution of Pt(NH₃)₄(NO₃)₂ and adjusted to a pH of about 9.5 with NH₄NOH. The amount of Pt adsorbed was determined by inductively coupled plasma (ICP). After drying at 100°C, the Pt was reduced in hydrogen, and the reduced metal particle size was determined by hydrogen chemisorption. Increasing the calcination temperature from 250° to 600°C prior to reduction lowered dispersion.

Extended x-ray absorption fine structure (EXAFS) measurements were made on the insertion device beamline of the Materials Research Collaborative Access Team (MR-CAT, sector 10) at the APS. Measurements were made in transmission mode, and the data were collected by continuously scanning the monochromator.

The sample thickness was chosen to give an absorbance ($\Delta\mu x$) of about 1.0 in the Pt edge region, corresponding to approximately 100 mg of catalyst. The sample was

centered in a continuous-flow *in situ* EXAFS reactor tube fit with polyimide windows. The calcined catalysts were measured in air at room temperature. The catalysts were then reduced in 5% H₂ (balance He) at 300°C for 1 h and cooled to room temperature. The EXAFS data of the reduced catalysts were collected at room temperature in H₂/He. Thereafter, the pre-reduced catalysts were purged with He and subsequently heated to 300°C in 5% O₂ (balance He) for 1 h, and the EXAFS data were collected at room temperature in 5% O₂.

Standard procedures were used to analyze the EXAFS data by using WINXAS97 software [1]. Phase-shift and backscattering amplitudes were obtained from reference compounds: Na₂Pt(OH)₆ for Pt-O and Pt foil for Pt-Pt.

Results

Although the particle size of the reduced metallic Pt particles was dependent on the calcination temperature prior to reduction, there was little difference in the EXAFS of the calcined particles calcined below about 500°C. Each had six Pt-O neighbors at a distance of 2.05 Å, characteristic of Pt oxide. Above 500°C in air, metallic Pt was present in the calcined samples (results not given). The EXAFS results and H/Pt values for the reduced and oxidized catalysts are given in Table 1. For reduced particles up to a dispersion of about 0.5 (about 20 Å), the particles were sufficiently small that a contribution from the support could be determined. This metal-support distance (Pt-O*) is about 2.2 Å. For larger particles, the contribution from the support was too small to resolve. For reduced particles smaller than about 13 Å (H/Pt = 0.79), exposure to O₂ at 300°C led to complete oxidation (four Pt-O at 2.05 Å). As the size of the reduced particles increased, the degree of oxidation decreased (see Fig. 1). In a 50-Å metallic Pt particle (H/Pt = 0.19), for example, a significant fraction of the Pt remains metallic in 300°C air (i.e., the Pt-Pt coordination number is 9.3).

The reaction rate for CO oxidation for Pt on silica increases as the size of the reduced particle increases. On a per-gram-of-catalyst basis, the activity of the Pt/silica when H/Pt = 0.29 is 2.5 times higher than its activity when H/Pt = 0.79. If, however, the rates are based on the surface area of the reduced catalyst, the activity of the former is 6 times higher. These results are in agreement with previous kinetic studies [2-6].

Table 1. Results from EXAFS fits.

Treatment	H/Pt	Scattering path	Coord. no.	R (Å)	$\Delta\sigma^2$ ($\text{\AA}^2 \times 10^3$)	ΔE_0 (eV)
Reduced	1.28	Pt-Pt	5.0	2.74	1.6	-3.0
		Pt-O*	0.9	2.22	7.2	17.6
Oxidized		Pt-O	4.1	2.05	4.1	1.9
Reduced	0.79	Pt-Pt	5.2	2.75	1.6	-4.1
		Pt-O*	1.1	2.22	7.0	17.9
Oxidized		Pt-O	4.4	2.06	4.1	1.5
Reduced	0.63	Pt-Pt	7.0	2.74	1.6	-4.4
		Pt-O*	0.9	2.23	7.0	21.0
Oxidized		Pt-Pt	2.1	2.98	3.5	-11.4
		Pt-O	3.9	2.05	3.6	0.4
Reduced	0.51	Pt-Pt	7.7	2.75	1.6	-2.9
		Pt-O*	0.9	2.18	8.4	16.4
Oxidized		Pt-Pt	3.4	2.74	3.0	-1.9
		Pt-O	3.3	2.05	3.7	-0.6
Reduced	0.29	Pt-Pt	9.3	2.76	1.6	-2.0
Oxidized		Pt-Pt	5.7	2.75	3.5	0.7
		Pt-O	2.7	2.05	3.4	0.8
Reduced	0.19	Pt-Pt	10.9	2.76	1.1	-1.0
Oxidized		Pt-Pt	9.3	2.77	1.3	-0.9
		Pt-O	1.2	2.04	2.4	0.7
Reduced	0.11	Pt-Pt	11.3	2.76	1.1	-1.0
Oxidized		Pt-Pt	10.4	2.77	1.0	-0.8
		Pt-O	0.9	2.03	2.3	-1.2

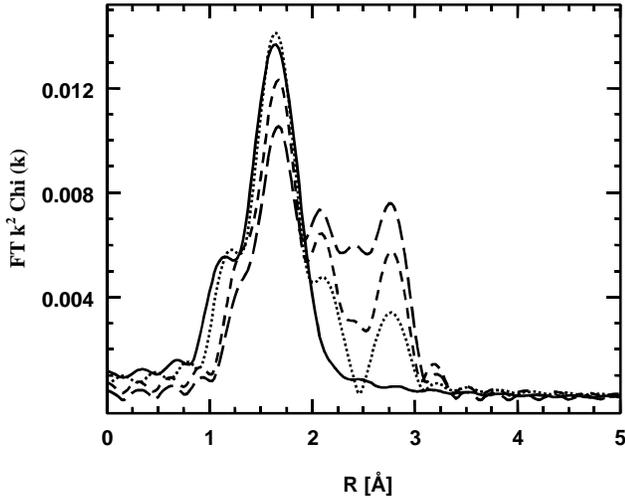


FIG. 1. Fourier transform (k^2 , $\Delta k = 2.9-12.4 \text{ \AA}^{-1}$, and $\Delta r = 0.9-3.1 \text{ \AA}$) of (pre-reduced) 2% Pt/silica oxidized at 300°C . Solid line indicates $H/Pt = 0.79$, dotted line indicates $H/Pt = 0.63$, short dashed line indicates $H/Pt = 0.51$, and long dashed line indicates $H/Pt = 0.29$.

Discussion

The concept of an active site in heterogeneous catalysts is fundamental for understanding the catalytic process. Structural identification and determination of the number of sites allow one to determine the turnover rate, or the rate per surface atom. While H_2 or CO chemisorption is often used to count the number of surface metal atoms in reduced catalysts, a similar technique has not been established for supported, noble metal oxidation catalysts. The EXAFS spectra indicate that very small, reduced metal particles are fully oxidized under the reaction conditions. These particles also have low activity. As the (reduced) particle size increases, the size of the metallic core (in the oxidized catalyst) increases, and so does the activity. The EXAFS results indicate that large particles have a metallic core and an oxidized surface. Catalytic reactions, however, occur at the particle surface. In a previous study, infrared spectra of CO adsorbed on an oxidized Pt catalyst showed that although a fraction of the surface is oxidized, a significant portion remains reduced. In that study, the activity of the catalysts paralleled the number of exposed, metallic Pt atoms. Infrared spectroscopy of adsorbed CO is being obtained for the catalysts with different particle sizes to determine the fraction of metallic Pt present. We hope to establish that

the active site for oxidation is exposed metallic Pt. If this is true, the number of metallic Pt atoms should increase as the size of the metal particles becomes larger. If that can be established, it will then be possible to determine the number of sites by chemisorption of CO or infrared spectroscopy of adsorbed CO and to calculate turnover rates.

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