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

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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) H₂-free CO at any temperature or (ii) CO/H₂ 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 SnO_x species, leading to Pt-Sn segregation, alongside carbon deposition. XPS and XANES analyses confirmed Sn reoxidation. While a contamination by traces of O₂ 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 O₂. 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 → SnO + C) is as favourable as Boudouard reaction (2 CO → CO₂ + 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 O₂.

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 H₂ (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 Pt₃Sn 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/H₂ 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

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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 H₂ 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/H₂ 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 H₂ 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 H₂ removal (Figs. 1 and S2). This indicates that the Pt-Sn nanoalloy was unstable and segregated once H₂ was removed from the feed. The changes were essentially reversible when H₂ 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 $E_{app} = -38 \pm 4\text{ kJ mol}^{-1}$ was calculated. An activation energy of $-35 \pm 4\text{ kJ mol}^{-1}$ 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% H₂ in He just before removing H₂ 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 H₂ 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.

activation energy will be the sum of the true activation energy and the CO heat of adsorption [24]. Knowing that the heat of adsorption of CO on this Pt-Sn sample at 523 K is about -84 kJ mol^{-1} (Fig. S5 and Table S1), a positive true activation energy of ca. $+36 \text{ kJ mol}^{-1}$ can be calculated from the apparent activation energy of -38 kJ/mol for the reaction step of adsorbed CO with a tin surface atom.

Quasi in situ X-ray photoelectron spectroscopy (XPS) was used to determine whether or not the segregation process involved a change in oxidation state for any of the metals initially present in the Pt-Sn alloy. The Pt-Sn/alumina sample was first reduced under a flow of pure hydrogen at 723 K for 30 min in a reaction chamber before being transferred into the XPS analysis chamber under ultra-high vacuum (UHV).

The main contribution of the C 1s core level spectrum was used as energy reference at 284.6 eV, corresponding to graphite-like sp^2 adventitious carbon [25]. This is consistent with the fact that the sample was treated *in situ* at temperatures sufficiently high to remove sp^3 species. The Pt 4f XPS signal could not be interpreted due to overlapping with Al 2p contribution.

The Sn 3d XPS spectra exhibited the simultaneous presence of metallic (at 484.8 eV) and oxidized (at 486.6 eV) tin contributions (Fig. 3A). The atomic percentages of these two tin species are given in Table 1. It is likely that the metallic tin fraction (ca. 62 at.%) corresponded entirely to tin present in the Pt-Sn alloy nanoparticles, while the remainder (ca. 38 at.%) corresponded to SnO_x species strongly interacting with the alumina. SnO_x species strongly bound to the support have been proposed on similar systems [26,27], these species possibly being instrumental in immobilizing supported metal particles [28]. Such species are typically hard to reduce; the tin component of $\text{SnO}_2\text{-Al}_2\text{O}_3$ gels free of noble metals reduces under H_2 only above 1073 K [29].

The same sample was then exposed to a flow of 2% CO/He at 498 K for 90 min, then evacuated under secondary vacuum and transferred back into the XPS analysis chamber. Surprisingly, tin was more oxidized than before the CO treatment, as the proportion of Sn^0 dropped from 62 at.% down to 31 at.% (Fig. 3B and Table 1). This result indicates that, surprisingly, CO had acted as an oxidizer, at least as far as tin was concerned. CO has already been reported as being able to oxidize Ag nanoparticles at room temperature, with the concomitant formation of elemental carbon through Boudouard reaction [30].

The C 1s XPS spectrum of the sample reduced at 723 K exhibited two contributions at high binding energies, beside the main C-C sp^2 peak at 284.6 eV used as a reference (Fig. 3C). The peak at 286.8 eV corresponded to CO linearly adsorbed on Pt [31,32] and that at 289.2 eV could be attributed to the formation of CO_x -type groups such as carbonates and carboxylates [25].

Fig. 3. (A) Sn 3d and (C) C 1s XPS spectrum of Pt-Sn/alumina after reduction under hydrogen at 723 K. (B) and (D) Same analyses on the same sample that had been subsequently exposed for 90 min at 498 K to 2% CO/He.

Table 1

X-ray photoelectron spectroscopy binding energies of various Sn and C species and the corresponding atomic percentages.

Sn or C compound	Binding energy (eV)	Atomic % after H_2 at 723 K	Atomic % after CO at 498 K
Sn^0	484.8	62	31
SnO_x	486.6	38	69
C-C sp^2	284.6	70	78
CO(ads)	286.8	5	9
CO_x	289.2	25	13

The evolution of the XPS C 1s signal following exposure to 2% CO/He at 498 K was quite remarkable (Fig. 3D and Table 1). A marked increase in the proportion of C-C sp^2 bond typical of graphitic carbon was observed, alongside the expected increase of the signal associated with CO(ads). In contrast, the band associated with more oxidized CO_x species decreased. These observations suggest that CO reacted through a direct decomposition to yield graphitic elemental carbon and oxygen (Eq. (1)) rather than through Boudouard reaction (Eq. (2)):

The oxygen formed could subsequently have reacted with the Sn present in the alloy, explaining the increased fraction of oxidized tin following exposure to CO (Table 1). The conversion of CO in the absence of H_2 was investigated over the Pt and Pt-Sn/alumina materials (Fig. S6). The production of CO_2 was found to be negligible below 573 K, supporting our earlier observation that Boudouard reaction (Eq. (2)) is negligible at lower temperatures over these materials.

The chemical state of Sn in the Pt-Sn/alumina and the effect of the feed composition at 498 K were investigated by *in situ* X-ray Absorption Spectroscopy (XAS). The details and sequence of the XAS measurements are given as Supporting Information. Fig. 4 presents the XANES data at the Sn K-edge. The overall edge shifts to higher energies and the increase in the white line intensity of the

Fig. 4. Normalized Sn K-edge XANES spectra of the Pt-Sn/alumina sample exposed to different atmospheres and spectrum of a Sn^0 standard. The inset zooms in the edge position, highlighting a shift towards higher energies of the white line position when the sample was exposed to 2% CO + 60% H_2 at 373 K or only 2% CO at $T = 498 \text{ K}$. He was used as diluent.

alloy-related spectra as compared to those of the metallic Sn° reference (black line) could be mainly due to two effects. First, alloying Sn with Pt induces a transfer of electrons from Sn towards the more electronegative Pt causing a partial filling of the Pt d band vacancies [33]. Second, oxidized Sn species strongly interacting with the alumina may be present, even after the reduction in H₂ at 723 K, as already indicated by the XPS analysis (Fig. 3).

The modification of the Sn K-edge XANES spectra of the Pt-Sn/alumina under various feed compositions were relatively limited but could still be resolved (inset of Fig. 4). The edge clearly shifted to higher energies under 2% CO/He (pink line) as compared to 60% H₂/He (blue line), indicating a more oxidized state of Sn in the presence of CO. The edge shifted back to lower energies to the state equivalent to that obtained under 60% H₂/He when exposed to 2% CO + 60% H₂ (green line). However, Sn became again more oxidized once temperature was dropped to 373 K (red line), still under 2% CO + 60% H₂.

These XANES Sn K-edge data are consistent with the interpretation of the *in situ* DRIFTS data reported above. Pt-Sn alloy nanoparticles were present at 498 K under CO + H₂, associated with CO (ads) DRIFTS bands at ca. 2046 cm⁻¹ (Fig. 1). The Pt-Sn phase segregated when no H₂ was present, leading to a metallic Pt-rich phase associated with a CO(ads) band at 2061 cm⁻¹. Importantly, the XANES Sn K-edge data indicate that Sn gets oxidized during this process and thus supports the conclusions obtained from the XPS data (Fig. 3) that exposure to H₂-free CO does indeed lead to the oxidation of tin at 498 K.

The XANES analysis (Fig. 4, red line) highlights a similar Pt-Sn segregation involving Sn oxidation when temperature is decreased to 373 K, consistent with earlier observations derived from *in situ* DRIFTS data that segregation was triggered even in the presence of H₂ when temperature was decreased below 448 K⁶.

Pt L3-edge XANES data only revealed the presence of metallic Pt under all conditions (Fig. S7 and XANES and EXAFS Analyses in the Supporting Information). White line increase and shift were observed upon adsorption of CO, which overall withdrew electronic density from Pt. The Pt-CO bonding involves the filled 5σ (HOMO) and empty 2π* (antibonding LUMO) orbitals of CO overlapping with Pt 5d orbitals. The HOMO of CO donates electron to Pt, while the LUMO of CO accepts electron from Pt, the later transfer being dominant. The weaker heat of adsorption of CO (Fig. S5 and Table S1) measured on Pt-Sn phases, which exhibit an electron-rich Pt as compared to the case of pure Pt particles, indicates that the additional electronic density supplied by Sn to Pt decreased the bond strength between Pt and CO. This indicates that the sigma donation from CO to Pt was more decreased (because the Pt becomes less acceptor) than the donation from Pt to CO LUMO was increased.

The EXAFS data collected at the corresponding Pt and Sn edges both indicated the presence of alloy nanoparticles on the reduced sample (Figs. S8–S11 and Table S2). However, the precision of the EXAFS data could not clearly evidence phase segregation in the presence of CO only. This may be due to the disorder and compositional variations in the Pt-Sn particles, in addition to variations in particle size (Fig. S1).

Overall, the combination of DRIFTS, XPS and XANES Sn K-edge data clearly indicates that the present mode of alloy segregation involved the oxidation of some of the tin initially present in the alloyed nanoparticles.

It is important to note that the segregation process was essentially reversed simply by exposing the sample to a H₂ or CO/H₂-containing feed at temperature above ca. 448 K (Fig. S3). An *in situ* DRIFTS experiment realized over a sample initially segregated at 323 K showed that the pure Pt domains were gradually converted back into Pt-Sn domains as the temperature was increased (Fig. 5). These spectra show clearly resolved bands of

Fig. 5. *In situ* DRIFTS spectra collected under 2%CO + 10% H₂ in He over Pt-Sn/alumina during a temperature program from 323 up to 573 K using a ramp of 10 K min⁻¹. Spectra are reported every 25 K. The sample was initially reduced at 673 K under H₂, before being fully segregated under the full stream at 323 K for 2 h. Total flow was always 50 mL min⁻¹.

CO either adsorbed on Pt (bands at 2076–2066 cm⁻¹) or Pt-Sn (ca. 2050 cm⁻¹) during the temperature program (Fig. 5). (The lower signal intensity at higher temperature is merely due to temperature-dependent surface coverage of CO, see Fig. S5).

The possibility that the segregation was triggered by contaminant traces of O₂ in the present cases was carefully considered. A concentration of 2 vol% of O₂ was shown to readily segregates the alloy phase [16], even in the presence of CO and H₂ at 498 K. Additional experiments were carried out with the addition of significantly lower O₂ concentration (i.e. 100 ppm) that led to a fast band shift from 2050 to 2064 cm⁻¹ (Fig. S12). The far slower segregation rate observed in previous experiments realized on different setups (DRIFTS cell, XPS setup, synchrotron setup) would therefore have to be related to far lower concentrations of O₂.

Potential leakage of ambient air into our DRIFTS cell was considered. In fact, hydrogenation reactions at low temperatures have been routinely performed over Ni-based catalysts, which are highly oxygen-sensitive. Toluene hydrogenation at 70 °C over Ni nanoparticles embedded in a zeolite (sample preparation reported elsewhere [34]) led a fast irreversible deactivation when 300 ppm of O₂ was introduced (Fig. S13). In contrast, the deactivation rate was close to zero when no O₂ was added to the feed (Fig. S13). The minute apparent deactivation rate, if truly significant and due to O₂, would lead to an O₂ concentration of about 1.1 ppm (note that other causes of deactivation could also be expected in this case, Ni sintering, surface reconstruction and carbonaceous deposits). In conclusion, our DRIFTS cell can be considered as essentially leak-free.

The data reported in Fig. S6 showed that no CO₂ could be observed as long as Boudouard reaction had not become relevant, indicating that CO₂ level was below 10 ppm (analysis threshold) for these reactions carried out under 15.8% CO/He. The corresponding O₂ contamination level in our typical 2% CO/H₂ feed would then be less than 1 ppm.

The additional graphite-like carbon build-up observed under XPS conditions (Fig. 3 and Table 1) is a further support for the CO-induced oxidation, likely involving direct CO dissociation (Eq. (1)) rather than Boudouard reaction (Eq. (2)). Instead, an increased presence of CO_x species would have been expected if the oxidation were due to the occurrence of Boudouard reaction, or even O₂ traces, and this was clearly not the case. Furthermore, the negative activation energy measured for the segregation process (Fig. 2) fits well with CO adsorption on platinum, which is reversible at these temperatures, but not with O₂ adsorption. Increasing the temperature from 498 to 548 K would not lead to a lower oxygen surface concentration, as oxygen does not desorb from Pt nanoparticles significantly at these temperatures [35]. An increase in the

Fig. 6. Gibbs energy of reaction associated with the oxidation of bulk Pt and Sn by CO and the concomitant formation of carbon. The curves were calculated for a partial pressure of CO of 2 kPa.

segregation rate with increasing temperature would thus be expected if O_2 were involved, while the opposite was observed experimentally (Fig. 2).

Based on the DRIFTS, XPS and XANES results we can conclude that the segregation of Pt-Sn by CO occurred via the oxidation of Sn only, since the state of Pt appeared to remain metallic (Figs. 1 and S7). The thermodynamics of the oxidation by CO of bulk Pt and Sn supported this observation. The Gibbs energy of the oxidation of Sn by CO to SnO or SnO₂, with the concomitant formation of carbon, was always negative up to 773 K (Fig. 6).

In contrast, the equilibria involving Pt were always unfavourable over this temperature range. These findings, although corresponding to bulk phases, provide a rational for the reactivity and segregation of our Pt-Sn nanoparticles. The oxidation of metallic silver by CO and concomitant carbon deposition was already proposed by Bechoux et al. based on *in situ* IR analyses [30].

On a kinetic point of view, platinum is a poor catalyst for CO dissociation. Somorjai and co-workers have yet shown that Pt steps could dissociate CO at room temperature [36] and also on Pt(1 0 0) at 498 K [37]. The kinetics of dissociation on pure Pt phases may not be favored by the fact that each Pt site is likely to be covered and strongly poisoned by CO. In contrast, the CO-free Sn of Pt-Sn surfaces may provide a more favourable path for the dissociation of CO with subsequent adsorption of the formed oxygen on the oxophilic Sn. The exclusion of CO adsorption on the Sn sites was also suggested by Wang and Hsing as one of the reasons for the improved electrocatalytic performance of Pt-Sn electrodes for CO oxidation [20].

The roles of temperature and H_2 on the occurrence and rate of segregation (resp. re-alloying) likely relate to the formation (resp. removal) of O(ads) formed from CO dissociation. If no hydrogen is present or if the temperature is too low to enable water formation from the reaction between H_2 and O(ads), then O(ads) will react with the Sn component of the alloy leading to segregation (Fig. 1). If H_2 is brought back and the temperature is high enough, the reduction of SnOx occurs and the Pt-Sn alloy will be restored (Figs. 4, 5 and S3).

3. Conclusion

In summary, we unravel here for the first time a new mode of segregation of Pt-Sn alloy nanoparticles occurring as a consequence of the dissociation of CO leading to Sn oxidation and carbon deposition. This segregation mode is favored at low temperatures

(ca. <448 K) and in the absence of H_2 . In effect, CO acts as an oxidising agent, with concomitant deposition of carbon. The process is yet reversible. 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. It would be of paramount interest to investigate the relevance of this process during the operation of other alloy-based electrodes used for H_2 oxidation, in which CO traces can be present at low temperatures, and may lead to the oxidation of the most oxophilic metal of the alloy.

4. Experimental Section

4.1. Materials and gases

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 method. A mixture of a Pt complex [i.e. $Pt(dba)_2$ (dba = dibenzylidene acetone)] and octylsilane, which acted as a ligand, was used for the synthesis of Pt monometallic NPs. Pt-Sn NPs were obtained by contacting Pt ($dba)_2$ and tributyltin hydride [(n-Bu)₃SnH] without the addition of any other ligand [21]. The precursors were dissolved in dry tetrahydrofuran (THF) and pressurized with H_2 (3 bar) 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 γ -Al₂O₃ support (BET surface area of 106 m²/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 593 K in order to remove most of the alkyl fragments. High purity He and H_2 from Air Liquide (Alphagaz, 99.999% purity) further purified with using VICI® traps (models P-100-2 and P-200-2 for He and H_2 , respectively) were used, which should have brought down O_2 level below 1 ppm. High purity CO (>99%, main impurity $N_2 \sim 0.4$ mol.% and $H_2 \sim 0.5$ mol.%) was used without further purification.

4.2. Diffuse reflectance FT-IR

DRIFTS experiments were performed at ambient pressure with a high temperature DRIFT cell (from Spectra-Tech®) fitted with KBr windows, using a collector assembly. A description and properties of the cell can be found elsewhere [38]. The spectrophotometer used was a Nicolet 6700 (ThermoFischer Scientific) fitted with a liquid-N₂ cooled MCT detector. The DRIFT spectra were recorded at a resolution of 4 cm⁻¹ and 8 or 32 scans accumulation depending on the time-resolution desired. The DRIFTS spectra are reported as log (1/R), where R is the sample reflectance. This pseudo-absorbance gives a better linear representation of the band intensity against surface coverage than that given by the Kubelka-Munk function for strongly absorbing media such as those based on metals supported on oxides [39]. The contribution of gas-phase CO was subtracted using a CO(g) spectrum collected at the reaction temperature over a SiC powder [40].

4.3. X-ray absorption spectroscopy

Scheme S1 shows the treatment applied to the catalysts during the XAS experiments at the Pt-L₃ and Sn-K edges. The catalysts

were initially reduced under 30% H_2 /He up to 673 K (10 K/min) and maintained at this temperature for 40 min. The temperature was then decreased to 498 K where the EXAFS spectra were collected (I). The atmosphere was then switched to 2%CO/60% H_2 /He and EXAFS spectra were collected at the Pt-edge (II). H_2 was subsequently removed from the feed (balanced by He to keep the same total flow) and EXAFS spectra were measured (III) at both edges. Finally, H_2 was added back to the feed and the last EXAFS spectra at 498 K were collected (IV). For the final data collection at the Sn-edge, the atmosphere was changed to 30% H_2 /He and the temperature was ramped up until 673 K (10 K/min). After 40 min, the temperature was decreased to 373 K where another EXAFS spectra was collected (V). A stabilization period of 30 min was used before the EXAFS measurements each time conditions were changed. Three EXAFS spectra were collected and averaged for data analysis.

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