

The effect of Sn on the electronic state of M/ γ -Al₂O₃ (M = Pd, Pt) catalysts and the influence in the catalytic combustion of methane

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Pd-Sn and Pt-Sn catalysts supported on γ -Al₂O₃ were prepared by co-precipitation and the Pt characterized dispersion of reduced samples was determined by H₂ chemisorption for Pt and Pt-Sn catalysts, The Pd dispersion was determined by CO adsorption on Pd and Pd-Sn catalysts. The catalysts were characterized by the electron binding energy values determined by XPS. The results are explained on the basis of the Pt and Pd species electron binding energy changes due to the electronic properties of Sn. The catalytic activity in methane oxidation under lean burn conditions was measured. The results reveal that the tin addition causes a change in the catalytic activity of the supported catalysts, showing a greater catalytic activity on the CH₄-O₂ reaction for the bimetallic Pd-Sn/ γ -Al₂O₃.

Key words: Methane oxidation, Platinum, Platinum-Tin, Palladium, Palladium-Tin, XPS.

Introduction

The combustion of hydrocarbons is of interest to functionalize inexpensive feed stocks and because catalytic combustion offers a possible means to generate energy without creating excessive amounts of nitrogen oxides. The engine out total hydrocarbons composition reflects the fuel CH₄/NMHC ratio, typically 93% methane, 5% NMHC [1]. Methane is the most difficult hydrocarbon to oxidize since it contains no C-C bond, but only C-H bonds, which are more difficult to break [2]. Although methane does not contribute to tropospheric ozone production, it is a potent greenhouse gas estimated to have a 20-year global warming potential 21 times that of carbon dioxide at equivalent emission rates [3]. The complete oxidation of methane can be performed over either noble metals or transition metal oxides [4-7]. Few studies have been made on platinum catalysts [8-11] compared to palladium ones [12-16]. Burch and Loader. observed T₅₀ (temperature at 50% conversion) for Pt or Pd supported on high surface area γ -Al₂O₃ catalysts within 100 °C of each other, Pd having the higher activity [11].

A mechanism for the oxidation of methane on Pt suggests that the metal would activate the almost non-polar C-H bonds of methane through a homolytic mechanism (dissociate adsorption of CH₄ at free metal sites), oxygen species

acting as an inhibitor for the reaction at full coverage [17]. The extent of oxidation of the Pt or Pd surface would be a key factor in the catalytic behavior, a less oxidized platinum surface being more active compared to a more oxidized surface. On this basis, operating under methane-rich conditions is expected to lower the oxidation extent of a Pt or Pd surface. Deng et al. [18] and Lampert et al. [19] showed an increase in the Pd3d_{5/2} electron binding energies and the formation of sulfate on alumina supported PdO. Lampert et al. [19] give a detailed mechanism for sulfur inhibition of methane oxidation activity and explained the deactivation of PdO by sulfur oxides by both a decrease in the chemisorption of CH₄ on the sulfated PdO and a decrease in the availability of oxygen from the PdO due to an increase in the Pd oxidation state.

Now, Roth et al. [5] found that SnO₂ strongly promoted the oxidation of methane over Pt catalysts. However, when Pt was supported on SnO₂ grafted on Al₂O₃ (15 wt% Sn), the activity found after ageing, was lower than Pt/Al₂O₃. Thus, on the basis of these results, we investigated in this work, the effect of lower amounts of tin additions on 1%Pt/ γ -Al₂O₃ and 2%Pd/ γ -Al₂O₃ activities for CH₄ oxidation and the effect of the electronic state of Pt and Pd.

Experimental

Catalyst preparation

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. All

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catalysts were prepared by impregnation using acidic aqueous solutions (0.1 M HCl), and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Merck, minimum. 98% purity) for the platinum catalyst or PdCl_2 (Merck, minimum. 98% purity) in palladium catalysts and simultaneously incorporating the solution of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (Alfa/Johnson Matthey) for Pd-Sn or Pt-Sn catalysts. After impregnation, the catalysts were dried at 120 °C overnight, and then calcined in flowing air for 6 h at 600 °C. Finally, the catalysts were reduced in a pure hydrogen flow for 8 h at 500 °C. A reference alumina support was prepared in the same way using only diluted hydrochloric acid. 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). The measures of reduced accessibility of the catalysts were obtained at room temperature in a static volumetric apparatus. For platinum catalysts the measurements were obtained by the $\text{H}_2\text{-O}_2$ titration method using the stoichiometric $(\text{H}/\text{Pt})_{\text{surf}} = 1$. We use of the method of CO absorption method using the stoichiometric $(\text{CO}/\text{Pd})_{\text{surf}} = 1$ for palladium catalysts.

XPS characterization

Photoelectron spectra were recorded over 2%Pd/ γ - Al_2O_3 , 1%Pt/ γ - Al_2O_3 , 2%Pd-1%Sn/ γ - Al_2O_3 and 1%Pt-2%Sn/ γ - Al_2O_3 catalysts after $\text{CH}_4\text{-O}_2$ reaction using a VG Escalab 200R electron spectrometer equipped with a hemispherical analyzer, operating in a constant pass energy mode, and a monochromatic $\text{MgK}\alpha$ ($h\nu = 1253.6$ eV, $1 \text{ eV} = 1.603 \times 10^{-19} \text{ J}$) 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, as due to the relative by high surface area and the small particle size the photoelectron intensity was very low. 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.

Catalytic activity studies

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. Measurements over the samples were performed using a feed volume flow rate of $100 \text{ cm}^3 \text{ minute}^{-1}$ consisting of 2 vol% CH_4 , 15 vol% of O_2 . The catalyst loading in the reactor was of 200 mg. The reactor out flow was analyzed using a Shimadzu gas chromatograph provided with a thermoconductivity detector (TCD). The chromatograph used a Chromosorb 2,000 column to analyze the CH_4 evolutions and a molecular sieve 13X column for the separation of O_2 and N_2 . Before testing the catalytic activity, the samples were pretreated for 1 h in the reactant stream at 600 °C. The samples were then cooled and measurements taken as the temperature was increased stepwise. Measurements were made as the samples were heated in the range 25–600 °C. The catalyst was left at each temperature for 1 h until a steady state was reached. The conversions of CH_4 to all products were calculated based on the following equation:

$$\text{conversion}(\%) = \frac{(X_{\text{in}} - X_{\text{out}})}{X_{\text{in}}} 100 \quad (1)$$

X_{in} = the concentration of X introduced in the experiment
 X_{out} = concentration of X at the reactor outlet

Table 1. Characterization data of catalyst

Catalyst	Pt (wt%)	Pd (wt%)	Sn (wt%)	Cl (wt%)	Pt Dispersion	Pd Dispersion
$\gamma\text{-Al}_2\text{O}_3$	-	-	-	0.99	-	-
2% Pd/ $\gamma\text{-Al}_2\text{O}_3$	-	2.1	-	1.0	-	0.29
1% Pt/ $\gamma\text{-Al}_2\text{O}_3$	1.02	-	-	1.02	0.35	-
2% Pd-1% Sn/ $\gamma\text{-Al}_2\text{O}_3$	-	2.0	1.1	1.2	-	0.29
1% Pt-2% Sn/ $\gamma\text{-Al}_2\text{O}_3$	1.0	-	2.2	1.2	0.26	-

Table 2. Light-off₅₀ values obtained for methane oxidation (°C), and binding energies (eV) of core electrons of the catalysts studied

Catalyst	Light-off ₅₀ CH_4 $\text{CH}_4\text{-O}_2$	Pd 3d _{5/2} (eV)	Sn 3d _{5/2} (eV)	Pt 4d _{5/2} (eV)	Al 2P (eV)
2% Pd/ $\gamma\text{-Al}_2\text{O}_3$	420	336.3	-	-	74.5
1% Pt/ $\gamma\text{-Al}_2\text{O}_3$	560	-	-	315.3(56%) 318.0(44%)	74.5
2% Pd-1% Sn/ $\gamma\text{-Al}_2\text{O}_3$	485	337.0	486.9	-	74.5
1% Pt-2% Sn/ $\gamma\text{-Al}_2\text{O}_3$	540	-	486.8	315.5(60%) 318.5(40%)	74.5

Results

Characterization of catalysts

The catalyst characterization data are summarized in Table 1. Comparable Pd and Pt dispersion values were obtained for the mono and the bimetallic catalysts.

Methane oxidation

In Table 2, temperatures of 50% conversion (light-off temperatures) for methane in the $\text{CH}_4\text{-O}_2$ reaction on all catalysts studied are given. $\gamma\text{-Al}_2\text{O}_3$ was not active for methane propane oxidation at the temperatures studied in this investigation.

CH_4 oxidation over 2%Pd/ $\gamma\text{-Al}_2\text{O}_3$ and 2%Pd-1%Sn/ $\gamma\text{-Al}_2\text{O}_3$ in $\text{CH}_4\text{-O}_2$ reactions

In Fig. 1, we compare the evolution of CH_4 during the $\text{CH}_4\text{-O}_2$ reaction over 2%Pd/ $\gamma\text{-Al}_2\text{O}_3$ and 2%Pd-1%Sn/ $\gamma\text{-Al}_2\text{O}_3$. The tin addition to 2%Pd/ $\gamma\text{-Al}_2\text{O}_3$ resulted also in a decrease in the methane oxidation performance of palladium. The temperature required to reach 50% methane conversion is 420 °C for the catalyst 2%Pd/ $\gamma\text{-Al}_2\text{O}_3$ and 485 °C for the catalyst 2%Pd-1%Sn/ $\gamma\text{-Al}_2\text{O}_3$. This decrease in palladium activity for methane oxidation cannot be explained by an increase of residual chloride [20] due to SnCl_4 addition since the results presented in Table 1 show comparable amounts of chloride in 2%Pd/ $\gamma\text{-Al}_2\text{O}_3$ and 2% Pd-1%Sn/ $\gamma\text{-Al}_2\text{O}_3$ catalysts.

CH_4 oxidation over 1%Pt/ $\gamma\text{-Al}_2\text{O}_3$ and 1%Pt-2%Sn/ $\gamma\text{-Al}_2\text{O}_3$ in $\text{CH}_4\text{-O}_2$ reactions

The evolution of $\text{CH}_4\text{-O}_2$ reaction over 1%Pt/ $\gamma\text{-Al}_2\text{O}_3$ and 1%Pt-2%Sn/ $\gamma\text{-Al}_2\text{O}_3$ catalysts is shown in Fig 1. In this figure, it can be seen the temperature required to reach a 50% methane conversion is 560 °C on 1%Pt/ $\gamma\text{-Al}_2\text{O}_3$ and 540 °C on the 1%Pt-2%Sn/ $\gamma\text{-Al}_2\text{O}_3$ catalyst. Hence the addition of tin to platinum catalyst leads to an increase in the catalytic activity for the combustion of methane.

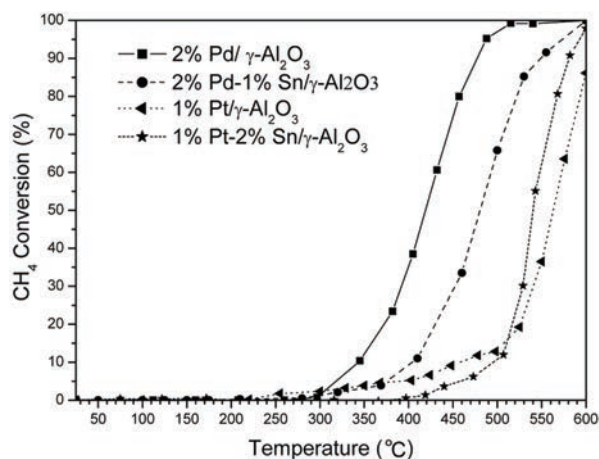


Fig. 1. Methane conversion as a function of temperature on the $\text{CH}_4\text{-O}_2$ reaction, Reaction feed: 2% CH_4 , 15% O_2 , balance He.

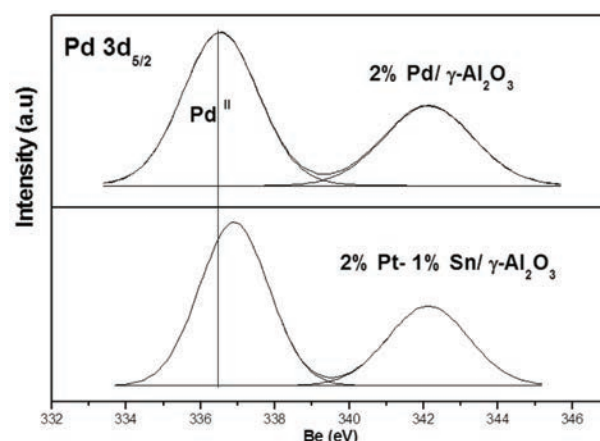


Fig. 2. Pd $3d_{5/2}$ Core level spectra of catalysts 2% Pd/ $\gamma\text{-Al}_2\text{O}_3$ and 2% Pd-1% Sn/ $\gamma\text{-Al}_2\text{O}_3$.

X-ray photoelectron spectroscopy

Binding energies of core electrons of the catalysts after the $\text{CH}_4\text{-O}_2$ reaction are reported in Table 2, and shown in Fig. 2 for the catalysts 2%Pd/ $\gamma\text{-Al}_2\text{O}_3$ and 2%Pd-1%Sn/ $\gamma\text{-Al}_2\text{O}_3$ after the $\text{CH}_4\text{-O}_2$ reaction, the binding energy Pd $3d_{5/2}$ for 2%Pd/ $\gamma\text{-Al}_2\text{O}_3$ (336.2 eV) indicates that Pd is present as PdO [21, 22]. The Sn addition to 2%Pd/ $\gamma\text{-Al}_2\text{O}_3$ resulted in an increase in the degree of Pd oxidation as shown by the increase in the Pd $3d_{5/2}$ electron binding energy (337.0 eV).

Photoelectron spectra were recorded over 1%Pt/ $\gamma\text{-Al}_2\text{O}_3$ and 1%Pt-2%Sn/ $\gamma\text{-Al}_2\text{O}_3$ catalysts after the $\text{CH}_4\text{-O}_2$ reaction, and are shown in Fig. 3 where the binding energy Pt $4d_{5/2}$ for the 1%Pt/ $\gamma\text{-Al}_2\text{O}_3$ sample indicates that Pt is present as Pt(0) (315.3 eV). 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 [21]. Now, it has been reported [23, 24], for PtO_2 a binding energy component (318 eV) of the Pt $4d_{5/2}$ that can be assigned to (Pt^{4+}). However, for the 1%Pt-2%Sn/ $\gamma\text{-Al}_2\text{O}_3$ sample, the binding energy of the Pt $4d_{5/2}$, revealed a higher binding energy component

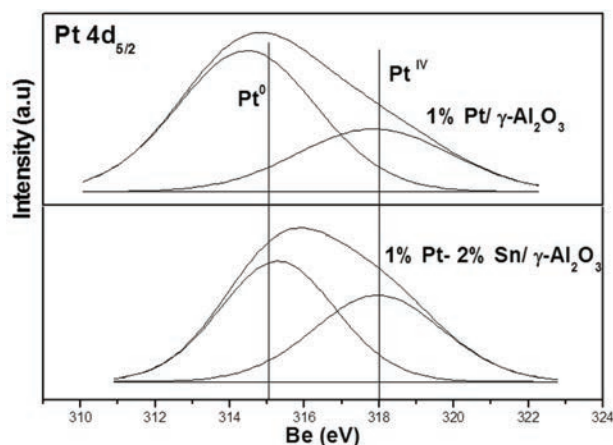


Fig. 3. Pt $4d_{5/2}$ Core level spectra of catalysts 1% Pt/ $\gamma\text{-Al}_2\text{O}_3$ and 1% Pt-2% Sn/ $\gamma\text{-Al}_2\text{O}_3$.

Table 3. Atomic surface ratios of supported Pd, Pd-Sn, Pt and Pt-Sn catalysts determined by XPS

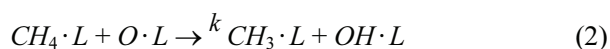
Catalyst	Sn/Al	Pd/Al	Pt/Al
2% Pd/ γ -Al ₂ O ₃	-	0.021	-
1% Pt/ γ -Al ₂ O ₃	-	-	0.0020
2% Pd-1% Sn/ γ -Al ₂ O ₃	0.039	0.025	-
1% Pt-2% Sn/ γ -Al ₂ O ₃	0.043	-	0.0053

(318.5 eV) that can be associated to an increase in the highly oxidized Pt component with respect to the Pt⁰ component. The binding energy of the Sn3d_{5/2} reveals that Sn is present as Sn²⁺ [21, 25, 26] on both catalysts

Discussion

The use of palladium based catalysts in hydrocarbon abatement for natural gas engines and for catalytic combustion is well documented. In NGV lean burn applications, palladium oxidation catalysts exhibit initially high total hydrocarbon conversions, but their methane activity declines rapidly [12, 19, 27-29]. Possible deactivation mechanisms include hydrothermal sintering of the palladium and the support, carbon residues deposition and sulfur poisoning. The results of methane combustion over all catalysts (Fig. 1), are consistent with reports in the literature, showing that Pd catalysts present higher methane activity related to Pt catalysts. The temperature required to reach 50% methane conversion on 2%Pd/ γ -Al₂O₃ and 1%Pt/ γ -Al₂O₃ is 420°C and 560°C respectively. The same figure shows that the addition of Sn to the catalysts results in a decrease of the temperature to reach 50% conversion of methane for CH₄-O₂ over 1%Pt/ γ -Al₂O₃. However, Sn addition to Pd catalyst resulted in an increase of the temperature to reach 50% conversion of methane for this reaction.

These results reveal the following facts: (i) Sn addition to the catalyst, led to an increase in the degree of Pd oxidation for 2%Pd/ γ -Al₂O₃; (ii) 2%Pd/ γ -Al₂O₃ activity for methane oxidation declined as the degree of Pd oxidation increased. Now, Farrauto et al. [33] and Mueller et al. [34] proposed the methane oxidation mechanism in terms of Mars-van Krevelen reduction-oxidation pathways, where the rate determining step is the abstraction of the first hydrogen on the adsorbed methane molecule:



L is an active site (PdO). This site must provide oxygen atoms to oxidize the chemisorbed CH_xL species. Deactivation of PdO for CH₄ oxidation may be due to: (i) a decrease in methane adsorption on the PdO sites, and (ii) a decrease in the availability of oxygen from PdO. This decrease in the availability of oxygen may be due to an increase in the Pd oxidation state generated by tin species. Pd-O bond energy would be higher, thus higher temperatures would be necessary for the oxidation of

the chemisorbed CH_xL species.

On the other hand, Table 2 shows the increased proportion of oxidized platinum atoms on 1%Pt-2%Sn/ γ -Al₂O₃ relative to 1%Pt/ γ -Al₂O₃. These highly oxidized Pt species may have been generated as a result of the interaction between Pt and SnO at the surface of the catalyst. The SnO deposit which lies in close proximity to the edge of a Pt particle would have withdrawn electron density from the Pt particle, conferring on Pt species a higher positive charge. A new catalytic site consisting of adjacent cationic Pt^{δ+} and anionic SnO^{δ-} moieties could then develop and this would facilitate the initial (heterolytic) C-H bond activation in a similar way to that proposed earlier to explain methane activation over oxide catalysts [35] and propane combustion over sulfated Pt/Al₂O₃ catalysts [36, 37].

Conclusions

The XPS results presented in this investigation confirm that a Sn addition to 2%Pd/ γ -Al₂O₃ catalyst resulted in an increase of the oxidation state of PdO. Deactivation of PdO by the Sn species, on methane oxidation may be due to an increase in the degree of oxidation of Pd which may lead to an increase in the Pd-O bond energy and therefore, to a decrease in the availability of oxygen from the PdO to oxidize methane adsorbed species at a given temperature. The photoelectron spectroscopy data revealed the formation of highly oxidized surface Pt atoms on the 1%Pt-2%Sn/ γ -Al₂O₃ catalyst. The increased proportion of oxidized platinum atoms on 1%Pt-2%Sn/ γ -Al₂O₃ relative to 1%Pt/ γ -Al₂O₃, could be due to polarization of these atoms for by addition of Sn in the support.

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