Kinetics, Operando FTIR and Controlled Atmosphere EXAFS Study of the Effect of Sulfur on Pt-Supported Catalysts During CO Oxidation*

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Introduction

Small amounts of SO_2 (10 to 60 ppm) present in automobile exhaust gas are known to poison noble metal catalysts. Although the poisoning mechanism during oxidation reactions is not completely understood, it has been proposed that the formation of surface sulfates on the support base metal oxide plays a role in sulfur poisoning. Since such sulfates decompose in the temperature range of 500 to 700ºC [1], catalysts operating above 500ºC can, eventually, be more tolerant to sulfur poisoning. Operando IR is used to probe adsorbates on the working surface during reaction and activity measurements are used to investigate nature of poisoning by H_2S and SO_2 on Pt/SiO_2 and Pt/Al_2O_3 catalysts during CO oxidation. In-situ XANES and EXAFS are used to characterize the catalyst before and after reaction.

Methods and Materials

Catalysts containing 2.0% Pt were prepared on silica and alumina supports using $Pt(NH_3)_4(NO_3)_2$. Calcination at temperatures from 250 to 600 °C rendered samples with different dispersions ranging from 0.10 to 0.70 as determined by hydrogen chemisorption [2]. The catalysts were reduced prior to determination of the CO oxidation rate, XAFS and IR spectroscopies. Catalyst activities were determined in a continuous-flow, fixed-bed reactor. Catalysts were pretreatment with H_2S or continously co-feed with 20 ppm SO_2 in 1%CO and 5% O_2 (balance in He). Transmission infrared spectra of pressed disks of Pt/SiO_2 were collected in-situ and under *operando* conditions. The samples were pretreated at various conditions prior to study of CO adsorption and reaction. Measurements using XAFS spectroscopy were made in transmission on the insertion-device beam line of the Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon Source, Argonne National Laboratory. The sample holder was centered in a continuous-flow in-situ XAFS reactor.

Results

H_2S poisoning. A portion of the silica-supported catalysts was treated ex-situ with H_2S at 200ºC for 2 hrs followed by reduction pre-reduction at 200ºC. Compared to the S-free catalysts, H_2S increases the light-off temperature (LOT, i.e. temperature at 50% conversion) for all catalysts. The poisoning effect was greatest for the catalyst with highest dispersion, e.g., an increase of 50ºC for the highest dispersion compared to an increase of 30ºC for the lowest dispersion, suggesting an influence of the particle size. IR spectra taken under reaction conditions at 100°C (Figure 1) show that the linearly adsorbed CO on Pt shifts from 2071 cm^{-1} to 2086 cm^{-1} but the integrated absorbance intensity is only slightly affected by the presence of the adsorbed H_2S. The bridge-bonded CO signal (1815 cm^{-1}) disappears in the poisoned catalyst.

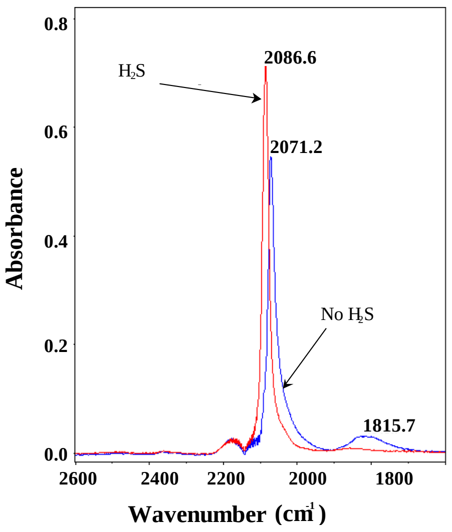

Figure 1. IR spectra of Pt/SiO_2 during reaction

EXAFS data were also obtained after reduction of the H_2S poisoned catalysts under conditions similar to that for the catalytic reaction. Table 1 summarizes the XANES and EXAFS results for the Pt/silica catalysts with different dispersion.

Table 1. EXAFS and XANES fits: 2%Pt/SiO_2 with different dispersion after H_2S poisoning and reduction

Sample	Fraction Pt^{+2}	Fraction Pt^0	Scattering atoms	CN (±10%)	R, Å (±0.02)	DWF (x 10^3)
$Pt(0.10)/SiO_2$	-	1.0	Pt-Pt	12.0	2.77	1.6
$Pt(0.10)/SiO_2$ + H_2S	-	1.0	Pt-Pt	12.0	2.76	1.6
$Pt(0.33)/SiO_2$	-	1.0	Pt-Pt	9.3	2.75	1.6
$Pt(0.33)/SiO_2$ + H_2S	0.05	0.95	Pt-Pt	7.2	2.75	1.6
			Pt-S	1.0	2.33	4.0
$Pt(0.63)/SiO_2$	-	1.0	Pt-Pt	7.8	2.74	1.6
$Pt(0.63)/SiO_2$ + H_2S	0.80	0.20	Pt-Pt	3.4	2.73	1.6
			Pt-S	2.0	2.33	4.0

Poisoning by H_2S leads to partial oxidation of a portion of the surface metallic Pt and the formation of Pt-S bonds. Figure 2 shows the k^2-weighted magnitude of the Fourier transform for the reduced and H_2S poisoned (and reduced) Pt/silica catalyst with a dispersion of 0.63. In the Fourier transform, the peaks for Pt-Pt (between about 1.8 and 3.1 Å) overlap with the Pt-S peak at about 2.9 Å.

EXAFS fits (Table 1) of the S-poisoned $Pt(0.10)/SiO_2$ give a Pt-Pt CN and bond distance of 11.6 and 2.77 Å, respectively, and confirm that this catalyst possesses large Pt crystallites. The particles are sufficiently large that it was not possible to detect oxidized Pt by XANES or Pt-S bonds by EXAFS at the particle surface. As the Pt dispersion increases, there is a small increase in the white line intensity and the number of Pt-S bonds. The XANES and EXAFS are consistent with oxidation of the surface Pt atoms to Pt^{+2} with the formation of Pt-S bonds. The core of the particle, however, remains metallic.

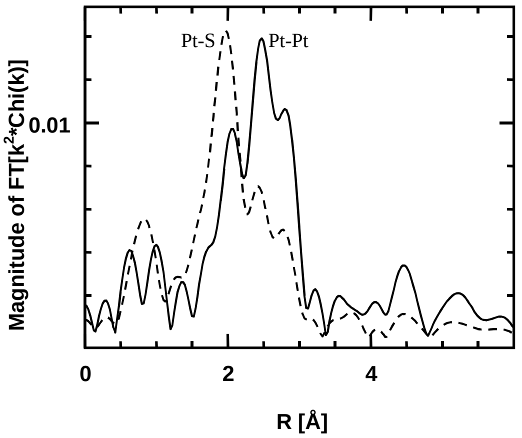

Figure 2. Magnitude of the k^2-weighted Fourier transform for Pt(0.63)/Silica (k = 2.75 to 13.3 $Å^{-1}$). Solid line, reduced in H_2 at 250 °C; dashed line, pre-reduced, H_2S at RT and re-reduced at 250 °C.

SO_2 poisoning. During oxidation reactions, it is likely that S will be present as SO_2. For gasoline with 300 ppm of sulfur, the exhaust gases entering the automotive exhaust catalyst would contain about 20 ppm of SO_2. Thus, to emulate the S concentration in the exhaust gas from an engine, 20 ppm of SO_2 was continuously added to the reactant mixture of 1% CO -10% O_2 in He.

Typical activity results for Pt supported on SiO_2 and Al_2O_3 with 0.63 and 0.68 dispersions, respectively, are shown in Figure 3.

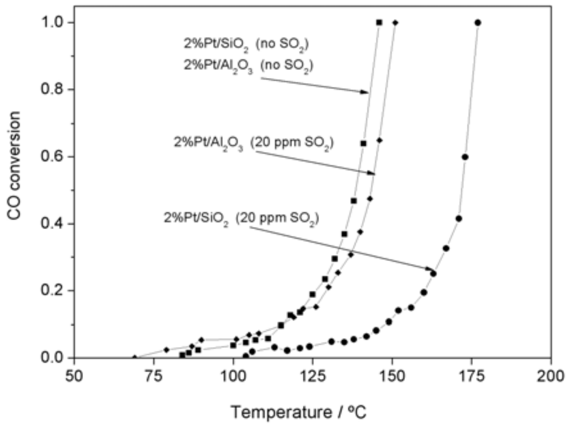

Figure 3. Conversion versus temperature for Pt supported on SiO_2 and Al_2O_3 with and without SO_2 poisoning.

SO_2 strongly supresses the CO conversion of Pt/silica increasing the LOT. In addition, the poisoning effect is largest for the catalysts with highest dispersion, or smallest particles. Figure 3 also shows an apparent support effect. Consecutive activity tests on the Pt/A_2O_3 catalyst show a gradual increase in LOT with increasing exposure to SO_2 and eventually reaches an activity equivalent to that of the Pt/SiO_2 catalyst. Operando IR results show that after consecutive runs SO_2 is adsorbed on Al_2O_3 which acts as a sulfur trap forming sulfates. Initially this prevents the poisoning of the Pt, however, eventually the alumina is saturated and the Pt is poisoned by the SO_2.

The Pt/alumina and Pt/silica catalysts with different dispersion and tested for oxidation of CO with 20 ppm SO_2 were analyzed by XANES and EXAFS, Table 2.

Table 2. 2% Pt Oxidation catalysts poisoned by SO_2

Composition (Dispersion)	Fraction Pt^{+4}	Fraction Pt^0	Scatter	CN	R, Å	DWF (x 10^3)
SiO_2 (0.10)	0.10	0.90	Pt-Pt	10.0	2.77	1.0
			Pt-O	0.5	2.05	1.5
SiO_2 (0.33)	0.25	0.75	Pt-Pt	5.1	2.74	1.6
			Pt-O	2.1	2.05	1.5
SiO_2 (0.63)	0.35	0.65	Pt-Pt	2.9	2.71	1.6
			Pt-O	2.7	2.05	1.5

Following the reaction there are significant amounts of oxidized Pt and presence of Pt-Pt, and Pt-O bonds, with no Pt-S bonds. For several samples, the height of the white line was larger than that of the Pt^{+2} reference, thus no fit could be obtained using only Pt^{+2} and Pt^0. However, excellent fits were obtained with a linear combination of Pt^{+4} and Pt^0. Acceptable fits were also possible using Pt^{+2}, Pt^{+4} and Pt^0. While the absolute values of the various Pt oxidation states differ with the two fits, the trends were the same. For Pt/silica with different dispersions, the XANES show that the extent of Pt oxidation increases with decreasing particle size. For example, for the largest particles about 10% of the Pt is oxidized, while for smallest particles about 35% is oxidized. The degree of oxidation of the Pt/alumina catalysts is very similar, or perhaps slightly higher, than that on silica with similar dispersion. For catalysts with dispersions around 0.7, the Pt-Pt coordination numbers (CN) are small, less than about 3. The true CN is higher since all the Pt is not metallic. For example, in Pt(0.63) the fraction of metallic is 0.65, thus the true Pt-Pt CN is 4.5. An estimate of the particle size from the Pt-Pt CN is about 10 Å [3]. Consistent with this small particle size, the Pt-Pt bond distance is about 2.72 Å. The EXAFS were also obtained after reduction of the SO_2-poisoned catalysts. The fits are given in Table 3.

Table 3. 2% Pt/Silica poisoned by SO_2 and reduced at 250°C.

Composition	Scatter	CN (±10%)	R, Å	DWF (x 10^3)
SiO_2 (0.10)	Pt-Pt	11.3	2.77	1.6
SiO_2 (0.33)	Pt-Pt	9.0	2.76	1.6
	Pt-S	0.5	2.30	4.0
SiO_2 (0.63)	Pt-Pt	7.5	2.75	1.6
	Pt-S	0.7	2.30	4.0

While there were no Pt-S bonds in the SO_2-poisoned oxidation catalyst, the fits of the reduced catalysts clearly indicate Pt-S as well as Pt-Pt bonds. In addition, there are no Pt-O bonds after reduction, Figure 4. Within the limits of accuracy, the size of the reduced particle is unchanged after SO_2 poisoning. The presence of Pt-S in the reduced Pt/silica catalysts suggests that SO_2 is bonded to Pt atoms in the oxidized catalysts since the silica support does not form surface sulfates as observed on alumina. In addition, since there were no Pt-S contributions to the EXAFS in the SO_2-poisoned oxidation catalysts, the SO_2 is likely bonded through the oxygen atom, i.e., Pt-O-S-O bond or similar species.

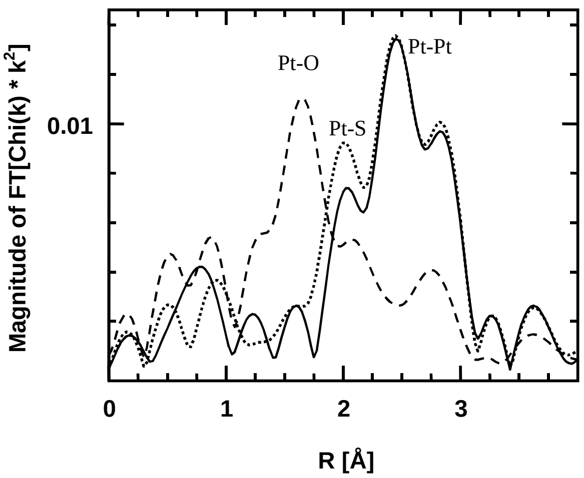

Figure 4: Magnitude of the Fourier Transform for 2% Pt(0.63)/Silica (k^2: Δk = 2.75-13.2 Å^{-1}). Solid line, reduced (no S); dashed line, oxidized by SO_2; dotted line, oxidized by SO_2 and reduced.

For Pt(0.63)/silica, the structure of Pt is very similar after one or four reactions (and reductions) with SO_2, consistent with the catalytic and IR results indicating that the Pt is rapidly poisoned. For Pt(0.68)/alumina, however, after one catalyst test, the amount of Pt-S is significantly lower than after four reactions. As with the IR and catalytic tests, EXAFS indicates that at short times on stream, the Pt/alumina is less poisoned by SO_2 than Pt/silica.

Discussion

The results of this study show that the effect of sulfur on Pt catalysts during CO oxidation is a dynamic phenomena, which strongly depends on the catalyst's history including : 1) how and what type of sulfur is added, 2) the catalyst pretreatment, 3) the type of support, 4) the Pt crystallite size, 5) the reaction conditions, and 6) the time on stream.

IR results of S-poisoned catalysts show that the CO surface coverage is very similar to that of the S-free catalyst although there is a shift in the position of the linearly bonded CO band to higher frequency. While S appears to have little influence on the quantity of linearly bonded CO, in the S-poisoned catalysts there is little bridge bonded CO suggesting few adjacent S-free Pt atoms. The latter are thought to be required for dissociation of O_2. Thus, we propose that the lower activity of the S poisoned catalyst results from inhibition of oxygen adsorption and dissociation. At elevated temperatures, CO reacts with adsorbed S species to lower the surface coverage and making possible the activation of O_2, albeit at a lower rater than on S-free Pt.

On some supports like alumina that react with SO_x to form sulfates, at short times-on-stream, the support appears to protect the catalyst from the detrimental effects of S. However, the effect is transitory. Once the support surface is saturated, the Pt is readily poisoned.

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