



# CO PROX over Pt–Sn/Al<sub>2</sub>O<sub>3</sub>: A combined kinetic and in situ DRIFTS study



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## ABSTRACT

Preferential oxidation of CO (PROX) in hydrogen-rich mixtures was studied over alumina-supported Pt and Pt–Sn catalysts, which exhibited a well-defined metal particle size. The reaction rate was much faster over Pt–Sn/Al<sub>2</sub>O<sub>3</sub> than over Pt/Al<sub>2</sub>O<sub>3</sub>. Significantly different apparent activation energies and oxygen reaction orders were found for both samples. Whereas the CO PROX kinetics over Pt/Al<sub>2</sub>O<sub>3</sub> could be described by oxygen adsorption as being rate-determining step, this was not the case for Pt–Sn. In situ Diffuse Reflectance Infrared Fourier Transformed Spectroscopy (DRIFTS) showed that Pt–Sn, initially under a mixture of 1% CO/80% H<sub>2</sub>, segregated upon the introduction of 2% O<sub>2</sub>, even at temperatures where the alloy was stable under reducing conditions. For the CO PROX reaction over Pt–Sn/Al<sub>2</sub>O<sub>3</sub> a bifunctional mechanism is proposed with CO and H being adsorbed on the platinum sites and oxygen being channeled from neighboring SnO<sub>x</sub> sites. This work suggests a Mars–Van Krevelen type of mechanism for the SnO<sub>x</sub> site, in agreement with the low value of 0.2 for the oxygen reaction order over Pt–Sn.

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## 1. Introduction

PEM fuel-cell technology requires very pure hydrogen, i.e. free from any components likely to adsorb on the platinum-based electrode. One of these components is carbon monoxide, which is always present when hydrogen is produced from carbon-containing resources via reforming or partial oxidation reactions. CO preferential oxidation (PROX) aims at removing small amounts of CO in hydrogen rich streams by catalytic oxidation of CO at low temperatures, with minimal production of water. Bimetallic Pt–Sn catalysts have shown much higher activities for CO oxidation [1–5] and CO PROX than those of Pt catalysts [6–8]. The actual state of the active phase under reaction conditions is being debated [1–8]. To further explore this issue, a combined DRIFTS (Diffuse Reflectance Infrared Fourier Transformed Spectroscopy) and kinetic study under similar CO PROX reaction conditions was performed on alumina-supported Pt–Sn and Pt exhibiting both well-controlled particle sizes.

The carbonyl IR bands present at the surface of the Pt–Sn sample were investigated using a modified DRIFTS reaction cell to determine the nature of the phase present under typical reaction

conditions. The pre-reduced sample at 400 °C was studied at 150 and 225 °C. These two temperatures were chosen because those are either side of 175 °C, which was shown in previous work to be a critical temperature delimiting the stability domains of different metallic phases under reducing (i.e. O<sub>2</sub>-free) conditions [9]. An alloy phase characterized by a Pt–CO band at ca. 2054 cm<sup>-1</sup> was observed above 175 °C [9]. This alloy phase, the composition of which is yet unclear, was characterized by a remarkably low heat of CO adsorption on Pt of 95 kJ/mol at low CO coverage, which is about half the value usually displayed by pure Pt nanoparticles. The alloy phase was unstable below 175 °C and a Pt-rich phase was formed exhibiting a Pt–CO band at around 2071 cm<sup>-1</sup>. The effect of the presence of O<sub>2</sub> will be of particular interest in the present study, as molecular oxygen can readily lead to the oxidation of tin [2,5,6] and therefore favor the segregation of Pt and Sn.

## 2. Experimental

### 2.1. Catalysts synthesis and characterization

Pt-containing mono and bimetallic supported catalysts were synthesized using a two-step methodology. Pt and Pt–Sn nanoparticles (NPs) were first prepared using a colloidal route according to the literatures [10,11]. A mixture of a Pt complex (i.e. Pt(dba)<sub>2</sub>, dba = dibenzylidene acetone) and octylsilane (ABCR), which acted

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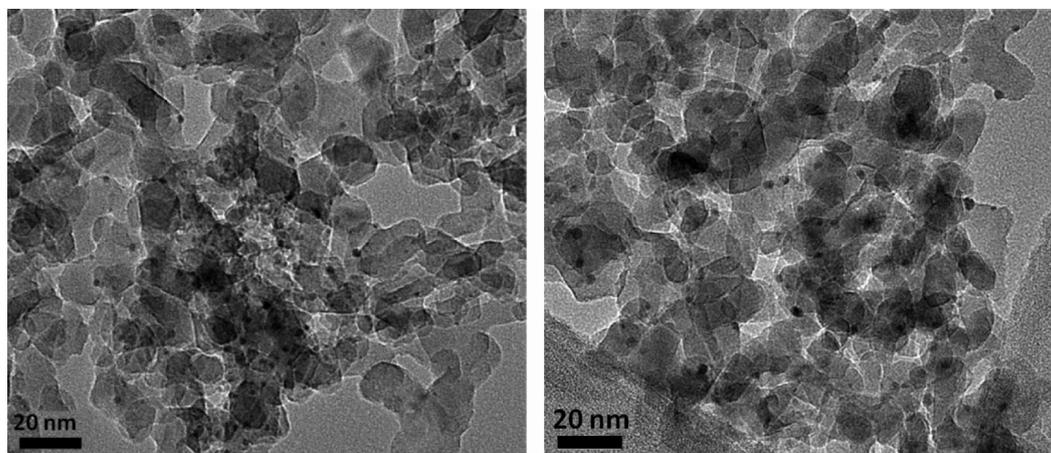


Fig. 1. TEM picture and particle size distribution of NPs supported onto  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Pt (left) and PtSn (right).

as a ligand, was used for the synthesis of Pt monometallic NPs. Pt–Sn NPs were obtained by contacting Pt(dba)<sub>2</sub> and tributyltin hydride [(*n*-Bu)<sub>3</sub>SnH](Sigma Aldrich) without the addition of any other ligand. The precursors were dissolved in dry tetrahydrofuran (Sigma Aldrich) and pressurized with 3 bar of H<sub>2</sub> during 10 h at room temperature. The colloidal suspension was further used for the second step of the catalyst preparation.

Following the evaporation of the solvent, a small volume of the suspension was added to the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support (Alfa Aesar, BET surface area of 106 m<sup>2</sup>/g) under continuous stirring and non-oxidative atmosphere and then dried overnight under Ar. The dry crude catalysts were subsequently calcined under flowing dry air at 320 °C in order to remove most of the alkyl fragments.

Transmission electron microscopy for both the colloidal nanoparticles and solid materials was carried out using a High Resolution Electron microscope JEOL 2100F at 200 kV. The samples were dispersed in THF and the carbon-coated copper grids were impregnated with a droplet of the mixtures. The mean size of the Pt and Pt–Sn nanoparticles in the colloidal state was ~2 nm. The narrow particle size distribution was maintained after the deposition onto the support and after calcination at 320 °C. From the particle size distribution by assuming a cuboctahedral particle shape and the formulas given in Ref. [12], a dispersion of 0.50 and 0.47 was calculated for the Pt and Pt–Sn catalysts, respectively.

The ICP technique was used for the determination of the elemental composition of the Pt–Sn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> samples. After an acidic treatment of the samples, the nominal loading found was 0.86 wt.% for Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 0.65 wt.% Pt for Pt–Sn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The tin content in the Pt–Sn sample was 0.61 wt.%.

XRD analysis of Pt–Sn catalyst showed the presence of a Pt–Sn alloy phase, after in situ reduction by H<sub>2</sub> at 400 °C [9]. The XRD analysis was performed on the blank support  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and on both samples, Pt–Sn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Pt/Al<sub>2</sub>O<sub>3</sub> pre-reduced in situ under H<sub>2</sub> flow (20 ml/min) at 400 °C for 1 h. The samples were then cooled down to 25 °C under H<sub>2</sub>. The diffraction patterns were collected in the  $2\theta$  angle range of [25°–90°]. The presence of Pt–Sn crystallites was supported by the presence of two peaks at  $2\theta = 41$ –45° and  $2\theta = 79$ °, which are consistent with the phase Pt<sub>0.996</sub>Sn<sub>1.004</sub>. Pt crystallites are represented by two peaks at  $2\theta = 40$ ° and 81°, respectively. Due to the anisotropy of metal crystallite size in the case of Pt/Al<sub>2</sub>O<sub>3</sub>, some of the rays were hardly visible.

## 2.2. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

For the DRIFTS studies, a commercial High Temp/Ambient Pressure Chamber DRIFTS cell from Spectra-Tech was used, modified in

a similar way as that described in details elsewhere [13]. The DRIFTS assembly was fitted in a Magna 550 Nicolet spectrometer using a MCT detector. The cell dome was fitted with ZnSe windows. The samples were used in the powder form and about 6 mg was placed into a ceramic crucible on top of a SiC layer. A thermocouple was located at the center of the sample bed. Spectra were collected using 32 scans at a resolution of 4 cm<sup>-1</sup>. The DRIFTS data are reported as  $\log 1/R$ , with  $R = I/I^0$ , where  $R$  is the sample reflectance,  $I^0$  is the intensity measured on the sample after exposure to the CO-free feed and  $I$  is the intensity measured under reaction condition. The pseudo-absorbance  $\log 1/R$  gives a better linear representation of the band intensity against sample surface coverage than that given by the Kubelka–Munk function for strongly absorbing media [14].

A mass spectrometer was used on-line to estimate the CO conversion. To maximize the DRIFTS signal the sample powder was on deposited as a thin layer on top of the SiC filler and not mechanically mixed as was the case for the plug-flow reactor studies. The ratio catalyst weight to CO molar flowrate ( $W/F_{CO}$ ) was 8 kg<sub>cat</sub> s mol<sup>-1</sup> in the case of the experiment carried out in the DRIFTS cell, against 33.6 kg<sub>cat</sub> s mol<sup>-1</sup> in the case of the plug flow reactor.

## 2.3. Kinetic experiments

The kinetic study was conducted in the temperature range of 25–260 °C with 25 mg of catalyst (100–200  $\mu$ m) diluted in 225 mg of SiC packed in a quartz tube with an inner diameter of 4 mm. Experiments were conducted with a total flow of 100 Nml/min with a composition of 1% CO, 2% O<sub>2</sub>, 80% H<sub>2</sub> and 17% N<sub>2</sub> at a total pressure of 1 bar. For the determination of the reaction orders the CO partial pressure was varied between 0.25 and 1.5 kPa and the oxygen partial pressure between 0.3 and 2.5 kPa. These experiments were carried out at 150 °C for Pt and at 100 °C for Pt–Sn. The activation energy was determined from isothermal experiments at 115, 130, 150 and 190 °C for Pt and 75, 100, 115, 130 °C for Pt–Sn. The analysis of CO, CO<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub> was carried out by using a micro-chromatograph equipped with a molecular sieve and poraplot column.

The selectivity of the CO oxidation was calculated from:

$$S = \frac{0.5 \text{ (moles of CO}_2 \text{ at exit)}}{\text{(moles of O}_2 \text{ inlet} - \text{moles of O}_2 \text{ outlet)}} \quad (1)$$

## 3. Results

### 3.1. TEM analysis

Fig. 1 shows TEM images of both the Pt/Al<sub>2</sub>O<sub>3</sub> and PtSn/Al<sub>2</sub>O<sub>3</sub> samples. A number of these images were used to determine the

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