











## PAPER

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[View Journal](#) | [View Issue](#)Cite this: *Catal. Sci. Technol.*, 2020,  
10, 4726Dynamic structural changes of supported Pd,  
PdSn, and PdIn nanoparticles during continuous  
flow high pressure direct H<sub>2</sub>O<sub>2</sub> synthesis†Dmitry E. Doronkin, <sup>\*,ab</sup> Sheng Wang, <sup>ac</sup> Dmitry I. Sharapa, <sup>a</sup>  
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The direct synthesis of hydrogen peroxide over TiO<sub>2</sub>-supported mono- and bimetallic Pd, PdSn, and PdIn nanoparticles (NPs) was performed in a continuous plug-flow reactor at 80 bar in ethanol with H<sub>2</sub>:O<sub>2</sub> ratios varied from 10:1 to 1:10. At the same time the catalysts were monitored by *operando* X-ray absorption spectroscopy (XAS). The setup optimized for XAS allowed productivities that are among the highest reported up to now. A rate of up to 580 mmol<sub>H<sub>2</sub>O<sub>2</sub></sub> g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> and a H<sub>2</sub>O<sub>2</sub> concentration of 80 mmol l<sup>-1</sup> were obtained which were only limited by the supply of reactants. During H<sub>2</sub>O<sub>2</sub> synthesis, the studied NPs revealed a face centered cubic (fcc) Pd(Sn/In) metal (alloy) structure at H<sub>2</sub>:O<sub>2</sub> ratios equal to or smaller than 1 and the corresponding  $\beta$ -hydride structure at H<sub>2</sub>:O<sub>2</sub> > 1. Under all conditions, additional SnO<sub>2</sub>/In<sub>2</sub>O<sub>3</sub> species were observed for the bimetallic catalysts. XAS supported by DFT calculations showed that alloying Pd with In or Sn limited the H<sub>2</sub> uptake capacity and the corresponding lattice expansion of the bimetallic NPs. Different catalysts performed best at different H<sub>2</sub>:O<sub>2</sub> ratios. All catalysts were stable at H<sub>2</sub>:O<sub>2</sub> > 1. Significant leaching of the active Pd and PdIn species could be observed for H<sub>2</sub>:O<sub>2</sub>  $\leq$  1 (quantified by XAS), while PdSn was relatively stable under these conditions. The higher stability of PdSn NPs is proposed to be due to a SnO<sub>2</sub> shell providing strong bonding between the NPs and the titania support.

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## Introduction

Hydrogen peroxide is an important environmentally friendly oxidant widely used in chemical synthesis, paper, pulp, and textile bleaching, wastewater treatment, mining, and

others.<sup>1–4</sup> Nearly all industrially produced H<sub>2</sub>O<sub>2</sub> is derived from the anthraquinone auto-oxidation<sup>4</sup> process introduced by Riedl and Pfeleiderer.<sup>5</sup> This process is only economic on a large scale and produces harmful organic waste. Economy of scale brings the need for energy-intensive concentration of the H<sub>2</sub>O<sub>2</sub> solution to 70 wt% at production plants, transportation of the resulting hazardous material to end users and further dilution at the end-user sites to obtain required concentrations (often <9 wt%).<sup>3</sup> Hence, there is a need to develop alternative processes for H<sub>2</sub>O<sub>2</sub> production which are green, sustainable and economically viable on a small scale.

Direct catalytic synthesis of H<sub>2</sub>O<sub>2</sub> from H<sub>2</sub> and O<sub>2</sub> is a promising reaction which allows the small-scale, decentralized production of H<sub>2</sub>O<sub>2</sub> without generation of harmful byproducts.<sup>2–4</sup> Commercial implementation of the direct H<sub>2</sub>O<sub>2</sub> synthesis is mainly hampered by safety concerns as the process requires high partial pressures, potentially forming explosive mixtures. The safety concerns hinder studies of working catalysts which limits the knowledge-based catalyst and process development. To meet the safety regulations, most of the studies on the direct catalytic H<sub>2</sub>O<sub>2</sub> synthesis were performed with highly diluted gases in (semi-) batch reactors.<sup>1,2</sup> In addition, new and intrinsically safe

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† Electronic supplementary information (ESI) available: PDF describing catalyst synthesis and characterization; indirect online determination of catalytic activity and selectivity using mass spectrometry; titration of H<sub>2</sub>O<sub>2</sub> with Ce(SO<sub>4</sub>)<sub>2</sub>; DFT-optimized PdSn and PdIn structures used for theoretical evaluation of hydride formation; exemplary raw *k*<sup>2</sup>-weighted EXAFS data; XANES and FT EXAFS spectra of reference compounds (bulk Pd, Sn, In metals and their oxides); calculated reference XANES spectra of In<sup>0</sup>, In<sub>2</sub>O<sub>3</sub>, and In-doped Pd nanoparticles; exemplary XANES and EXAFS fits; detailed results of EXAFS analysis of the experimental spectra; XAS evidence of leaching of Pd, Sn, and In species; high resolution transmission electron microscopy of used PdSn and PdIn NPs. See DOI: 10.1039/d0cy00553c



concepts, that make use of membrane reactors<sup>6,7</sup> and electrochemical H<sub>2</sub>O<sub>2</sub> production,<sup>3</sup> have emerged. Recently, *operando* studies of the catalysts for H<sub>2</sub>O<sub>2</sub> production were reported by eliminating the explosion hazard by using thin capillaries as *in situ* reactors<sup>8</sup> or dissolving H<sub>2</sub> and O<sub>2</sub> at high pressures in separate liquid streams.<sup>9</sup>

Platinum-group metal nanoparticles (NPs) are presently the most active catalysts for the direct H<sub>2</sub>O<sub>2</sub> synthesis.<sup>1,3</sup> Among those supported Pd particles are often used as catalysts for the direct H<sub>2</sub>O<sub>2</sub> synthesis. However, Pd also catalyses the side reactions, *i.e.* H<sub>2</sub>O<sub>2</sub> decomposition or overhydrogenation to water, reducing the overall H<sub>2</sub>O<sub>2</sub> selectivity. Promoting Pd with other metals, for example Au and Sn, allows improving the catalyst selectivity by suppressing these side reactions.<sup>1,10–12</sup> Information on the structure of bimetallic NPs and its correlation with catalytic activity and selectivity during H<sub>2</sub>O<sub>2</sub> is scarce and, for the most part, obtained indirectly *via* DFT calculations, kinetic experiments and *ex situ* catalyst characterization. However, so far the structure of the bimetallic NPs producing quantitative amounts of H<sub>2</sub>O<sub>2</sub> was not directly observed. In addition, catalytic testing is usually done under very limited sets of conditions, *e.g.* H<sub>2</sub>:O<sub>2</sub> ratio often shifted to excess O<sub>2</sub>. Previously we have reported on a setup for *operando* XAS studies of H<sub>2</sub>O<sub>2</sub> synthesis catalysts in a continuous plug-flow reactor cell at high pressures and variable H<sub>2</sub>:O<sub>2</sub> ratios. This setup unravelled the structure of Pd NPs and their hydrides during direct H<sub>2</sub>O<sub>2</sub> synthesis in water at 10 bar.<sup>9</sup> In this work, a modified continuous flow setup is used to provide direct information on the structure, dynamics, activity and selectivity of supported monometallic Pd and bimetallic PdSn and PdIn NPs, including formation of hydrides. All data are obtained during the direct catalytic synthesis of H<sub>2</sub>O<sub>2</sub> at 80 bar in ethanol while the feed composition was varied in a wide range from high H<sub>2</sub> excess to high O<sub>2</sub> excess. The data are used to provide structure–activity correlations, define catalyst stability regions and outline the most promising operating conditions for the subsequent process optimization.

## Materials and methods

### Catalyst synthesis

Mono- and bimetallic catalysts were synthesized by depositing Pd(M) nanoparticles on TiO<sub>2</sub> (Aeroxide® P25) pre-treated with diluted H<sub>2</sub>SO<sub>4</sub> (denoted as s-TiO<sub>2</sub>) as reported previously<sup>13,14</sup> to obtain Pd/s-TiO<sub>2</sub> (4.5 wt% Pd); PdSn/s-TiO<sub>2</sub> (4.1 wt% Pd and 2.8 wt% Sn); PdIn/s-TiO<sub>2</sub> (3.4 wt% Pd and 1.2 wt% In) catalysts. For convenience, the synthesis procedure is summarized in the ESI.† Detailed characterisation (TEM, EDX mapping, XRD, XAS) of the isolated unsupported bimetallic nanoparticles and the supported catalysts is reported in our recent publication.<sup>14</sup> TEM analysis reported in the cited work<sup>14</sup> reveals relatively broad NP size distribution between 2 and 6 nm with maxima at 3–4 nm.

### Operando setup and experimental test procedure

The experimental setup used in this study is based on the concept described by us earlier.<sup>9</sup> Essentially, in order to avoid mixing O<sub>2</sub> and H<sub>2</sub> in the gas phase, they are dissolved in separate solvent streams and the obtained liquid H<sub>2</sub> and O<sub>2</sub> solutions are mixed before the *in situ* cell. A scheme of the setup and a photo of the stainless steel liquid flow *in situ* cell used as a catalytic reactor are given in Fig. 1. The setup and the cell are built of stainless steel passivated with 30 wt% HNO<sub>3</sub> according to ref. 15 with 2 mm thick polyether ether ketone (PEEK) X-ray windows. Two HPLC pumps pump the acidic ethanol (Normapur, denatured with 1 wt% methyl ethyl ketone, MEK, with 0.12 M H<sub>2</sub>SO<sub>4</sub>, and a trace amount of 0.3 ± 0.03 wt% water) from separate containers flushed with technical N<sub>2</sub>. In a separate experiment the catalytic activity in ethanol denatured with MEK was found to be comparable to the activity observed in absolute ethanol. Due to high consumption of ethanol during catalytic experiments and cost reasons, denatured ethanol was used for the *operando* measurements. The solvent streams were then mixed with H<sub>2</sub> or O<sub>2</sub> gas streams in SiC-packed columns at high pressure to allow complete dissolution of the respective gases. The obtained liquid solutions were mixed together, flown through the *in situ* cell, and depressurized after a back pressure regulator (BPR) into a product container flushed with N<sub>2</sub> at 280 ml min<sup>−1</sup>. The flushing gas containing unreacted H<sub>2</sub> and O<sub>2</sub> was eventually sampled by a quadrupole mass spectrometer (MS, Pfeiffer Vacuum OmniStar GSD 320).

The setup was operated at 296 K (ambient temperature) and 80 (±2) bar. 25 mg of pressed and sieved catalyst (sieve fraction 80–160 μm) was used resulting in a catalyst bed volume of 4 (±0.5) mm (length) × 5 mm (depth defining the X-ray path length) × 1 mm (height). The catalyst was packed between two quartz wool plugs and supported on both sides by 6–8 mm long SiC packed beds for better stability. Combined liquid flow was 3 ml min<sup>−1</sup> resulting in the liquid hourly space velocity (LHSV) 9000 h<sup>−1</sup> and the residence time in the catalyst bed 0.4 s. For the measurements at different H<sub>2</sub>:O<sub>2</sub> ratios the liquid flows were kept constant and the gas flows were varied.

Note that the experiment is potentially dangerous and can be operated only with pressure-rated equipment and after appropriate testing. Protection measures should include nitrogen purge, overpressure protection of the HPLC pumps and/or pressure relief valves as well as tubing and cells with small volume and openings (max. 1–2 mm) which would act as flame arrestors.<sup>16</sup> Parts (especially, MFC and shut-off valves) that are in direct contact with gaseous oxygen at high pressure require special cleaning (grease-free).

The liquid and gas flows used are listed in Table 1 in the same order as the measurements were performed. For each set of conditions, after changing the gas flows, a waiting time of approx. 60–80 minutes (or until stable MS readings were obtained) was allowed before starting XAS measurements. The exact timings of each experiment are discussed in the section



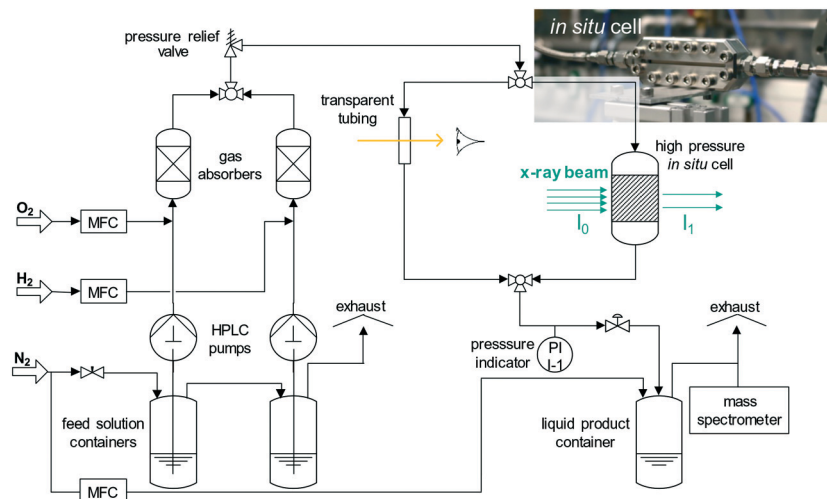


Fig. 1 Scheme of the experimental setup for *operando* studies of the direct  $\text{H}_2\text{O}_2$  synthesis and a photo of the reactor (*in situ* cell, top right).

**Table 1** Reaction conditions during *operando* XAS measurements listed in the same order as they were performed. Flows are given in  $\text{ml}_{\text{STP}} \text{min}^{-1}$  (calibrated at 273.15 K and 1013.25 hPa)

$\text{H}_2:\text{O}_2$ ratio	$\text{H}_2$ gas flow [ $\text{ml min}^{-1}$ ]	Liquid flow ( $\text{H}_2$ channel) [ $\text{ml min}^{-1}$ ]	$\text{O}_2$ gas flow [ $\text{ml min}^{-1}$ ]	Liquid flow ( $\text{O}_2$ channel) [ $\text{ml min}^{-1}$ ]
$\text{H}_2$ only	10	1.5	0	1.5
10:1	10	1.5	1	1.5
3:1	10	1.5	3.33	1.5
1:1	10	1.5	10	1.5
1:3	3.33	1.5	10	1.5
1:10	1	1.5	10	1.5
$\text{O}_2$ only	0	1.5	10	1.5
3:2 <sup>a</sup>	10	1.5	6.67	1.5

<sup>a</sup> This step was performed only during the PdIn catalyst test.

“Leaching of Pd, Sn, and In during synthesis of  $\text{H}_2\text{O}_2$ ” in which longer gaps between the measurements were due to two reasons: (a) waiting for injection of electrons in the synchrotron storage ring (PdSn/s- $\text{TiO}_2$  and Pd/s- $\text{TiO}_2$  at 4–6 h time on stream, TOS), and (b) due to continuously changing concentrations of the  $\text{H}_2$  and  $\text{O}_2$  at the outlet (Pd/s- $\text{TiO}_2$  at 10–12 h TOS and PdIn/s- $\text{TiO}_2$  at 8–13 and 14–17 TOS). The order in which measurements were performed was defined by the fact that less time is needed to stabilize reactant and product concentrations at higher  $\text{H}_2:\text{O}_2$  ratios which, as will be shown in the discussion, directly affects catalyst stability. This stepwise change from stabilizing to leaching conditions made it possible to use one catalyst loading per each catalyst sample. At the end of the study reversibility of the catalyst structure and operation was checked by returning the leached PdIn/s- $\text{TiO}_2$  catalyst sharply from oxidizing conditions back to reducing  $\text{H}_2:\text{O}_2$  ratio of 3:2.

After stabilization of  $\text{H}_2$  and  $\text{O}_2$  outlet concentrations the product container was replaced with a clean and dry one and the product solution was collected while the XAS measurements were performed. XAS spectra were recorded once near the inlet (probing the zone at 0.5–1.5 mm from the inlet) and once near the outlet (probing the zone at 2.5–3.5

mm out of 4 from the inlet) of the catalyst bed at Pd-K and, if applicable, at Sn-K/In-K edges. Each spectrum measurement took approx. 30 min.

$\text{H}_2\text{O}_2$  yield and selectivity were monitored and quantified in several ways. Indirect online monitoring was based on the negligible solubility of  $\text{H}_2$  and  $\text{O}_2$  at ambient pressure which led to separation of unreacted  $\text{H}_2$  and  $\text{O}_2$  from the liquid solution after depressurization and allowed their semi-quantitative ( $\pm 10\%$  relative error) quantification using the MS, the detailed procedure and results are provided in the ESI.† This quantification for  $\text{H}_2:\text{O}_2$  ratios between 3:1 and 1:3 yielded results in a good agreement with results obtained by titration of  $\text{H}_2\text{O}_2$  (ESI,† Table S1).

Precise evaluation of the  $\text{H}_2\text{O}_2$  yields was done *via* titration of the product solution. Titration was performed immediately after the respective experiment whenever possible, otherwise product solutions were stored in glass vials in a dark cold ( $-27^\circ\text{C}$ ) environment to ensure no  $\text{H}_2\text{O}_2$  decomposition before titration. To ensure reproducibility of the results, product solutions were titrated independently using two different methods.  $\text{H}_2\text{O}_2$  concentration reported in the main text was obtained *via* reaction with a  $\text{TiOSO}_4/\text{H}_2\text{SO}_4$  reagent after which the absorption of the formed complex was



analysed using a UV-vis spectrophotometer (Specord S600, Analytik Jena).<sup>17</sup> H<sub>2</sub>O<sub>2</sub> in the obtained product solution was also titrated with Ce(SO<sub>4</sub>)<sub>2</sub> (cf. experimental details and results in the ESI†).<sup>18</sup>

The amount of water in the product solution was determined by Karl Fischer (KF) titration<sup>19</sup> on a Metrohm Titrando 841 titrator using HYDRANAL-Methanol dry and HYDRANAL-Composite 5 (Sigma Aldrich) as a solvent and a reagent for the titration, respectively. H<sub>2</sub>O<sub>2</sub> yield and selectivity to H<sub>2</sub>O<sub>2</sub> were calculated from concentrations of H<sub>2</sub> and O<sub>2</sub> dissolved in the feed solution as well as produced H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub> concentrations determined by titration as:

$$Y_{\text{H}_2\text{O}_2} = \frac{C_{\text{H}_2\text{O}_2}}{\min(C_{\text{H}_2}, C_{\text{O}_2})}, \quad (1)$$

$$S_{\text{H}_2\text{O}_2} = \frac{C_{\text{H}_2\text{O}_2}}{C_{\text{H}_2\text{O}_2} + C_{\text{H}_2\text{O}}}. \quad (2)$$

### X-ray absorption spectroscopy and data analysis

The XAS measurements at Pd-K, Sn-K, and In-K absorption edges (24 350 eV, 29 200 eV, and 27 940 eV, correspondently) were performed at the CAT-ACT beamline of the KIT synchrotron (Karlsruhe, Germany).<sup>20</sup> The CAT experimental station was designed for *operando* studies of heterogeneous catalysts and has the necessary infrastructure for catalytic experiments including high pressure gas dosing infrastructure and analytics.<sup>20</sup> Before the beamtime the experiment was set up and thoroughly tested without X-ray beam.

X-rays were generated using a 2.5 T wiggler source (40 poles, 48 mm period length) and the photon energy was selected with a double crystal monochromator with a Si (311) crystal pair. Higher harmonics rejection was performed using Rh-coated mirrors. Energy was calibrated using spectra of reference Pd/Sn/In metal foils measured simultaneously with spectra of the catalysts. The beam size was 0.9 mm (vert.) × 1 mm (hor.). The experiments were performed in transmission geometry using the nominal high energy ionization chambers to determine the X-ray intensity before the sample, after the sample, and after the reference metal foil.

The spectra were normalized and the extended X-ray absorption fine structure (EXAFS) spectra were background subtracted using the ATHENA program from the IFEFFIT software package.<sup>21</sup> *k*<sup>1</sup>-, *k*<sup>2</sup>-, and *k*<sup>3</sup>-weighted EXAFS functions were Fourier transformed in the *k* range of 2.5–12.5 Å<sup>−1</sup> (Pd-K edge), 2.0–13.0 Å<sup>−1</sup> (Sn-K edge), and 2.0–10.5 Å<sup>−1</sup> (In-K edge) and multiplied by a Hanning window function with sill size of 1 Å<sup>−1</sup>. The structural model for fitting the Pd-K edge spectra was based on the Pd metal structure (ICSD collection code 52251). The model for fitting the In-K edge spectra was based on a mixture of the first In–O shell from the In<sub>2</sub>O<sub>3</sub> crystal structure (ICSD collection code 14387) and the first In–Pd shell from the model of the Pd metal structure with In as a central atom (fits using pure In metal structure as a model were unsuccessful). The corresponding theoretical

backscattering amplitudes and phases were calculated by FEFF 6.0.<sup>22</sup> Structure refinement was performed using ARTEMIS software (IFEFFIT).<sup>21</sup> The theoretical data were then adjusted to the experimental spectra by the least square method in *R*-space between 1.2 and 3 Å (Pd-K spectra) or 1.0 and 3 Å (In-K spectra). First, the amplitude reduction factors (*S*<sub>0</sub><sup>2</sup> = 0.78 for Pd and *S*<sub>0</sub><sup>2</sup> = 0.75 for In) were calculated from the fits of reference spectra of Pd and In foils and then the coordination numbers, interatomic distances, energy shift ( $\delta E_0$ ) and mean square deviation of interatomic distances ( $\sigma^2$ ) were refined. The absolute misfit between theory and experiment was expressed by  $\rho$ .<sup>21</sup> Pd, Sn, and In nearest neighbors could not be distinguished in the fits due to similar scattering factors.

### Density functional theory calculations

DFT calculations were performed using the VASP package (version 5.4.1).<sup>23</sup> The bulk alloys were modelled with a 2 × 2 × 2 supercell (corresponding to 32 metal atoms in one unit cell). The structures were fully optimized with respect to the position of atoms, the cell volume, and the cell shape. PdSn and PdIn alloys were modelled with 4 Pd atoms in the supercell being exchanged with In or Sn (corresponding to a 12.5 at% doping). An energy cutoff of 450 eV was used as negligible change of the lattice constant was observed for higher cutoffs (see Fig. S1†) (compare to ref. 24) and a *k*-point sampling of 6 × 6 × 6 was used. Two independent sets of calculations with different GGA-functionals were performed for each system: the BEEF-vdW,<sup>25</sup> that is known to provide accurate adsorption energies and reaction barriers on transition metal surfaces,<sup>26,27</sup> was used to calculate the reaction energies, while PBE-sol,<sup>28</sup> a functional known to provide accurate bulk parameters, was used to calculate interatomic distances.

In the first step an optimal distribution of In and Sn dopants in Pd metal was computed. Among the six starting distributions five that had no neighbouring dopant atoms (no short In–In or Sn–Sn contacts) were found to have low differences in energy, while the one with tetrahedral dopant clusters appears to be energetically unfavourable (In–In repulsion significantly distorts the crystal structure). This agrees with the fact that Pd–In and Pd–Sn alloys are known not to contain any clusters of dopant atoms or any short In–In or Sn–Sn contacts.<sup>29–31</sup> For further investigation, structures with the most distant dopant atoms were chosen (see ESI†).

### Transmission electron microscopy

For transmission electron microscopy (TEM), the samples were deposited in dry state on Cu grids covered with holey carbon film. The samples were examined in an FEI Titan 80-300 aberration corrected electron microscope operated at 300 kV. Scanning transmission electron microscopy (STEM) images were acquired using a Fischione model 3000 HAADF (high-angle annular dark-field) STEM detector and energy dispersive X-ray spectra (EDX) were acquired using an EDAX SUTW EDX





detector. TEM images were evaluated using ImageJ.<sup>32</sup> Particle size was estimated as an average of minor and major axes of an ellipse enclosing the corresponding particle.

## Results and discussion

### Activity and selectivity to H<sub>2</sub>O<sub>2</sub> measured during spectroscopic study

The catalytic data on the three tested catalysts measured during *operando* XAS experiments are summarized in Fig. 2.

H<sub>2</sub>O<sub>2</sub> concentrations obtained by TiOSO<sub>4</sub> photometric determination (Fig. 2a, c and e) agree with those obtained by Ce(SO<sub>4</sub>)<sub>2</sub> titration (with a systematic discrepancy of approx. 10%, Table S1†) and qualitatively agree with the results of online MS monitoring (Table S1†). Due to the experiment design in which the space velocity was kept the same but the amount of dissolved gases was decreased to obtain different H<sub>2</sub>:O<sub>2</sub> ratios, the maximum achievable H<sub>2</sub>O<sub>2</sub> concentrations were also different (red circles in Fig. 2a, c and e). The monometallic Pd catalyst (Pd/s-TiO<sub>2</sub>) showed rather high

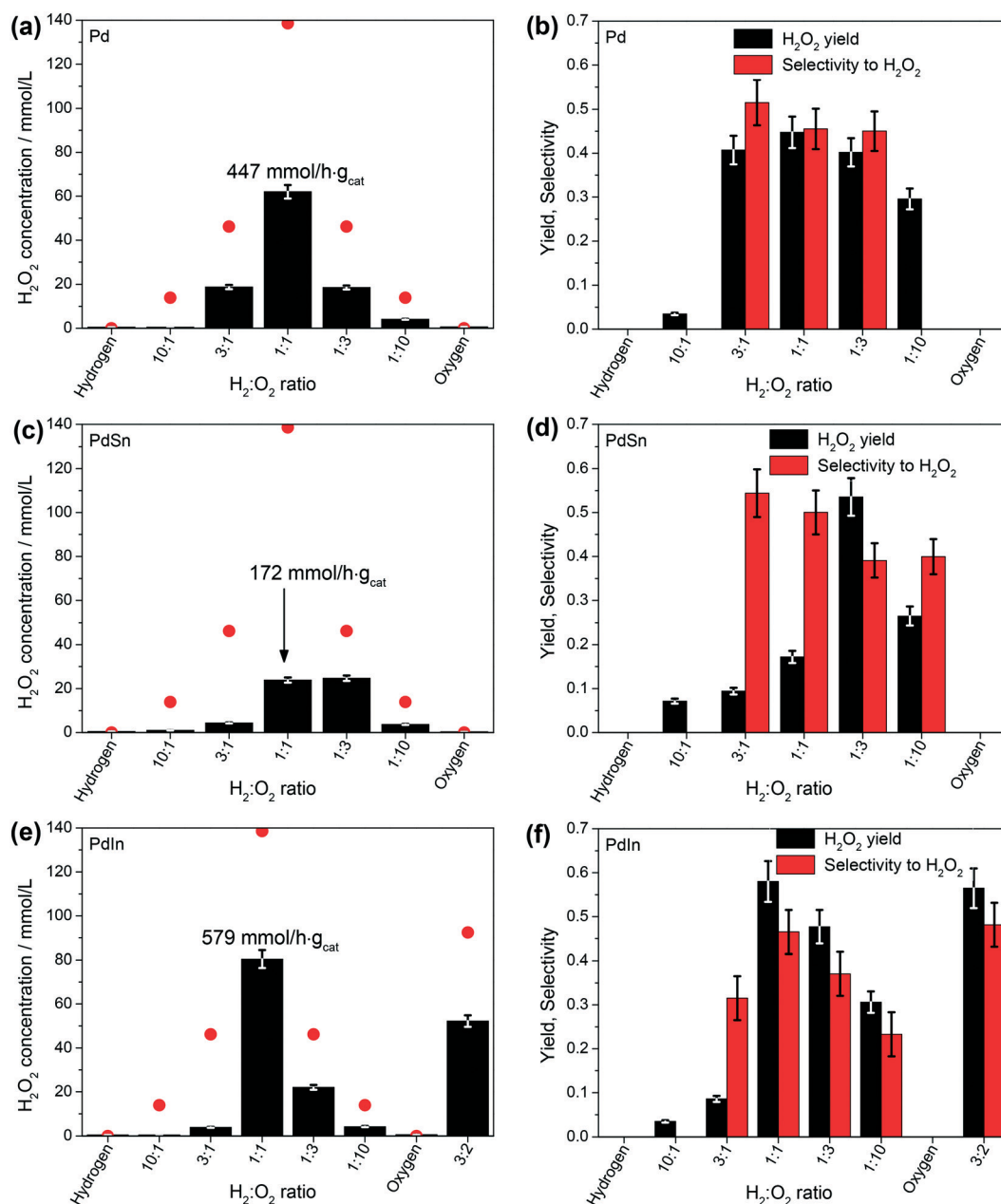


Fig. 2 (a, c and e): Theoretically achievable (red circles) and experimentally determined (black bars) H<sub>2</sub>O<sub>2</sub> concentrations together with achieved H<sub>2</sub>O<sub>2</sub> production rates at H<sub>2</sub>:O<sub>2</sub> = 1:1. (b, d and f): H<sub>2</sub>O<sub>2</sub> yields and selectivities observed during *operando* XAS measurements. H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O concentrations presented here were obtained by photometric titration with TiOSO<sub>4</sub> and Karl Fischer titration, respectively, for the online MS and Ce(SO<sub>4</sub>)<sub>2</sub> titration data see Table S1.†



H<sub>2</sub>O<sub>2</sub> yields and selectivities, both in the range of approx. 40–50%, implying full conversion of the limiting reactant at H<sub>2</sub>:O<sub>2</sub> ratios between 3:1 and 1:3 (*cf.* Table S1† for conversions of H<sub>2</sub> and O<sub>2</sub> obtained from MS data). The Pd catalyst showed similar H<sub>2</sub>O<sub>2</sub> yields and selectivities at H<sub>2</sub>:O<sub>2</sub> = 3:1–1:3, independent of the exact H<sub>2</sub>:O<sub>2</sub> ratio. Doping Pd with Sn and In in PdSn (PdSn/s-TiO<sub>2</sub>) and PdIn (PdIn/s-TiO<sub>2</sub>) catalysts significantly altered the catalytic behaviour of the resulting catalysts. Compared to Pd, the catalytic activity was drastically decreased under hydrogen excess (Fig. 2b, d and f). Approaching stoichiometric and oxygen-rich conditions led to an improvement in H<sub>2</sub>O<sub>2</sub> yields over PdIn (very active already at H<sub>2</sub>:O<sub>2</sub> = 1:1) and PdSn which showed H<sub>2</sub>O<sub>2</sub> yields above 50% only in excess of oxygen (H<sub>2</sub>:O<sub>2</sub> = 1:3). Under oxygen-rich conditions productivity of all three catalysts was similar.

The high activity of the catalyst means that the maximum H<sub>2</sub>O<sub>2</sub> productivity was limited by the availability of reactants and could be achieved at H<sub>2</sub>:O<sub>2</sub> ratio 1:1 (as the maximum amount of the gases was dosed in this experiment) for Pd/s-TiO<sub>2</sub> and PdIn/s-TiO<sub>2</sub>. This does not allow determination of the specific activity of the catalysts, instead only a lower limit on the H<sub>2</sub>O<sub>2</sub> productivities could be identified as 447 mmol<sub>H<sub>2</sub>O<sub>2</sub></sub> g<sub>cat</sub><sup>−1</sup> h<sup>−1</sup> and 579 mmol<sub>H<sub>2</sub>O<sub>2</sub></sub> g<sub>cat</sub><sup>−1</sup> h<sup>−1</sup> for Pd/s-TiO<sub>2</sub> and PdIn/s-TiO<sub>2</sub> catalysts, respectively. The highest obtained H<sub>2</sub>O<sub>2</sub> concentration was 80 mmol L<sup>−1</sup> or approx. 0.3 wt%.

Although the setup was optimized for spectroscopy, the obtained productivities are, to our knowledge, among the highest published in the literature. They are at least three times higher than productivities obtained in (semi-)batch reactors as reviewed by Edwards *et al.*<sup>1</sup> and only two times lower than productivities reported by Gudarzi *et al.*<sup>33</sup> over Pd and PdAu supported on activated carbon cloth. Since in our case H<sub>2</sub>O<sub>2</sub> production rates were limited not by kinetics but by the concentrations of dissolved gases (max. 139 mmol L<sup>−1</sup> for each of H<sub>2</sub> and O<sub>2</sub>), optimization of the reaction parameters (contact time, pressure and amount of dissolved gases) could further increase the H<sub>2</sub>O<sub>2</sub> production rates.

### Operando X-ray absorption spectroscopy

XAS spectra in terms of XANES and EXAFS were measured in a spatially defined way near the inlet and near the outlet of the catalyst bed in each *operando* experiment. In all cases the Pd–K edge spectra measured in the same experiment were similar and, therefore no gradients in speciation were evident along the catalyst bed. Therefore, only one set of spectra measured near the inlet of the catalyst bed will be shown and discussed. Fig. 3 shows *operando* XANES and Fourier transformed (FT) *k*<sup>2</sup>-weighted EXAFS spectra of the three catalyst samples measured at the Pd–K edge under all test conditions. Fig. S2 (ESI†) shows the *k*<sup>2</sup>-weighted EXAFS data to allow evaluating the raw data quality. Qualitatively, all recorded Pd–K edge spectra show the same features as the Pd metal spectrum (Fig. S3†), independently on the experimental

conditions or catalyst composition (monometallic Pd and bimetallic PdSn and PdIn).

Hence, in all cases Pd species are composed of Pd NPs. No spectral features attributed to either PdO phase (high backscattering on O or Pd at uncorrected distances of 1.5 and 3 Å, correspondingly, in FT EXAFS, Fig. S3†) or chemisorbed oxygen species on the Pd NP surface (higher white line and a peak at 24375 eV in XANES) could be observed in any of the experimental Pd–K edge spectra in this work, even under excess O<sub>2</sub>. This is different to our previous observations on the H<sub>2</sub>O<sub>2</sub> synthesis over Pd/TiO<sub>2</sub> in water where surface chemisorbed oxygen species could be identified in the *operando* spectra.<sup>9</sup> The difference is attributed to the effect of ethanol solvent which provides net reducing environment since it is a dominating reagent in the system, even if O<sub>2</sub> is dissolved. Full reduction of Pd NPs in alcohols was evidenced previously by Grunwaldt *et al.*<sup>34</sup> and, in relation to H<sub>2</sub>O<sub>2</sub> synthesis in methanol, also by Kanungo *et al.*<sup>8</sup> While surface chemisorbed O was visible in aqueous solution,<sup>9</sup> the same Pd NPs were fully reduced in a separate experiment with pure ethanol (even containing dissolved O<sub>2</sub>).<sup>35</sup> The other contributing factor, as compared to our previous study,<sup>9</sup> is that NPs of larger size were used in this work which results in a very small fraction of surface Pd (<1%)<sup>36</sup> (almost invisible for conventional XAS) and could further explain the inability to observe surface oxygen in this study. Furthermore, it was demonstrated that larger (>4 nm) Pd NPs reduce easier than NPs with sizes below 2 nm.<sup>37,38</sup>

The observed spectral features shifted with changing H<sub>2</sub>:O<sub>2</sub> ratio between H<sub>2</sub>-rich and O<sub>2</sub>-rich feeds (Fig. 3). Two descriptors were used to evaluate the spectral changes, one for XANES (position of the 2nd peak above the absorption edge, predominantly, reflecting changes in the electronic structure of Pd), and one for EXAFS (average Pd–Pd(In,Sn) bond distance reflecting local structural changes around Pd atoms). Exemplary Pd–K EXAFS fits are provided in the ESI† Fig. S6 and the detailed fitting parameters are listed in the Tables S3–S5.† In the H<sub>2</sub> only feed and at H<sub>2</sub>:O<sub>2</sub> ratios 10:1 and 3:1 the XANES maxima shift to lower energies while EXAFS shows backscattering at a larger distance (Fig. 3). Such changes in the XANES and EXAFS spectra of Pd NPs under excess H<sub>2</sub> were observed by us in the previous work<sup>9</sup> and attributed to the formation of Pd hydride.<sup>34,39–41</sup> The two clearly separated groups of spectra (in H<sub>2</sub> excess and O<sub>2</sub> excess) of Pd/s-TiO<sub>2</sub> and PdIn/s-TiO<sub>2</sub> catalysts reveal evident structure expansion (β-hydride formation) while the spectra of PdSn/s-TiO<sub>2</sub> measured in H<sub>2</sub> excess and O<sub>2</sub> excess differ less clearly from each other and require further analysis to identify structural changes.

To identify the state of the second metal in the PdSn/s-TiO<sub>2</sub> and PdIn/s-TiO<sub>2</sub> catalysts, the corresponding Sn–K edge and In–K edge *operando* XAS spectra were recorded (Fig. 4, raw EXAFS data in Fig. S2†). Sn–K edge XANES spectra are similar to the SnO<sub>2</sub> reference spectrum (Fig. S4†). This similarity is further supported by FT EXAFS data with only the first shell at 1.5 Å (not corrected for the phase shift)



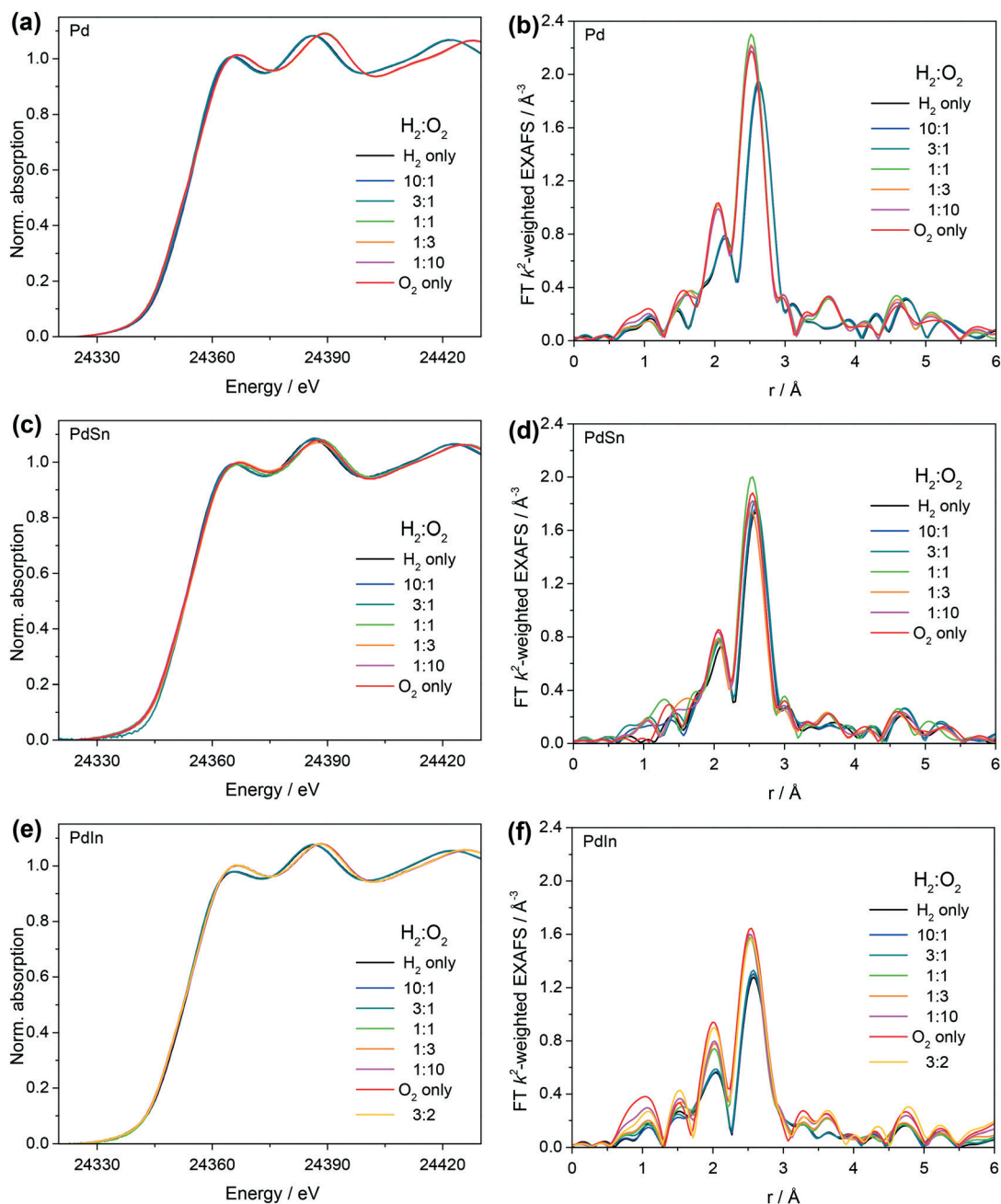


Fig. 3 Operando XANES and FT  $k^2$ -weighted EXAFS (uncorrected for the phase shift) measured at Pd-K absorption edge during direct synthesis of  $H_2O_2$  at 80 bar over (a and b) Pd/s-TiO<sub>2</sub>, (c and d) PdSn/s-TiO<sub>2</sub>, and (e and f) PdIn/s-TiO<sub>2</sub> catalysts. Catalytic properties are reported in Fig. 2.

visible corresponding to O neighbours. Noteworthy, no second shell is found in the EXAFS of PdSn/s-TiO<sub>2</sub> compared to the SnO<sub>2</sub> spectrum (Fig. S4†), hence, the majority of the observed SnO<sub>x</sub> species in the PdSn/s-TiO<sub>2</sub> are highly disordered. As shown in the previous work,<sup>14</sup> during the metal deposition both Pd and Sn were kept in tight contact as PdSn nanoparticles, hence we suppose that, in lieu of high temperature pretreatment, SnO<sub>x</sub> species are still in tight contact with Pd, possibly as a thin layer covering Pd NPs.<sup>11</sup> With respect to the dynamics of Sn species in the PdSn/s-TiO<sub>2</sub>, the intensity of the XANES white

line (peak at 29210 eV) slightly lowers under H<sub>2</sub> excess suggesting reversible reduction of a small fraction of SnO<sub>x</sub> species. The fraction of Sn<sup>4+</sup> was determined using linear combination analysis (LCA) of the *operando* XANES spectra in the range 29185–29235 eV using Sn-K edge spectra of Sn<sup>0</sup> and SnO<sub>2</sub> as references (Fig. 5a). Exemplary LCA XANES fits at the Sn-K edge are given in Fig. S7†. At the start of the experiment (under H<sub>2</sub> excess) approx. 30% of Sn species are reduced whereas under O<sub>2</sub> excess this number decreases to approx. 22%. The obtained absolute numbers should be taken with caution as the reference spectra do not perfectly



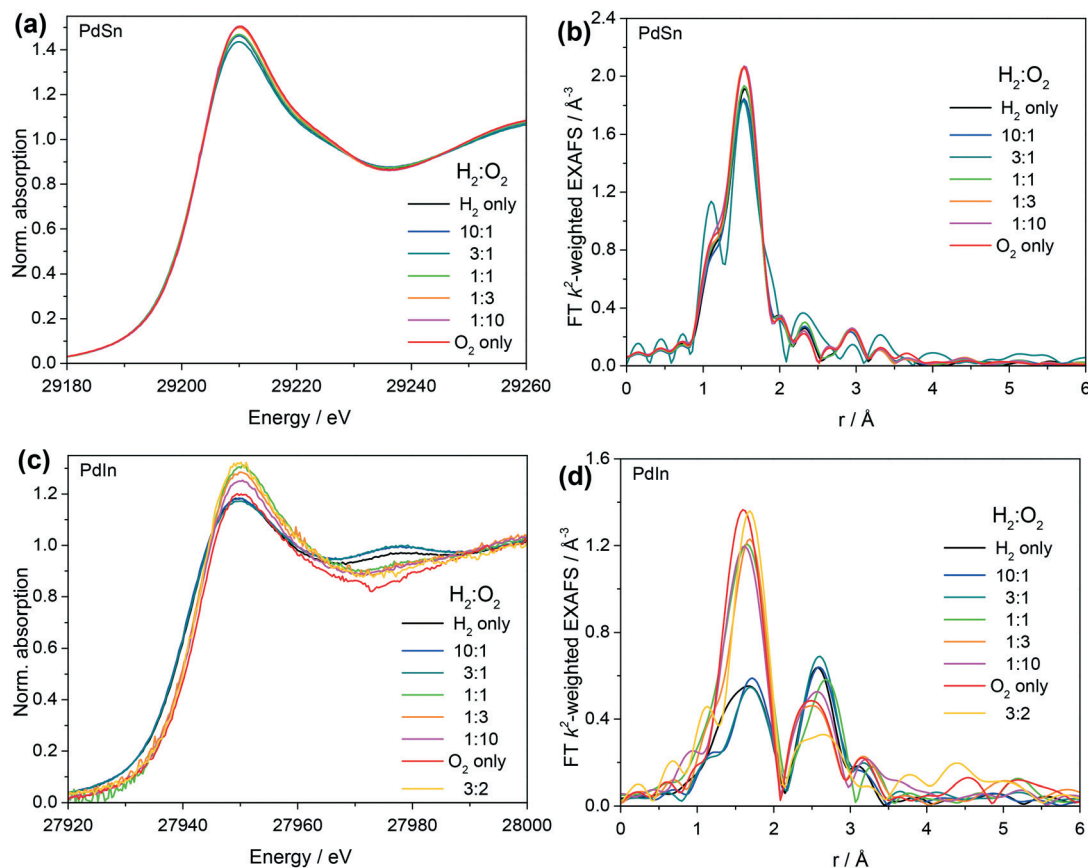


Fig. 4 Operando XANES and FT  $k^2$ -weighted EXAFS (uncorrected for the phase shift) measured at (a and b) Sn-K and (c and d) In-K absorption edges during direct synthesis of  $H_2O_2$  at 80 bar over (a and b) PdSn/s- $TiO_2$  and (c and d) PdIn/s- $TiO_2$ . Catalytic properties are reported in Fig. 2.

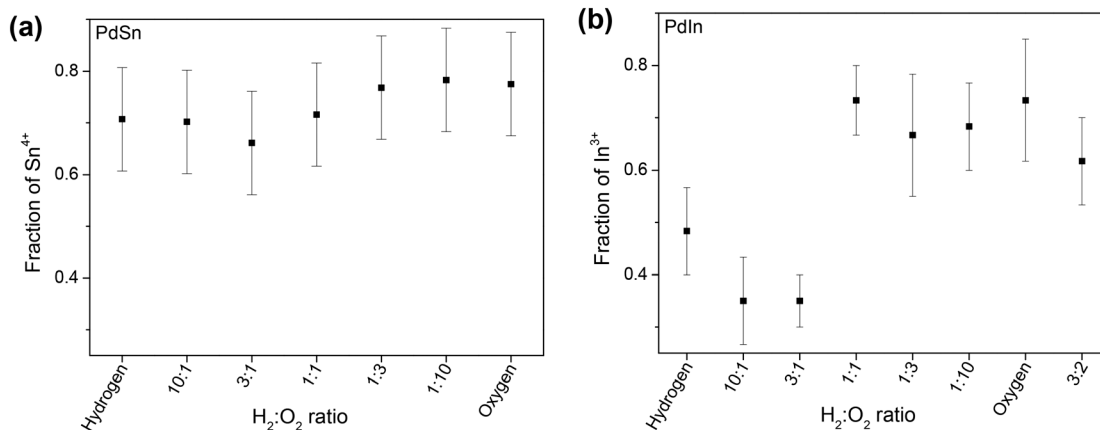


Fig. 5 Molar fractions of  $Sn^{4+}$  (in the  $Sn^0$ - $SnO_2$  mixture) and  $In^{3+}$  species (in the  $PdIn^0$ - $In_2O_3$  mixture) obtained from (a) linear combination analysis of operando Sn-K XANES and (b) coordination number of (O) in the first shell around In obtained from In-K edge EXAFS spectra measured during direct synthesis of  $H_2O_2$  at 80 bar over (a) PdSn/s- $TiO_2$  and (b) PdIn/s- $TiO_2$ .

reproduce the pure states seen in the particular catalyst and this is reflected in the corresponding error bars, however the trends are reliable due to low noise in the original data (Fig. 4a).

Unlike the Sn-K spectra, operando XANES and FT EXAFS spectra of the PdIn/s- $TiO_2$  measured at the In-K edge

(Fig. 4c and d) change significantly with  $H_2:O_2$  ratio. XANES spectra measured under  $O_2$  excess reveal features (white line peak at 27950 eV and a valley with a minimum at 27975 eV) characteristic for  $In_2O_3$  oxide (Fig. S5†). The spectra change under  $H_2$  excess (Fig. 4c), the absorption edge shifts to lower energies, the white line intensity decreases, and a new peak





at 27980 eV appears. The absorption edge shift and decreased white line intensity are typical signs of reduction of transition metals, however, the In-K edge spectra under  $H_2$  excess are markedly different from the metallic In spectrum (Fig. S5†). Therefore, the reduced In species cannot be assigned to pure In NPs. An alternative model for In species is In-doped Pd NPs. The corresponding theoretical XANES spectrum of this species was calculated and indeed shows features (most importantly, the peak at approx. 2975 eV which is not present in either  $In_2O_3$  or metallic In reference spectra) similar to the ones in the experimental spectra (Fig. S8†). The same structural model is received from the detailed analysis of the EXAFS spectra (Table S2†). Two backscattering peaks at 1.6 Å and 2.6 Å (not corrected for the phase shift) can be distinguished in the In-K edge *operando* FT EXAFS spectra (Fig. 4d). The peak at 1.6 Å can be attributed to backscattering on the first shell composed of oxygen neighbours (similar to  $In_2O_3$ , Fig. S5†), the intensity of this peak decreases if more  $H_2$  is present in the feed. The second peak at 2.6 Å, intensity of which increases under  $H_2$  excess, cannot be attributed to In-In interaction in metallic In (approx. 3.0 Å) or in  $In_2O_3$  (3.3 Å, Fig. S5†). However, it corresponds to the Pd-Pd interaction in the metallic Pd lattice (Fig. S3†). In fact, assuming an In-doped Pd lattice as a structural model leads to good fit results (Table S2†). Hence, the In-K edge spectra confirm that a fraction of In atoms forms PdIn alloy while the rest form In oxide species. Due to the lack of reference XANES spectra of a well-defined PdIn alloy, LCA of XANES spectra cannot be used to quantify the oxidation state of In. Instead, coordination numbers in the first shell (CN(O), Table S2†, exemplary EXAFS fits in Fig. S7†) are used to evaluate the  $In^0$  fraction in a mixture with  $In^{3+}$  assuming octahedral coordination of  $In^{3+}$  in oxidic species (Fig. 5b). Because of the very slow reduction, the first experimental spectrum measured in  $H_2$  only feed shows higher In oxidation state than in the spectra taken later. Compared to the oxidation state of Sn, the fraction of reduced In during  $H_2O_2$  synthesis is with 65%  $In^0$  in excess  $H_2$  much higher. Under excess  $O_2$  the fraction of reduced In decreases to 25–30% which is comparable with the  $SnO_2$  fraction in the PdSn sample. Due to statistical uncertainties in the coordination number determination from EXAFS, the absolute error bars resulting from such an analysis are high.

Coordination numbers in the first shell around metallic In sites (Table S2†) corrected by the fraction of metallic In (Fig. 5b) correspond to the coordination numbers around Pd atoms in the PdIn/s- $TiO_2$  catalyst (Table S5†) confirming random bulk alloy structure.

### Structure of Pd, PdSn, and PdIn hydride species determined by *operando* XAS

$PdH_x$  formation and stoichiometry reveals itself in the Pd-K edge XANES and EXAFS spectra in numerous ways. The most straightforward way to detect interstitial hydride is by determining the Pd lattice expansion by X-ray diffraction<sup>42</sup> or

elongation of Pd-Pd bonds in EXAFS.<sup>9,39,40,43</sup> This direct proof, however, allows detecting only  $\beta$ - $PdH_x$ . In case of formation of the intermediate  $\alpha$ - $PdH_x$  phase and the corresponding very small lattice expansion EXAFS is not sensitive enough but XANES may be used. Both  $\alpha$ - $PdH_x$  and  $\beta$ - $PdH_x$  can be detected *via* shifts of the rising edge position and the XANES peak positions (due to core-hole shielding effect).<sup>40</sup> An increase in the Debye-Waller factor due to inhomogeneous H distribution in Pd nanoparticles and the resulting broader distribution of Pd-Pd interatomic distances can also indirectly prove the formation of  $\alpha$ - $PdH_x$  and  $\beta$ - $PdH_x$  hydrides.<sup>43–46</sup>

The structural parameters could be extracted by fitting the *operando* Pd-K edge EXAFS spectra of Pd/s- $TiO_2$ , PdSn/s- $TiO_2$ , and PdIn/s- $TiO_2$  catalysts. The fit results are summarized in Tables S3–S5.† All mentioned structural parameters for all three studied catalysts abruptly change when  $H_2$ -rich conditions change to stoichiometric  $H_2:O_2$  ratio = 1:1 and  $O_2$ -rich feed indicating decomposition of  $\beta$ -Pd(Sn, In) $H_x$  NPs (Fig. 6a–c). Since EXAFS shows only weak sensitivity to  $\alpha$ - $PdH_x$ , the XANES data need to be analysed as well. Fig. 6 shows the interatomic distances as the most important structural descriptor obtained from EXAFS (showing  $\beta$ -hydride formation) along with the position of the 2nd peak in the *operando* XANES spectra (showing both  $\alpha$ - and  $\beta$ -hydride). In all three catalysts both EXAFS and XANES spectra measured at Pd-K edge change at the same time during switch of the  $H_2:O_2$  ratio from 3:1 to 1:1. This simultaneous change of both EXAFS and XANES spectra implies decomposition of  $\beta$ -Pd(Sn, In) $H_x$  hydrides directly to metallic Pd(Sn, In) NPs without an intermediate  $\alpha$ -hydride phase. This result is markedly different from our previous study of Pd NPs at lower partial pressures in water<sup>9</sup> and ethanol<sup>35</sup> where  $\alpha$ - $PdH_x$  was observed in the catalyst producing  $H_2O_2$ . The difference may originate from a much higher concentration of  $H_2$  and  $O_2$  in the liquid feed, higher pressure, different catalyst with larger more uniform Pd(Sn, In) NPs (which form  $\beta$ -hydrides under milder conditions and in this way may influence also the catalytic properties)<sup>47</sup> and a different, acid-pretreated, support.

Although the catalysts display similar structural dynamics during  $H_2O_2$  synthesis, Fig. 6 also highlights important differences between the structure of monometallic Pd and structures of bimetallic PdSn and PdIn NPs. The EXAFS and XANES data (known to be highly sensitive to the crystal structure type<sup>48,49</sup>) with features matching the Pd reference spectrum (Fig. S3†) confirm the fcc Pd lattice structure in all three catalysts. However, average interatomic distances and structure expansion factors are different in all three cases. The Pd-Pd distance in the monometallic Pd NPs was calculated to be 2.739 ( $\pm 0.008$ ) Å and it increased to 2.836 ( $\pm 0.004$ ) Å under  $H_2$  excess as a result of  $\beta$ - $PdH_x$  formation (Table S3, exemplary fits in Fig. S6†). On the other hand, the minimal observed Pd-M (where M can be Pd, Sn, or In) distances in bimetallic PdSn and PdIn NPs in non-hydride state were longer than in monometallic Pd NPs at approx.



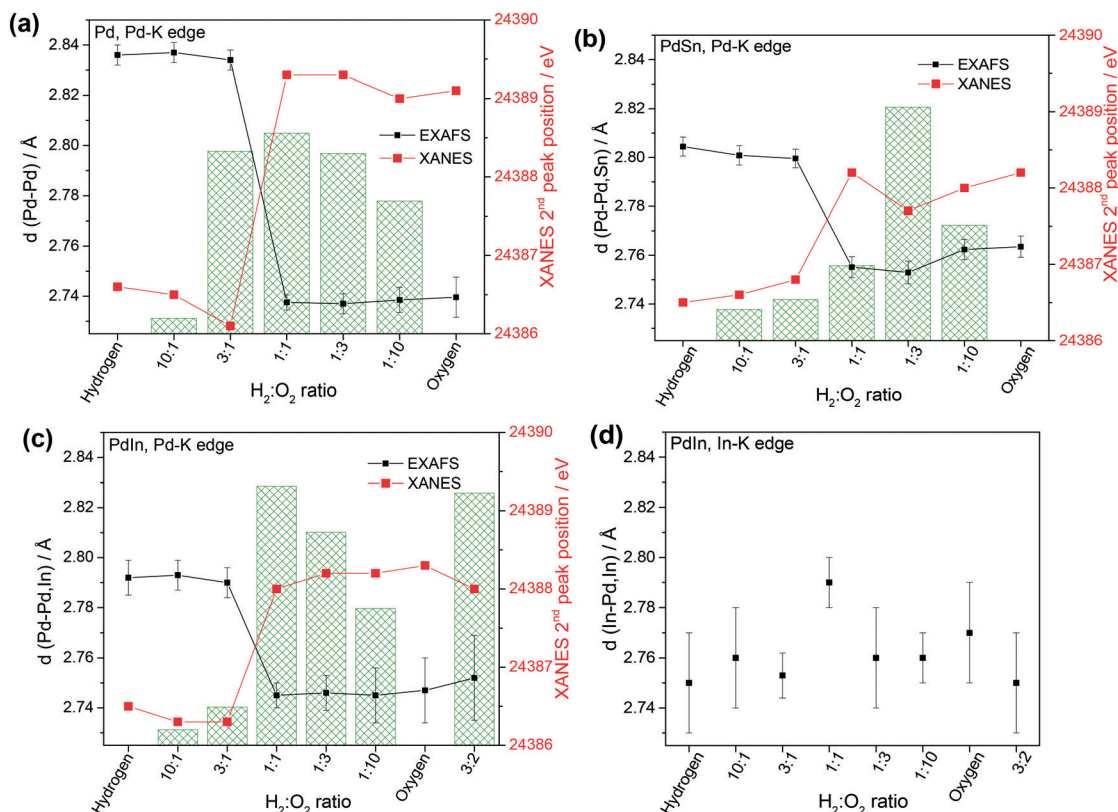


Fig. 6 Pd-Pd(Sn,In) and In-Pd(In) interatomic distances obtained from analysis of *operando* Pd-K and In-K edge EXAFS and position of the 2nd peak after absorption maximum in the *operando* Pd-K edge XANES spectra obtained during direct synthesis of  $H_2O_2$  at 80 bar over (a) Pd/s-TiO<sub>2</sub>, (b) PdSn/s-TiO<sub>2</sub>, and (c and d) PdIn/s-TiO<sub>2</sub> catalysts. Lines connecting the data points serve as guides to the eye. Hatch patterns serve to illustrate the trends in  $H_2O_2$  yields reported in Fig. 2.

2.753 ( $\pm 0.005$ ) Å and 2.745 ( $\pm 0.005$ ) Å correspondingly (Tables S4 and S5, exemplary fits in Fig. S6†). Under  $H_2$  excess the Pd-M distances increased to 2.805 ( $\pm 0.005$ ) Å and 2.792 ( $\pm 0.007$ ) Å which are significantly shorter than in the corresponding monometallic  $\beta$ -PdH<sub>x</sub>. It should be noted that absolute error bars for interatomic distances are higher than obtained from the statistics of the fits and can be up to 1%.<sup>50</sup> These errors stem from imperfect calculation of the theoretical scattering function by FEFF<sup>22</sup> and also correlation of the interatomic distances with  $E_0$  (edge energy) which, in turn, can be defined in several ways and depends on the instrumental resolution of the beamline. Li *et al.* checked the accuracy of FEFF calculations and obtained  $\pm 0.007$  Å for an Ag-Ag scattering pair (the same scattering function as Pd-Pd employed in this work).<sup>51</sup> On the other hand, relative bond distance variations can be observed with higher precision and the detection limit of relative shifts as low as 0.0001 Å was demonstrated by Purans *et al.* using difference EXAFS analysis.<sup>52</sup> In our analysis all parameters influencing interatomic distances were kept the same and, hence, we believe that the trends are accurately represented even if systematic errors mentioned above may be higher than the reported error bars.

In order to further highlight the different structure of the Pd, PdSn, and PdIn nanoparticles and since the shifts of

interatomic distances are near the lower limit of EXAFS sensitivity, the trends visible in EXAFS are also supported by a direct comparison of the edge region of the Pd-K edge XANES spectra of all three catalysts under hydride-forming conditions and under  $O_2$  (Fig. S9†). This leads to two conclusions. First, longer Pd-M distances under  $O_2$  feed strongly suggest doping of Pd lattice by the second (larger) metal, in our case Sn and In. This conclusion is fully supported for the PdIn/s-TiO<sub>2</sub> catalyst by the In-K edge XANES spectra (Fig. S5†) and the In-K edge EXAFS showing the same In-M and Pd-M distances (Tables S2 and S5† and Fig. 6c and d) in the non-hydride state. Unfortunately, SnO<sub>x</sub> species mask spectral features of reduced Sn making a similar analysis impossible for the Sn-K edge spectra. Average Pd<sup>0</sup>:Sn<sup>0</sup> and Pd<sup>0</sup>:In<sup>0</sup> atomic ratios under non-hydride forming conditions are 5.5 : 1 and 8.7 : 1, respectively.

Second,  $\beta$ -hydride formation leads to significant structure expansion of the undoped Pd lattice while expansion of the Sn- and In-doped PdSn and PdIn lattices is not so pronounced. Interestingly, whereas the average Pd-M distance in PdIn NPs increases with absorption of H (Fig. 6c), the corresponding In-M distance remains the same even in the hydride NPs (Fig. 6d). Hence, doping Pd by Sn or In limits the lattice expansion during  $\beta$ -hydride formation. This may be tentatively explained by a lower amount of H<sup>-</sup> which



can be stabilized in the doped Pd lattice, possibly because  $H^-$  do not occupy interstitial sites near the dopant atoms as confirmed by the unchanged local geometry around In in the case of  $\beta$ -PdInH<sub>x</sub>. Interestingly, Kanungo *et al.*<sup>8</sup> observed a similar lattice expansion in both monometallic Pd and alloyed PdAu NPs with Pd–Au distances lengthening to the same degree as Pd–Pd distances, although the formed PdAuH<sub>x</sub> hydride was less stable compared to PdH<sub>x</sub>. This means that introducing a second metal into the Pd lattice does not always limit lattice expansion upon hydrogen uptake since a higher hydrogen solubility was also found in PdAg, PdAu, PdCu, PdCe, and PdY alloys.<sup>53</sup> The nature of the second metal and the doping level, structure of the alloy (random or core-shell), formation of intermetallic structures *etc.* can be decisive factors in determining the hydrogen uptake capacity and the resulting lattice expansion.

### DFT calculations

To evaluate the theoretical hydrogen uptake capacity in the monometallic and bimetallic Pd lattices and confirm the structure of bimetallic PdSn and PdIn hydrides derived from *operando* EXAFS measurements, DFT calculations were performed. As a starting structure the  $2 \times 2 \times 2$  supercell containing 32 metal atoms was employed. The Pd:M ratio was set to 7:1, similar to the values obtained from the XAS analysis (the structures are reported in the ESI†). The hydrogen uptake of the PdM clusters was calculated and is shown in Fig. 7. It was found, that structures containing H atoms next to In or Sn dopant atoms are energetically unfavourable. Stable structures contain hydrogen atoms that are highly distributed while at the same time avoiding interstitial sites near dopant atoms. We note that the dissolution energies were calculated using the BEEF-vdW functional, while the interatomic distances were obtained using PBE-sol. In case of pure palladium, the hydrogen dissolution energy stays negative for the entire range of H:

Pd ratios investigated (Fig. 7a) as also observed in earlier theoretical studies.<sup>54</sup> Therefore, structures with high hydrogenation degrees should be easily accessible, in practice even H: Pd ratios above 1 have been achieved.<sup>55–57</sup> The average Pd–Pd interatomic distance in the model with a H: Pd ratio of 0.625 was found to be very similar to the average Pd–Pd distance experimentally determined under H<sub>2</sub> excess (Fig. 6a and 7b).

The hydrogen dissolution energies calculated for the PdIn and PSn alloys are drastically different from those obtained for pure palladium. Investigations of the PdSn and PdIn alloys reveal that while initial hydrogen dissolution energies are similar to those of Pd, an increase in the H: (Pd + M) ratio above 1/4 (stoichiometry H<sub>0.4</sub>Pd<sub>(1-x)</sub>M<sub>x</sub>) is prohibitively endergonic due to repulsion between hydrogen and Sn or In (Fig. 7a). As a result of the lower degree of hydrogenation, the averaged lattice expansion in the alloy hydrides is also smaller than that of the pristine Pd lattice (Fig. 7b), in agreement with the trends obtained from EXAFS analysis (Fig. 6). Hence, DFT calculations support the experimental conclusion that doping Pd with a second metal limits its lattice expansion by limiting the amount of dissolved hydrogen.

### Leaching of Pd, Sn, and In during synthesis of H<sub>2</sub>O<sub>2</sub>

An important factor determining catalyst stability and, according to some reports,<sup>58</sup> also activity in the direct H<sub>2</sub>O<sub>2</sub> synthesis is leaching of Pd species from the solid to the liquid phase.<sup>59</sup> During the reported experiments, leaching of transition metal species could be unambiguously seen from the decreased height of the absorption edge in non-normalized XANES spectra (Fig. 8a and S10†). The leaching of active species did not affect the XAS spectra, either because the amount of dissolved species was too low compared to the solid phase or because Pd(M) NPs detached from the support as a whole rather than being dissolved slowly. During the experiment no spatial gradients in the

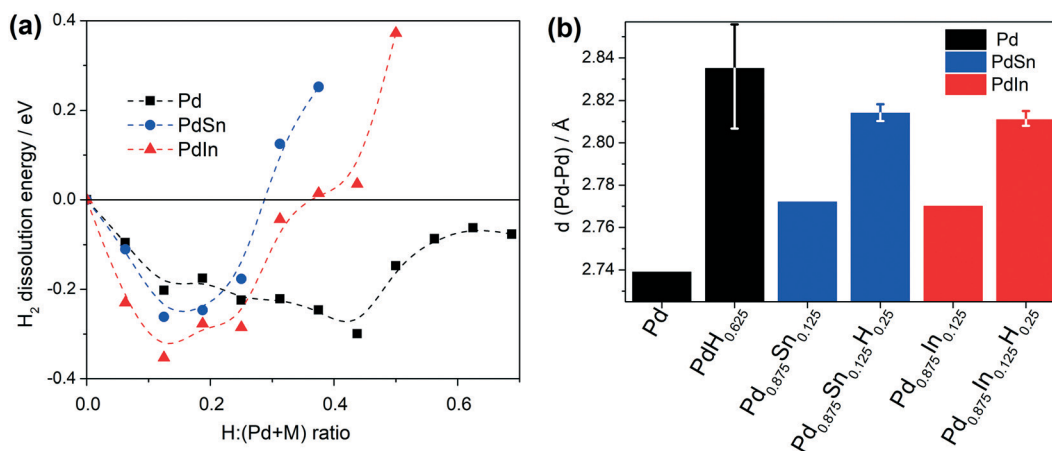
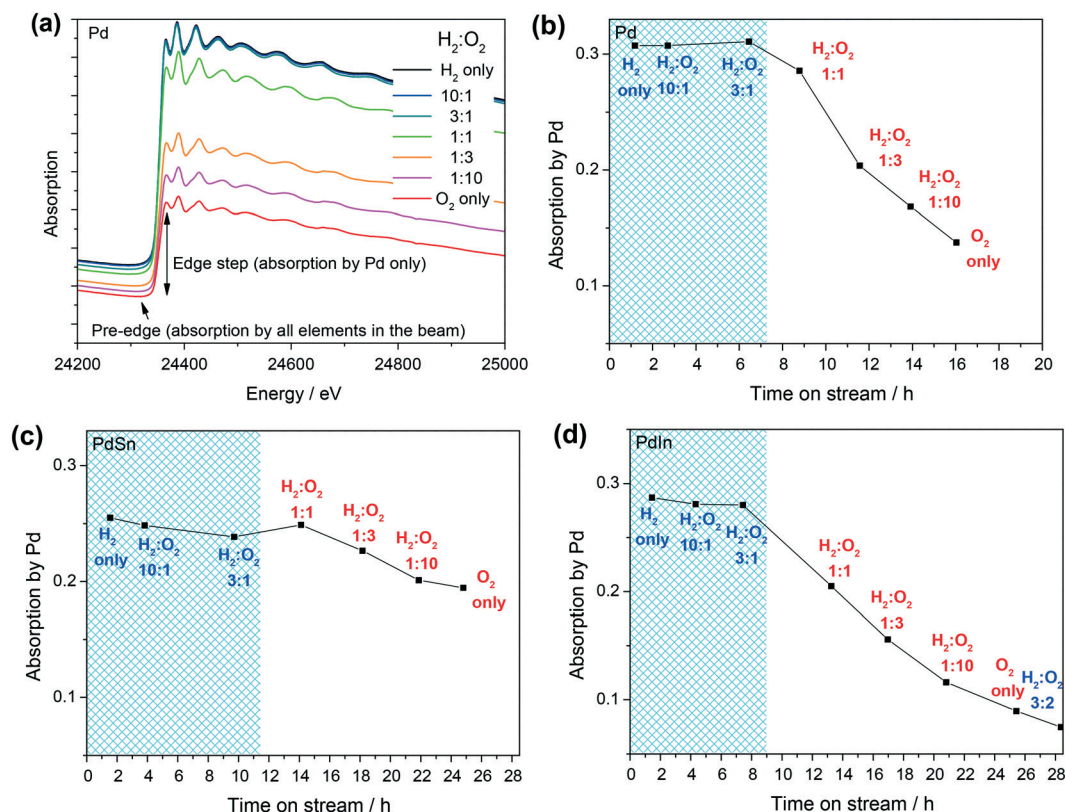


Fig. 7 (a) Calculated differential dissolution energies of hydrogen in monometallic Pd and bimetallic PdSn and PdIn lattices. Dissolution energies are calculated relative to the pure metal and H<sub>2</sub> in the gas-phase. (b) Calculated average Pd–M distances in the Pd, PdSn, and PdIn lattices and the corresponding hydrides. Error bars indicate the scatter of the theoretically determined bond distances.





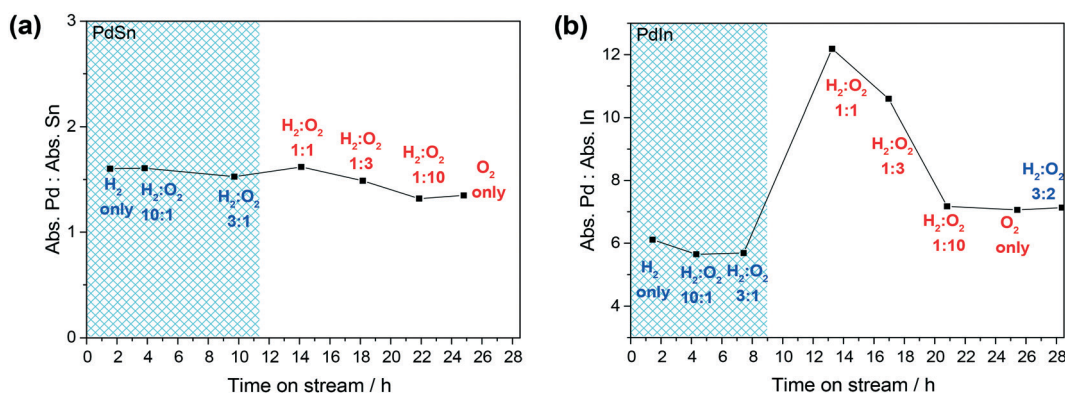


**Fig. 8** (a) Decrease in the X-ray absorption as seen in the non-normalized *operando* Pd-K edge XANES spectra of the Pd/s-TiO<sub>2</sub> catalyst measured during H<sub>2</sub>O<sub>2</sub> synthesis experiments (time-on-stream during changing conditions from H<sub>2</sub> only to H<sub>2</sub> + O<sub>2</sub> mixtures and, finally, to O<sub>2</sub> only). (b–d): Variation of X-ray absorption by Pd (inlet of the catalyst bed, corrected for absorption by X-ray windows and normalized by the total absorption of the catalyst) with time on stream and H<sub>2</sub>:O<sub>2</sub> ratio during the direct synthesis of H<sub>2</sub>O<sub>2</sub> at 80 bar over (b) Pd/s-TiO<sub>2</sub>, (c) PdSn/s-TiO<sub>2</sub>, and (d) PdIn/s-TiO<sub>2</sub>. Hatch patterns designate hydride-forming conditions (H<sub>2</sub> excess).

concentrations of active species were found, *i.e.* the species leached out at the inlet of the catalyst bed were not trapped by the s-TiO<sub>2</sub> support at the outlet.

To be able to semi-quantitatively evaluate the fraction of the leached Pd species, the X-ray absorption in the pre-edge region (−30 eV from the edge position) was corrected for the amount of X-rays absorbed by the X-ray windows in the cell.<sup>60</sup>

The Pd-K, Sn-K, and In-K edge heights were then normalized by the corrected total absorption which allows to compensate for the restructuring of the catalyst bed in the liquid flow (densification, movement of catalyst grains). The obtained values are proportional to the concentrations of the respective species in the probed volume. Fig. 8b–d shows the decrease in the corrected absorbance by Pd in the X-ray beam



**Fig. 9** Ratios of X-ray absorption by Pd to X-ray absorption by (a) Sn and (b) In (inlet of the catalyst bed, corrected for absorption by X-ray windows and normalized by the total absorption by the catalysts) with time on stream and H<sub>2</sub>:O<sub>2</sub> ratio during the direct synthesis of H<sub>2</sub>O<sub>2</sub> at 80 bar over PdSn/s-TiO<sub>2</sub> and PdIn/s-TiO<sub>2</sub>. Hatch patterns designate hydride-forming conditions (H<sub>2</sub> excess).



during the *operando* XAS study on the Pd/s-TiO<sub>2</sub>, PdSn/s-TiO<sub>2</sub>, and PdIn/s-TiO<sub>2</sub> catalysts. Pd species in the Pd/s-TiO<sub>2</sub> remain stable in the solid phase under H<sub>2</sub> excess (all conditions under which  $\beta$ -PdH<sub>x</sub> is observed), while the amount of supported Pd rapidly decreases after changing to H<sub>2</sub>:O<sub>2</sub> ratio 1:1 and further to more oxidizing conditions. Within approx. 9 hours more than half of Pd was removed from the support (and also from the probed volume of the *in situ* cell).

The bimetallic PdSn/s-TiO<sub>2</sub> catalyst showed much higher stability. Pd species are stable under hydride-forming conditions and at a H<sub>2</sub>:O<sub>2</sub> ratio of 1:1 (Fig. 8b). Even after switching to the feeds with O<sub>2</sub> excess, the amount of leached Pd was markedly lower than for Pd/s-TiO<sub>2</sub> and PdIn/s-TiO<sub>2</sub> with approx. 23% after 14 hours on stream. The ratio of the Pd:Sn normalized absorption edge heights was nearly constant during the whole experiment (Fig. 9a) proving that Sn species in the catalyst were also rather stable and were leached out at a similar rate to Pd species.

Unlike the PdSn/s-TiO<sub>2</sub>, the PdIn/s-TiO<sub>2</sub> showed low stability in oxidizing feeds. The leaching rate of Pd species from PdIn/s-TiO<sub>2</sub> in the oxidizing media was high and comparable to that observed for the monometallic Pd/s-TiO<sub>2</sub> (Fig. 8c). Noteworthy, leaching of active species from the PdIn catalyst after switching to H<sub>2</sub>:O<sub>2</sub> = 1:1 resulted in a very long time before the catalytic activity was stabilized and the spectra could be measured. Comparison of the relative concentrations of Pd and In (Fig. 9b) also shows that In was leached out much faster than Pd after exposure to oxidizing conditions. After switching to H<sub>2</sub>:O<sub>2</sub> = 1:1 the Pd:In ratio was increased by two times, *i.e.* more than half of In was lost from the catalyst bed before the steady-state H<sub>2</sub>O<sub>2</sub> production was observed. However, during the following hours the Pd leaching rate was faster than that of In so at the end of the experiment the Pd:In ratio was similar to that in the fresh catalyst.

Transformation and leaching of Pd species in methanol solution (excess O<sub>2</sub>) in the presence of halide ions at ambient pressure was also observed by Centomo *et al.*<sup>61</sup> using *in situ* XAS. Furthermore, Pd complexes leached in the presence of halogens are generally accepted as active species of C-C coupling reactions in the basic media.<sup>62</sup> Our current observations, on the other hand, are made in the halogen-free acidic solution which is new, furthermore the dependence on the partial pressure of O<sub>2</sub> is derived. This dependence may also explain the fact that we could not previously observe Pd leaching at 10 bar in aqueous solution near stoichiometric H<sub>2</sub>:O<sub>2</sub> ratio.<sup>9</sup>

### Transmission electron microscopy

TEM images with particle size distributions of the as-received catalysts are reported elsewhere.<sup>14</sup> The corresponding images of the studied catalysts after the *operando* measurements are shown in Fig. 10. The high Pd and In leaching rates in Pd/s-TiO<sub>2</sub> and PdIn/s-TiO<sub>2</sub> resulted in only few NPs visible in the images of especially PdIn/s-TiO<sub>2</sub>. The relative fraction of very

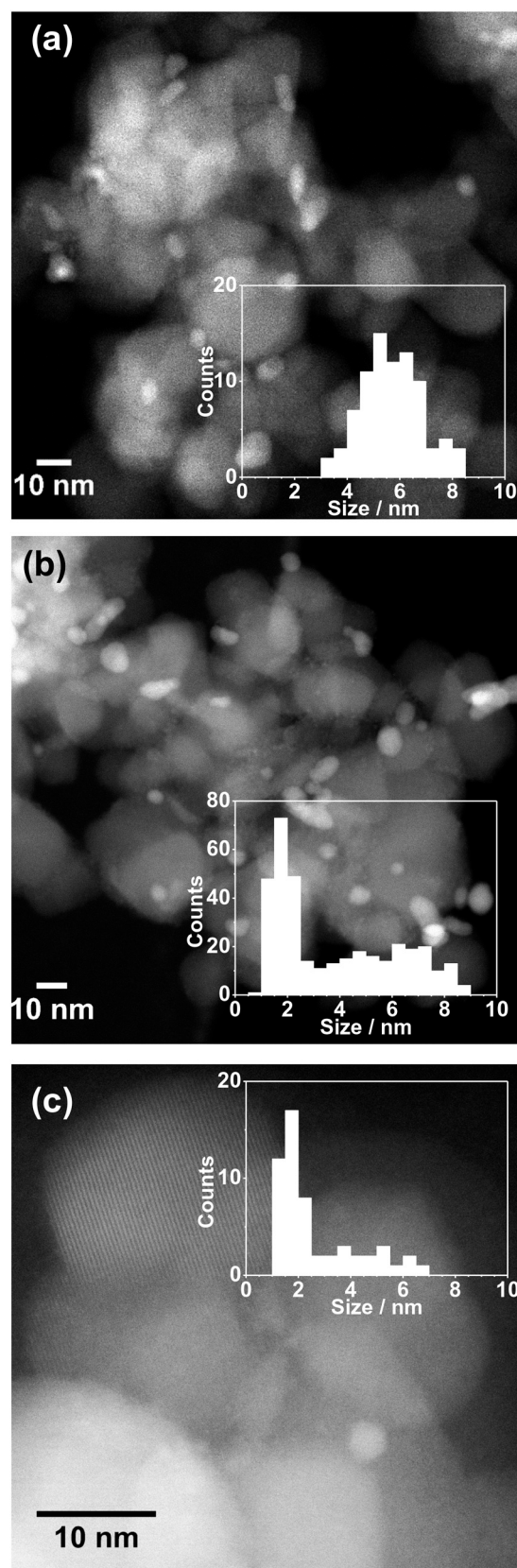


Fig. 10 STEM-HAADF images of the catalysts after *operando* XAS measurements and the corresponding particle size distributions for: (a) Pd/s-TiO<sub>2</sub>, (b) PdSn/s-TiO<sub>2</sub>, and (c) PdIn/s-TiO<sub>2</sub>.



small ( $\leq 1$  nm) particles/clusters did not increase after  $\text{H}_2\text{O}_2$  synthesis experiments (compare Fig. 10a and c). Absence of very small particles and no signs of Pd–O interaction in the XAS spectra (even under the most oxidizing conditions with the highest leaching rate) lead to the suggestion that during  $\text{H}_2\text{O}_2$  synthesis Pd(M) NPs detach from the s-TiO<sub>2</sub> support as a whole rather than break up or dissolve as ionic  $\text{Pd}^{2+}$  species. Weak bonding between the Pd(In) NPs and the support is probably due to the absence of calcination step during catalyst synthesis. Hence, future experiments in terms of catalyst pretreatment could further enhance the stability of these catalysts under different operating conditions.

The PdSn catalyst showed much slower leaching rate of Pd/Sn species compared to the Pd and PdIn catalysts. We relate this stabilization by Sn to the formation of a  $\text{SnO}_2$  shell around PdSn NPs under  $\text{O}_2$ -excess conditions analogously to the observations by Freakley *et al.*<sup>11</sup> made after catalyst calcination. The  $\text{SnO}_2$  layer is visible in high resolution TEM (HRTEM) images (Fig. S12a†) and may facilitate strong bonding between the s-TiO<sub>2</sub> support and the resulting core@shell PdSn@ $\text{SnO}_2$  NPs, thus, hindering detachment and leaching of active species during catalysis. The synthesis of PdSn NPs and their deposition on s-TiO<sub>2</sub> were performed under inert conditions (see ESI† and detailed characterisation of unsupported and supported NPs in ref. 14). Hence, the  $\text{SnO}_2$  shell must have been formed after exposure of the as-prepared supported catalyst to air. Since no thermal treatment was performed on the catalyst we exclude the possibility of the s-TiO<sub>2</sub> morphology change and formation of a TiO<sub>2</sub> shell rather than  $\text{SnO}_2$ . On the contrary, no such protective layer is formed by oxidized In species (Fig. S12b†) leading to high Pd and In leaching rates.

## Discussion

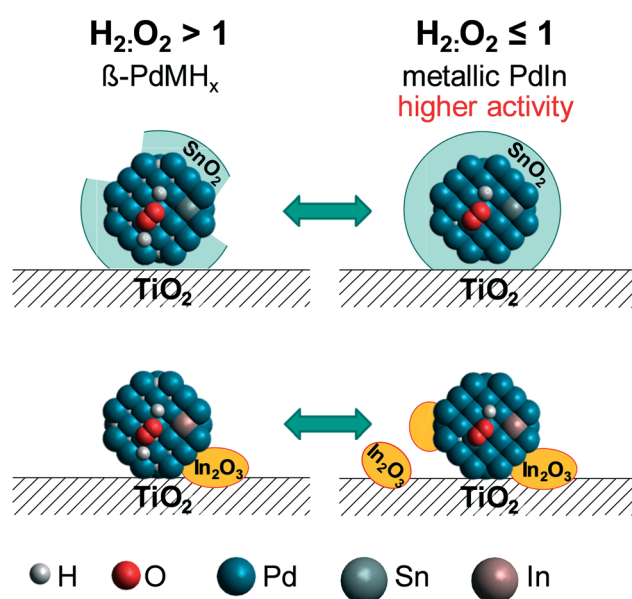
In this work supported monometallic Pd and bimetallic PdSn and PdIn NPs were used as model catalysts and systematically tested in the continuous direct synthesis of  $\text{H}_2\text{O}_2$  in the liquid phase at 80 bar and  $\text{H}_2:\text{O}_2$  ratios varying from strongly reducing to strongly oxidizing conditions. The observed  $\text{H}_2\text{O}_2$  production rates are among the highest rates compared to recent literature,<sup>1,33</sup> despite the employment of an *in situ* XAS cell as the reactor. Due to this compromise it could not be perfectly operated in the kinetic regime and the activity was limited by the supply of reagents (in most of the cases at nearly 100% conversion of the limiting reactant). Therefore, the already high  $\text{H}_2\text{O}_2$  production rates could be further improved in the future, *e.g.* by substantially increasing the flow of the reaction feed. This would also allow obtaining kinetic data in future work.

Whereas previously catalysts were mostly tested in a narrow window of  $\text{H}_2:\text{O}_2$  ratios with excess of  $\text{O}_2$ ,<sup>1,10–12,14</sup> in this work the  $\text{H}_2:\text{O}_2$  ratio was varied from 10:1 to 1:10 and it was found that trends in activity and stability of the catalysts strongly depend on the  $\text{H}_2:\text{O}_2$  ratio (Fig. 2). For instance, under reducing conditions ( $\text{H}_2:\text{O}_2 = 3:1$ ) the

monometallic Pd/s-TiO<sub>2</sub> outperformed both alloyed catalysts producing *ca.* 4 times more  $\text{H}_2\text{O}_2$  with a comparable selectivity. Under stoichiometric conditions the PdIn/s-TiO<sub>2</sub> catalyst was more active than Pd/s-TiO<sub>2</sub>, while production of  $\text{H}_2\text{O}_2$  over PdSn/s-TiO<sub>2</sub> was substantially slower. Under the most commonly tested oxidizing conditions (in our case  $\text{H}_2:\text{O}_2 = 1:3$ ) otherwise not so active PdSn/s-TiO<sub>2</sub> showed the highest  $\text{H}_2\text{O}_2$  yield followed by Pd/s-TiO<sub>2</sub> and PdIn/s-TiO<sub>2</sub>. On the other hand, Pd/s-TiO<sub>2</sub> and PdIn/s-TiO<sub>2</sub> were not stable in oxidizing media while PdSn/s-TiO<sub>2</sub> demonstrated high stability under all test conditions (Fig. 8). Hence, no single catalyst formulation could cover all applications. Different catalysts are suitable for different reaction conditions, *e.g.* Pd/s-TiO<sub>2</sub> is active and stable under reducing conditions while PdSn/s-TiO<sub>2</sub> would be the catalyst of choice, both active and stable, in oxidizing media.

The improved leaching resistance of the PdSn/s-TiO<sub>2</sub> catalyst may be attributed to the formation of a  $\text{SnO}_2$  shell over the PdSn NPs (Scheme 1). This model of a shell is supported by earlier results by Freakley *et al.*<sup>11</sup> PdIn NPs in the PdIn/s-TiO<sub>2</sub> catalyst did not have a similar  $\text{In}_2\text{O}_3$  shell (Scheme 1) and showed high leaching rates in contrast to the PdSn/s-TiO<sub>2</sub>. Hence, formation of an oxide shell over PdM NPs depends on the nature and/or concentration of the second metal and may increase the catalyst durability.

The structure of the Pd(M) NPs in all three catalysts abruptly changed between metallic and  $\beta$ -hydride phases depending on the  $\text{H}_2:\text{O}_2$  ratio (Scheme 1). The Pd lattice expansion could be reproducibly controlled in a wide range by varying the  $\text{H}_2:\text{O}_2$  ratio and the nature of the dopant metal. The monometallic Pd/s-TiO<sub>2</sub> showed high activity in both hydride and metallic states (the highest and the lowest observed Pd–Pd distances) while PdSn and PdIn were not



**Scheme 1** Schematic representation of transformations of PdSn and PdIn NPs in the reaction feed with different  $\text{H}_2:\text{O}_2$  ratios.



active in the hydride state despite having intermediate Pd–Pd(M) distances (Fig. 6). Moreover, Pd–Pd(M) distances in PdSn and PdIn catalysts were similar but the activity was different, *e.g.* at  $\text{H}_2:\text{O}_2 = 1:1$ . The observations rule out a direct dependence of activity and selectivity of Pd(M) catalysts on the Pd–Pd bond length and/or  $\text{PdH}_x$  formation in the tested catalysts. Instead, the chemical nature of the dopant which changes electronic structure of Pd species may play a role in the direct  $\text{H}_2\text{O}_2$  synthesis.

The observed structure–activity correlations rule out leached species as active sites for  $\text{H}_2\text{O}_2$  direct synthesis because Pd/s- $\text{TiO}_2$  demonstrated high activity and PdIn/s- $\text{TiO}_2$  – considerable activity also under hydride-forming conditions. Under reducing conditions the catalysts were very stable and no leaching could be observed. This conclusion is also in agreement with our previous *operando* study of the direct synthesis of  $\text{H}_2\text{O}_2$ .<sup>9</sup> On the other hand, both bimetallic catalysts showed high activity only at  $\text{H}_2:\text{O}_2 \leq 1$  which we tentatively attribute to partial leaching of the second metal oxide species which results in reconstruction of the shell around metallic PdM NPs and provides access of the reactants to the Pd surface. This effect, although very small, is especially important for the PdSn/s- $\text{TiO}_2$  in which >70% Sn forms oxide even under net reducing conditions blocking access to the Pd surface. As a result of very slow leaching of Pd and Sn species the PdSn/s- $\text{TiO}_2$  displays high activity only under  $\text{O}_2$  excess, long after the first leaching inducing conditions were applied.

## Conclusions

The used *in situ* setup for direct hydrogen peroxide synthesis provided both realistic catalytic data with  $\text{H}_2\text{O}_2$  production rates close to the highest reported in literature and structural analysis by *operando* XANES and EXAFS. The highest obtained  $\text{H}_2\text{O}_2$  concentration was 80 mmol  $\text{L}^{-1}$  (approx. 0.3 wt%) over the bimetallic PdIn/s- $\text{TiO}_2$  catalyst, corresponding to a productivity of 579 mmol $_{\text{H}_2\text{O}_2}$  g $_{\text{cat}}^{-1}$  h $^{-1}$ .

Along the wide range of  $\text{H}_2:\text{O}_2$  ratios a strong influence of reaction conditions on hydride formation in Pd, PdIn, and PdSn-based catalysts was found. The observed hydrogen uptake could be supported by theoretical calculations. Doping Pd NPs with a second metal limited hydrogen uptake to a stoichiometry of  $\text{H}_{0.4}\text{Pd}_{(1-x)}\text{M}_x$ . Also the leaching could be directly observed by XAS, demonstrating stabilization by Sn (Scheme 1).

## Conflicts of interest

There are no conflicts to declare.

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