# Improved effect on the reduction of NO by propane under oxidizing conditions on sulfated Pt–Sn/Al$_2$O$_3$ catalysts

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## Abstract

Sulfation of the 1%Pt–1%Sn/γ-Al$_2$O$_3$ catalyst, resulted in an enhancement of the conversion of NO and C$_3$H$_8$ during the C$_3$H$_8$–NO–O$_2$ reaction. IR study showed the formation of bulk aluminum sulfate and surface tin sulfate. The presence of tin sulfate in the catalyst enhances C$_3$H$_8$ oxidation by probably conferring on Pt atoms a stronger partial positive charge than in the case of sulfated 1%Pt/Al$_2$O$_3$. The improvement of NO conversion on 1%Pt–1%Sn/γ-Al$_2$O$_3$ is explained on the basis of the enhancement of NO oxidation to NO$_2$ induced by Sn surface species over the catalyst. © 2002 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

For engines available today, there is a contradiction in the emission of NO$_x$ that is formed in the combustion process and the fuel consumption. The most fuel-efficient engines apply combustion in oxygen excess. However, the exhaust from these engines is strongly oxidizing and under these conditions three-way catalysts are no longer effective for NO$_x$ removal [1–8]. There is thus, a major drive to achieve efficient NO$_x$ reduction, in oxygen excess, without increasing the fuel consumption or even in order to be able to lower the fuel consumption further.

Several technical approaches are possible for reducing the NO$_x$ pollution by vehicles powered by lean-burn and diesel internal combustion engines, including the use of tailpipe adsorbents and catalysts. One of the most attractive solutions to the NO$_x$ problem is continuous catalytic reduction of the NO$_x$ molecules in the exhaust gas using the unburned hydrocarbons from the fuel (HC-SCR). The search for catalysts that are active in a broad temperature window and that are sufficiently stable over extended time periods has been the subject of numerous studies [4,9]. Technically, the purification of exhaust from a lean burning engine requires the removal of nitric oxide, a reaction which has been reported successful over supported noble metals [10].

However, in spite of the important diminution of sulfur content on gasoline, the NO decomposition must be carried out in the presence of the SO$_2$ formed during the combustion of sulfur compounds. Over Pt/Al$_2$O$_3$, exhaust SO$_2$ is a significant poison for the NO decomposition, since SO$_2$ in the presence of an oxidation catalyst will be oxidized to sulfur trioxide (SO$_3$), which can form sulfates and be adsorbed on the sites at which NO reduction occurs [11–14]. In the present

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work, we investigated the effects of catalyst sulfation on the $C_3H_8$–NO–$O_2$ reaction over Pt/$\gamma$-$Al_2O_3$ and Pt–Sn/$\gamma$-$Al_2O_3$. In particular, the differences in the sulfation effects for both catalysts are presented and discussed in terms of a reaction mechanism involving sulfates formation.

## 2. Experimental

### 2.1. Preparation of the catalysts

The support used was $\gamma$-$Al_2O_3$ 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 co-impregnation using acidic aqueous solutions (0.1 M HCl) of $SnCl_4 \cdot 5H_2O$ (Alfa/Johnson Matthey) and $H_2PtCl_6 \cdot 6H_2O$ (Merck, minimum 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.

The reduced catalysts were then sulfated. Sulfation was performed on samples heating to 500 °C in flowing air (100 $cm^3 min^{-1}$). The feed was then changed at 500 °C for a nitrogen flow containing 50 ppm $SO_2$, 5% $O_2$ (100 $cm^3 min^{-1}$) for 10 h. The samples were then cooled to 25 °C.

### 2.2. Metal accessibility measurements

Platinum accessibility measurements on reduced catalysts, were obtained by the $H_2$–$O_2$ titration method at room temperature in a static volumetric apparatus and using the stoichiometric H/Pt = 1. Isotherms were obtained in the 0–50 Torr range. Extrapolation to the original value was used to calculate the number of Pt exposed atoms and dispersion (Table 1). Comparable Pt dispersion values of 35 and 28% were obtained for the mono and the bimetallic catalysts respectively.

The metal content of the catalysts was determined by energy disperse X-ray spectrometer interfaced to a scanning electron microscope.

### 2.3. IR study

For infrared studies, a self supporting sample disk of about 10 mg $cm^{-2}$ prepared by pressing the sulfated catalyst powder was placed in an IR cell with KBr windows. All the IR spectra were recorded at room temperature using a Nicolet Magna-IR$^{TM}$ 750 spectrometer at a resolution of 10 $cm^{-1}$.

### 2.4. Activity measurements

Steady state catalyst testing was carried out using a quartz tubular down flow reactor (i.d. 7 mm). Reactant gases were fed from independent mass flow controllers. Measurements were obtained, using a feed volume flow rate of 100 $cm^3 min^{-1}$ consisting of 1000 ppm of NO, 5 vol.% $C_3H_8$, 10 vol.% of $O_2$, and balance $N_2$. The catalyst load in the reactor was of 200 mg. The reactor out flow was analyzed using a Shimadzu gas chromatograph with a TCD detector. The chromatograph used a Chromosorb 2000 column to analyze the $C_3H_8$ evolution. The NO and $SO_2$ evolutions were followed using a KM 9106 Quintox Gas Analyzer. Measurements were taken as the temperature was increased stepwise. The catalyst was left at each temperature for 1 h until the steady state was reached.

## 3. Results

### 3.1. $C_3H_8$–NO–$O_2$ reactions over Pt/$\gamma$-$Al_2O$ and 1%Pt-1%Sn/$\gamma$-$Al_2O_3$ unsulfated samples

The evolution of the reaction for unsulfated Pt/$\gamma$-$Al_2O_3$ and 1%Pt–1%Sn/$\gamma$-$Al_2O_3$ catalysts is shown in Fig. 1. In this figure and in Table 2, it can be seen that
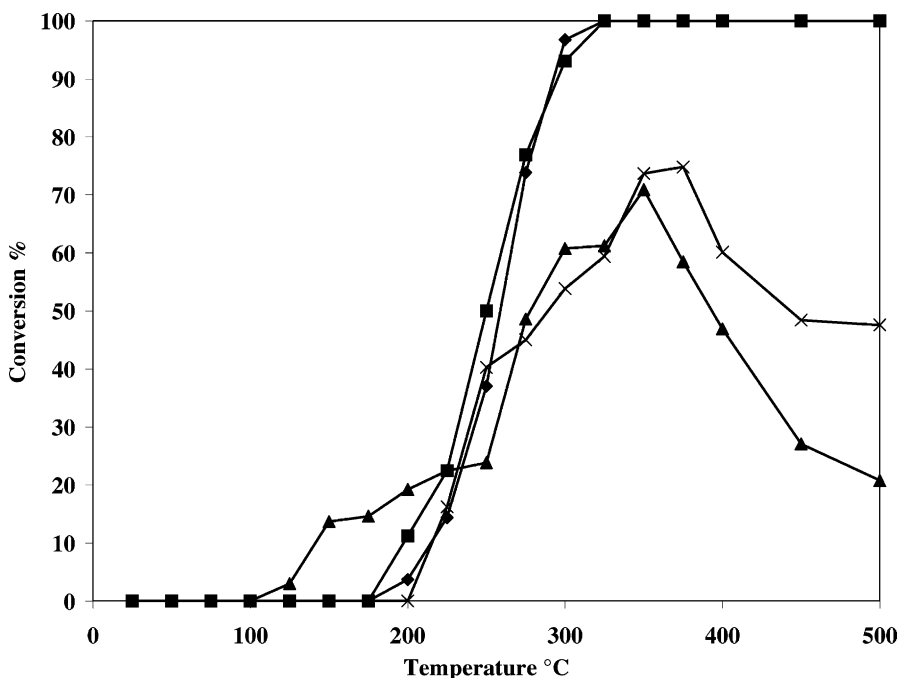
Table 1
Catalysts characterization

| Catalyst | Pt (wt.%) | Sn (wt.%) | Cl (wt.%) | Pt dispersion |
|---|---|---|---|---|
| 1%Pt/$\gamma$-$Al_2O_3$ | 1.02 | 0 | 1.2 | 0.35 |
| 1%Pt–1%Sn/$\gamma$-$Al_2O_3$ | 1.0 | 1.2 | 1.2 | 0.28 |

Fig. 1. Effect of temperature on the $C_3H_8$–NO–$O_2$ reaction. % $C_3H_8$ conversion over unsulfated Pt/$\gamma$-Al$_2$O$_3$ ($\blacklozenge$); and unsulfated 1% Pt–1%Sn/$\gamma$-Al$_2$O$_3$ (+). % NO conversion over unsulfated Pt/$\gamma$-Al$_2$O$_3$ ($\blacktriangle$); and unsulfated 1% Pt–1%Sn/$\gamma$-Al$_2$O$_3$ ($\blacksquare$). Feed: 4.5% $C_3H_8$, 15% $O_2$; 1000 ppm NO.

the temperature for the conversion of 50% of propane is of the same order for mono and bimetallic catalysts (260 and 255 °C, respectively). Thus, the propane combustion is not notably affected by the presence of tin on the catalysts. The effect of temperature on NO conversion during $C_3H_8$–NO–$O_2$ reaction is also shown on Fig. 1. In this figure, it can be seen that the temperature required for 50% NO conversion is also of the same order for both catalysts (285 and 290 °C, respectively).

### 3.2. $C_3H_8$–NO–$O_2$ reactions over Pt/$\gamma$–Al$_2$O and 1%Pt-1%Sn/$\gamma$–Al$_2$O$_3$ sulfated samples

The effect of catalyst sulfation on the $C_3H_8$–NO–$O_2$ reactions over Pt/$\gamma$-Al$_2$O and 1%Pt–1%Sn/$\gamma$-Al$_2$O$_3$ is illustrated in Figs. 2 and 3, respectively.

Comparing these figures and in Table 2, it can be seen that both $C_3H_8$ and NO decompositions over sulfated 1%Pt–1%Sn/$\gamma$-Al$_2$O$_3$ light off more rapidly than over sulfated 1%Pt/$\gamma$-Al$_2$O$_3$. The temperature

Table 2

Catalytic determinations of $C_3H_8$–NO–$O_2$ reactions over sulfated and unsulfated 1%Pt/$\gamma$-Al$_2$O$_3$ and 1%Pt–1%Sn/$\gamma$-Al$_2$O$_3$

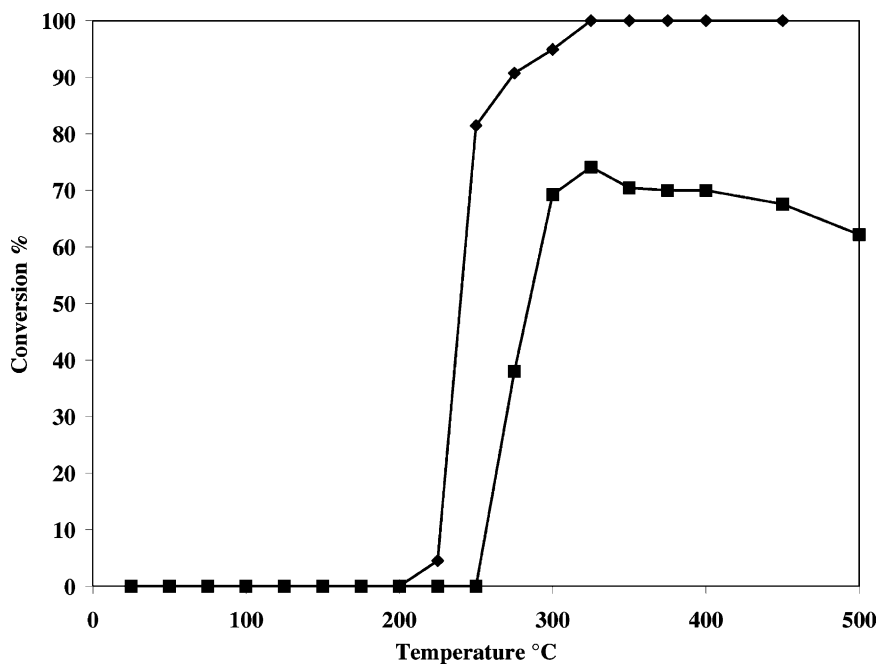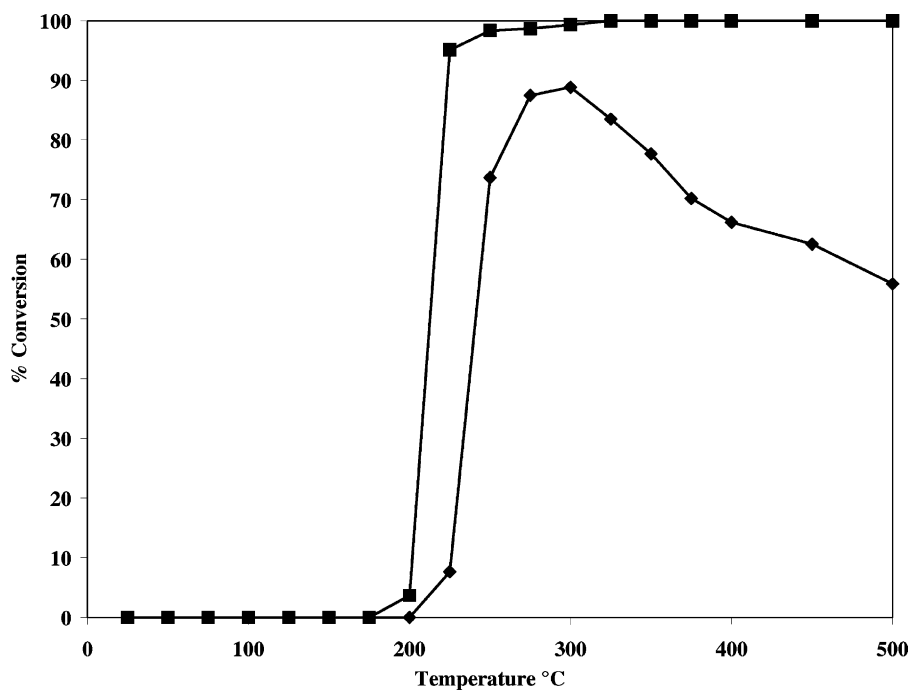| Catalyst | | | | Maximum NO conversion(%) | Temperature maximum NO |
|---|---|---|---|---|---|
| Supported on $\gamma$-Al$_2$O$_3$ | Sulfated | Temperature at 50% $C_3H_8$ conversion (°C) | Temperature at 50% NO conversion (°C) | | |
| 1%Pt | Yes | 260 | 285 | 70 | 350 |
| 1%Pt | No | 225 | 290 | 70 | 325 |
| 1%Pt–1%Sn | Yes | 255 | 290 | 75 | 375 |
| 1%Pt–1%Sn | No | 205 | 230 | 85 | 300 |

Fig. 2. Effect of temperature on the $C_3H_8$–NO–$O_2$ reaction over sulfated Pt/$\gamma$-Al$_2$O$_3$. Feed: 4.5%C$_3$H$_8$, 15% O$_2$; 1000 ppm NO ((♦): C$_3$H$_8$; (■): NO).



Fig. 3. Effect of temperature on the $C_3H_8$–NO–$O_2$ reaction over sulfated 1%Pt–1%Sn/$\gamma$-Al$_2$O$_3$. Feed: 4.5% C$_3$H$_8$, 15% O$_2$; 1000 ppm NO ((♦): C$_3$H$_8$; (■): NO).
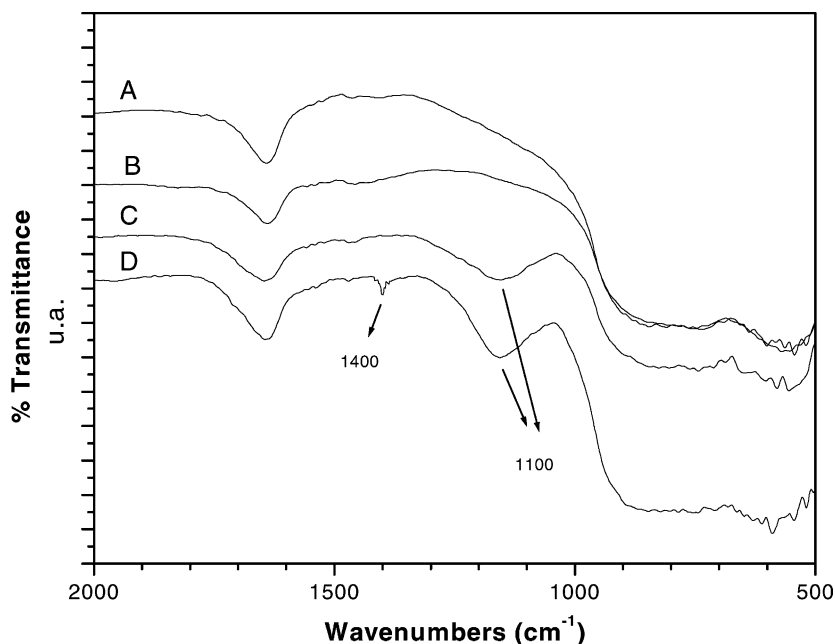
Fig. 4. FT-IR spectra of (A) 1%Pt/γ-Al$_2$O$_3$; (B) 1%Pt–1%Sn/γ-Al$_2$O$_3$; (C) sulfated 1%Pt/γ-Al$_2$O$_3$; (D) sulfated 1%Pt–1%Sn/γ-Al$_2$O$_3$.

required for 50% propane conversion is 225 °C on sulfated Pt catalyst and 205 °C on sulfated Pt–Sn catalyst.

Temperature required for 50% NO conversion is much higher over sulfated 1%Pt/γ-Al$_2$O$_3$ relative to sulfated 1%Pt–1%Sn/γ-Al$_2$O$_3$ (290 °C, compared with 230 °C).

### 3.3. Nature of sulfate species formed on sulfated Pt/γ-Al$_2$O and 1%Pt–1%Sn/γ-Al$_2$O$_3$

Previous IR studies of metal oxides sulfation have evidenced two types of sulfate species: surface species characterized by one or more bands in the 1410–1370 cm$^{-1}$ frequency range and bulk like species leading to wide bands in the 1200–1000 cm$^{-1}$ range [15–17]. In a recent paper [18], it has been shown that Pt does not affect the sulfate formation nor the nature of adsorbed species. Spectra reported in Fig. 4 show that only bulk like sulfate species are present on sulfated 1%Pt/γ-Al$_2$O (Fig. 4 C) while both species are present on sulfated 1%Pt–1%Sn/γ-Al$_2$O$_3$ (Fig. 4 D).

## 4. Discussion

### 4.1. C$_3$H$_8$ conversion

The Pt/γ-Al$_2$O$_3$ catalyst was sulfated under oxidizing conditions, which is expected to result in the formation of sulfate species on the Al$_2$O$_3$ support, but does not result in any sulfur species being deposited on Pt [19,20].

The C$_3$H$_8$ oxidation is unaffected by Sn present in the Pt/γ-Al$_2$O$_3$ catalyst, which is then consistent with the mechanism proposing that the reaction occurs only on the Pt surface. However, sulfation of the Pt/γ-Al$_2$O$_3$ results in a lowering of the C$_3$H$_8$ light-off temperature (Table 2).

According to Burch et al. [21], exposure of the Pt/γ-Al$_2$O$_3$ catalyst to an SO$_2$ + O$_2$ mixture at 500 °C results in the formation of SO$_3$ on Pt. However, SO$_3$ is not stable on Pt and will migrate to the Al$_2$O$_3$ surface forming aluminum sulfates. These authors propose a model involving the built-up of an electronegative sulfate (SO$_4{}^{2-}$) deposit which lies in close proximity to the edge of a Pt particle (Fig. 5). This would
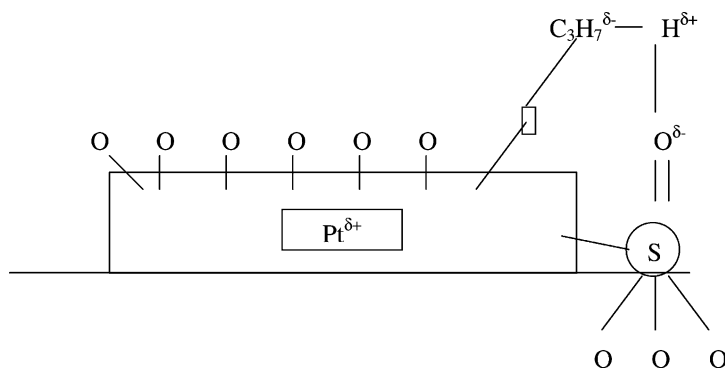
Fig. 5. Promoting effect of sulfation on the $C_3H_8$ combustion reaction over Pt/$\gamma$-$Al_2O_3$.

withdraw electron density from the Pt particle thereby, conferring on Pt atoms at the perimeter a partial positive charge. A catalytic site consisting of adjacent cationic and anionic moieties could then develop and this would facilitate the initial (heterolytic) C–H bond activation at the basic anionic (sulfate) site.

The strong lowering of the $C_3H_8$ light-off temperature on sulfated 1%Pt–1%Sn/$\gamma$-$Al_2O_3$ can be explained assuming that tin is interacting with alumina forming a tin aluminate and Pt is associated with this tin aluminate (eggshell model) as has been proposed by Adkins and Davis [22].

Sulfation pretreatment of the bimetallic catalyst would lead also to a built-up of an electronegative sulfate ($SO_4^{2-}$) but associated with tin. This ($SO_4^{2-}$) and tin aluminates would increase the electron density withdrawal from the Pt particle conferring on Pt atoms a stronger partial positive charge than in the case of sulfated Pt/$Al_2O_3$.
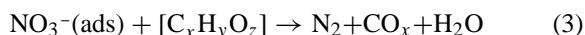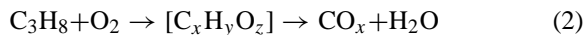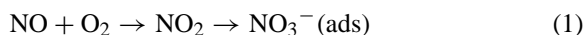
The IR spectra of the catalysts gave evidence of the formation of aluminum sulfates and tin sulfates during presulfation of the samples. IR spectra (Fig. 4) suggest that the absorption band obtained at $1163\,cm^{-1}$ on oth sulfated 1%Pt-/$\gamma$-$Al_2O_3$ and sulfated 1%Pt–1%Sn/$\gamma$-$Al_2O_3$, can be ascribed to bulk like sulfate species formed on $Al_2O_3$ during the sulfating pretreatment of the catalysts, while the peak obtained at $1400\,cm^{-1}$ on 1%Pt–1%Sn/$\gamma$-$Al_2O_3$ can be attributed to tin sulfate surface species.

The formation of sulfate phases could be expected on thermodynamic ground; the Gibbs free energies of the sulfates formation $\Delta G_f$, calculated at $500\,°C$ are: $-737\,kJ/mol$ for $SnSO_4$ and $-8312\,kJ/mol$ for $Al_2(SO_4)_3$ [23]. These values show that both species

are stable and could be formed under the conditions in which the catalysts were presulfated.

### 4.2. NO conversion

It is well known that selective reduction of NO with hydrocarbons is a very complex reaction comprising several parallel or consecutive reaction steps. Burch et al. [13] proposed a reaction mechanism of NO reduction by propane over Pt/$\gamma$-$Al_2O_3$. NO reduction appears to occur via reaction of $NO_2$ with $C_3H_8$ on the support and/or at the metal-support interface. Sulfation of the $Al_2O_3$ results in a decrease in the number of sites available for the nitrate species to be adsorbed and hence in the number of adsorbed nitrate species with which propane or propane derived species can react.

$$NO + O_2 \rightarrow NO_2 \rightarrow NO_3^-(ads) \tag{1}$$

$$C_3H_8 + O_2 \rightarrow [C_xH_yO_z] \rightarrow CO_x + H_2O \tag{2}$$

$$NO_3^-(ads) + [C_xH_yO_z] \rightarrow N_2 + CO_x + H_2O \tag{3}$$

The inhibition effect of sulfation on the catalytic activity for NO reduction by hydrocarbons has been reported for many alumina-based catalysts [11–13]. This negative effect of sulfation is probably due to the strong adsorption of sulfates on the alumina sites at which $NO_2$ adsorption occurs.

Sulfation of 1%Pt-1%Sn/$\gamma$-$Al_2O_3$ catalysts should also result in a decrease in the number of sites available on the $\gamma$-$Al_2O_3$ for the nitrate species to be adsorbed and hence in the number of adsorbed species with which $C_3H_8$ can react. Surprisingly, NO conversion on sulfated 1%Pt–1%Sn/$\gamma$-$Al_2O_3$ was not

decreased but increased. Now, it has been shown that for the NO selective catalytic reduction by hydrocarbons (HC–SCR), oxidation of NO to $NO_2$ is the important initial step [13,24,25]. A possible explanation for this result is that the addition of Sn to Pt/$\gamma$-$Al_2O_3$ catalyst enhances NO oxidation to $NO_2$, probably due to the enhancement of adsorbed oxygen on the metallic surface induced by Sn surface species over the catalyst. This explanation is supported by our earlier study about the effect of Sn on NO oxidation over Pt/$\gamma$-$Al_2O_3$ [26].

From the above mentioned results, $SO_2$ pretreatment on 1%Pt–1%Sn/$\gamma$-$Al_2O_3$ may cause two effects on catalytic performance:

- Sulfate formation on alumina $NO_2$ adsorption sites on which NO reduction proceeds (reaction 1).
- Acceleration of reaction 2 by surface Pt atoms with a strong partial positive charge due to electronegative sulfates and tin aluminate.

## 5. Conclusions

Results have been presented for $C_3H_8$–NO–$O_2$ reaction with sulfated and unsulfated 1%Pt/$\gamma$-$Al_2O_3$ and 1%Pt–1%Sn/$\gamma$-$Al_2O_3$.

IR study showed that $SO_2 + O_2$ pretreatment at 500 °C of this catalyst leaded to the formation of bulk aluminum sulfate and to surface tin sulfate. $C_3H_8$ and NO conversions as a function of temperature showed that while propane combustion is not notably affected by the presence of tin on the catalysts, sulfation of the 1%Pt–1%Sn/$\gamma$-$Al_2O_3$, resulted in an enhancement of the conversion of NO and $C_3H_8$ during the $C_3H_8$–NO–$O_2$ reaction.

An explanation of the higher activity of $C_3H_8$ conversion is proposed on the basis of the presence of tin sulfate that would confer on Pt atoms a stronger partial positive charge than in the case of sulfated Pt/$Al_2O_3$. This partial positive change would improve the activation of the first C–H bond in propane.

NO conversion is enhanced on 1%Pt–1%Sn/$\gamma$-$Al_2O_3$ probably due to the improvement of NO oxidation to $NO_2$ induced by Sn surface species over the catalyst and to the acceleration of propane oxidation (reaction 2) by surface Pt atoms with a strong partial positive charge due to electronegative sulfates and tin aluminate.

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