



Intermetallic Nanoparticles

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Visualizing Formation of Intermetallic PdZn in a Palladium/Zinc Oxide Catalyst: Interfacial Fertilization by PdH_x

Yiming Niu⁺, Xi Liu⁺, Yongzhao Wang, Song Zhou, Zhengang Lv, Liyun Zhang, Wen Shi, Yongwang Li, Wei Zhang,* Dang Sheng Su,* and Bingsen Zhang*

Abstract: Controllable synthesis of well-defined supported intermetallic catalysts is desirable because of their unique properties in physical chemistry. To accurately pinpoint the evolution of such materials at an atomic-scale, especially clarification of the initial state under a particular chemical environment, will facilitate rational design and optimal synthesis of such catalysts. The dynamic formation of a ZnOsupported PdZn catalyst is presented, whereby detailed analyses of in situ transmission electron microscopy, electron energy-loss spectroscopy, and in situ X-ray diffraction are combined to form a nanoscale understanding of PdZn phase transitions under realistic catalytic conditions. Remarkably, introduction of atoms (H and Zn in sequence) into the Pd matrix was initially observed. The resultant PdH_x is an intermediate phase in the intermetallic formation process. The evolution of PdH_x in the PdZn catalyst initializes at the PdH_{χ}/ZnO interfaces, and proceeds along the PdH_{χ} (111) direction.

ntermetallic materials with well-defined structures and tunable compositions afford unique catalytic properties, and are thus highly desirable for heterogeneous catalysis.^[1] For instance, L1₀-type PdZn with lattice parameters of a = b =4.0915 Å and c = 3.3426 Å in space group P4/mmm, is regarded as a promising catalyst for methanol steam reforming (MSR), the water–gas shift reaction (WGS), alkane dehydrogenation, and selective hydrogenation reactions.^[2–7] The excellent catalytic performance of intermetallic PdZn is derived from reduction of the ZnO-supported Pd, which give rise to unique electronic properties and structural stability. However, despite enormous efforts to acquire supported PdZn intermetallic catalysts in a controllable fashion, there is a lack of convincing evidence about the key elementary steps associated with the intermetallic process; thus, mechanistic clarification and rational design of catalysts is hindered. Firstly, PdZn formation was investigated under ultrahighvacuum conditions, based on some model systems, in which the interaction between deposited Zn layers and the singlecrystal Pd surface was studied at elevated temperatures in the absence of a gaseous atmosphere.^[8-10] According to the (sub)surface structural evolution of PdZn, determined by surface-sensitive techniques, it was determined that the deposited Zn layer starts to diffuse into Pd (111) at about 350 K, followed by formation of a 1:1 PdZn multilayer intermetallic at about 500 K because of further diffusion of Zn into the Pd bulk. Similar processes also took place on a Pd (110) surface, but at higher temperatures.

However, considering the very different chemical environment and material gap between the model and real systems, a study on technologically applied PdZn supported catalyst under working conditions is necessary to gain insightful understanding regarding the real intermetallic process. Based on in situ X-ray absorption spectroscopy (XAS) investigations, it was reported that the intermetallic process was initiated from the surface of Pd nanoparticles (NPs) and continued inwards during MSR.^[11] But details about the microstructural evolution of the PdZn intermetallic at nano or atomic scales remains challenging. Furthermore, the role of H₂ in formation of the bimetallic alloy has not been rationalized. Visualization of the formation of the active species with high spatial resolutions will contribute to fundamental studies as well as practical applications. To date, rapid development of transmission electron microscopy (TEM) and complementary techniques, such as in situ gas-

[*]	 Y. Niu,^[+] Y. Wang, Dr. L. Zhang, W. Shi, Prof. D. S. Su, Prof. B. Zhang Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences Shenyang 110016 (China) E-mail: dangsheng@fhi-berlin.mpg.de bszhang@imr.ac.cn Y. Niu,^[+] Y. Wang, W. Shi School of Materials Science and Engineering University of Science and Technology of China Shenyang 110016 (China) 		S. Zhou School of Chemistry and Chemical Engineering University of Chinese Academy of Sciences Beijing, 100049 (China) Prof. W. Zhang School of Materials Science & Engineering, Electron Microscopy Center, and Key Laboratory of Automobile Materials MOE Jilin University Changchun 130012 (China) E-mail: weizhang@ilu.edu.cn
	Dr. X. Liu, ^[+] S. Zhou, Dr. Z. Lv, Prof. Y. Li State Key Laboratory of Coal Conversion, Institute of Coal Chemistry Chinese Academy of Sciences Taiyuan 030001 (China) and SynCat@Beijing, Synfuels China Technology Co., Ltd. Beijing 101407 (China)	[⁺] [·]	These authors contributed equally to this work. Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/anie.201812292.

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heating and electron energy-loss spectroscopy (EELS), facilitate direct detection of solid-gas interactions at nanoscales, and some promising in situ TEM results regarding Fischer-Tropsch synthesis, the low-temperature WGS reaction, and other catalytic process, have been reported.^[12-21]

To the best of our knowledge, herein we present the first atomic-scale visualization of a complete phase transition from Pd/PdH_x to PdZn on a ZnO support under H₂ atmosphere, which has been systematically analyzed by integrating in situ TEM, EELS, and X-ray diffraction (XRD) data. Significantly, the interfacial PdH_x species were generated quickly under an H₂ atmosphere and at elevated temperature these species were identified as key intermediates in the following transformation. Subsequently, a consecutive phase transition started at the PdH_x/ZnO interface at higher temperature, then proceeded along the PdH_x (111) direction until the whole NP was converted to the PdZn structure. The acetylene partial hydrogenation reaction was selected as a fingerprint reaction to examine the catalytic activity of the formed PdZn in comparison to monometallic Pd catalysts.

ZnO nanorods with an approximate 15.6 nm diameter prepared by a surfactant-assisted alcohol thermal method^[22] were chosen as supports to uniformly anchor Pd NPs with controllable size, while serving as a potential Zn source. The surfactant on ZnO nanorods was removed by calcination at 400 °C in air for 2 h. After calcination, the ZnO nanorods (Supporting Information, Figure S1) remained as a wurtzite phase (Figure S2). Subsequently, Pd was decorated on the calcined ZnO support through a wet impregnation method. A subsequent calcination process in static air at 400°C was performed to produce oxidized Pd NPs with a uniform size distribution. XRD results (red curve in Figure S3) confirm that Pd NPs have been completely oxidized into PdO NPs (JCPDS 85-0624). PdO NPs are uniformly dispersed upon well-preserved ZnO nanorods (Figure S4a) and the size distribution of PdO NPs ranges from 2.0 to 8.0 nm with an average size of approximately 4.1 nm (Figure S4a inset).

Temperature-programmed reduction mass spectrometry (TPR-MS) was conducted to determine the phase-transition temperatures and the variation of gas-phase composition during the PdO/ZnO reduction process. The mass signals at m/e = 2 and 18 representing H₂ and H₂O were detected and normalized as a function of time (Figure S5a), respectively. With increasing temperature, a sharp negative peak associated with the H_2 signal appeared at about 90 °C, concomitant with a corresponding positive peak associated with the H₂O signal at 100°C. At higher temperature, another broad positive peak corresponding to the H₂O signal emerged at 260 °C and ended at 400 °C. Based on additional ex situ XRD results (Figure S3), we conclude that metallic Pd and PdZn were formed consecutively in the two processes, respectively.

In situ XRD experiments were performed to gain insights into the evolution of the crystalline structure under 1 bar of H₂ pressure and at elevated temperature. As shown in Figure 1a, Pd transformed into β -PdH NPs under an H₂ atmosphere at 50°C. As the temperature increased, the β -PdH phase disappeared gradually while the α -PdH remained and finally transformed into a PdZn phase at 340 °C. The crystal structure of ZnO was well-preserved



Figure 1. a) In situ XRD patterns of a Pd/ZnO sample under H_2 atmosphere during heating treatment across a temperature range. b) Selected in situ XRD patterns related with the evolution of PdH_x species at elevated temperatures ranging from 50°C to 130°C. c) Four kinds of distinct Pd-based species during the phase-transition process. d) Selected in situ XRD patterns related with the phase-transition process from PdH, to PdZn above 260°C.

during the process. The hydrogen content in PdH was determined from peak positions through Vegard's law.^[23] It was observed that there were two PdH peaks at 50°C, indicating that there were two phase structures of PdH NPs assigned to $PdH_{0.9}$ (45.3°) and $PdH_{0.6}$ (46.1°). When the temperature was increased, the peak of PdH_{0.9} gradually weakened and disappeared at 130 °C, but the peak associated with PdH_{0.6} shifted to PdH_{0.1} (46.7°) and remained until 260 °C (Figure 1b). At about 270°C, the PdH_{0.1} phase started to transform into PdZn and the process completed at 340°C (Figure 1 d). The in situ XRD experiments explicitly revealed the structural evolution and identified the PdH_x phase acting as an intermediate phase for the formation of intermetallic PdZn (Figure 1c).

To record the structural evolution and the hydrogen distribution in Pd NPs during the intermetallic process at nanoscales, in situ TEM experiments were carried out using a commercial gas-heating holder with a homemade gas supply system (Supporting Information) under various conditions. According to the aforementioned in situ XRD experiments and previous investigations, the PdH structure exhibits a larger lattice parameter (a = b = c = 4.035 Å) compared to Pd (3.891 Å). Thus, Pd NPs kept in H_2/He (10 vol %) and pure He atmospheres at 100°C were studied using in situ TEM. High-resolution (HR)TEM images of the Pd/ZnO sample under these two atmospheres (Figures 2a,b) were compared in terms of lattice constants. Therein, Pd (111) was chosen as a typical plane for studying lattice-constant differences. The average d-spacing of the NP was measured as 2.24 Å under a He atmosphere (Figure 2c), which was indexed as the Pd (111) plane. After introducing a H₂ atmosphere to replace pure He, the average d-spacing of the identical NP at the same temperature expanded to 2.30 Å (Figure 2c). The induced variation is attributed to the incorporation of H into the Pd NPs. Considering that the atomic ratio of palladium

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Figure 2. HRTEM images of the same Pd NP on ZnO in a) He and b) H₂/He (10 vol%), which has been turned into PdH_x; both images were taken from the [011] zone axis. c) Corresponding lattice distance measurements of the (111) plane based on the HRTEM images shown in (a) and (b), respectively. d) Superimposed FFTs corresponding to Pd and PdH_x in (a) and (b); the reciprocal spacings of Pd(11-1) (green circles) and PdH_x(11-1) planes (red circles). e) Atomic diagrams describing the interplanar spacing of (111) planes in Pd (top) and PdH (bottom); Pd (dark green balls) and H (white balls) atoms. Working conditions: 700 mbar, flow rate 1.5 mLmin⁻¹, 100°C, dose rate 900 e Å⁻² s⁻¹.

hydride is elusive because of its close relevance to H₂ pressure, the measured value is slightly less than that of PdH (111) (2.33 Å, JCPDS 65-0557). The generated palladium hydride is denoted as PdH_x (0 < x < 1). Such experimental results agree with the theoretical interplanar spacing of Pd and PdH (111) planes described by atomic diagrams (Figure 2e). The superimposed local fast Fourier transforms (FFTs) correlate with the HRTEM images (Figure 2d), and the larger reciprocal spacings of Pd (11-1) planes (green circle in Figure 2d) indicates a smaller d-spacing, and vice versa. Selected area electron diffraction (SAED) was also conducted for further confirmation (Figure S6), and HRTEM images and superimposed FFTs (Figure S7) were included to obtain an accurate comparison of the variations in the lattice parameter. To get a broader picture of the structural evolution, 32 sets of FFT spots were examined from the Pd (111) plane of different Pd NPs under different atmospheres (Figures S8 and S9). Similar to Figure 2d, the smaller

reciprocal spacings of PdH_x (111) planes (red circle in Figure S7) for NPs under H_2 atmosphere verify expansion of the lattice parameter. These results confirm that the PdH_x NPs were formed under a H_2/He (10 vol %) atmosphere at 100 °C and are consistent with the in situ XRD results.

Previous studies have demonstrated that interfacial metallic atoms exhibit different properties compared with those away from the interface.^[24-26] In this case, two kinds of Pd hydride species (for example, PdH_{0.9} and PdH_{0.6}) appeared during in situ XRD experiments. Considering the uniform size distribution of Pd NPs, it is reasonable to assume that H may display an inhomogeneous distribution in Pd NPs supported on ZnO and the interfacial Pd may have a stronger capability for binding with H. To verify the hypothesis, the formed hydride was analyzed using EELS to obtain spectroscopic evidence (Figure 3; Figure S10). Previous investigations have demonstrated that Pd exhibits a red shift from approximately 7 to 5 eV in its plasmon resonance after hydrogen absorption.^[27-29] Thus, we used the peak at about 5 eV as the fingerprint assigned to PdH, formation in the following EELS measurements, whereas quantitatively identifying the hydrogen content in Pd NPs under H₂ atmosphere is still challenging in a real system. EEL spectra of a hydride particle were acquired at 50°C under He atmosphere, which had formed at 100 °C under H₂ atmosphere. The EELS signal from 2-50 eV was recorded across the Pd NP to the ZnO support, as shown in Figure 3a. No PdH_x signals were observed in the area (curves a and b in Figure 3b) away from the interface, between Pd NP and ZnO. On approaching



Figure 3. a) High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of the PdH_x/ZnO sample at 50 °C under He atmosphere after in situ reduction. b) EEL spectra of different regions on the PdH_x/ZnO sample as marked in (a). c) HRTEM image of the PdZn/ZnO sample at 300 °C under an H₂ atmosphere; the Figure inset is the corresponding FFT. d) Zn and Pd L-edge EEL spectra of the area of interest in Figure S10b.

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the interface area, the PdH_x peak emerged at approximately 5 eV and gradually enhanced (Figure 3b; Figure S10a). For the ZnO supports, no peaks were found in the EELS results (curves f and g in Figure 3b). Combined with the aforementioned analysis, it is concluded that Pd atoms in the interface area with ZnO have a stronger capability for binding with hydrogen to form the PdH_x structure. The PdZn structure was acquired after 300 °C reduction and corroborated by HRTEM and EELS (Figures 3 c,d).

The phase transition from PdH_r to PdZn was investigated using HRTEM. According to the aforementioned XRD results, a Pd NP in an α -PdH state at elevated temperature was chosen as the starting material. When the temperature increased to 300 °C, the PdZn phase appeared at the NP/ZnO support interface, as indicated by the lattice d-spacing ascribed to the PdZn composite and a lattice mismatch that emerged at the PdH_x/PdZn interface. Co-existence of PdH_x (11-1) (red lines) and PdZn (1-1-1) (green lines) planes was evident in the HRTEM images (Figures 4 a,b), which was also demonstrated in the corresponding FFTs (Figures 4c,d). The corresponding inverse FFTs (IFFTs), correlated with the spots in Figures 4 c,d, were conducted (Figures 4 e,f) to obtain the distribution of PdH_x and PdZn phases at 20 and 40 minutes, respectively. For the phase transition after 20 minutes, the PdZn structure (green dots) occupied a relatively small area at the edge of the PdH_x structure (red dots). For phase transition after 40 minutes, the green area invaded the red area, and the PdH_x structure was transformed into the PdZn structure. The expanding green area corresponds to the gradual growth of the PdZn phase at the expense of the PdH_r phase. The shared lattice plane (white lines in the HRTEM images, Figures 4 e,f) of PdZn and PdH_x phases were ascribed to PdH_x (11-1), indicating that the growth direction of PdZn was parallel to PdH_x (111), as demonstrated by the atomic model in Figure S12. This is consistent with previous studies, which indicate that Zn atoms diffuse more readily into Pd for the formation of the PdZn structure on the Pd (111) plane than on the Pd (110) plane.^[9,10,30] Therefore, the PdH_v structure was initially generated under H₂ atmosphere and acted as an intermediate during the phase transition. Zn atoms that are reduced from ZnO by interstitial H in PdH_v preferentially diffuse into PdH_x NPs along the PdH_x (111) direction to form the PdZn phase as H atoms are removed in the form of water. The process is illustrated in Figure 5.

Although the electron dose was controlled to relatively low levels (below 900 $e Å^{-2}s^{-1}$) for in situ HRTEM investigation, electron-beam irradiation was nevertheless inevitable and likely accounts for the few amorphous areas that emerged on the Pd NP surface after long periods of observation by TEM, similar to previous ex situ TEM investigations.^[31] Thus, an ex situ TEM image of Pd/ZnO was acquired at the initialized state and at the end of this process (Figure S15). The Pd and PdZn NPs are homogenously dispersed in ZnO nanorods (Figures S15a,b). Particle size distribution (PSD) histograms (Figures S15a,b insets) confirm the uniform size distribution of supported Pd and PdZn NPs. The microstructural features of Pd/ZnO and PdZn/ZnO catalysts exhibited an evolution from face-centered cubic (fcc) Pd to PdZn NPs with a tetragonal structure, according to





Figure 4. HRTEM images of an identical Pd/ZnO sample at 300 °C maintained under H₂ atmosphere for a) 20 and b) 40 minutes. c,d) The corresponding local FFTs are displayed; crystal planes assigned to PdH_x (red circles), the crystal plane indexed to PdZn (green circles). e,f) Superimposed IFFTs formed using spots in the corresponding FFT images shown in (c) and (d); PdH_x (red), PdZn (green). White lines indicate the PdH_x/PdZn interface, which is confirmed to be PdH_x (11-1) planes. White arrows show the growth direction of PdZn, which is perpendicular to the PdH_x (11-1) planes.

HRTEM images (Figures S15c,d), in good agreement with the in situ TEM (Figures 2–4) and XRD (Figure 1; Figure S3) analysis. Thus, the possibility of phase transition induced by electron-beam irradiation is excluded. The catalytic performance of the PdZn structure was also tested and compared with mono Pd catalysts (Pd/Al₂O₃; Figure S16) for the partial hydrogenation of acetylene. The PdZn catalyst exhibited superior selectivity and stability compared to Pd/Al₂O₃ catalyst (Figure S17), which confirmed the efficacy of the preparative method as a basis for the in situ TEM study.

In summary, our work demonstrates the direct visualization of the phase transition from Pd to PdZn on a ZnO nanorod support at atomic scale under real chemical environments. The in situ XRD results provide structural information for the transition from Pd to PdH_x and PdZn, in sequence, under H₂ atmosphere. Combined with H₂-TPR and in situ TEM studies, H atoms diffuse into the Pd NP at a relatively low temperature, leading to the formation of PdH_x phases.

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Figure 5. A diagram depicting the proposed phase-transition process from Pd to PdZn.

The microstructural evolution as a function of temperature, which was monitored by in situ TEM, unveils the sequence of the phase transitions from Pd to PdZn via the intermediate PdH_x under H₂ atmosphere. The Pd NPs exist in PdH_x forms under H₂ atmosphere below 260 °C. The alloying process started at the interface between PdH_x NPs and ZnO supports in the PdH_x (111) direction. Our results convincingly depict the transformation from Pd/ZnO to intermetallic PdZn, which displayed unique catalytic performance for selective hydrogenation of acetylene, at atomic scale under real chemical environments. This work not only discloses detailed microstructural information in reference to the catalyst activation, but also sheds light on the rational design and optimum synthesis of intermetallic composite catalysts.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: EELS \cdot heterogeneous catalysis \cdot in situ TEM \cdot PdH_x \cdot PdZn intermetallics

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Visualizing Formation of Intermetallic PdZn in a Palladium/Zinc Oxide Catalyst: Interfacial Fertilization by PdH_x



A palladium catalyst supported on ZnO is monitored in situ and in chemical environments relevant to catalysis. Structural evolution of PdZn intermetallic metal nanoparticles (NPs), visualized at an atomic scale, reveals the evolution of a PdH_x intermediary species at the interface between PdH_x and the ZnO support.

