

# PROX reaction over Pt<sub>3</sub>Sn/Al<sub>2</sub>O<sub>3</sub>: Structural investigation by *operando* DRIFTS

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## Introduction

Pt<sub>3</sub>Sn based catalysts have presented exhibit enhanced activities for preferential CO oxidation (PROX) as compared to analogous Pt catalysts. Yet, often ‘ill-defined’ PtSn phases present on the catalyst prevent a full understanding of the reaction mechanism and active sites involved. Therefore we used for this study well-defined Pt and Pt<sub>3</sub>Sn catalysts, obtained by impregnation of pre-formed Pt or Pt<sub>3</sub>Sn nanoparticles [1]. Our 1% Pt<sub>3</sub>Sn/γ-Al<sub>2</sub>O<sub>3</sub> and 1% Pt/γ-Al<sub>2</sub>O<sub>3</sub> catalysts were used in the CO PROX. Experiments were carried out under controlled conditions to obtain intrinsic kinetics. Additionally an investigation of CO adsorption under the reaction mixture was carried out by *operando* DRIFTS over the samples. An unusual evolution of the adsorbed CO was noted while ramping up the temperature.

## Materials and Methods

Pt and Pt<sub>3</sub>Sn nanoparticles were prepared using a colloidal approach [1]. The colloidal suspension is deposited onto the γ-Al<sub>2</sub>O<sub>3</sub> support (106 m<sup>2</sup>/g) under continuous stirring and inert atmosphere. Pt/γ-Al<sub>2</sub>O<sub>3</sub> and Pt<sub>3</sub>Sn/γ-Al<sub>2</sub>O<sub>3</sub> catalysts were calcined and then reduced with 10% H<sub>2</sub>/N<sub>2</sub> flow at 400°C for 2 h. The CO PROX reaction was conducted in a fixed-bed reactor under atmospheric pressure at a temperature range between 50-260°C ramped up/down with 1°C/min. A gas flow consisted of 1 NmL/min CO, 2 NmL/min O<sub>2</sub>, 18 NmL/min N<sub>2</sub> and 79 NmL/min H<sub>2</sub> was used. DRIFTS analysis was performed under the same reaction conditions, using a modified Spectra-Tech fixed-bed cell.

## Results and Discussion

TEM analysis showed that the average metal particle size was 1.7 nm for both samples with a rather narrow distribution indicating that the above synthesis method indeed allows a control of the particle size. The catalytic results are summarized in **Table 1** for the two samples. As reported in the literature, the Pt<sub>3</sub>Sn catalyst was more active for preferential CO oxidation than the Pt one, reflected in a lower light-off temperature and also lower activation energy of 32 compared to 75 kJ/mol for Pt<sub>3</sub>Sn and Pt, respectively [2].

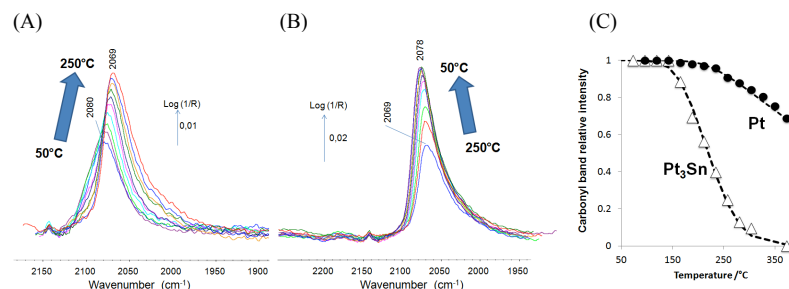
**Table 1.** Comparison of light-off temperature, selectivity and apparent activation energy for Pt<sub>3</sub>Sn/Al<sub>2</sub>O<sub>3</sub> and Pt/Al<sub>2</sub>O<sub>3</sub>. The last column gives the heat of CO adsorption determined through a Temkin model at zero (E0) and full (E1) coverage, respectively.

Catalyst	T <sub>light-off</sub> (°C) (X <sub>CO</sub> =50%)	$S = \frac{\Delta O_2^{(CO)}}{\Delta O_2^{(CO)} + \Delta O_2^{(H_2)}} \times 100\%$	E <sub>act</sub> (kJ/mol)	-ΔH <sub>ads</sub> CO (kJ/mol)
Pt <sub>3</sub> Sn/Al <sub>2</sub> O <sub>3</sub>	175	45	32	E0 = 95; E1 = 75
Pt/Al <sub>2</sub> O <sub>3</sub>	240	70	75	E0 = 180; E1 = 85

The carbonyl IR band evolution during PROX over PtSn/Al<sub>2</sub>O<sub>3</sub> as a function of temperature is shown in Fig. 1. Surprisingly, by raising the temperature the amount of carbonyl species increases, while at the same time the wavenumber decreased (red-shift). The increase of the carbonyl species was the result of both surface enrichment of platinum atoms induced by CO adsorption at the surface of the alloy and by various extent of blocking of Pt sites by SnO. By decreasing the reaction temperature a blue shift is then observed as well as an increase of the amount CO carbonyls due to an increase in surface coverage of a Sn-rich alloy surface.

These interpretations were confirmed by isothermal experiments carried out at various temperatures and under various reaction feed (not shown), proving that CO (in the absence of O<sub>2</sub>) could induced surface segregation of Pt while maintaining a reduced alloy, in contrast to the effect of O<sub>2</sub> which is known to produce segregated oxides.

The heat of CO adsorption at low and high coverage on the Pt-Sn alloy was calculated using the Adsorption Equilibrium IR method (Fig. 1.C). The CO heat of adsorption was dramatically lowered on the Pt-Sn as compared to Pt case (Table 1), explaining the improved catalytic property of the alloy, which is less prone to CO poisoning (Fig.1.C).



**Figure 1.** (A) and (B): *Operando* DRIFTS spectra over Pt<sub>3</sub>Sn/Al<sub>2</sub>O<sub>3</sub> in 1% CO/2% O<sub>2</sub>/50% H<sub>2</sub> and Ar when temperature is increased (A) and decreased (B). (C) Evolution with temperature of the DRIFTS band intensity of carbonyl under 2%CO in H<sub>2</sub>. The dotted lines correspond to a Temkin adsorption model using the E0 and E1 values reported in Table 1.

## Significance

*Operando* DRIFTS proved, for the first time, that CO induced structural changes on PtSn alloys under reaction conditions, particularly at temperatures below 175°C. This has consequences for the interpretation of the kinetic results and is consistent with hysteresis effects sometimes observed over similar formulations. The CO heat of adsorption on the Pt-Sn alloy could be measured and found to be much lower than that of Sn-free Pt.

## References

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