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CO dissociation on Pt-Sn nanoparticles triggers Sn oxidation and alloy segregation

Alina Moscu [a,b], Christina Theodoridi [a], Luis Cardenas [a], Chloé Thieuleux [b], Debora Motta-Meira [c], Giovanni Agostini [c], Yves Schuurman [a], Frederic Meunier [a,*]

[a] Institut de Recherches sur la Catalyse et l'Environnement de Lyon, IRCELYON, Université Lyon 1, CNRS, 2, Av. Albert Einstein, 69626 Villeurbanne, France
[b] Université de Lyon, Institut de Chimie de Lyon, LC2P2, UMR 5265 CNRS-CPE, Lyon-UCBL, CPE Lyon, 43 Bvd du 11 Novembre 1918, 69100 Villeurbanne, France
[c] European Synchrotron Radiation Facility (ESRF), 6 Rue Jules Horowitz, BP 220, Grenoble Cedex 9 38043, France

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ABSTRACT

Identifying the causes of the segregation of Pt-based alloy nanoparticles is crucial for the design and operation of the corresponding catalysts and electrodes. This article describes a yet unreported mode of alloy segregation upon exposure to CO. *In situ* IR studies indicated that Pt-Sn alloy nanoparticles were not stable under (i) H_2-free CO at any temperature or (ii) CO/H_2 mixtures at temperatures below ca. 450 K. This was rationalized by the ability of Pt to dissociate CO. The oxygen adatoms readily reacted with metallic Sn to form a SnOx species, leading to Pt-Sn segregation, alongside carbon deposition. XPS and XANES analyses confirmed Sn reoxidation. While a contamination by traces of O_2 at the sub-ppm level cannot be excluded, the data reported indicate that the structural modifications undergone by the Pt-Sn nanoparticles are more consistent with a reaction involving CO rather than one involving O_2. In particular, the XPS analysis after CO exposure revealed an increased fraction of graphitic carbon, while that of oxidized carbon decreased. Thermodynamic calculations indicate that the oxidation of tin by CO, with concomitant carbon formation ($Sn + CO \rightarrow SnO + C$) is as favourable as Boudouard reaction ($2\ CO \rightarrow CO_2 + C$) at low temperatures. Alloy stability in the presence of CO must therefore be a concern when CO dissociation is possible and one of the alloyed metal is oxophilic.

1. Introduction

Alloy nanoparticles receive ever-increasing interest as catalyst and electrode materials with structural properties that can largely differ from those of bulk samples [1]. The composition and ordering of the surface of as-prepared alloys may differ from those existing in the sample bulk [2,3]. More, alloy nanoparticles may readily decompose or restructure under conditions of use due to the presence of some reactive or strongly adsorbing molecules [4–12]. Alloy segregation induced by oxidation appears to be a process of utmost complexity [2,13]. A first segregation mode can be referred to as "adsorbate-induced surface segregation". The adsorption of CO was shown to lead to surface segregation over many materials, due to the preferential formation of strong chemical bonds between CO and one of the metals present in the alloy, e.g. Pd in the case of a Au-Pd catalyst [14] and Pt in the case of a Pt-Co electrode [9]. A second segregation mode of alloys involves the reoxidation of one or more of the metal components by strong oxidizers such as O_2. Pt-Sn nanoparticles were shown to be readily converted into an intimate mixture of metallic Pt clusters and oxidic tin domains during the oxidation of CO [15] and during the preferential oxidation of CO in the presence of large excess of H_2 (PROX) [16].

Pt-Sn alloy is the crucial component of an industrial catalyst for the production of alkenes from alkanes [17,18] and is also a promising electrode material for Proton-Exchange Membrane Fuel Cells (PEM-FC), as Pt_3Sn supported on carbon showed much improved resistance to CO poisoning as an anode electrocatalyst as compared to Pt and many other alloys [4,19]. The improved resistance to CO poisoning was later attributed in part to lower CO adsorption coverage on the Pt sites [20]. The heat of adsorption of CO on Pt in Pt-Sn alloy nanoparticles is ca. 95 kJ mol^{-1}, while a value of 180 kJ mol^{-1} is reported on pure Pt [6].

We reported in an earlier paper [6] a segregation process that took place over alumina-supported Pt-Sn nanoparticles under a CO/H_2 mixture, which occurred only below ca. 450 K and appeared to be reversible when temperature was raised back above 450 K. The origin of this segregation was unclear and we report here a thorough investigation on this matter. We demonstrate that a yet unreported mode of segregation took place, involving CO

* Corresponding author.
E-mail address: fcm@ircelyon.univ-lyon1.fr (F. Meunier).

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dissociation with subsequent reoxidation of the non-noble metal leading to the decomposition of the alloy phase.

2. Results and discussion

The alumina-supported Pt and Pt-Sn samples were prepared using a colloid-based method reported earlier [6,21] (Exp. Section and Supporting Information). The narrow particle size distribution was centered around 1.8 ± 0.4 nm (Fig. S1). The global composition based on ICP was 0.37 wt% Pt and 0.23 wt% Sn. The nature of the alumina-supported Pt-Sn particles was investigated by *in situ* diffuse reflectance spectroscopy. CO adsorption can be used to reveal the nature of the sample surface, as markedly different band positions are obtained whether Pt is alloyed with Sn or not [4,22]. The IR stretching band of CO adsorbed on pure metallic Pt at 498 K under a mixture of CO and H_2 was located at ca. 2070 cm^{-1} (Fig. 1A), while that adsorbed on a Pt atom of a Pt-Sn alloy absorbs at ca. 2046 cm^{-1} (Fig. 1B). It should be stressed that CO adsorption on metallic tin is negligible in the present conditions [23], so all the carbonyl bands observed were related to surface Pt atoms only.

Our earlier study showed that the alloy was stable under a CO/H_2 stream at 523 K and only started to segregate below 448 K, as evidenced by a shift of the CO(ads) band to higher wavenumbers, which are typical of pure Pt [6]. To assess whether or not the observed segregation was only related to temperature changes, the stability of the alloy was tested isothermally after removing H_2 from the feed. Three temperatures were used, 498, 523 and 548 K, all well above the 448 K threshold. At all these temperatures the CO(ads) band position shifted to higher wavenumbers following H_2 removal (Figs. 1 and S2). This indicates that the Pt-Sn nanoalloy was unstable and segregated once H_2 was removed from the feed. The changes were essentially reversible when H_2 was brought back, though a slight increase of DRIFTS signal was observed, for instance at 523 K (Fig. S3), indicating that Pt dispersion was affected to a minor extent by these treatments.

The band shift appeared to be more limited at higher temperature (compare Figs. 1 and S2). The kinetics of this structural modification was followed by plotting the DRIFTS band intensity at 2024 cm^{-1} (position shown by the red arrow in Fig. 1) as a function of time (Fig. 2). At short times this intensity was mostly representative of the disappearance of the Pt-Sn alloy. The initial segregation rate was taken to be proportional to the slope of the curves at the origin of time (Fig. 2, dotted lines). Interestingly, the segregation rate appeared to decrease with increasing temperatures.

The corresponding Arrhenius-type plot was drawn (Fig. 2, inset), from which a negative apparent activation energy Eapp = −38 ± 4 kJ mol^{-1} was calculated. An activation energy of −35 ± 4 kJ mol^{-1} was obtained if the segregation process was quantified by following the wavenumber shift of the low wavenumber side of the alloy band at half height (Fig. S4). The two methods used to evaluate the rate of segregation appeared thus consistent.

The fact that both rate and extent of segregation decreased with increasing temperature indicates that the cause of the segregation was kinetically and thermodynamically not favored at higher temperatures. It also indicates that the segregation was a complex process consisting of multiple elementary steps, most likely involving absorption step with a large (negative) heat of adsorption, such as CO sorption on Pt. The CO coverage on Pt atoms of the Pt-Sn phase significantly decreased with temperature over the range of interest, as shown by adsorption isobars measured by DRIFTS (Fig. S5).

If the rate-determining step of the segregation process were the reaction between an adsorbed CO molecule on platinum and an adjacent surface tin atom, a lower surface coverage of CO would lead to a lower segregation rate. At low coverages, the apparent

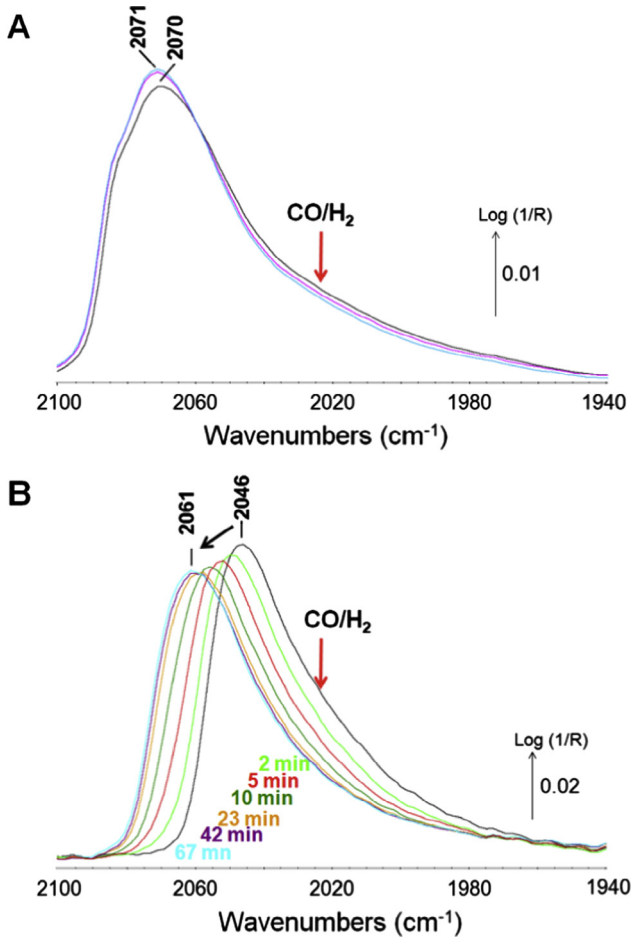

Fig. 1. *In situ* DRIFTS spectra collected under 2%CO/He at 498 K over (A) Pt/alumina after 10 (pink) and 30 min (blue) and (B) Pt-Sn/alumina at 2 (light green), 5 (red), 10 (green), 23 (orange), 42 (purple) and 67 min (blue). The black spectrum in both figures is the steady-state spectrum collected under 2%CO + 10% H_2 in He just before removing H_2 from the feed. Total flow was always 50 mL min^{-1}.

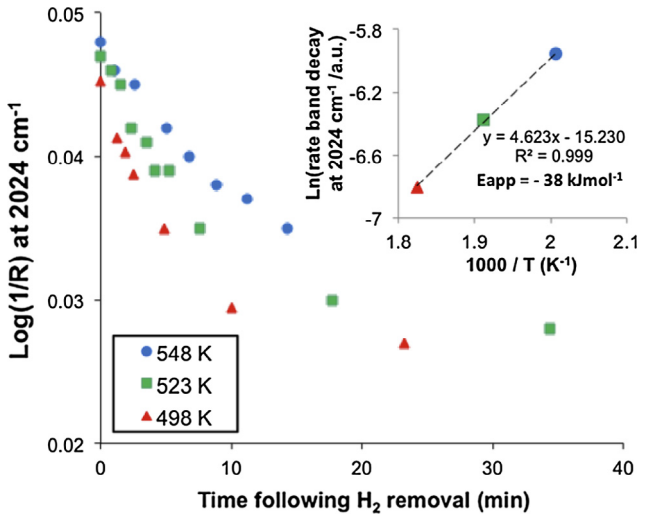

Fig. 2. DRIFTS intensity of the CO(ads) band at 2024 cm^{-1} on the Pt-Sn/Al_2O_3 as a function of time at 498, 523 and 548 K following the removal of H_2 from the feed. Feed: 2%CO in He. (Inset) Corresponding Arrhenius-type plots reporting the slopes of the tangent to the curves at the origin of time as a function of the reciprocal temperature.