

**From pure oxides over oxide-supported metal and  
bimetallic particles to mixed oxides: model systems  
for catalytic and structural studies**

**Habilitationsschrift**

zur Erlangung der Lehrbefugnis für das Fach  
Physikalische Chemie



von

Univ. Ass. Dr. rer. nat. Simon Penner

Institut für Physikalische Chemie  
Leopold Franzens Universität Innsbruck  
Innrain 52a

Innsbruck, im Juli 2010

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## Abstract

The present thesis deals with the preparation and structural and catalytic characterization of model systems of three important classes of heterogeneous catalysts. These include pure oxides, oxide-supported bimetallic particles of Pd and Rh and mixed oxides. Structural characterization is based on Analytical High-resolution Electron Microscopy, X-ray diffraction, Atomic Force Microscopy and Low-energy Ion Scattering. Complementary spectroscopic techniques include X-ray Photoelectron Spectroscopy, Thermal Desorption, Raman and in-situ FT-Infrared Spectroscopy and Electric Impedance Spectroscopy. Volumetric Adsorption techniques were employed to quantify the adsorbed molecules. Catalytic testing was performed in methanol steam reforming and CO hydrogenation as test reactions.

Concerning methanol steam reforming, special emphasis was put on the determination of the catalytic contribution of the pure oxides ( $\text{Ga}_2\text{O}_3$ ,  $\text{In}_2\text{O}_3$ ,  $\text{SnO}$ ,  $\text{SnO}_2$  and  $\text{GeO}_2$ ) to the activity and selectivity of the respective oxide-supported Pd-based bimetallic phases and the eventual preparation of single-phase oxide-supported bimetallic particles. For  $\text{In}_2\text{O}_3$ , also the interaction with hydrogen was studied to reveal the oxide's reducibility, the hydrogen bonding and the related defect chemistry and reactivity. These studies were complemented by comparing strong metal-support interaction effects in the oxide-supported Pd metal and bimetallic particles and their influence on catalytic performance. Significant differences in the activity and  $\text{CO}_2$ -selectivity between the studied oxides were observed, ranging from inactive ( $\text{SnO}$ ,  $\text{GeO}_2$ ) over active, but unselective ( $\text{Ga}_2\text{O}_3$ ) to active and selective pure oxide catalysts ( $\text{SnO}_2$ ,  $\text{In}_2\text{O}_3$ ). The surface chemistry of the oxides and, more specifically, the distribution of acidic and basic surface sites, along with their redox properties, are identified to possibly steer the catalytic selectivity. Easily reducible oxides with predominantly basic surface sites tend to favour  $\text{CO}_2$  formation in methanol steam reforming.

Pd particles embedded in a **thin film** of each oxide were observed to undergo transformation to the respective bimetallic state upon annealing in hydrogen at temperatures around 523 K. PdZn,  $\text{Pd}_5\text{Ga}_2$ , PdIn,  $\text{Pd}_2\text{Sn}/\text{PdSn}$  and  $\text{Pd}_2\text{Ge}$  particles were formed on the thin film model catalysts, along with the suppression of Pd-hydride formation or formation of a heavily hydrogen-distorted Pd lattice as observed for Pd on  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ . However, considerable differences regarding structural and thermal stability of the bimetallic phases and particles and the extent of strong metal-support interaction were detected. The exceptional structural and thermal stability of PdZn was ascribed to both an excellent crystallographic match of the structures of Pd metal and PdZn and the high thermodynamic stability of the PdZn phase, resulting in a pronounced "strong particle-stabilization effect". On  $\text{Ga}_2\text{O}_3$ ,  $\text{In}_2\text{O}_3$  and

SnO/SnO<sub>2</sub>, the analogous crystallographic relationships also favour the formation of partially ordered bimetallic phases. On GeO<sub>2</sub>, the missing crystallographic match results in formation of the thermodynamically most stable Pd<sub>2</sub>Ge phase. Bimetallic formation upon reduction in these cases was accompanied by rather substantial particle sintering. Due to the easy reducibility of In<sub>2</sub>O<sub>3</sub>, metal-support interaction was most pronounced on the Pd-In<sub>2</sub>O<sub>3</sub> catalyst, leading to bimetallic formation during catalyst preparation and subsequent bimetallic particle encapsulation by indium oxide species. Pd on Ga<sub>2</sub>O<sub>3</sub> was only affected by such effects at high annealing temperatures ( $T \geq 673$  K), whereas on amorphous GeO<sub>2</sub> and SnO/SnO<sub>2</sub> thin films, Pd was not affected by additional metal-support interaction effects (except of bimetallic formation) under similar experimental conditions.

Correlation of these thin film experiments to the technically more relevant **powder systems** revealed the importance of the area of the metal-oxide interface regarding formation of bimetallic phases. Due to the smaller extent of this interface, the onset temperature of bimetallic formation is shifted to higher temperatures by about 50-100 K. Pd particles supported on In<sub>2</sub>O<sub>3</sub> powder and on different polymorphs of GeO<sub>2</sub> appear to be the exception to the rule. Whereas encapsulation of Pd-In bimetallic particles was observed on the respective Pd-In<sub>2</sub>O<sub>3</sub> powder catalyst, strong metal-support interaction on GeO<sub>2</sub> was observed to strongly depend on the specific polymorph used. On tetragonal GeO<sub>2</sub>, due to its increased reducibility, oxide re-crystallization and encapsulation of metal/bimetallic particles frequently occurs upon annealing in hydrogen. In contrast, on hexagonal GeO<sub>2</sub> no such effects were observed (as on the amorphous film), but a small part of hexagonal GeO<sub>2</sub> was found to be transformed to the tetragonal phase upon annealing at elevated temperatures.

A CO<sub>2</sub>-selective bimetallic state was easily established on the ZnO, Ga<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub>-supported catalysts. In contrast, Pd particles supported on GeO<sub>2</sub> and SnO/SnO<sub>2</sub> never approach such a selective state, despite bimetallic formation at comparable temperatures. On SnO/SnO<sub>2</sub> this was interpreted in terms of the absence of active geometric site ensembles for methanol conversion upon formation of more Sn-enriched bimetallics. Pd<sub>2</sub>Ge on amorphous and hexagonal GeO<sub>2</sub> converts methanol via dehydrogenation to CO and H<sub>2</sub>. Classical metal-support interaction effects were found to account for the missing activity if Pd<sub>2</sub>Ge is supported on tetragonal GeO<sub>2</sub> powder.

Formation of similar bimetallics has been obtained for Pd supported on SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, albeit at higher temperatures ( $T \geq 673$  K), and Rh supported on V<sub>2</sub>O<sub>3</sub>. In the first two cases, hydrogen reduction at low temperatures ( $T \sim 473$  K) yields an amorphous Pd-hydride phase, most likely associated by the formation of a heavily distorted Pd lattice. For Rh on V<sub>2</sub>O<sub>3</sub>,

formation of Rh-V bimetallics causes a considerable loss in CO hydrogenation activity, which is nevertheless accompanied by a selectivity shift towards methane.

Materials chemistry-related work was primarily focussed on the formation of different oxide nano-architectures and, depending on the preparation conditions (substrate temperature, deposition rate, oxygen partial pressure, post-annealing temperature), resulted in nano-spheres ( $\text{Ga}_2\text{O}_3$ ), nano-pyramids ( $\text{In}_2\text{O}_3$ ), plates and needles ( $\text{V}_2\text{O}_5$ ) and dendrites (co-deposited  $\text{Ga}_2\text{O}_3$ - $\text{WO}_3$ ), also suitable as nanostructured thin film model systems for heterogeneous catalysts, as proven in this work. Formation and transformation of a range of different oxide structures has been also observed upon studying the annealing behaviour of  $\text{WO}_3$  thin films in various gas atmospheres.

The studies were finally supplemented by growth studies of PdO on Pd (supported on  $\text{SiO}_2$ ), revealing three-dimensional cluster growth, in strong contrast to growth of  $\text{Rh}_2\text{O}_3$  on Rh forming an epitaxial shell around the individual Rh particles.