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AN XPS EVIDENCE OF Pt⁴⁺ PRESENT ON Pt-Sn/ γ -Al₂O₃ AND ITS EFFECT ON SO₂ OXIDATION.

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Abstract

A deactivating effect on 1%Pt/ γ -Al₂O₃ activity on SO₂ oxidation is induced by Sn addition. XPS determinations revealed an increased formation of a Pt⁴⁺ species on 1%Pt-2%Sn/ γ -Al₂O₃ suggesting that Sn species would withdraw electron density from adjacent Pt particles increasing Pt⁴⁺ species which may lead to lower electronic interactions with the anti-bonding orbital of SO₂ molecule, thus, lowering its dissociate adsorption.

Keywords:

SO₂, Pt⁴⁺, Platinum/alumina catalyst, Platinum-tin/alumina.

1. Introduction.

Exhaust SO₂ is a significant poison for noble metal catalysts contained on the catalytic automotive converter. Its poisoning effects will become increasingly serious as emission standards tighten. SO₂ in the exhaust is also a problem in controlling diesel engine particulate emission. At present, the development of a sulfur-resistant HC-SCR catalyst activity at low temperature may be regarded as a major challenge in catalytic research of diesel engine pollution control. The large amounts of sulfur present in diesel fuel impede the application of particulate matter filter technologies in which a NO_x catalyst-assisted process is used to facilitate filter regeneration [1]. In the presence of an oxidation catalyst, SO₂ will be oxidized to sulfur trioxide (SO₃), which can form sulfates by reacting with water and other compounds in the exhaust and be adsorbed on the soot [1, 2]. At the moment, the NO_x trap approach is successful only with low sulfur fuels, as SO₂ forms sulfates with the storage metals [3], especially with barium. Because the sulfates are more stable than the equivalent nitrates, there is competition for adsorption on the active sites between NO_x and SO_x, and the sites become progressively poisoned by sulfate formation [3, 4]. In spite of the important concentration of SO₂ in the gas exhaust, especially in diesel automotive trucks, only small efforts have been done to develop catalysts which diminish SO₂ oxidation on platinum converter catalysts working under oxidizing conditions. Minimum generation of sulfate by catalytic oxidation of gaseous SO₂ becomes the most demanding requirement.

With this aim, in the present study, we determined by XPS the nature of the active sites of 1%Pt/γ-Al₂O₃ and 1%Pt-2%Sn/γ-Al₂O₃. SO₂+O₂ temperature programmed reaction and SO₂ temperature programmed adsorption were studied over the catalysts in order to determine the effect of Sn addition in the SO₂ oxidizing activity of 1%Pt/γ-Al₂O₃. Results obtained suggested a very interesting relationship between the SO₂ oxidation and the changes induced by Sn on the binding energy of Pt4d_{5/2}.

2. Experimental

The support used was γ-Al₂O₃ Merck with a grain size of 0.063-0.200 mm (70-230 mesh ASTM). Before use, the support was calcined for 6 h at 600 °C in air. Pt and Pt-Sn catalysts supported on alumina were prepared by impregnation using acidic aqueous solutions (0.1 M HCl) of SnCl₄·5H₂O (Alfa/Johnson Matthey) and H₂PtCl₆ · 6H₂O (Merck, min. 98% purity). After impregnation, the catalysts were dried at 120 °C overnight, and then calcined in flowing air for 6 h at 500 °C. Finally, the catalysts were reduced in pure hydrogen flow for 8 h at 500 °C. A reference alumina support was prepared in the same way using only diluted hydrochloric acid.

Platinum accessibility measurements on reduced catalysts, were obtained by the H₂-O₂ titration method at room temperature in a static volumetric apparatus and using the stoichiometric (H/Pt)_{surf} = 1. Isotherms were obtained in the 0-50 Torr (1 Torr = 1.33 mbar) range. Extrapolation of the linear part of the isotherm to zero pressure gave the monolayer coverage. This amount of H₂ chemisorbed in monolayer was then used to calculate the number of exposed Pt atoms and dispersion (Table 1). Comparable Pt dispersion values were obtained for the mono and the bimetallic catalysts respectively.

The chemical microanalysis of the catalyst was determined by energy dispersive X-ray spectroscopy (EDS), (NORAN) performed in conjunction with a scanning electron microscope (JEOL, model JSM-6300). Catalysts metal contents are reported in Table 1.

Photoelectron spectra were recorded over fresh samples using a VG Escalab 200R electron spectrometer equipped with a hemispherical analyzer, operating in a constant pass energy mode, and a non-monochromatic MgK α ($h\nu = 1253.6$ eV, 1 eV = 1.603×10^{-19} J) X-ray source operated at 10 mA and 12 kV. The energy regions of the photoelectrons of interest were scanned a number of times in order to get good signal-to-noise ratios. The intensities of the peaks were estimated by determining the integral of each peak after subtracting an S-shaped background and fitting the experimental peak to Lorentzian/Gaussian lines (80%L/20%G). The binding energies (BE) were referenced to the Al 2p peak, the BE of which was fixed at 74.5 eV. Using this reference, BE values of C 1s peak coming from adventitious carbon appeared at 284.9 ± 0.2 eV.

The catalyst tests were performed in a continuous flow tubular quartz reactor (inner diameter 7 mm) placed in a programmable furnace. The catalyst temperature was controlled by a thermocouple mounted internally. Reactant gases were fed from independent mass flow controllers. SO₂ evolutions were followed using a KM 9106 Quintox Gas Analyzer. The SO₂ adsorption measurements over the samples were obtained using a feed volume flow rate of $100 \text{ cm}^3 \text{ min}^{-1}$ consisting of 50 ppmV of SO₂ and balance He, whereas the oxidation activity was carried out with a feed flow composition consisting of 50 ppmV of SO₂, 10 vol % of O₂ and balance He. The catalyst loading in the reactor was of 200 mg for both experiments. The concentrations of SO₂ and O₂ consumed were detected every minute and recorded during the experiments using a KM 9106 Quintox Gas Analyzer. Temperature programmed SO₂ adsorption and SO₂ oxidation reaction curves were obtained following the evolution of SO₂ as a function of temperature (25-500 °C).

The conversions of SO₂ to all products were calculated based on the following equation:

$$SO_2 \text{ conversion}(\%) = \frac{(SO_{2in} - SO_{2out})}{SO_{2in}} 100$$

SO_{2in} = the concentration of SO₂ introduced in the experiment

SO_{2out} = concentration of SO₂ at the reactor outlet.

3. Results

The catalyst characterization data are summarized in Table 1. Comparable Pt dispersion values of 0.35, and 0.28 were obtained for the mono and the bimetallic catalysts respectively.

Table 1. Chemical microanalysis of the catalysts determined by energy dispersive X-ray spectroscopy and Pt dispersion determined by H₂ chemisorption data.

Catalyst	wt%Pt	wt%Sn	wt%Cl	Pt Dispersion
γ -Al ₂ O ₃	---	---	0.99	---
1%Pt/ γ -Al ₂ O ₃	1.02	---	1.2	0.35
1%Pt-2%Sn/ γ -Al ₂ O ₃	1.0	2.2	1.2	0.28

In Figure 1, the SO₂ temperature programmed adsorption is illustrated for γ -Al₂O₃, 1%Pt/ γ -Al₂O₃, and 1%Pt-2%Sn/ γ -Al₂O₃ catalysts. SO₂ adsorption began at 25 °C and the maximum SO₂ uptake was found around 150 °C. At higher temperatures, SO₂ adsorption diminishes and no additional uptake was observed up to 500 °C. The similarity of the SO₂ adsorption profiles for alumina, platinum and bimetallic platinum-tin catalysts, in spite of its metallic composition, suggests that SO₂ is adsorbed mainly on the support. However, small amounts of SO₂ on the metallic particles cannot be discarded [5].

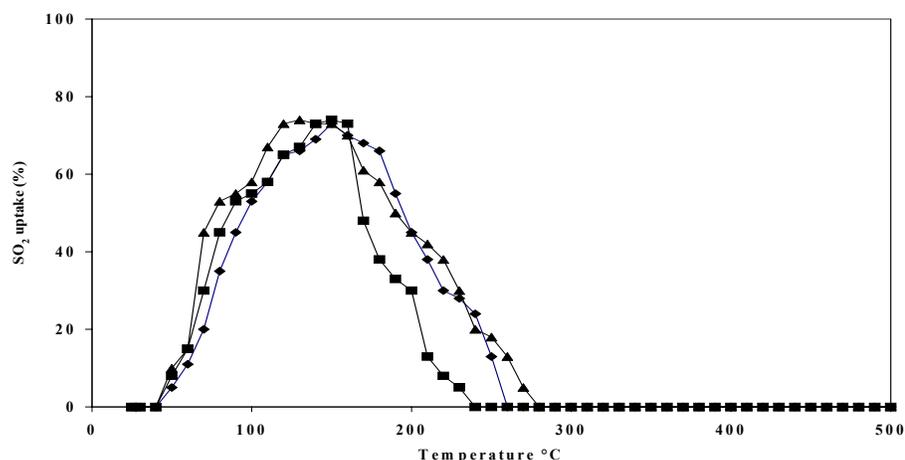


Figure 1. SO₂ adsorption as a function of temperature over: γ -Al₂O₃ (▲); 1%Pt/ γ -Al₂O₃ (◆) and 1%Pt-2%Sn/ γ -Al₂O₃ (■). Feed: 50 ppmV of SO₂ and balance He.

Figure 2 shows the SO₂ signals recorded from SO₂ + O₂ reaction over 1%Pt/γ-Al₂O₃ and 1%Pt-2%Sn/γ-Al₂O₃ catalysts. In this figure it can be seen that the first low temperature SO₂ signal adsorption occurred at the same temperature over the two catalysts. The second SO₂ uptake began at 200°C over 1%Pt/γ-Al₂O₃ and at higher temperature over 1%Pt-2%Sn/γ-Al₂O₃ (300°C). Thus, over the bimetallic catalyst, an important diminution of platinum activity on SO₂ oxidation is induced by tin.

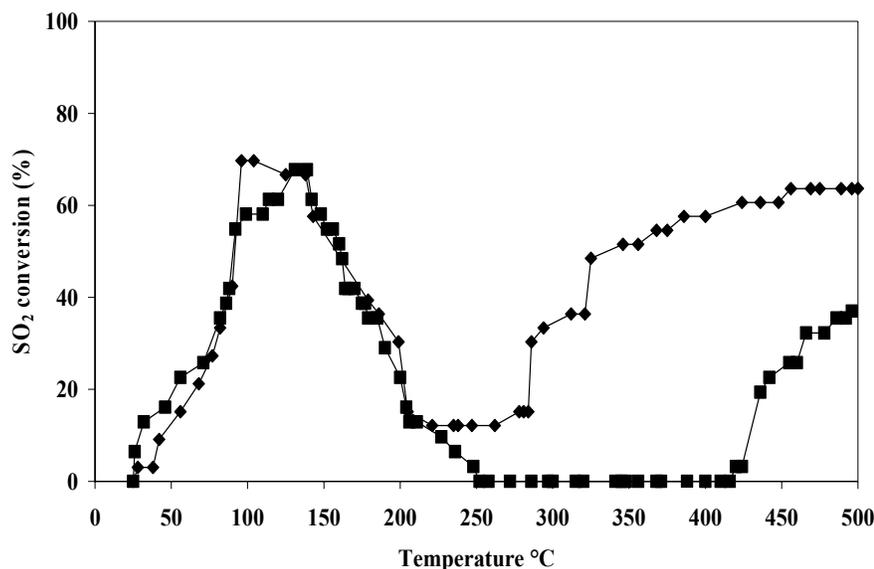


Figure 2. Effect of temperature on the SO₂ + O₂ reaction over Pt/Al₂O₃ (◆) and 1% Pt-2%Sn/Al₂O₃ (■). Feed: 50 ppmV of SO₂, 10 vol.% of O₂ and balance He.

Binding energies of core-electrons are reported in Table 2. The binding energy of Pt4d_{5/2} for 1%Pt/γ-Al₂O₃ (315.3 eV) indicates that Pt is present as Pt⁰ [6]. A second Pt component is observed at higher binding energies (318.0 eV) corresponding to an oxidized species of Pt, perhaps in the form of Pt-Cl-Al bridges [6]. Now, it has been reported [7-8], for PtO₂ a binding energy component (318 eV) of the Pt4d_{5/2} that can be assigned to (Pt⁴⁺). However, for the 1%Pt-2%Sn/γ-Al₂O₃ sample, the binding energy of the Pt4d_{5/2}, revealed a higher binding energy component (318.5 eV) that can be associated to an increase in the highly oxidized Pt component with respect to the Pt⁰ component. For the catalyst with Sn, the binding energy of Sn3d_{5/2} (close to 487 eV) reveals that Sn is present as Sn⁺² [6-10].

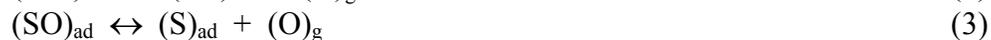
Table 2.
 Binding energies (eV) of core electrons of alumina supported Pt-Sn catalysts

Catalyst	Sn 3d _{5/2}	Pt 4d _{5/2}
1%Pt / γ -Al ₂ O ₃	---	315.3 (56) 318.0 (44)
1%Pt-2%Sn/ γ -Al ₂ O ₃	486.8	315.5 (60) 318.5 (40)

4. Discussion

The results obtained from the quantitative analysis of SO₂ temperature programmed adsorption and SO₂ + O₂ temperature programmed reaction over 1%Pt / γ -Al₂O₃ and 1%Pt-2%Sn/ γ -Al₂O₃ catalysts (Figures 1 and 2) revealed that *in the absence of oxygen*, SO₂ adsorption occurs at low temperature (<200 °C). However, this adsorbed SO₂ must be mainly adsorbed on the support. This conclusion is based on the fact that very similar amounts of SO₂ reacted over γ -Al₂O₃, 1%Pt/ γ -Al₂O₃ and 1%Pt-2%Sn/ γ -Al₂O₃ catalysts despite its metal relation and content at temperatures lower than 200 °C. *With oxygen present*, at low temperature, oxygen does not interfere with SO₂ adsorption. In addition, the oxidation of SO₂ occurs at higher temperatures (>300 °C). Finally, over 1%Pt-2%Sn/ γ -Al₂O₃ catalysts, Sn induces an important diminution of SO₂ oxidation activity of platinum.

These results reveal that Sn induces a strong effect on Pt behavior in SO₂ oxidation. Now, SO₂ adsorption on metallic Pt [11, 12] and on Pt supported on SiO₂ [13] have been reported as SO₂ dissociative adsorption over the metal according to the following reactions:



The results in Figure 2 show that the activity for the SO₂ oxidation reaction diminishes when tin is added to platinum catalyst. Thus, tin plays an essential role on the oxidation of SO₂. Tin may modify the SO₂ reactivity following two hypotheses: (i), Tin acts as a dilution agent of the Pt atoms ensembles required for the SO₂ dissociate adsorption. This dilution effect of tin on platinum ensembles has been reported previously [14, 15]; and (ii), SO₂ dissociate adsorption is diminished due to the modification of the electron density on platinum induced by the tin oxide entities surrounding the platinum particles (egg-shell model), that might lower SO₂ adsorption strength [16, 17].

5. Conclusions

The lower activity in SO₂ oxidation observed over 1%Pt-2%Sn/ γ -Al₂O₃ relative to 1%Pt/ γ -Al₂O₃, can be explained in basis of the lowering of SO₂ dissociate adsorption, due to the modification of the electron density on platinum induced by the tin oxide entities surrounding the platinum particles, that might lower SO₂ adsorption strength and consequently lowering further SO₂ interaction with adsorbed oxygen.

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