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# Hydrogen reduction and metal-support interaction in a metastable metal-oxide system: Pd on rhombohedral $In_2O_3$

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ABSTRACT

Structural and chemical consequences of reactive metal-support interaction (RMSI) effects occurring under hydrogen reduction in a metastable metal-oxide system have been exemplified for small PdO particles loaded onto rhombohedral $In_2O_3$ (PdO/rh-$In_2O_3$) using synchrotron-based *in situ* X-ray diffraction experiments at temperatures up to 500 °C. rh-$In_2O_3$ is a meta-stable $In_2O_3$ polymorph that is prone to gas-phase dependent phase transformation to cubic $In_2O_3$ (c-$In_2O_3$). Cross-influence of metal-support interaction and phase transformation can therefore be expected in similar temperature regimes. To separate both effects, comparable experiments have also been conducted on pure rh-$In_2O_3$. Phase transformation of pure rh-$In_2O_3$ to cubic $In_2O_3$ in hydrogen occurs between 415 °C and 450 °C. On Pd/rh-$In_2O_3$, a sequence of PdO reduction to Pd metal, followed by $PdH_{0.706}$ hydride formation and subsequently, InPd and $In_3Pd_2$ intermetallic compound formation have been observed between 30 °C and 500 °C. After the intermetallic compound formation is finished at around 400 °C, the phase transformation to c-$In_2O_3$ sets in at exactly the same temperature as on pure rh-$In_2O_3$ and extends over the same temperature range. This proves that the phase transformation of rh-$In_2O_3$ to c-$In_2O_3$ is not influenced by the reduction and the intermetallic compound formation. In contrast to Pd on c-$In_2O_3$, In-Pd compound formation from rh-$In_2O_3$ occurs at much lower temperatures (230 °C *vs.* 300 °C), despite finally approaching the same compound stoichiometries (InPd and $In_3Pd_2$). This points to a high structural stability of reduced rh-$In_2O_3$/stability of oxygen vacancies (compared to c-$In_2O_3$) as well as to facilitated diffusion of reduced In(-O) species at low temperatures.

## 1. Introduction

Reactive metal-support interaction (RMSI), *i.e.* the formation of intermetallic compounds starting from oxide-supported small (noble) metal particles by pre-reduction in hydrogen, is an increasingly important topic in catalytic research [1]. To date mostly viewed as a more or less unwanted by-product of the so-called "strong metal-support interaction" (the latter usually leading to diminished catalytic activity through structural and electronic alterations) [2], the irreversible formation of such intermetallic compounds by RMSI has recently gained increased attention due primarily to two factors: increased knowledge of the catalytic properties and use of single-phase intermetallic compounds [3–7], and on the other hand introduction of bifunctional synergisms of oxide-supported intermetallic compounds [8–11]. The latter have proven to be a very powerful tool in *e.g.* explaining the high $CO_2$ selectivity of Pd-based intermetallic compounds in methanol steam reforming [8]. For the archetypical ZnPd/ZnO system, a bifunctional share of catalytic duties between ZnPd (activation of methanol) and ZnO (water activation) has been directly proven by various methods both on real and model systems, experimentally as well as theoretically [8,9,12–14]. Pd on cubic $In_2O_3$ (c-$In_2O_3$) is an equally interesting system [15] due to the outstanding high $CO_2$ selectivity of $In_2O_3$ itself [16], the easy reduction of cubic $In_2O_3$ and the easy intermixing and subsequent intermetallic compound formation between In and Pd [15]. Different In-Pd phases, most notably InPd [10,17,18], $In_3Pd_2$ [10,17], $In_7Pd_3$ [19], and $InPd_2$ [20] have been shown to exhibit activity and selectivity in methanol steam reforming, selective semi-hydrogenation of acetylene or $CO_2$ methanation. The role

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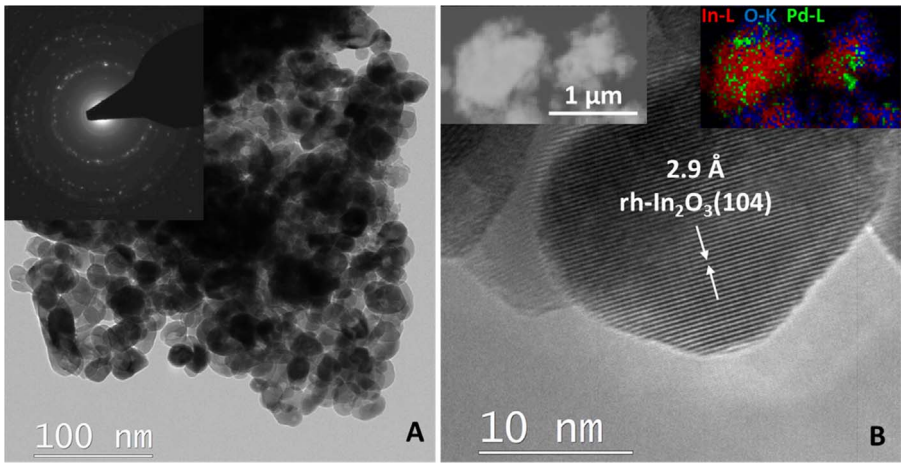


**Fig. 1.** Transmission electron microscopy data of the initial PdO/rh-$In_2O_3$ sample. Panel A: TEM overview image with SAED pattern shown as inset. Panel B: High-resolution image of a single-crystalline rh-$In_2O_3$ grain displaying {104} lattice fringes. HAADF image (left) and corresponding EDX map (right) with overlaid In-L (red), O-K (blue) and Pd-L (green) intensities are shown as insets.

of c-$In_2O_3$ in these processes has been scrutinized in detail [21,22]. To clarify the role of c-$In_2O_3$, its catalytic and physicochemical properties have recently been compared directly to its most prominent metastable modification in the In-O phase diagram, *i.e.* rhombohedral (rh-)$In_2O_3$ [23,24]. Reduction is very much influenced by the eventual gas-phase dependent phase transformation into its thermodynamically stable c-$In_2O_3$ counterpart [23,24]. Due to the application possibilities of rh-$In_2O_3$, also in contact with metals as potential catalyst or sensor material [25–27], the clarification of RMSI in a metal – rh-$In_2O_3$ system is of particular importance. Generally, as the preparation of single intermetallic In-Pd compounds on the respective $In_2O_3$ oxide is a prerequisite for subsequent physico-chemical or catalytic characterization, understanding the elementary steps of reduction affecting both metal and oxide component, is imperative. To connect to the catalytically most interesting system, we will exemplarily highlight this process for small PdO particles in contact with rh-$In_2O_3$. Several specific research questions will be addressed by this approach: (i) is the intermetallic compound formation between In and Pd as a function of reducibility of the oxide comparable between c- and rh-$In_2O_3$, (ii) does the phase transformation influence the intermetallic compound formation and (iii) what are the structural prerequisites (change of lattice parameters of participating phases) for the intermetallic compound formation? We, thus, exemplify a thorough and detailed investigation for such a metal – on – metastable oxide system.

Methodologically, these research questions are addressed by a combination of electron microscopy and most importantly, by synchrotron-based *in situ* X-ray diffraction. Using the latter, the phase evolution and transformations can be directly followed and by Rietveld analysis the structural questions answered properly.

## 2. Experimental

### 2.1. Preparation of materials

rh-$In_2O_3$ has been prepared following a hydrothermal synthesis routine highlighted in detail earlier [28]. For preparation of the PdO/rh-$In_2O_3$ material, a classical wet impregnation routine has been employed. Therefore, a defined amount of rh-$In_2O_3$ was suspended in ≈ 25 mL deionized water. Subsequently, $Pd(NO_3)_2{\cdot}2H_2O$ (Sigma Aldrich) was dissolved in approximately 35 mL of deionized water and the resulting solution added dropwise to the vigorously stirred rh-$In_2O_3$ suspension. The preparation is finished by calcination of the material in air at 300 °C for 30 min, resulting in PdO particles on rh-$In_2O_3$, as evidenced by XRD. Most notably, no cubic $In_2O_3$ has been introduced by the impregnation process, confirming the stability of the initial PdO/rh-$In_2O_3$ material. Rietveld analysis (*cf.* Fig. 2) indicates a phase composition of 95.1(0.8) wt% rh-$In_2O_3$ and 4.9(0.6) wt% PdO.

### 2.2. In situ X-ray diffraction

*In situ* X-ray diffraction (XRD) has been performed at beamline 12.2.2 at the Advanced Light Source using a beam energy of 25 keV for pure rh-$In_2O_3$ and PdO/rh-$In_2O_3$, respectively. The sample holders were quartz capillaries with inner diameters of 700 µm, and the gas injection was accomplished using a 500 µm capillary with cut-open ends [29]. Heating, as well as cooling rates, realized in an low power infrared tube furnace [30], were chosen as 20 K $min^{-1}$ for all experiments. A Perkin Elmer flat panel detector (XRD 1621, with dark image and strain correction) is used to record the XRD patterns every 25 s. Rietveld refinement was performed using the FULLPROF program [31]. The profile function 7 (Thompson-Cox-Hastings pseudo-Voigt convoluted with axial divergence asymmetry function) [32] was used in all refinements. The resolution function of the instruments was determined from the structure refinement of the standard material $LaB_6$.

### 2.3. Transmission electron microscopy

Transmission electron microscopy (TEM) measurements were carried out using two microscopes, namely a ZEISS EM 10C (for overview imaging and selected area electron diffraction, SAED) and a FEI Tecnai F20 S-TWIN analytical (high-resolution) transmission electron microscope (200 kV), equipped with an Apollo XLTW SDD X-ray detector (for collecting energy-dispersive X-ray (EDX) data).

## 3. Results and discussion

The structure and morphology of the initial metastable Pd/rh-$In_2O_3$ material has been investigated by TEM (Fig. 1). As shown in Fig. 1A, the initial PdO/rh-$In_2O_3$ specimen consists of spherical grains of rh-$In_2O_3$ exhibiting typical sizes ranging between 30 and 50 nm. The crystal structure of rh-$In_2O_3$ and PdO in the initial specimen is further corroborated by the SAED pattern shown as inset in Fig. 1A. All reflections can be unequivocally assigned to either the rhombohedral structure of rh-$In_2O_3$ or tetragonal PdO. Due to the strong overlap of reflections corresponding to both phases, the presence of PdO cannot be derived straightforwardly only from electron diffraction. However – apart from the XRD patterns discussed below - the HAADF/EDX experiments confirm the presence of