

Supplementary Materials

# Local Structure of Pd<sub>1</sub> Single Sites on the Surface of PdIn Intermetallic Nanoparticles: A Combined DFT and CO-DRIFTS Study

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**Abstract:** Local structure of Pd<sub>1</sub> single sites on the surface of PdIn intermetallic nanoparticles supported on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was investigated by the combination of CO-DRIFT spectroscopy and DFT. CO-DRIFT spectra of PdIn/Al<sub>2</sub>O<sub>3</sub> catalyst exhibit only one asymmetric absorption band of linearly adsorbed CO comprising two peaks at 2065 and 2055 cm<sup>-1</sup> attributable to CO molecules coordinated to Pd<sub>1</sub> sites located at (110) and (111) facets of PdIn nanoparticles. The absence of bridged or hollow-bonded CO bands indicates that multipoint adsorption on PdIn nanoparticles is significantly hindered or impossible. DFT results show that on (110) facet multipoint CO adsorption is hindered due to large distance between neighboring Pd atoms (3.35 Å). On (111) facet multipoint CO adsorption on surface palladium atoms is impossible, since adjacent Pd atoms are located below the surface plane.

**Keywords:** single site alloy catalysts; PdIn intermetallic nanoparticles; CO adsorption; DRIFTS; DFT; bimetallic catalysts

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## Experimental Section

### *Catalyst Preparation*

The bimetallic PdIn/Al<sub>2</sub>O<sub>3</sub> (3 wt% Pd, 3.2 wt% In, molar ratio In:Pd=1) catalyst was prepared via incipient wetness impregnation of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> ( $S_{\text{BET}} = 8 \text{ m}^2/\text{g}$ ) by Alfa Aesar (Kandel, Germany) by aqueous solution of palladium and indium nitrates. The sample was dried at room temperature and reduced at 550 °C in flowing 5 %H<sub>2</sub>/Ar for 3 hours. Our previous study indicated that this temperature is sufficient for the formation of PdIn supported nanoparticles.[1] The monometallic 3 wt% Pd/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> reference catalyst was obtained using Pd(NO<sub>3</sub>)<sub>2</sub> as precursor with subsequent calcination at 550 °C in air flow for 4h and reduction at 500 °C in 5 %H<sub>2</sub>/Ar for 1h.

### *TEM*

The microstructure of the samples was studied by transmission electron microscopy (TEM), using an HT7700 instrument by Hitachi (Tokyo, Japan). The images were acquired in the transmitted electron detection mode (bright field imaging) at an accelerating voltage of 100 kV. Before the measurements, powdered samples were supported from an isopropanol suspension onto copper gauzes (O.D. 3 mm) covered with a carbon. The average size of metal particles was determined from the measurement of 120–150 nanoparticles in different areas of TEM images.

### *XRD*

Powder XRD patterns were obtained on a Bruker D8 ADVANCE X-ray diffractometer (Cu K $\alpha$ , Ni-filter, LYNX-EYE detector, reflection geometry) by Bruker (Ettingen, Germany). The experimental conditions were: 2 $\theta$  range from 10° to 80°, step scan 0.02°, and 2 s counting time per point. Crystallographic parameters were calculated using the Rietan-FT software, [2] which implements the Rietveld method.

### *DRIFT Spectroscopy of Adsorbed CO*

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) was performed with Tensor 27 Bruker spectrometer (Leipzig, Germany) equipped with a high temperature cell by Harrick (Pleasantville, NY, USA) and liquid-nitrogen-cooled MCT detector. The loading of powdered catalyst (20 mg) was placed in the sample compartment of the cell. Before measurements the sample was reduced in situ with a 5% H<sub>2</sub>/Ar mixture (30 cm<sup>3</sup>/min) at 500 °C for 1h and cooled from 500 to 200 °C in the H<sub>2</sub>/Ar flow. The subsequent cooling to 50 °C and recording of background spectrum was carried under Ar. DRIFT spectra of adsorbed CO were recorded at 50 °C under continuous 0.5 % CO/He flow (30 cm<sup>3</sup>/min). The reference spectrum of monometallic palladium catalyst was collected by the procedure described above.

The obtained spectra were deconvoluted between 2100 cm<sup>-1</sup> and 2000 cm<sup>-1</sup> in Origin software package [3] using two Gaussian curves. Curve fitting was performed by Levenberg-Marquardt method.

To estimate the strength of CO adsorption on PdIn catalyst the temperature-dependent series were performed. For a temperature series the temperature was varied between 50, 100 and 150 °C with preliminary registration of the background at given temperatures. The recording of the adsorption spectra was carried under flowing 0.5%CO/He (30 cm<sup>3</sup>/min).

### *Computational*

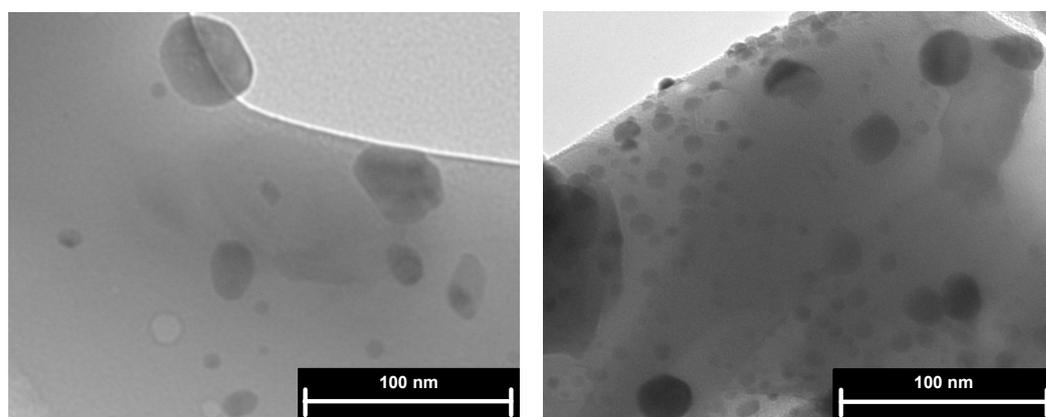
Density Functional Theory calculations were performed using the GPAW package [4,5] using the plane-wave basis set, where the exchange-correlation energy and potential were calculated within the generalized gradient approximation with the BEEF-vdW functional.[6] The lattice parameters of the Pd(fcc) and PdIn(B2) crystal structures were optimized using the stress tensor method available in the Atomic Simulation Environ-

ment (ASE) package.[7] The optimized lattice parameter of bulk Pd(fcc) is 4.01 Å in good agreement with the experimental values of 3.96 Å [8] and for PdIn(B2) we obtained a lattice constant of 3.35 Å also in agreement with the experimental lattice constant of 3.24 Å [9]. The calculation parameters are presented in table 1.

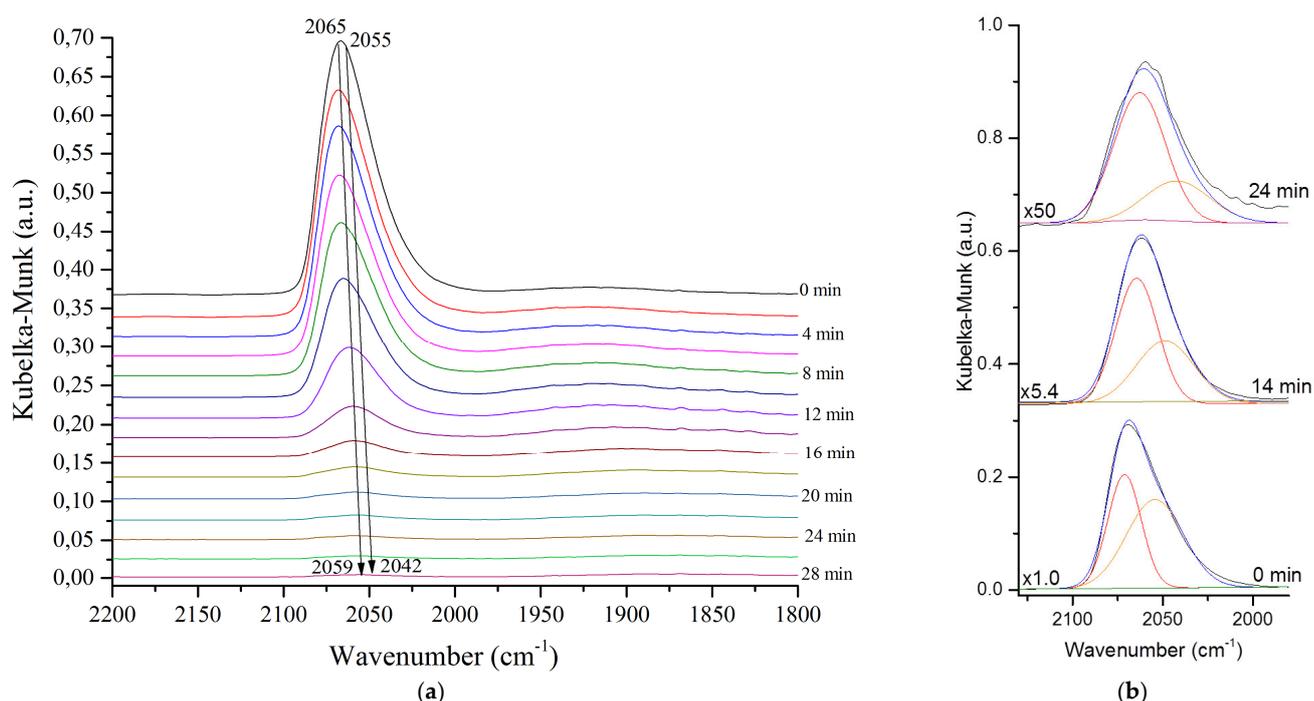
**Table S1.** Parameters used for DFT calculations.

Structure	Composition	#layers (#layers fixed)	k-points	Energy cutoff (eV), Plane waves
Pd fcc bulk	Pd <sub>4</sub>		8×8×8	1000
PdIn B2 bulk	PdIn		8×8×8	1000
CO gas molecule	CO		1×1×1	500
Pd(111)	Pd <sub>24</sub>	6 (3)	4×4×1	500
Pd(100)	Pd <sub>32</sub>	6 (3)	3×3×1	500
PdIn(110)	Pd <sub>24</sub> In <sub>24</sub>	4 (2)	3×3×1	500
PdIn(111)	Pd <sub>28</sub> In <sub>28</sub>	6 (3)	3×3×1	500

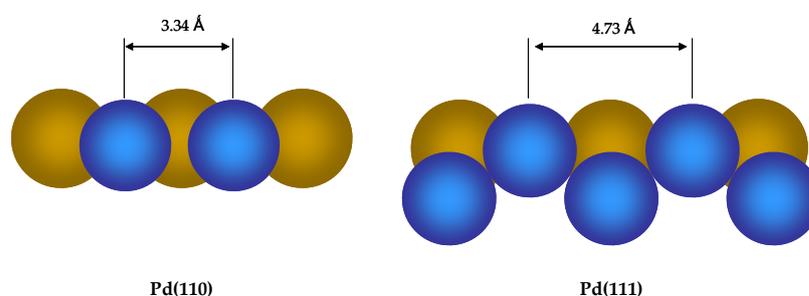
The adsorption of CO are modelled on Pd(111), Pd(100), PdIn(110), and PdIn(111) slabs. For all calculations the adsorbate and the atoms in the topmost layers are allowed to relax until forces became smaller than 0.03 eV/Å. The adsorption energy ( $E_{ads}$ ) of a CO molecule is obtained from:  $E_{ads}(CO) = E(\text{slab-CO}) - E(\text{slab}) - E(\text{CO}_{g})$ , where  $E(\text{surface-CO})$  is the total energy of the surface with one CO adsorbed,  $E(\text{surface})$  the energy of the bare surface, and finally  $E(\text{CO}_{g})$  is the energy of a free CO molecule in vacuum; a more negative  $E_{ads}$  indicates a stronger adsorption. The vibrational frequencies are calculated with a normal mode analysis by using a finite-difference approximation of the Hessian matrix as implemented in ASE.6. The finite-difference delta is 0.03 Å and 4 displacements per Cartesian coordinate. The scaling factor of 1.023 was used to facilitate the comparison between experimental and calculated vibration frequencies. [10]



**Figure S1.** Representative TEM images for Pd/Al<sub>2</sub>O<sub>3</sub> (left) and PdIn/Al<sub>2</sub>O<sub>3</sub> (right) catalysts.



**Figure S2.** CO-DRIFTS data for PdIn/Al<sub>2</sub>O<sub>3</sub> catalyst: **a)** CO desorption from PdIn/Al<sub>2</sub>O<sub>3</sub> in He flow at 50 °C; **b)** peak deconvolution after 0, 14 and 24 min of the experiment. Before the desorption experiment PdIn sample was reduced in situ at 500°C in 5%H<sub>2</sub>/Ar flow. After cooling to 50 °C He flow, flow of 0.5 vol.% CO/He was introduced to the cell and the spectra were collected. Then the adsorbed CO was purged by helium flow (30 ml/min) at 50 °C for 30min with subsequent recording of spectra.



**Figure S3.** Scheme of the neighboring Pd positions on the Pd (110) and Pd (111) surface planes. Pd atoms are blue and In atoms are brown.

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