

## Bimetallic Nanoparticles

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## Kinetics of Lifetime Changes in Bimetallic Nanocatalysts Revealed by Quick X-ray Absorption Spectroscopy

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**Abstract:** Alloyed metal nanocatalysts are of environmental and economic importance in a plethora of chemical technologies. During the catalyst lifetime, supported alloy nanoparticles undergo dynamic changes which are well-recognized but still poorly understood. High-temperature  $O_2$ - $H_2$  redox cycling was applied to mimic the lifetime changes in model  $Pt_{13}In_9$  nanocatalysts, while monitoring the induced changes by in situ quick X-ray absorption spectroscopy with one-second resolution. The different reaction steps involved in repeated  $Pt_{13}In_9$  segregation-alloying are identified and kinetically characterized at the single-cycle level. Over longer time scales, sintering phenomena are substantiated and the intraparticle structure is revealed throughout the catalyst lifetime. The in situ time-resolved observation of the dynamic habits of alloyed nanoparticles and their kinetic description can impact catalysis and other fields involving (bi)metallic nanoalloys.

**B**imetallic catalysts can exhibit drastically increased selectivity, activity, and stability compared to their monometallic siblings owing to an interplay of electronic and geometric effects. They are the workhorses in widespread technologies, such as car exhaust converters,<sup>[1]</sup> and fuel cells,<sup>[2]</sup> and have acquired a pivotal role in chemical industry. Within the library of bimetallic catalysts, archetypal Pt-based catalysts promote

a vast array of reactions,<sup>[3]</sup> such as  $NO_x$  reduction<sup>[1]</sup> (e.g. Pt-Rh) to alkane dehydrogenation<sup>[4-6]</sup> (e.g. Pt-In). In reaction, these catalysts operate at high temperature under rapidly changing reductive and oxidative environments.<sup>[7,8]</sup> For example, dehydrogenation catalysts require cyclic  $O_2$ - $H_2$  redox treatments to regenerate ( $O_2$ ) and reactivate ( $H_2$ ) Pt-In nanoalloys after coking in high-temperature alkane flows.<sup>[9-11]</sup>

Whilst catalysts were originally assumed to be static substances, intense research in the past decades has witnessed that (bi)metal catalysts are dynamically changing nanomaterials under reaction conditions.<sup>[12]</sup> During the catalyst lifetime, multiple atomic scale processes shape the working state of the catalyst and thereby influence its performance. It goes without saying that understanding these processes and detailing their kinetics is of crucial importance to control their occurrence and thus the catalyst performance. To this aim, techniques which provide high time resolution, but do not require long range order and can be applied in situ, are crucial for interrogating the kinetic behavior of (often disordered) bimetallic nanocatalysts under operating conditions. For example, in situ, dispersive and quick X-ray absorption spectroscopy (XAS) have established a role of utmost importance in uncovering the motifs of (bi)metallic nanoparticle restructuring.<sup>[13-18]</sup>

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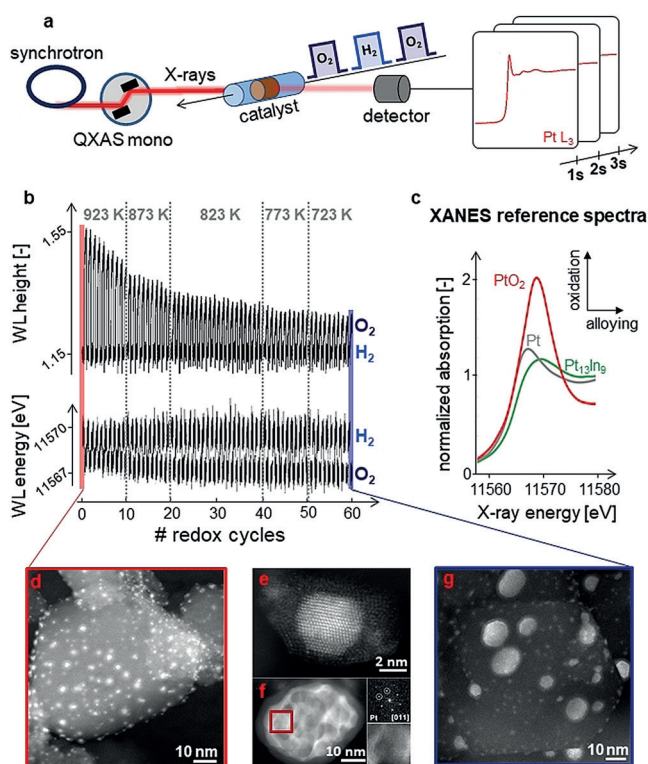
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Herein, we probe the dynamic lifetime changes in a  $\text{Pt}_{13}\text{In}_9$  model nanocatalyst induced by high-temperature  $\text{O}_2$ - $\text{H}_2$  redox cycling with quick X-ray absorption spectroscopy (QXAS). Such Pt-In catalysts show great promise for alkane dehydrogenation, hydroconversion of bio-based oxygenates, and as direct methanol and ethanol fuel cells.<sup>[3]</sup> Additionally, efforts have been undertaken recently by our groups<sup>[19–22]</sup> and others<sup>[23,24]</sup> to understand their formation and control their intermetallic composition. To monitor the kinetic habits of these catalysts in situ with high time resolution, QXAS spectra are recorded at the Pt  $L_3$ -edge with one second time resolution (Figure 1a). While pioneering in situ QXAS studies on the formation and working state of nanocatalysts are available,<sup>[7,25–30]</sup> the quantitative extraction of kinetic data and the construction of a full reaction mechanism has, to our best knowledge, not been reported for



**Figure 1.** a) Synchrotron source producing an X-ray beam by a quick-scanning channel-cut monochromator; the X-ray beam irradiates the catalyst bed, contained in a capillary by which cyclic  $\text{H}_2$ - $\text{O}_2$  pulses are flown to induce structural changes in the Pt-In nanocatalyst. The X-ray absorption spectrum is measured by the X-ray detector with 1 s time resolution. b) Pt  $L_3$ -edge XANES white line (WL) analysis yielding the (top) WL height in terms of normalized absorption and (bottom) WL energy (at the WL maximum) in eV, as a function of the number of  $\text{H}_2$ - $\text{O}_2$  redox cycles. The experiments are performed at variable temperature, ranging from 923 K down to 723 K. c) XANES reference spectra of  $\text{PtO}_2$ , Pt and  $\text{Pt}_{13}\text{In}_9$ . HAADF-STEM images of Pt-In nanoparticle catalysts after d, e) 1 and f, g) 60 redox cycles. e) HAADF-STEM of Pt-In nanoparticle after the first  $\text{H}_2$ - $\text{O}_2$  cycle, that is, after re-oxidation and alloy segregation, showing a bright contrast Pt core surrounded by a dark contrast In oxide shell. f) HAADF-STEM image of sintered nanoparticles after 60 redox cycles in oxidized (alloy segregated) state, showing Pt nanoworm network formation, surrounded by In oxide, together with magnified region (red square) and corresponding FFT.

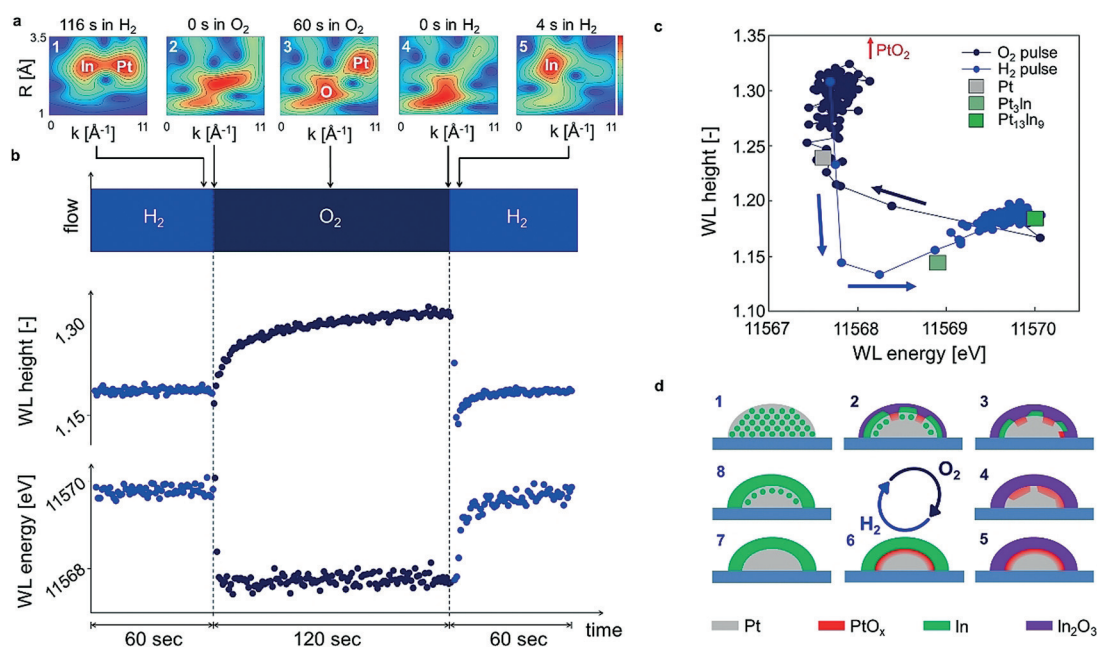
(bi)metallic nanoparticles. For this work, phase-pure Pt-In alloys were fabricated by atomic layer deposition<sup>[19]</sup> (ALD) and their XAS spectra measured to benchmark the QXAS data in their Pt-In composition during  $\text{O}_2$ - $\text{H}_2$  cycling. This allows to probe Pt-In nanoalloy-segregation dynamics on a quantitative level and to extract kinetic information.

The white line (WL) height and energy position of the X-ray absorption near edge structure (XANES) spectra are used to probe the state of Pt in situ during repetitive  $\text{H}_2$ - $\text{O}_2$  redox cycling (Figure 1b, Supporting Information, section S4). Reference XANES spectra show that 1) Pt oxidation mainly results in an increase in the WL height ( $\text{PtO}_2$ ), while 2) Pt alloying towards  $\text{Pt}_{13}\text{In}_9$  primarily results in a blue shift of the WL energy (Figure 1c; Supporting Information, sections S2.4). The WL height reversibly alternates from low to high values, respectively during  $\text{H}_2$  and  $\text{O}_2$  pulses, and vice versa for the WL energy. This suggests that Pt reversibly undergoes  $\text{PtO}_x$  reduction and Pt-In alloying ( $\text{H}_2$ ), followed by Pt-In alloy segregation and re-oxidation into  $\text{PtO}_x$  ( $\text{O}_2$ ).

The WL height and energy position remain constant at the end of each  $\text{H}_2$  pulse, implying that the alloy composition is stable for at least 60  $\text{H}_2$ - $\text{O}_2$  cycles. In contrast, the WL height strongly decreases in  $\text{O}_2$  with increasing number of redox cycles as a result of Pt nanoparticle (NP) sintering. HAADF-STEM confirms that initially well-dispersed NPs (ca. 2 nm, Figure 1d) sinter into larger ones (ca. 10 nm, Figure 1g), steered by  $\text{H}_2$ - $\text{O}_2$  cycling. A magnified view of a small NP obtained after one  $\text{H}_2$ - $\text{O}_2$  redox cycle, that is, in oxidized state, shows that the NP is composed of a metallic Pt core, surrounded by an  $\text{In}_2\text{O}_3$  crust (Figure 1e). Large NPs after 60  $\text{H}_2$ - $\text{O}_2$  redox cycles reveal a nanocomposite consisting of a Pt nanoworm network surrounded by  $\text{In}_2\text{O}_3$ , as confirmed by EDX (Supporting Information, section S7) and fast Fourier transformed (FFT) analysis showing face centered cubic (fcc) Pt (Figure 1f). Such nanocomposite structure suggests that nanoalloys decompose spinodally, as caused by kinetically rapid segregation.

The dynamic changes of Pt are now studied at the single cycle level. Figure 2a displays the Pt  $L_3$ -edge wavelet transformed (WT) quick extended X-ray absorption fine structure (EXAFS) magnitude at specific points in redox cycle 21.<sup>[20]</sup> At the end of the  $\text{H}_2$  pulse, the WT-EXAFS magnitude shows both Pt and In around Pt and mix to form a Pt-In alloy (Figure 2a,1; 116 s in  $\text{H}_2$ ). In the middle of the  $\text{O}_2$  pulse both Pt and O are observed, but no In, indicating that the Pt-In alloy has decomposed by segregation (Figure 2a,3; 60 s in  $\text{O}_2$ ). This results in phase-pure Pt with some degree of surface oxidation (suggested by XANES). After the start in  $\text{H}_2$ , only In is visible in WT-EXAFS, while Pt is barely observed (Figure 2a,5; 4 s in  $\text{H}_2$ ), showing that the Pt-In alloy is still evolving to a local equilibrium state and might be disordered. At the very start of the  $\text{O}_2$  and  $\text{H}_2$  pulses, WT-EXAFS plots show intermediate states with combined contributions from Pt, In and O (Figure 2a,2 and 2a,4; 0 s).

The XANES WL height and energy position in Figure 2b uncover the kinetics of the processes occurring within one  $\text{H}_2$ - $\text{O}_2$  redox cycle. During the  $\text{O}_2$  pulse, the decomposition of the initial Pt-In nanoalloy into fcc Pt and In (oxide) is rapid (WL energy shift), clarifying the spinodal nanostructure observed



**Figure 2.** a) Pt  $L_{3}$ -edge wavelet transformed (WT) quick EXAFS magnitude maps at five points in time (1–5) at the single cycle level after 21  $H_2$ - $O_2$  redox cycles. The plots reveal the element type ( $k$ -axis) and position ( $R$ -axis) of neighbors around Pt, namely In, O or Pt. The color bar represents the normalized intensity (0–1) of the WT QEXAFS magnitude. b) The WL height and energy versus time within the 21<sup>st</sup> redox cycle. Light blue (navy blue) corresponds to  $H_2$  ( $O_2$ ) gas environment resp. in panels (b–d). c) The transient evolution of the WL maximum during  $H_2$ - $O_2$  redox cycle 21 at 893 K, evolving from  $Pt_{13}In_9$  to a segregated  $PtO_x$  state ( $O_2$ ) and back to  $Pt_{13}In_9$  ( $H_2$ ) via the  $Pt_3In$  intermediate. The WL positions of Pt,  $Pt_3In$  and  $Pt_{13}In_9$  references are shown in the squares. d) Mechanism of reversible Pt-In segregation, Pt oxidation and Pt-In re-alloying at the single  $H_2$ - $O_2$  redox level: (2–5) simultaneous  $Pt_{13}In_9$  segregation, Pt surface oxidation, (5–8,1) consecutive Pt reduction and Pt-In alloying.

by HAADF-STEM for Pt- $In_2O_3$  nanonetworks. Simultaneous to alloy segregation, a slower Pt oxidation process takes place at the Pt surface, which is not entirely stabilized even within the 120 s  $O_2$  pulse (WL height). In contrast to Pt oxidation, Pt reduction at the start of the  $H_2$  pulse is completed in 2 s. Thereafter, Pt-In alloying takes place, which in contrast to Pt oxidation stabilizes within the  $H_2$  period.

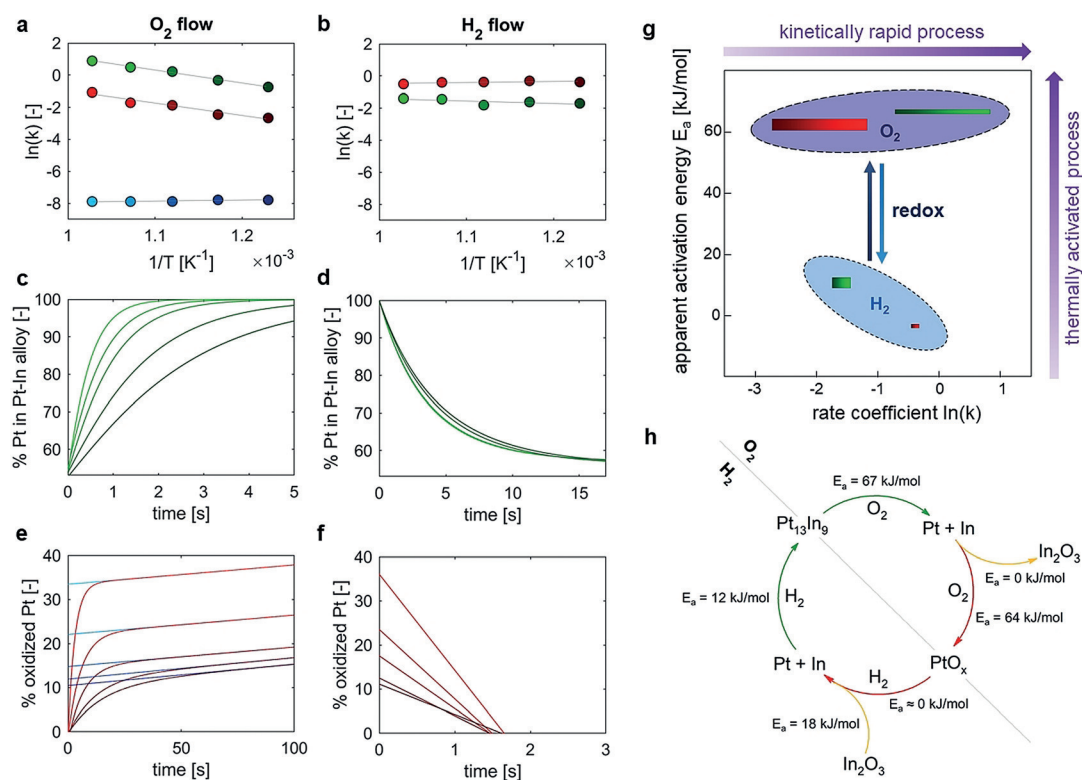
Figure 2c shows the evolution of the WL in time for both the  $O_2$  (navy blue) and  $H_2$  (light blue) pulses. Additionally, the white line positions of ALD-derived phase-pure Pt,  $Pt_3In$ , and  $Pt_{13}In_9$  are depicted (Supporting Information, S2). Notably, the final WL position in  $H_2$  matches to a stoichiometric  $Pt_{13}In_9$  alloy. There is a marked difference between the alloy formation and decomposition process. Pt-In alloy formation sets in after full reduction of  $PtO_x$  into Pt by a further drop in WL height (consecutive processes). The evolution from fcc Pt to  $Pt_{13}In_9$  presumably occurs via the fcc  $Pt_3In$  intermediate, established by the gradual but rapid incorporation of In into fcc Pt. Thereafter, the further uptake of In transforms  $Pt_3In$  (75% Pt) into intermetallic  $Pt_{13}In_9$  (59% Pt), which is kinetically slower. In contrast, Pt-In alloy decomposition occurs simultaneously with Pt surface oxidation to  $PtO_x$  (parallel processes). Instead of evolving via  $Pt_3In$  and Pt references towards  $PtO_x$ , the WL height shows a monotonic, upward trend that is intermediate to the phase-pure reference positions. Figure 2d illustrates the full redox process.

To perform a full kinetic analysis, the 60  $H_2$ - $O_2$  redox cycles are executed at temperatures ranging from 923 K down

to 723 K in steps of 50 K for each 10 cycles, except for 823 K which is kept for 20 cycles (Figure 1b). The WL height and energy are used for kinetic modeling of the degree of Pt oxidation and Pt-In alloying over time, respectively. First, WL-time data are averaged over all cycles at a given temperature to reduce noise (Supporting Information, section S6). Next, the WL time evolution is modelled by a zero- and/or first-order rate law. This yields rate coefficients for each temperature, from which Arrhenius plots are constructed and apparent activation energies  $E_a$  are estimated for the reduction/alloying and segregation/oxidation processes (Figure 3a,b). Additionally, 1) an estimated content of Pt in Pt-In alloys during segregation and alloying (resp. Figure 3c,d), and 2) the extent of Pt oxidation during  $H_2/O_2$  oxidation/reduction (resp. Figure 3e,f, S6) are extracted.

During the  $O_2$  pulse, the majority of In dealloys by segregating out of the  $Pt_{13}In_9$  alloy in 5 seconds by a first-order process (Figure 3c, green). The much slower Pt surface oxidation can only be modelled by combining a first-order rate law (Figure 3e, red) with a zero-order reaction with constant rate (Figure 3e, blue). The latter leads to a continuous increase in Pt oxidation state throughout the entire  $O_2$  pulse, and is presumably caused by diffusion controlled redispersion of Pt into smaller NPs after spinodal decomposition. The first-order processes, namely  $Pt_{13}In_9$  dealloying and initial Pt surface oxidation, show strong temperature dependence. Their Arrhenius plots (Figure 3a, red) exhibit linear correlations with relatively high slopes, yielding apparent activation energies of  $67 \pm 1 \text{ kJ mol}^{-1}$  for  $Pt_{13}In_9$





**Figure 3.** a) The Arrhenius plots for (green) Pt-In segregation, (red) Pt surface oxidation, and (blue) Pt diffusion-controlled oxidation process; c) green, and e) red and blue, respectively, are their modeled curves to WL XANES data (darker colors correspond to lower temperatures). b) Arrhenius plot for (green) Pt-In alloying and (red) Pt reduction, and their concomitant fits to the WL XANES during d) alloying (modeled) and f) reduction (Supporting Information, section S6) as a function of time. g)  $E_a$  versus  $\ln(k)$  for (red, top) Pt oxidation, (green, top) Pt-In segregation in  $O_2$  and (green, bottom) Pt-In alloying and (red, bottom)  $PtO_x$  reduction in  $H_2$ . The rectangle width represents the range that  $\ln(k)$  varies across the measured temperature range, while its height is the 66% confidence interval of  $E_a$ . h) reaction mechanism derived from Arrhenius plots in (a) and (b).  $In_2O_3$  activation energies are obtained from redox data collected at different temperature at the In K-edge as further detailed at the end of Supporting Information, section S6.

dealloying and  $64 \pm 4 \text{ kJ mol}^{-1}$  for initial Pt surface oxidation. The zero-order process approaches a zero activation energy (Supporting Information, section S6). Notably, the order of magnitude of the rate coefficients of Pt surface oxidation accords with an earlier study,<sup>[31]</sup> assessing Pt NP oxidation only.

During the  $H_2$  pulse, surface oxidized Pt is fully reduced to metallic Pt with a high rate (in 1.5 s; Figure 3 f). The activation energy retrieved in a qualitative way from the Arrhenius plot approaches zero (for more information see Supporting Information, section S6, and Figure 3 b). Similar to  $Pt_{13}In_9$  segregation, Pt-In alloying is described by a first-order rate law with now an activation energy of only  $12 \pm 3 \text{ kJ mol}^{-1}$  (Figure 3 d).

Figure 3 g and h present an overview of  $E_a$ - $\ln(k)$  space and a reaction mechanism for the  $Pt_{13}In_9$ - $PtO_x$ - $Pt_{13}In_9$  redox process. The  $E_a$ - $\ln(k)$  plot shows that the apparent activation energies for  $Pt_{13}In_9$  segregation and Pt oxidation in  $O_2$  are significantly higher compared to  $PtO_x$  reduction and Pt-In alloying in  $H_2$ , and therefore require thermal activation. While Pt surface oxidation (Figure 3 g,  $O_2$ -red) is the rate-determining step in  $O_2$ ,  $In_2O_3$  reduction (Supporting Information, section S6, last page) together with Pt-In alloying

(Figure 3 g,  $H_2$ -green) are kinetically the slowest processes in  $H_2$ . In  $O_2$  flow, the stability of  $In_2O_3/PtO_x$  drives the segregation of  $Pt_{13}In_9$  to segregated In/Pt, while the driving force for  $In_2O_3/PtO_x$  reduction and alloying in  $H_2$  is the stability of the  $Pt_{13}In_9$  nanoalloy (Figure 3 h).

In summary, we have demonstrated that kinetic modeling of in situ quick X-ray absorption spectroscopy data can result in the unrivaled identification of the reaction mechanism describing the dynamic restructuring of nanoparticles. The approach allowed to elucidate the steps involved in alloying-segregation of  $Pt_{13}In_9$  alloys into  $In_2O_3/PtO_x$  nanocomposites during high-temperature  $H_2$ - $O_2$  redox cycling. In  $O_2$ ,  $Pt_{13}In_9$  decomposition and Pt surface oxidation are discerned as simultaneous processes exhibiting high activation energy in which Pt oxidation is rate-determining. In contrast, the reverse processes in  $H_2$  drive the equilibrium state from  $In_2O_3/PtO_x$  back to  $Pt_{13}In_9$  through  $In_2O_3$  and  $PtO_x$  reduction followed by Pt-In alloying, both exhibiting low apparent activation energies. This QXAS approach can be applied to a wide variety of (bi)metallic nanocatalysts and by extension to any field studying dynamic changes in bimetallic nanoparticles and nanomaterials.

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## Conflict of interest

The authors declare no conflict of interest.

**Keywords:** alloying segregation · bimetallic nanoparticles · in situ time-resolved X-ray absorption spectroscopy · kinetics · oxidation–reduction

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