

Structural evolution of an intermetallic Pd-Zn catalyst selective for propane dehydrogenation

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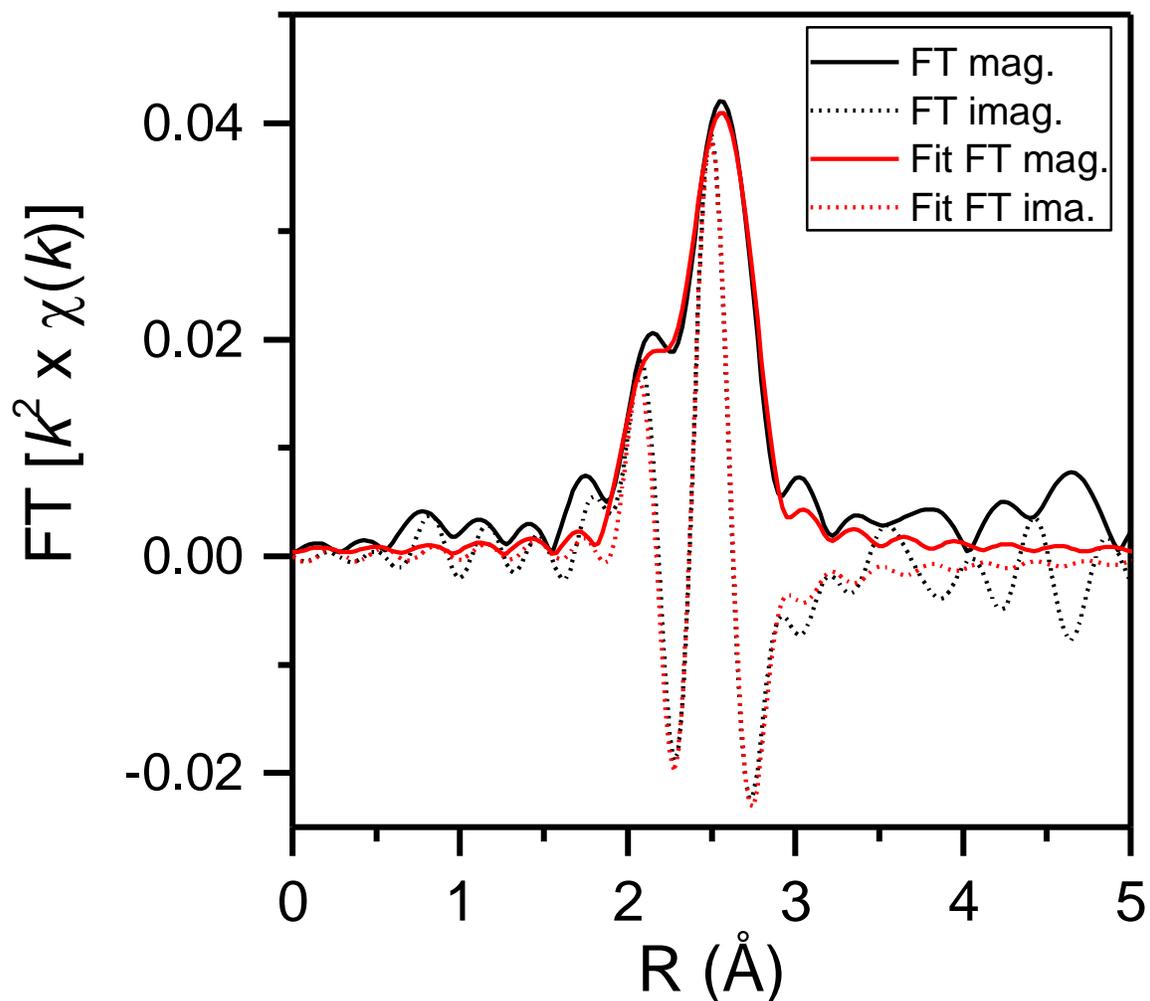
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Electronic Supplementary Information

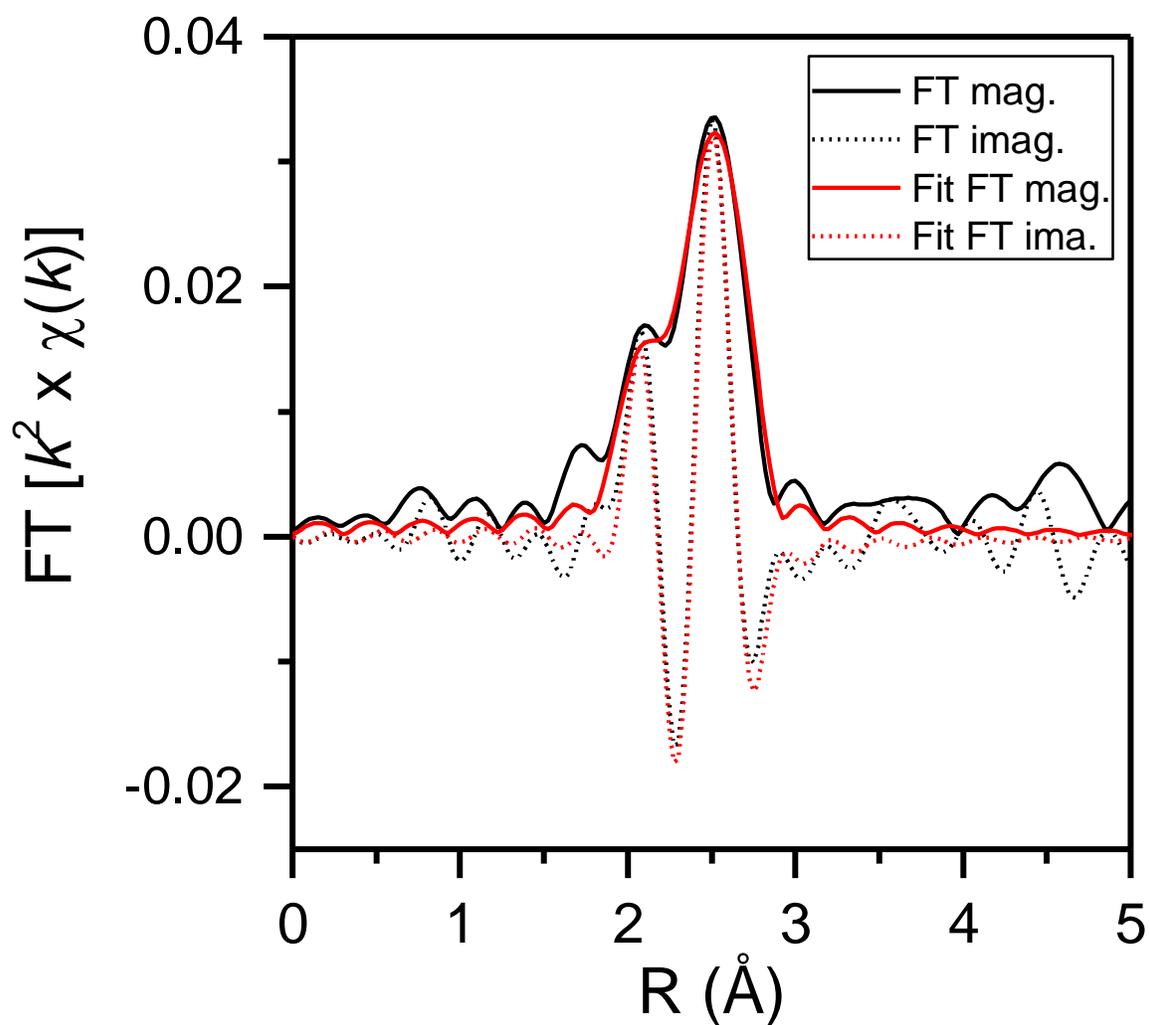
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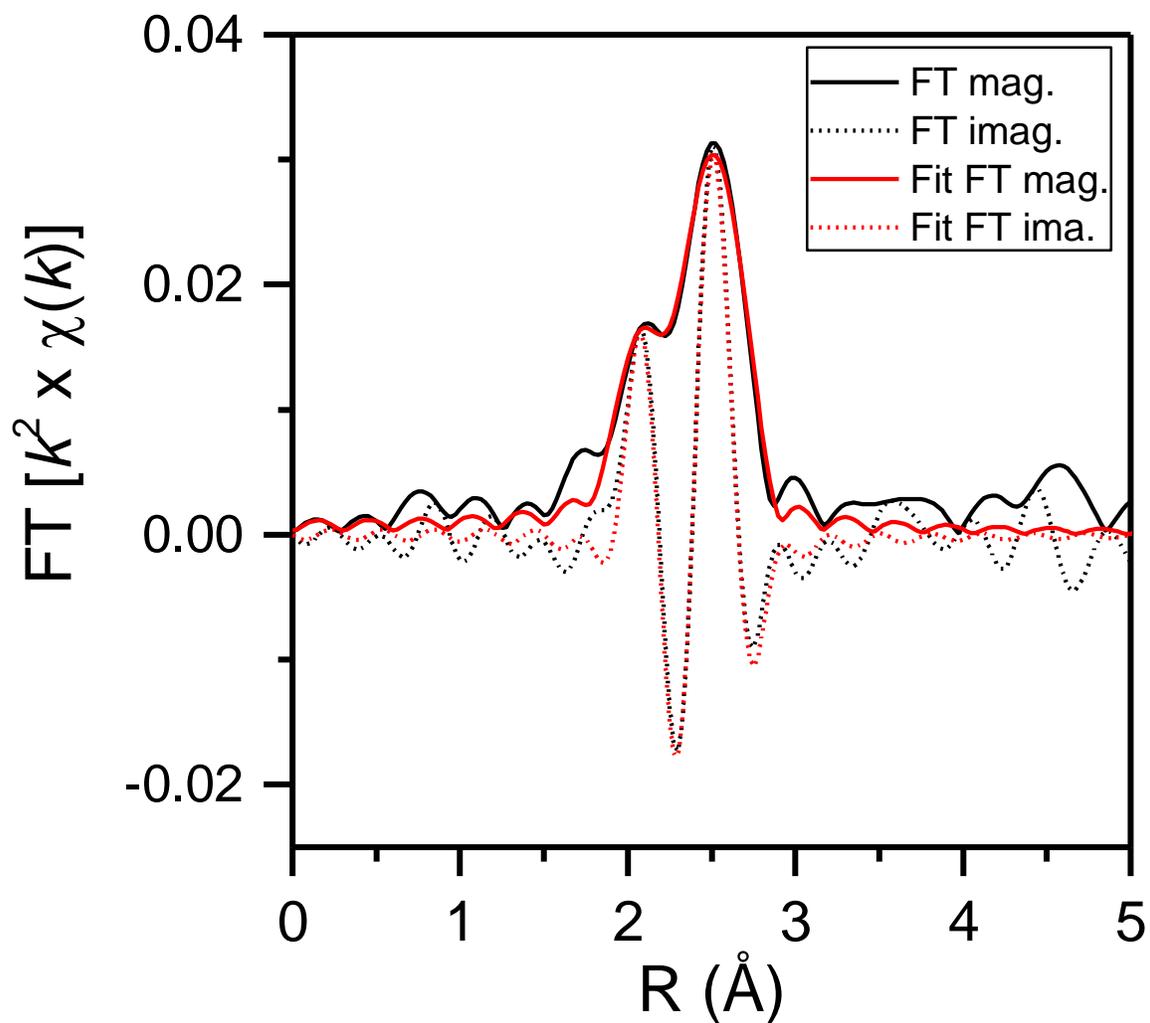
1. EXAFS



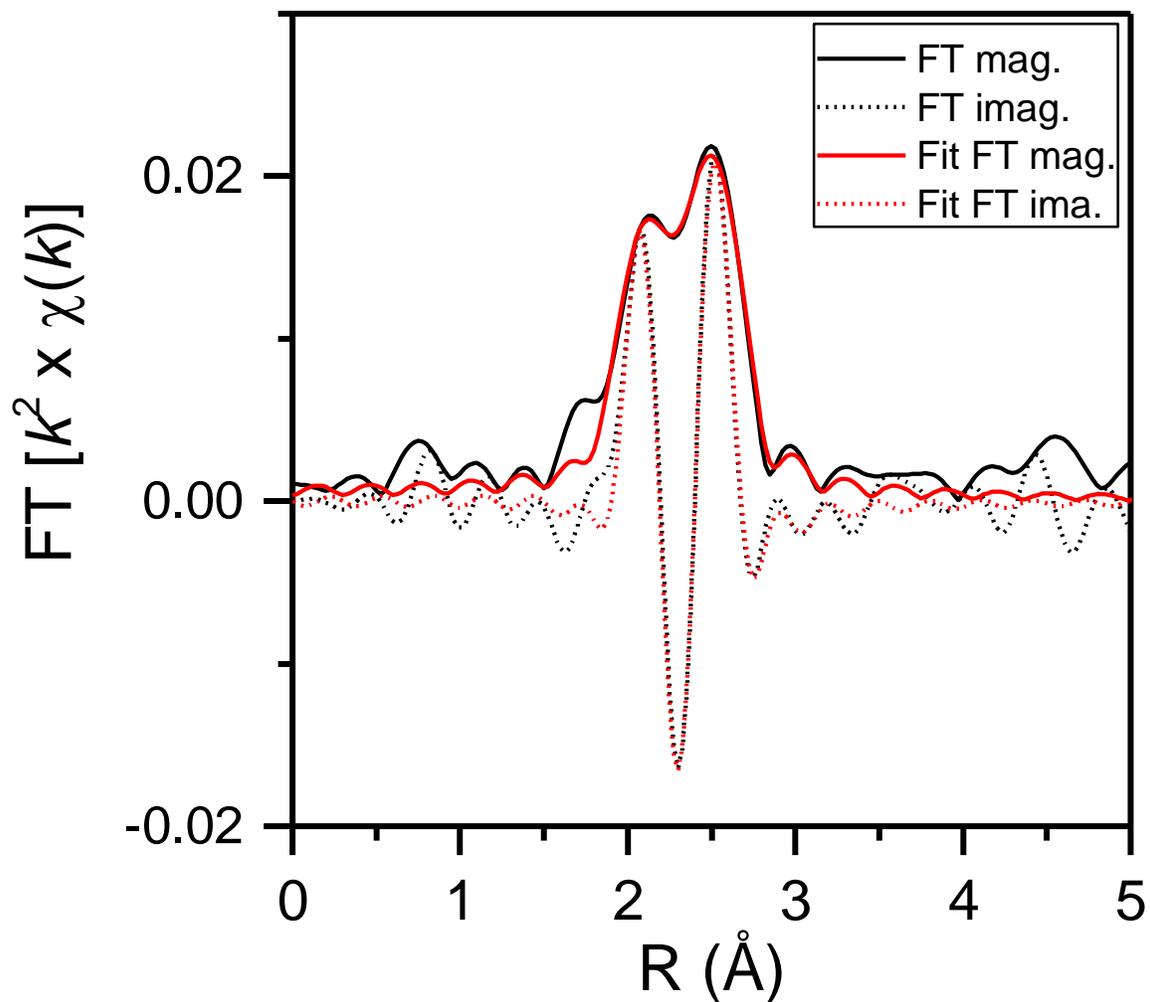
Supplementary Figure S1. *R*-space fitting results of the Fourier-transform (FT) of the k^2 -weighted EXAFS spectrum at the Pd K-edge of Pd/Al₂O₃ at room temperature in He after reduction in H₂ at 275 °C. The solid black line represents the magnitude of the FT, the dotted black line the imaginary part of the FT while the red solid and dotted lines are the fits of the magnitude and the imaginary part of the FT, respectively. ($2.8 \text{ \AA}^{-1} < k < 12.9 \text{ \AA}^{-1}$, $1.8 \text{ \AA} < R < 3.2 \text{ \AA}$). Residual = 4.9 %.



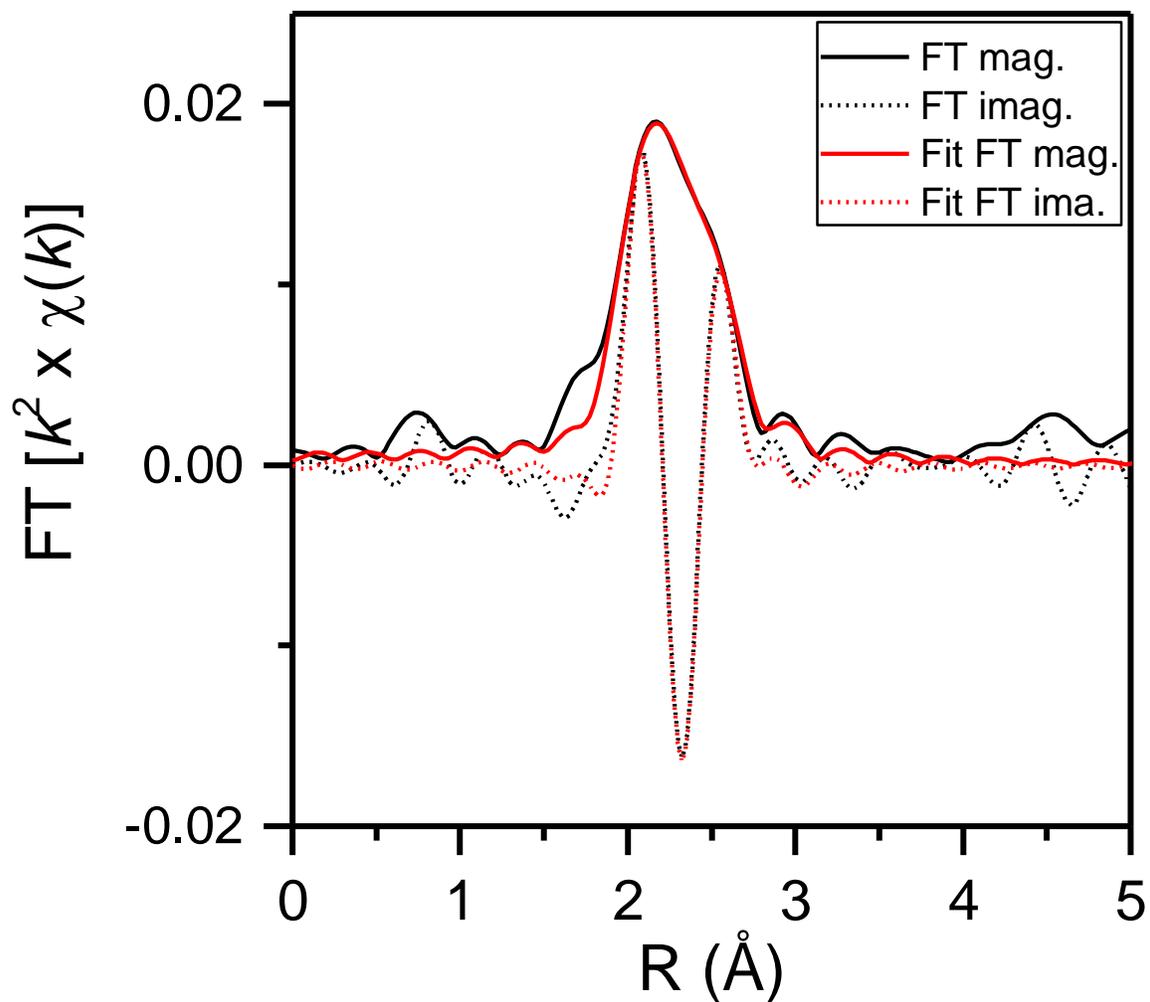
Supplementary Figure S2. *R*-space fitting results of the Fourier-transform (FT) of the k^2 -weighted EXAFS spectrum at the Pd K-edge of PdZn/Al₂O₃ at room temperature in He after reduction in H₂ at 230 °C. The solid black line represents the magnitude of the FT, the dotted black line the imaginary part of the FT while the red solid and dotted lines are the fits of the magnitude and the imaginary part of the FT, respectively. ($2.8 \text{ \AA}^{-1} < k < 12.9 \text{ \AA}^{-1}$, $1.8 \text{ \AA} < R < 3.2 \text{ \AA}$). Residual = 6.9 %.



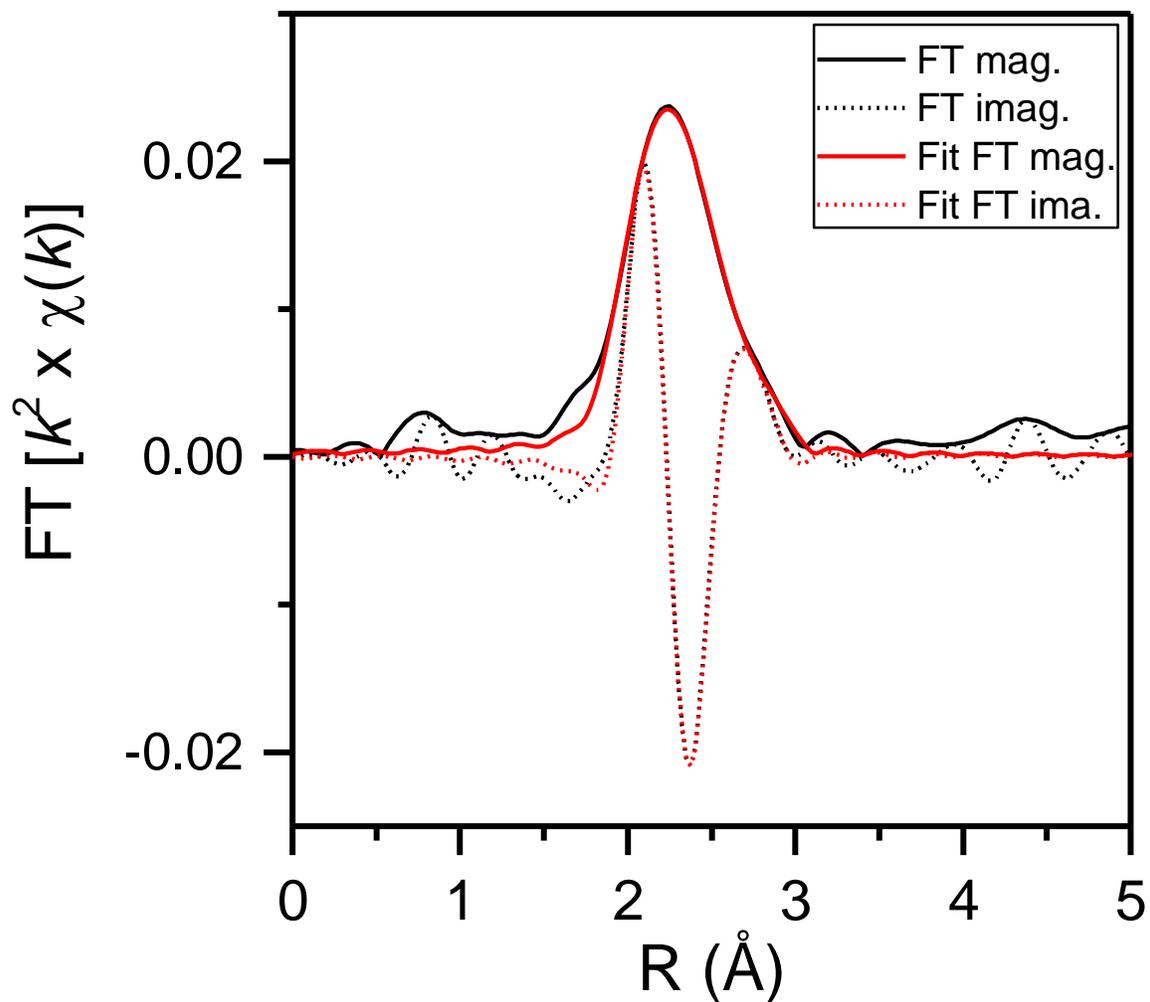
Supplementary Figure S3. *R*-space fitting results of the Fourier-transform (FT) of the k^2 -weighted EXAFS spectrum at the Pd K-edge of PdZn/Al₂O₃ at room temperature in He after reduction in H₂ at 275 °C. The solid black line represents the magnitude of the FT, the dotted black line the imaginary part of the FT while the red solid and dotted lines are the fits of the magnitude and the imaginary part of the FT, respectively. ($2.8 \text{ \AA}^{-1} < k < 12.9 \text{ \AA}^{-1}$, $1.8 \text{ \AA} < R < 3.2 \text{ \AA}$). Residual = 6.9 %.



Supplementary Figure S4. *R*-space fitting results of the Fourier-transform (FT) of the k^2 -weighted EXAFS spectrum at the Pd K-edge of PdZn/Al₂O₃ at room temperature in He after reduction in H₂ at 350 °C. The solid black line represents the magnitude of the FT, the dotted black line the imaginary part of the FT while the red solid and dotted lines are the fits of the magnitude and the imaginary part of the FT, respectively. ($2.8 \text{ \AA}^{-1} < k < 12.9 \text{ \AA}^{-1}$, $1.8 \text{ \AA} < R < 3.2 \text{ \AA}$). Residual = 4.5 %.

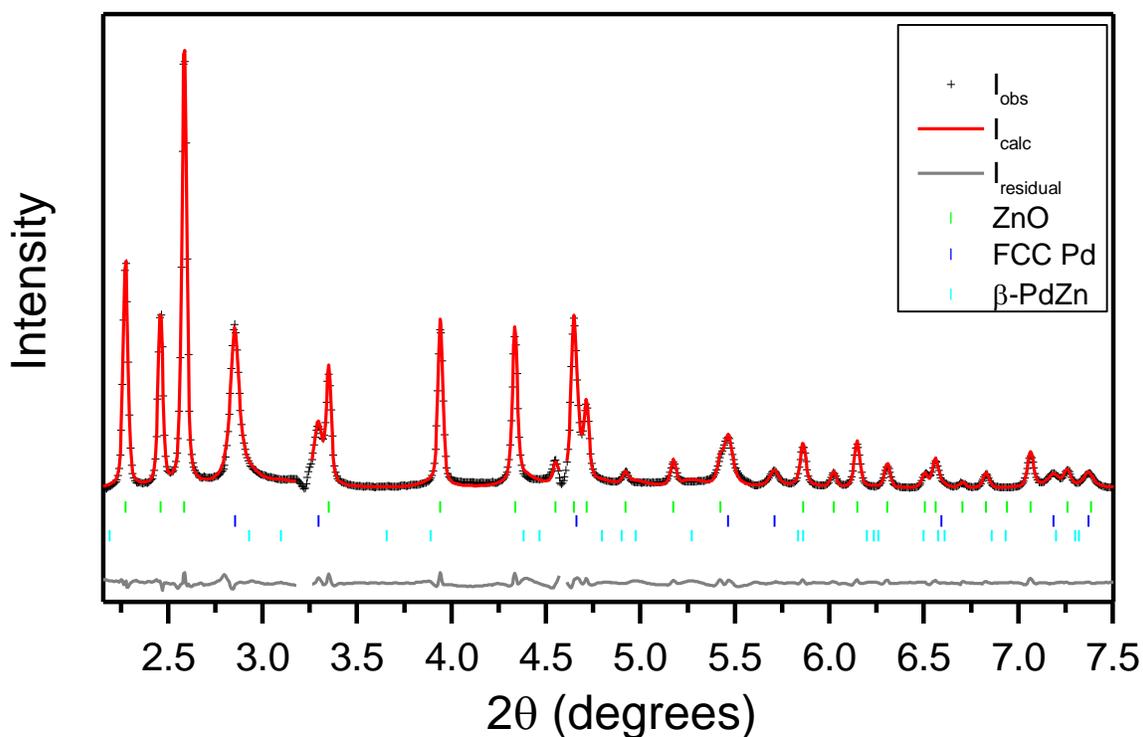


Supplementary Figure S5. *R*-space fitting results of the Fourier-transform (FT) of the k^2 -weighted EXAFS spectrum at the Pd K-edge of PdZn/Al₂O₃ at room temperature in He after reduction in H₂ at 425 °C. The solid black line represents the magnitude of the FT, the dotted black line the imaginary part of the FT while the red solid and dotted lines are the fits of the magnitude and the imaginary part of the FT, respectively. ($2.8 \text{ \AA}^{-1} < k < 12.9 \text{ \AA}^{-1}$, $1.8 \text{ \AA} < R < 3.2 \text{ \AA}$). Residual = 4.4 %.

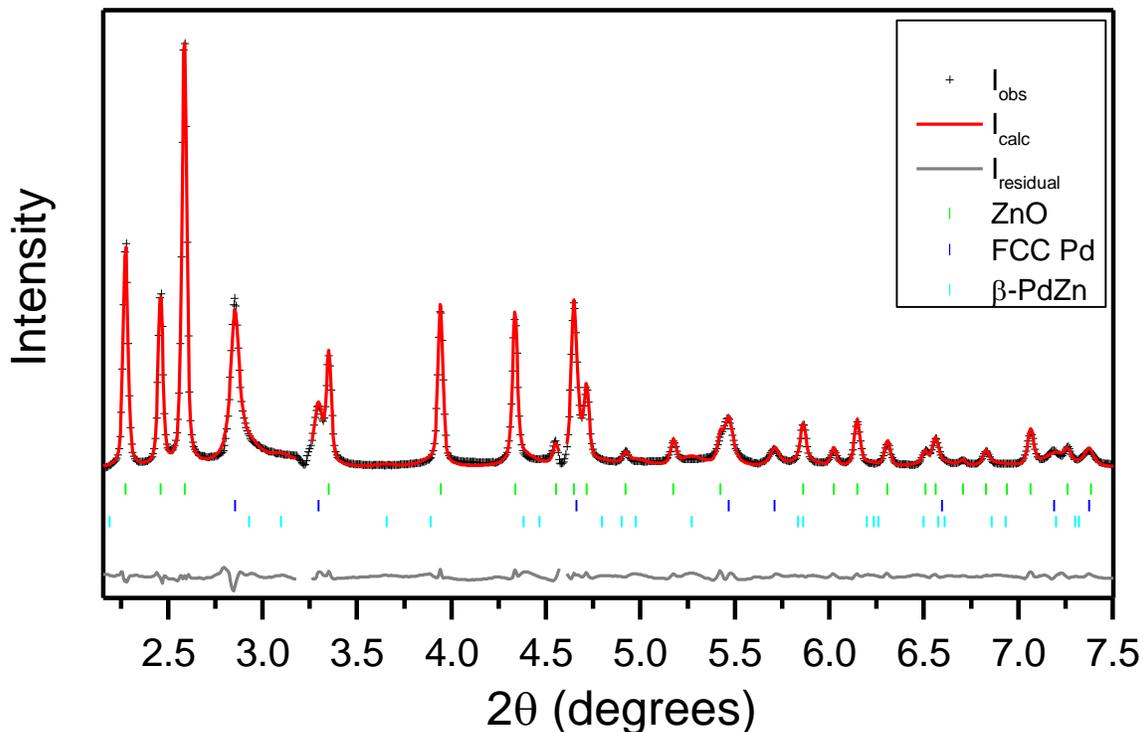


Supplementary Figure S6. *R*-space fitting results of the Fourier-transform (FT) of the k^2 -weighted EXAFS spectrum at the Pd K-edge of PdZn/Al₂O₃ at room temperature in He after reduction in H₂ at 500 °C. The solid black line represents the magnitude of the FT, the dotted black line the imaginary part of the FT while the red solid and dotted lines are the fits of the magnitude and the imaginary part of the FT, respectively. ($2.8 \text{ \AA}^{-1} < k < 12.9 \text{ \AA}^{-1}$, $1.8 \text{ \AA} < R < 3.2 \text{ \AA}$). Residual = 2.6 %.

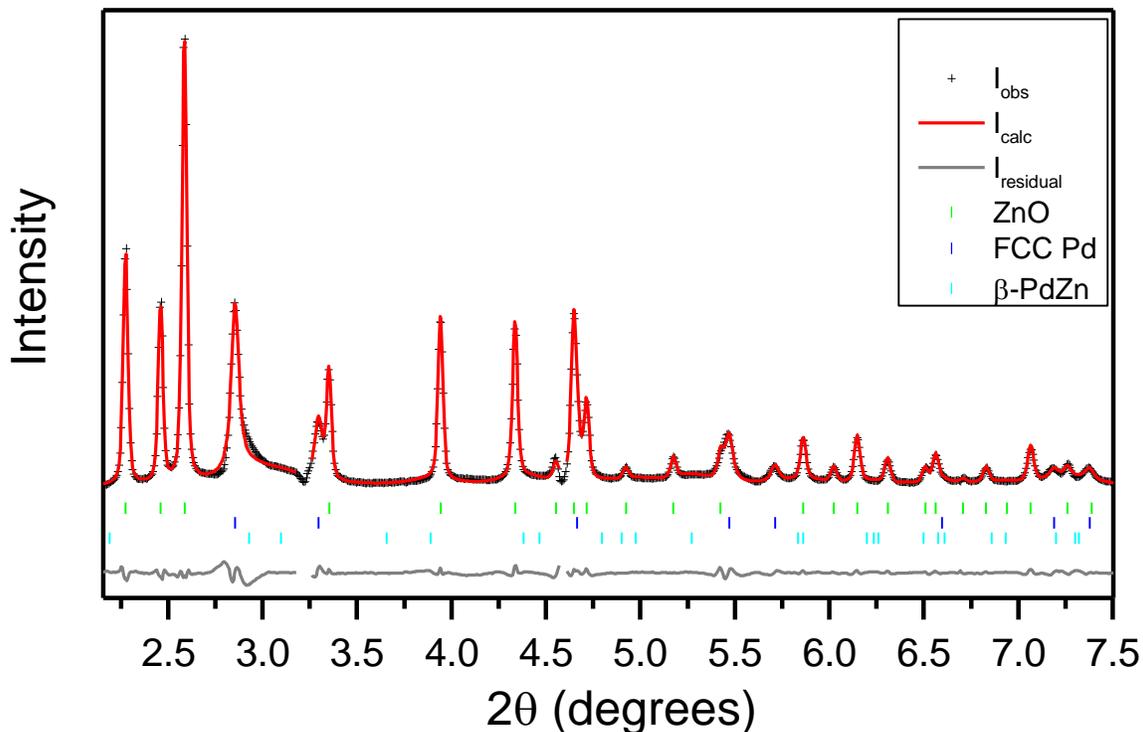
2. XRD



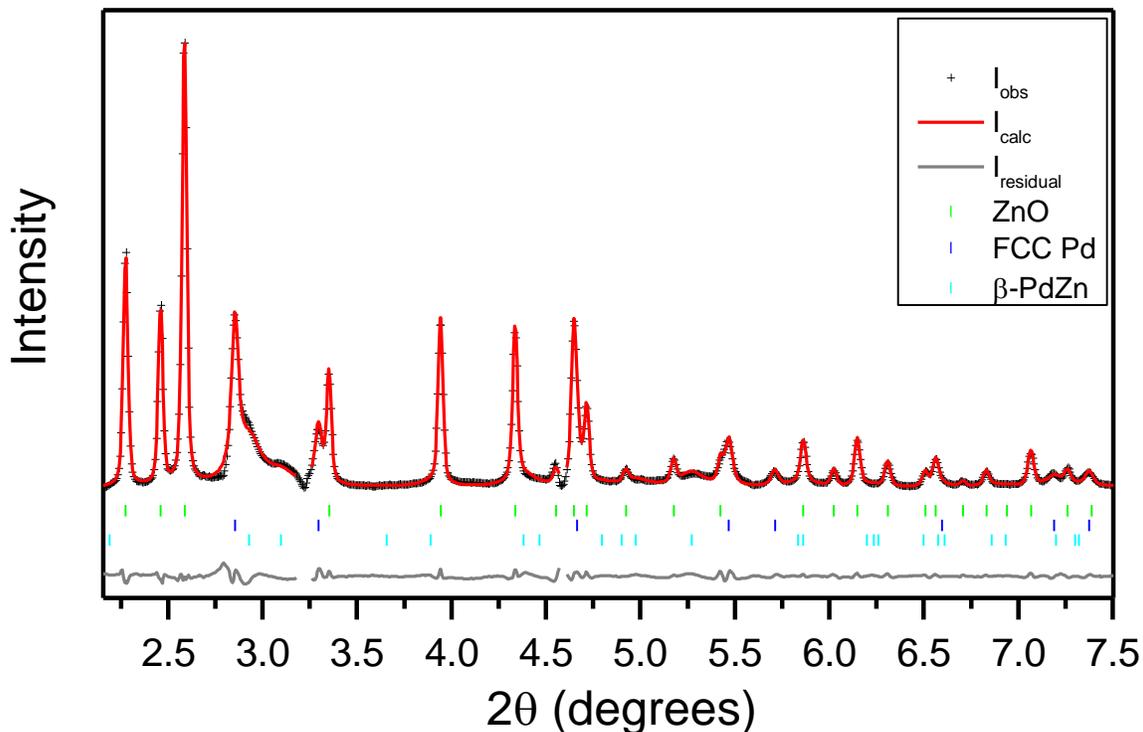
Supplementary Figure S7. Le Bail refinement of *in situ* synchrotron XRD data of PdZn/Al₂O₃ in He at 40 °C after reduction in H₂ at 230 °C after subtraction of the contribution due to the Al₂O₃ support. Black crosses represent observed data (I_{obs}) and the red solid line is the calculated pattern (I_{calc}); the solid grey line is the residual ($I_{\text{residual}} = I_{\text{calc}} - I_{\text{obs}}$) on the same scale, but offset for clarity. Gaps in I_{calc} and I_{residual} are regions which were excluded from the refinement due to significant artifacts from the support subtraction. Tick marks below the diffraction patterns are the refined positions of the reflections for each phase; ZnO (wurtzite) (top, green), FCC Pd (middle, blue) and β_1 -PdZn (bottom, cyan).



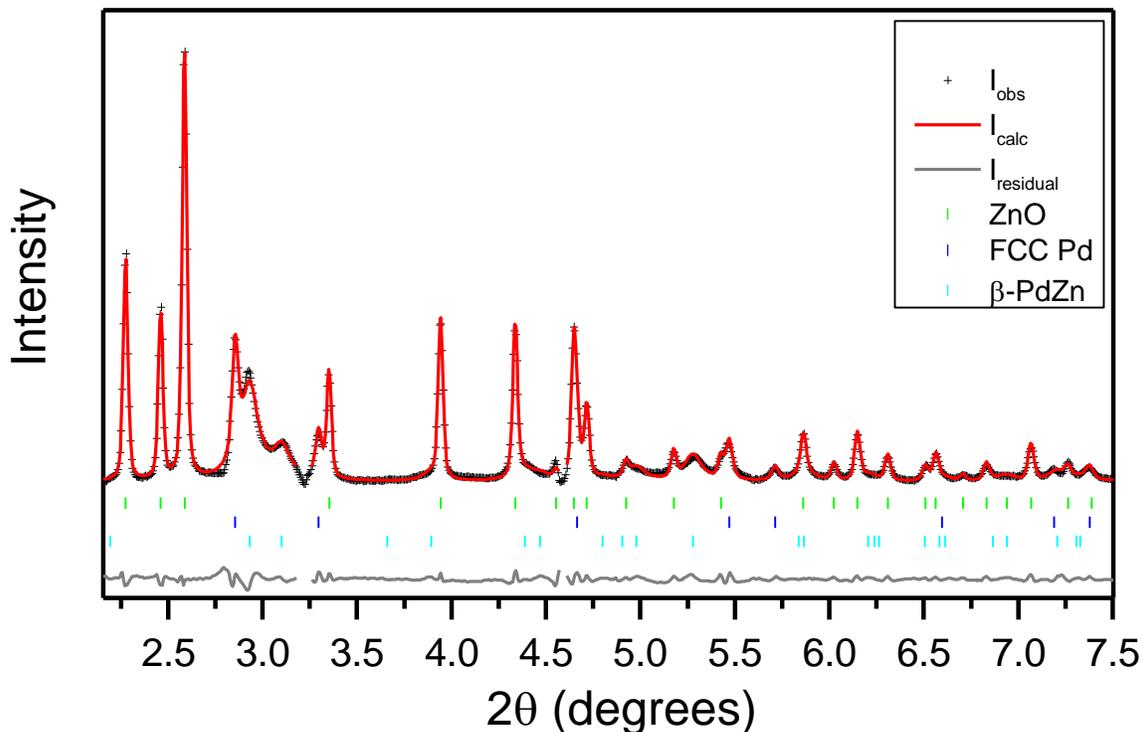
Supplementary Figure S8. Le Bail refinement of *in situ* synchrotron XRD data of PdZn/Al₂O₃ in He at 40 °C after reduction in H₂ at 325 °C after subtraction of the contribution due to the Al₂O₃ support. Black crosses represent observed data (I_{obs}) and the red solid line is the calculated pattern (I_{calc}); the solid grey line is the residual ($I_{\text{residual}} = I_{\text{calc}} - I_{\text{obs}}$) on the same scale, but offset for clarity. Gaps in I_{calc} and I_{residual} are regions which were excluded from the refinement due to significant artifacts from the support subtraction. Tick marks below the diffraction patterns are the refined positions of the reflections for each phase; ZnO (wurtzite) (top, green), FCC Pd (middle, blue) and β_1 -PdZn (bottom, cyan).



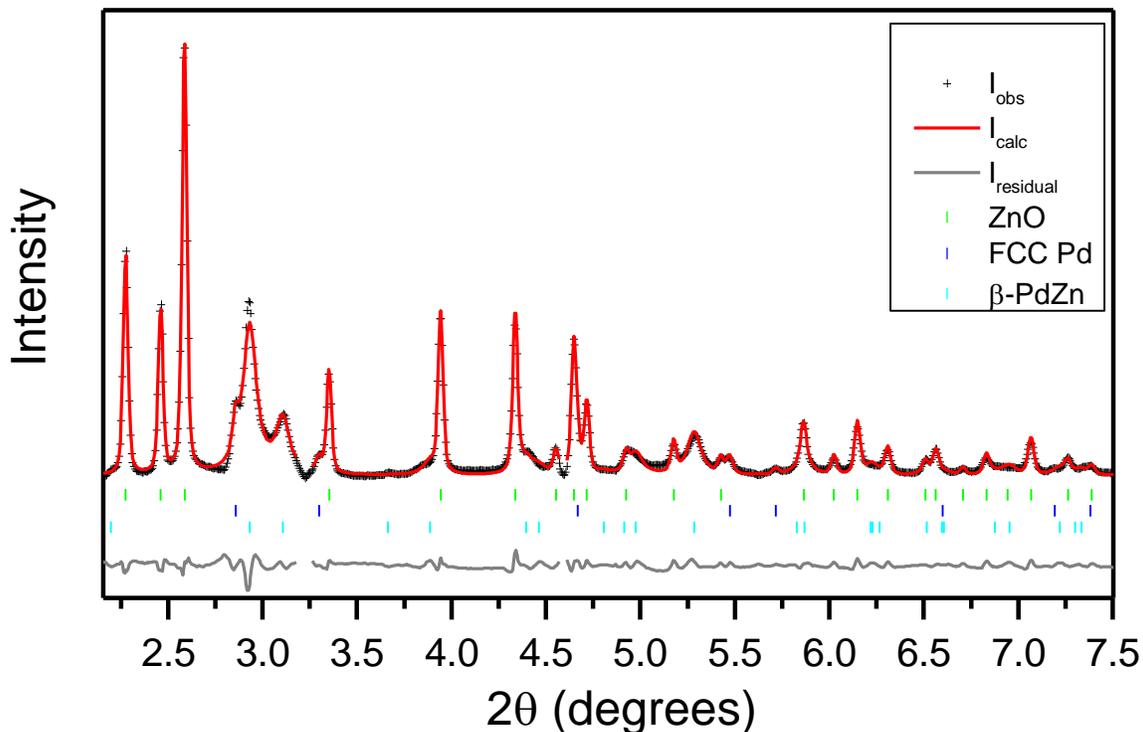
Supplementary Figure S9. Le Bail refinement of *in situ* synchrotron XRD data of PdZn/Al₂O₃ in He at 40 °C after reduction in H₂ at 350 °C after subtraction of the contribution due to the Al₂O₃ support. Black crosses represent observed data (I_{obs}) and the red solid line is the calculated pattern (I_{calc}); the solid grey line is the residual ($I_{\text{residual}} = I_{\text{calc}} - I_{\text{obs}}$) on the same scale, but offset for clarity. Gaps in I_{calc} and I_{residual} are regions which were excluded from the refinement due to significant artifacts from the support subtraction. Tick marks below the diffraction patterns are the refined positions of the reflections for each phase; ZnO (wurtzite) (top, green), FCC Pd (middle, blue) and β_1 -PdZn (bottom, cyan).



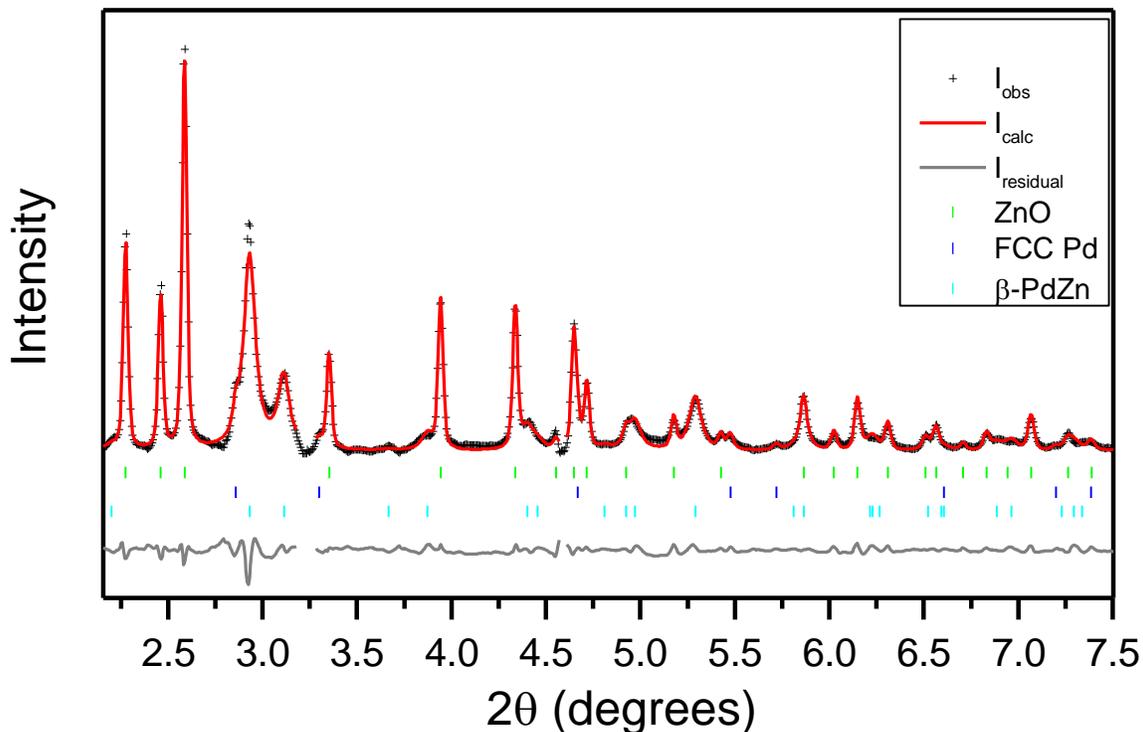
Supplementary Figure S10. Le Bail refinement of *in situ* synchrotron XRD data of PdZn/Al₂O₃ in He at 40 °C after reduction in H₂ at 375 °C after subtraction of the contribution due to the Al₂O₃ support. Black crosses represent observed data (I_{obs}) and the red solid line is the calculated pattern (I_{calc}); the solid grey line is the residual ($I_{\text{residual}} = I_{\text{calc}} - I_{\text{obs}}$) on the same scale, but offset for clarity. Gaps in I_{calc} and I_{residual} are regions which were excluded from the refinement due to significant artifacts from the support subtraction. Tick marks below the diffraction patterns are the refined positions of the reflections for each phase; ZnO (wurtzite) (top, green), FCC Pd (middle, blue) and β_1 -PdZn (bottom, cyan).



Supplementary Figure S11. Le Bail refinement of *in situ* synchrotron XRD data of PdZn/Al₂O₃ in He at 40 °C after reduction in H₂ at 425 °C after subtraction of the contribution due to the Al₂O₃ support. Black crosses represent observed data (I_{obs}) and the red solid line is the calculated pattern (I_{calc}); the solid grey line is the residual ($I_{residual} = I_{calc} - I_{obs}$) on the same scale, but offset for clarity. Gaps in I_{calc} and $I_{residual}$ are regions which were excluded from the refinement due to significant artifacts from the support subtraction. Tick marks below the diffraction patterns are the refined positions of the reflections for each phase; ZnO (wurtzite) (top, green), FCC Pd (middle, blue) and β_1 -PdZn (bottom, cyan).



Supplementary Figure S12. Le Bail refinement of *in situ* synchrotron XRD data of PdZn/Al₂O₃ in He at 40 °C after reduction in H₂ at 450 °C after subtraction of the contribution due to the Al₂O₃ support. Black crosses represent observed data (I_{obs}) and the red solid line is the calculated pattern (I_{calc}); the solid grey line is the residual ($I_{\text{residual}} = I_{\text{calc}} - I_{\text{obs}}$) on the same scale, but offset for clarity. Gaps in I_{calc} and I_{residual} are regions which were excluded from the refinement due to significant artifacts from the support subtraction. Tick marks below the diffraction patterns are the refined positions of the reflections for each phase; ZnO (wurtzite) (top, green), FCC Pd (middle, blue) and β_1 -PdZn (bottom, cyan).



Supplementary Figure S13. Le Bail refinement of *in situ* synchrotron XRD data of PdZn/Al₂O₃ in He at 40 °C after reduction in H₂ at 500 °C after subtraction of the contribution due to the Al₂O₃ support. Black crosses represent observed data (I_{obs}) and the red solid line is the calculated pattern (I_{calc}); the solid grey line is the residual ($I_{\text{residual}} = I_{\text{calc}} - I_{\text{obs}}$) on the same scale, but offset for clarity. Gaps in I_{calc} and I_{residual} are regions which were excluded from the refinement due to significant artifacts from the support subtraction. Tick marks below the diffraction patterns are the refined positions of the reflections for each phase; ZnO (wurtzite) (top, green), FCC Pd (middle, blue) and β_1 -PdZn (bottom, cyan).