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### **Supporting Information**

## Palladium Doping of In<sub>2</sub>O<sub>3</sub> towards a general and selective

## catalytic hydrogenation of amides to amines and alcohols

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1. GENERAL INFORMATION

2. XRD AND RAMAN ANALYSIS: FWHM AND CRYSTALLITE SIZE DETERMINATION

3. EXTENSION DATA FOR REACTION PROFILES INVESTIGATION

4. GENERAL PROCEDURES FOR THE CATALYST RECYCLING EXPERIMENTS

5. CHARACTERIZATION OF THE USED CATALYST Pd-In\_2O\_3 (5.3 wt.%)-R1

6. EXTENSION OF TABLE 2 AND SCHEME 2

7. CHARACTERIZATION DATA OF ISOLATED PRODUCTS

8. REFERENCES

9. <sup>1</sup>H AND <sup>13</sup>C NMR SPECTRA OF THE ISOLATED PRODUCTS

#### **1. GENERAL INFORMATION**

Reagents were obtained from commercial sources and were used as received. <sup>1</sup>H-NMR, <sup>13</sup>C-NMR spectra of isolated products were recorded on a Bruker Avance III HD 400 MHz spectrometer. All chemical shifts ( $\delta$ ) are reported in parts per million (ppm) and coupling constants (*J*) in Hz. For <sup>1</sup>H-NMR all chemical shifts are reported relative to tetramethylsilane ( $\delta$  0.0 ppm in CDCl<sub>3</sub>) or *d*-solvent peaks ( $\delta$  77.16 ppm CDCl<sub>3</sub>) for <sup>13</sup>C-NMR. The GC yields were determined by gas chromatography analyses using *n*-hexadecane as an internal standard. Agilent 7820A GC System equipped with a FID and a capillary column Agilent (HP-5, 30 m×0.32 mm×0.25 µm). Mass determination was carried out on a GC-Mass Agilent 5977E Network equipped with the same column as the GC and a Mass selective detector.

Powder X-ray diffraction (XRD) measurements were performed in a D4 Endeavor Bruker-AXS diffractometer using CuK $\alpha$  as the radiation source. Samples for electron microscopy studies were prepared by dropping a suspension of the In<sub>2</sub>O<sub>3</sub>- and Pd-doped In<sub>2</sub>O<sub>3</sub>-based catalysts in dichloromethane or ethanol directly onto the holey-carbon-coated nickel or copper grids. Some measurements were performed in a JEOL 2100F microscope operating at 200 kV both in transmission (TEM) and in scanning-transmission modes (STEM). C<sub>s</sub>-corrected Scanning Transmission Electron Microscopy (STEM) measurements were performed in probe corrector a Titan low-base operated at 300 kV. Raman spectra were recorded at room temperature on a Raman Horiba Scientific spectrometer coupled to a LabRAM HR Evolution microscope equipped with an argon ion laser, providing an excitation light at 532 nm. X-ray photoelectron spectra were acquired with a monochromatic Al K $\alpha$  X-ray source (1486.6 eV) using a pass energy of 20 eV on a Kratos AXIS ultra DLD spectrometer. The C1s peak at 284.6 eV was used to provide a precise energy calibration.

#### 2. XRD AND RAMAN ANALYSIS: FWHM AND CRYSTALLITE SIZE DETERMINATION

To further analyze the effect of the insertion of  $Pd^{2+}$  ions into the structure of  $In_2O_3$  matrix, the values of full width at half maximum (FWHM) for the 100% peak of the XRD patterns (Figure 1a in the manuscript) and for the band located at 306 cm<sup>-1</sup> in the Raman spectra (Figure 1b in the manuscript) were calculated for all samples. As shown in Table S1, it is possible to observe an increase in the FWHM with the Pd-doping, for both DRX peaks and Raman bands, indicating that the presence of  $Pd^{2+}$  ions in the structure affects both the long-range periodicity and the local organization.

**Table S1.** The values of FWHM for the peak (222) in the XRD patterns and for the band located at 306 cm<sup>-1</sup> in the Raman spectra. Estimated crystallite sizes obtained from Debye–Scherrer method.

	FWHM		Crystallite size (nm)
Catalyst	306 cm <sup>-1</sup>	(222)	Debye-Scherrer
	Raman band	DRX peak	
In <sub>2</sub> O <sub>3</sub>	18.44	0.68	13
Pd-In <sub>2</sub> O <sub>3</sub> (1 wt.%)	22.80	0.77	11
Pd-In <sub>2</sub> O <sub>3</sub> (1.5 wt.%)	20.97	0.84	10
Pd-In <sub>2</sub> O <sub>3</sub> (3.5 wt.%)	28.65	0.77	11
Pd-In <sub>2</sub> O <sub>3</sub> (5.3 wt.%)	45.13	0.77	11

The crystallite size (D) was calculated from the FWHM of the 100 % diffraction peak of the XRD pattern by using the Debye–Scherrer equation (eq. 1),<sup>1</sup> where k is a constant related to morphology,  $\lambda$  is the wavelength of the X-rays used,  $\beta$  is the full width at half maximum (FWHM),  $\theta$  is the Bragg angle, and D is the average crystallite size.

$$D = \frac{k\lambda}{\beta \cos\theta} \tag{1}$$

#### 3. EXTENSION DATA FOR REACTION PROFILES INVESTIGATION



**Figure S1.** Yield-time for the hydrogenation of benzanilide (1) in the presence of catalyst (a) Pd-In<sub>2</sub>O<sub>3</sub> (3.5 wt.%), (b) Pd-In<sub>2</sub>O<sub>3</sub> (1.5 wt.%), (c) Pd-In<sub>2</sub>O<sub>3</sub> (1 wt.%) and (d) In<sub>2</sub>O<sub>3</sub>.



**Figure S2.** Initial reaction rate ( $r_0$ ) for the hydrogenation of benzanilide (1) as a function of the Pd-doping degree of In<sub>2</sub>O<sub>3</sub> catalysts. Reaction conditions: 1 (0.1 mmol), catalyst (15 mg), toluene (1.6 mL), 60 bar H<sub>2</sub>, 160 °C.

#### 4. GENERAL PROCEDURES FOR THE CATALYST RECYCLING EXPERIMENTS

The general procedure for the hydrogenation of benzanilide (1) described in the main manuscript was applied for the catalyst recycling experiments. After reaction time (15 h), the autoclave was cooled down to room temperature and the pressure was carefully release. The reaction mixture was diluted with ethyl acetate and an aliquot was taken to be analysed by gas chromatography. Then, the catalyst was separated off by centrifugation, washed with ethyl acetate, diethyl ether and dry at 60 °C. For the catalyst reactivation, the dried catalyst was annealed at the desired temperature (250 or 400 °C) for 2 min in a conventional oven (5 °C/min) before using for the next run.

#### 5. CHARACTERIZATION OF THE USED CATALYST Pd-In<sub>2</sub>O<sub>3</sub> (5.3 wt.%)-R1



**Figure S3.** X-ray diffraction patterns of catalysts Pd-In<sub>2</sub>O<sub>3</sub> (5.3 wt.%) and Pd-In<sub>2</sub>O<sub>3</sub> (5.3 wt.%)-R1. The vertical lines below the XRD patterns indicate the expected reflection positions of body-centered cubic (bcc)-In<sub>2</sub>O<sub>3</sub>

#### 6. EXTENSION OF TABLE 2 AND SCHEME 2



Scheme S1. Hydrogenation of 4-chloro-*N*-phenylbenzamide over Pd-In<sub>2</sub>O<sub>3</sub> (5.3 wt.%).



Scheme S2. Synthesis of hexamethyleneimine from 6-amino-1-hexanol in the presence of catalyst Pd- $In_2O_3$  (5.3 wt.%).

#### 7. CHARACTERIZATION DATA OF THE ISOLATED PRODUCTS



**aniline:** The NMR spectrum is consistent with the reported data.<sup>2</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.18 – 7.09 (m, 2H), 6.74 (dd, *J* = 8.1, 6.7 Hz, 1H), 6.70 – 6.62 (m, 2H), 3.47 (s, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  146.43, 129.32, 118.59, 115.15. MS (EI): *m/z* (rel. int.) 93.



**4-methoxyaniline:** The NMR spectrum is consistent with the reported data.<sup>3</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.78 – 6.69 (m, 2H), 6.67 – 6.59 (m, 2H), 3.73 (s, 3H), 3.33 (s, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  152.86, 140.00, 116.44, 114.87, 55.77. MS (EI): *m/z* (rel. int.) 123.



**2-methoxyaniline:** The NMR spectrum is consistent with the reported data.<sup>3</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.82 – 6.74 (m, 2H), 6.71 (ddt, *J* = 9.5, 7.9, 2.1 Hz, 2H), 3.83 (s, 3H), 3.64 (s, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  147.38, 136.22, 121.13, 118.49, 115.06, 110.53, 55.46. MS (EI): *m/z* (rel. int.) 123.



*p*-toluidine: The NMR spectrum is consistent with the reported data.<sup>4</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.99 – 6.92 (m, 2H), 6.64 – 6.56 (m, 2H), 3.42 (s, 2H), 2.23 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  143.85, 129.77, 127.80, 115.28, 20.45. MS (EI): *m/z* (rel. int.) 107.

NH<sub>2</sub>

*m*-toluidine: The NMR spectrum is consistent with the reported data.<sup>5</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.02 (t, *J* = 7.6 Hz, 1H), 6.56 (d, *J* = 7.5 Hz, 1H), 6.45 (d, *J* = 8.3 Hz, 2H), 3.43 (s, 2H), 2.24 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  146.49, 139.16, 129.24, 119.50, 116.02, 112.35, 21.49. MS (EI): *m/z* (rel. int.) 107.



*o*-toluidine: The NMR spectrum is consistent with the reported data.<sup>4, 6 1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.01 (t, J = 7.5 Hz, 2H), 6.68 (td, J = 7.4, 1.2 Hz, 1H), 6.62 (d, J = 7.8 Hz, 1H), 3.45 (s, 2H), 2.13 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 144.68, 130.52, 127.04, 122.39, 118.69, 115.03, 17.38. MS (EI): m/z (rel. int.) 107.



**4-fluoroaniline:** The NMR spectrum is consistent with the reported data.<sup>71</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.89 – 6.78 (m, 2H), 6.63 – 6.54 (m, 2H), 3.40 (s, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  [157.62, 155.28 (d, <sup>1</sup>*J*<sub>*C*-*F*</sub> = 235.5 Hz)], [142.50, 142.48 (d, <sup>4</sup>*J*<sub>*C*-*F*</sub> = 2.2 Hz)], [116.14, 116.06 (d, <sup>3</sup>*J*<sub>*C*-*F*</sub> = 7.5 Hz)], [115.78, 115.56 (d, <sup>2</sup>*J*<sub>*C*-*F*</sub> = 22.4 Hz)]. MS (EI): *m*/*z* (rel. int.) 111.



*N*-methylaniline: The NMR spectrum is consistent with the reported data.<sup>8</sup><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.21 – 7.11 (m, 2H), 6.69 (tt, *J* = 7.2, 1.1 Hz, 1H), 6.61 – 6.53 (m, 2H), 3.55 (s, 1H), 2.77 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  149.48, 129.29, 117.31, 112.52, 30.78. MS (EI): *m/z* (rel. int.) 107.



**diphenylamine:** The NMR spectrum is consistent with the reported data.<sup>91</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.29 – 7.20 (m, 4H), 7.09 – 7.01 (m, 4H), 6.92 (td, *J* = 7.4, 1.2 Hz, 2H), 5.66 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  143.21, 129.39, 121.06, 117.90. MS (EI): *m/z* (rel. int.) 169.



**1,2,3,4-tetrahydroquinoline:** The NMR spectrum is consistent with the reported data.<sup>10 1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.97 – 6.87 (m, 2H), 6.57 (td, *J* = 7.4, 1.2 Hz, 1H), 6.40 (dd, *J* = 7.9, 1.2 Hz, 1H), 3.63 (s, 1H), 3.26 – 3.18 (m, 2H), 2.72 (t, *J* = 6.4 Hz, 2H), 1.94 – 1.83 (m, 2H).<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  144.94, 129.61, 126.84, 121.51, 117.01, 114.31, 42.11, 27.14, 22.33. MS (EI): *m/z* (rel. int.) 133.



**pyridin-2-amine:** The NMR spectrum is consistent with the reported data.<sup>111</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.05 (dd, J = 5.3, 1.8 Hz, 1H), 7.39 (ddd, J = 8.7, 7.2, 1.9 Hz, 1H), 6.64 – 6.57 (m, 1H), 6.47 (d, J = 8.3 Hz, 1H), 4.63 (s, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  158.63, 148.05, 137.67, 113.82, 108.60. MS (EI): m/z (rel. int.) 94.

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**benzyl alcohol:** The NMR spectrum is consistent with the reported data.<sup>12</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.35 – 7.18 (m, 5H), 4.56 (s, 2H), 2.79 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  140.95, 128.54, 127.58, 127.04, 65.07. MS (EI): *m/z* (rel. int.) 108.



(4-methoxyphenyl)methanol: The NMR spectrum is consistent with the reported data.<sup>13 1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.28 – 7.20 (m, 2H), 6.90 – 6.82 (m, 2H), 4.55 (s, 2H), 3.77 (s, 3H), 2.27 (s, 1H).<sup>13</sup>C

NMR (101 MHz, CDCl<sub>3</sub>) δ 159.16, 133.22, 128.63, 113.95, 77.43, 77.11, 76.79, 64.83, 55.29. MS (EI): *m*/*z* (rel. int.) 138.

# ОН

*m*-tolylmethanol: The NMR spectrum is consistent with the reported data.<sup>13 1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.19 (t, *J* = 7.5 Hz, 1H), 7.07 (dd, *J* = 14.8, 6.6 Hz, 3H), 4.52 (s, 2H), 2.89 (s, 1H), 2.31 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  140.96, 138.16, 128.45, 128.30, 127.81, 124.10, 65.05, 21.40. MS (EI): *m/z* (rel. int.) 122.

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cyclohexylmethanol: The NMR spectrum is consistent with the reported data.<sup>14</sup> <sup>1</sup>H NMR (400 MHz,

CDCl<sub>3</sub>)  $\delta$  3.41 (d, *J* = 6.4 Hz, 2H), 2.37 (s, 1H), 1.80 – 1.66 (m, 4H), 1.47 (dddd, *J* = 17.8, 8.1, 6.4, 3.2 Hz, 1H), 1.33 – 1.22 (m, 1H), 1.26 – 1.08 (m, 2H), 0.92 (qd, *J* = 13.3, 12.6, 3.4 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  68.52, 40.42, 29.58, 26.59, 25.83. MS (EI): *m/z* (rel. int.) 114.

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#### 9. <sup>1</sup>H NMR AND <sup>13</sup>C NMR SPECTRA OF THE ISOLATED PRODUCTS

























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