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# Formation of Intermetallic Compounds by Reactive Metal-Support Interaction:

# A Frequently Encountered Phenomenon in Catalysis

Dr. Simon Penner<sup>\*[a]</sup> and Prof. Dr. Marc Armbrüster<sup>[b], [c]</sup>

<sup>[a]</sup>Institute of Physical Chemistry, University of Innsbruck, Innrain 80-82, A-6020 Innsbruck

<sup>[b]</sup>Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Str. 40, D-01187

Dresden

<sup>[c]</sup> Institute of Chemistry, Technical University Chemnitz, Straße der Nationen 62, 09111 Chemnitz \*corresponding author: <a href="mailto:simon.penner@uibk.ac.at">simon.penner@uibk.ac.at</a>, Tel: 0043 512 507 58003

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#### Abstract

The review discusses the structural and catalytic aspects of the recently introduced reactive metal-support interaction (RMSI). This special term was coined to account for the inability of the original concept of strong-metal support interaction to accurately describe the structural, compositional and electronic changes frequently occurring in oxide-supported metal particle catalysts at very high temperatures upon reduction in hydrogen, in many cases leading to intermetallic compound or substitutional alloy formation. This inaccuracy predominantly refers to the requirement of full reversibility upon oxidation and mild reduction for a "strong" metal-support interaction. A close look at the formation of oxide-supported intermetallic compounds upon high-temperature reduction reveals that these compounds are very common in catalysis and the situation is much more complex compared to unsupported intermetallic compounds due to the presence of the intermetallic compound - oxide interface.

# 1. Introduction to the concept

Bi- or multimetallic systems, and among them the intermetallic compounds, represent an interesting class of materials in catalysis due to their structural and electronic properties, rendering them promising catalysts for a range of reduction or oxidation reactions<sup>[1,2]</sup>. A multimetallic system might come either as structurally well-defined intermetallic compound (defined as chemical compound of two or more metals with crystal structures different from the constituting metals; characteristic is the presence of covalent and/or ionic bonds) or as substitutional alloy (defined by a material composed of at least two elements as a single-or multiphase solid solution) depending on the corresponding phase diagram<sup>[1]</sup>. Whereas recent experimental and quantum mechanical studies focus on the successful knowledge-based matching of intermetallic compounds and catalytic reactions<sup>[1]</sup>, a deep literature-review reveals that intermetallic compounds are much more frequently encountered than previously assumed (for a comprehensive overview of the use of intermetallic compounds in catalysis, we refer to refs.<sup>[1,2]</sup>). This comprises materials, where an intermetallic compound is deliberately prepared to exploit distinct structural or electronic properties (e.g. with the wellknown preparation of the supported intermetallic compound ZnPd for CO<sub>2</sub>-selective steam reforming<sup>[3-6]</sup>) as well as materials where unintended intermetallic compound formation occurs as an outcome of preparation or use under catalytic reaction conditions<sup>[7-12]</sup>. It is worth noting, that the latter case represents the overwhelming majority of intermetallic compounds

discussed in the catalytic community. Supported intermetallic compounds are deliberately prepared either by promoting or modifying an oxide-supported metal (particle) with a second metal<sup>[1]</sup> by reaction with a highly reactive reagent or the oxide support itself takes part in the formation during the preparation of the intermetallic compound<sup>[1]</sup>. It is the latter example, which often creates the structurally and electronically most complex scenarios and on which this review is focused upon. Adding the metal atoms of the – usually oxidic – support as a reactant in the preparation of intermetallic compounds in most cases requires the oxide to be reduced at elevated temperatures by hydrogen (explicitly discussed e.g. in ref.<sup>[13-15]</sup>). There are many examples of this kind in literature with seemingly endless combinations of noble metal and oxide support<sup>[1,13-162]</sup></sup>. The chemical properties of the supporting oxide usually determine the requirements for intermetallic compound formation under given reduction conditions and in most cases are the source of complexity<sup>[1,13-15,163]</sup>. This is mainly due to the general presence of metal-support interactions and especially due to the so-called "strong metal-support interactions" (SMSI)<sup>[164-168]</sup>. The latter term, coined by Tauster et al., is reserved for structural re-arrangements and electronic changes exclusively occurring upon reduction in hydrogen at elevated temperatures with the presence of easily reduced oxides such as  $TiO_2$  or  $CeO_2^{[163]}$ . Hard-to-reduce oxides such as  $SiO_2$  or  $Al_2O_3$  were excluded. Although this appears to be a convenient term to also describe the formation of intermetallic compounds from supported metal nanoparticles, the use of this term does not come without strings attached - and finally led to the introduction of the new term of "reactive metalsupport interaction" (RMSI)<sup>[1]</sup>. The so-called reactive metal-support interaction here refers to a chemical reaction process occurring on the metal-oxide interface, but under extremely harsh conditions, i. e. at very high temperatures upon reduction in hydrogen, in many cases leading to the formation of intermetallic compounds or alloys. To be classified as "strong", a metalsupport interaction has to fulfill three strict requirements: i) the catalyst shows a conventional chemical behavior at low reduction temperatures, ii) upon increasing the reduction temperature, the chemisorption capability of the dispersed metal phase towards the "classic" probe molecules such as hydrogen or carbon monoxide is disturbed along with substantial changes in its catalytic behavior and iii), most importantly, the phenomenon must be fully reversible, i.e. the re-oxidation at an appropriate temperature followed by mild re-reduction re-establishes the catalytic behavior prior to entering the SMSI state<sup>[163]</sup>. As origin of strong metal-support interaction, perturbations associated with electronic interactions (also localized) occurring between the dispersed metal phase and the reduced oxide support and loss of active metal area by encapsulation, decoration and support migration (i.e. the active centers for chemisorption at the metal surface are blocked at high reduction temperatures by partial covering by a thin layer of the reduced oxide support) are discussed<sup>[166,169]</sup>. Figure 1 gives a schematic overview of a tentative degree of metal-support interaction, starting from changes in the chemisorption ability over changes in catalytic patterns to structural changes including as an extreme case formation of intermetallic compounds (Figure 1).



**Figure 1:** Tentative degree of metal-support interaction effects. Intermetallic compound formation is typically regarded as the most extreme form of "strong" metal-support interaction, but should be better viewed as a new type of "reactive" metal-support interaction. Adapted with permission from ref.<sup>[15, 166, 91]</sup>. Copyright Elsevier 1984 and 2003.

Focusing on the intermetallic compound and/or alloy formation as the most extreme case of "strong" metal-support interaction, requirement iii) is usually not fulfilled. Decomposition of the intermetallic compounds is only possible by harsh oxidation treatments, which do not reestablish the structural and electronic properties as before entering the intermetallic state<sup>[1]</sup>. Although the term "strong metal-support interaction" therefore is misleading and should be avoided, its structural and electronic manifestations nevertheless offer a convenient pathway to discuss the inherent complexity of oxide-supported intermetallic compounds. This complexity might both include structural and catalytic aspects. For oxidation reactions, this is in most cases due to the presence of an intermetallic-oxide interface, which forms upon entering the intermetallic state upon reduction. The reaction between the supported metal and the metal resulting from the reduction of the support leads to a set of questions, which are important for the properties of the materials: Which new phase(s) form? Which crystallographic and electronic structure results? Do the particles realize unusual particle morphologies? Do they grow topotactically? Is the intermetallic compound stable under reaction conditions? How does the reducibility of the support affect the intermetallic compound formation and does the preparation of the catalyst affect the extent of intermetallic compound formation?

The importance of addressing these questions becomes immediately clear by considering the effects on the catalytic properties, like changes in catalytic activity or selectivity upon entering the intermetallic compound state. Also the influence of the newly created interface (i.e. are special sites at the interface created upon entering the intermetallic state?) on the catalytic properties might be important.

By comparative studies of supported and unsupported intermetallic compounds, the question if the intermetallic compounds are the catalytically active and selective phases or just a part of a larger synergistic catalytic entity can be investigated, answering also the question, whether the supporting oxide contributes to the catalytic properties. In the larger context, the question can be answered, for which reactions an influence of intermetallic formation can indeed be expected.

A very important issue, also concerning the judgement whether a strong metal-support interaction in a strict definition of the term or a reactive metal-support interaction is present, is related to the general formation mechanism of the intermetallic compound. As the initial preintermetallic state of the catalyst are oxide-supported metal particles, four possible mechanisms are discussed in literature: i) a direct reaction between the noble metal and the oxide to the corresponding intermetallic compound and the associated noble metal oxide, e.g.

$$M_x + SiO_2 \rightarrow M_ySi + M_{x-y}O_2^{[21]},$$

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ii) a surface-specific reaction at the oxide-metal contact via chemisorbed oxygen on the metal surface, e.g.:

$$xM^{\delta +} - 0 - Si - 0 \rightarrow M_xSi + O_2 \uparrow + (x - 1)SiO_2^{[21]},$$

iii) a reaction via hydroxylated surface species, e.g.:

$$2Pd + SiOH + \frac{1}{2}H_2 \rightarrow Pd_2Si + H_2O^{[104]}$$

or iv) a direct reaction via reduction of the oxide in hydrogen, e.g.

$$2Pd + SiO_2 + 2H_2 \rightarrow Pd_2Si + 2H_2O$$
.<sup>[26,104]</sup>

Note that the first two mechanisms do not require hydrogen for formation of the intermetallic compound. As a matter of fact, the most crucial component determining the pathway of intermetallic compound formation is the supporting oxide, and, more specifically, its thermodynamic stability and the resulting reducibility. The first two mechanisms have been solely discussed for the hydrogen-free formation of M-Si intermetallic compounds by simple

thermal annealing. Furthermore, due to the very high formation enthalpy of SiO<sub>2</sub>, the first mechanism has been explicitely discarded for Rh-SiO<sub>2</sub><sup>[21]</sup> and Cu-SiO<sub>2</sub> systems<sup>[25]</sup>. In contrast, the prevalence of a mechanism which includes at least partial reduction of the support is nowadays favored and has been explicitly stated for Pt on SiO<sub>2</sub><sup>[13-15,29]</sup>, Al<sub>2</sub>O<sub>3</sub><sup>[13,14]</sup>,  $CeO_2$  <sup>[13,14]</sup>,  $VO_x$  <sup>[96]</sup> and  $TiO_2$  <sup>[116]</sup>, as well as for Pd on  $SiO_2$  <sup>[56,104]</sup> and Rh on  $SiO_2$  <sup>[26]</sup>,  $CeO_2$  $^{[53]}$ , ZnO<sup>[56]</sup> and V<sub>2</sub>O<sub>3</sub>  $^{[54,55,76]}$ . Surface specific mechanisms have been held accountable for the formation of Cu-Si<sup>[25]</sup> and Rh-Si<sup>[21]</sup>. The formation of the intermetallic compounds most probably includes the following reaction steps: 1) reduction of the oxidic support in the vicinity of the supported particles by hydrogen activated on the latter, 2) diffusion of these metallic species into the noble metal lattice and 3) formation of the respective intermetallic compound(s). For efficient formation of intermetallic compounds, steady removal of the formed water is a prerequisite, as is effective hydrogen activation on the noble metal surface <sup>[13-15]</sup>. It is worth noting, that evidence for this reaction mechanism has been collected for Pt particles on SiO<sub>2</sub><sup>[15]</sup> (Figure 2). Panels A and B of Figure 2 show Pt particles on SiO<sub>2</sub> in the as-grown state (panel A) and after reduction at 873 K (panel B). "A" and "B" denote reconstructed and irregular intermetallic Pt<sub>3</sub>Si and Pt<sub>12</sub>Si<sub>5</sub> particles. In this special case, EEL spectroscopy (panel C) revealed not only clear indications of SiO<sub>2</sub> reduction, but also clear differences in the extent of reduction as a function of distance from the metal particles. Thus, SiO<sub>2</sub> far away from the metal particles (and hence, far away from dissociatively activated hydrogen) only showed minor signs of reduction, whereas SiO<sub>2</sub> close to the metal surface showed clear indications of distortion of the SiO<sub>2</sub> building blocks by hydrogen reduction<sup>[15]</sup>. The necessity for dissociatively activated hydrogen was also explicitly stressed by Lamber for the formation of Pt<sub>2</sub>Si compounds<sup>[29]</sup>. Note that a possible reaction mechanism must also include kinetic diffusion limitations of the second metal phase to account for the formation of compound mixtures and particle size effects, as observed in a number of intermetallic compound systems (for details we refer to the following sections).

To highlight the possibility and feasability of intermetallic compound formation, we will shortly focus on the thermodynamics of the  $Pt/SiO_2$  system discussed in refs.<sup>[13,14]</sup>. For the reaction

$$3Pt + SiO_2 + 2H_2 \rightarrow Pt_3Si + 2H_2O$$

the standard reaction enthalpy at 900 K is +393 kJ mol<sup>-1</sup> (this can easily be calculated from the formation enthalpies of the reactants, including the one for Pt<sub>3</sub>Si, which can be calculated by density-functional theory to be -115.9 kJ mol<sup>-1</sup>)<sup>[13,14]</sup>. The standard formation entropy of the intermetallic compound is not known, but it is possible to give a rough estimate from the standard formation entropy of the isostructural Cu<sub>3</sub>Au compound (+238.6 J mole<sup>-1</sup>). The free reaction enthalpy at 900 K therefore is + 178 kJ mol<sup>-1</sup>, resulting in an equilibrium constant of  $4.5 \cdot 10^{-11}$ , indicating a highly endergonic reaction. Under the given experimental conditions (reactor volume 16 mL)<sup>[13,14]</sup>, a water pressure of ~  $10^{-3}$  bar will be built up at a hydrogen pressure of 1 bar. However, as the reduction experiments are performed under flowing conditions, the water is permanently removed – thus, the water partial pressure kept on a low level and the reaction forced towards the products. Water formation will be predominantly occur at the Pt-SiO<sub>2</sub> interface by reaction of diffusing atomic hydrogen with the SiO<sub>2</sub> substrate. The high formation energy and high stability of the intermetallic compounds formed also applies to compounds of differing stoichiometry, e.g. -127.8 kJ mol<sup>-1</sup> for a PtSi phase. Similar argumentations also hold for the corresponding Pt<sub>3</sub>Al (equilibrium constant  $1.3 \cdot 10^{-9}$ )<sup>[13,14]</sup> and Pt<sub>3</sub>Ce (equilibrium constant  $2.4 \cdot 10^{-6}$ )<sup>[13,14]</sup> compounds. In all these cases, classical thermodynamics does not limit intermetallic compound formation, because the experimental setup allows for permanent removal of reactant water.

As for the thermodynamics of supporting oxide reduction, this is basically dominated by the standard formation enthalpies of the oxides under question: for the  $Al_2O_3$  and  $CeO_2$  examples discussed above, these enthalpies are -1651 kJ mol<sup>-1</sup> and -1085 kJ mol<sup>-1</sup>, respectively,

indicating that intermetallic compound formation needs higher temperatures on  $Al_2O_3$ , corroborating the experimental results. Supporting the noble metals on oxides will lower formation enthalpies, e.g. ZnO, GeO<sub>2</sub> or Fe<sub>2</sub>O<sub>3</sub>, results in much lower temperatures required for the formation of intermetallic compounds.



**Figure 2:** TEM micrographs of a  $Pt/SiO_2$  catalyst in the as-prepared state (panel A) and after reduction at 873 K in flowing hydrogen (panel B). Panel C shows EEL spectra taken at

various spots on the catalyst to highlight the formation mechanism of the Pt-Si intermetallic compounds. Partially adapted from ref.<sup>[15]</sup>. Copyright Elsevier 2003.

This review tries to summarize the present dispersed and far from systematic knowledge on the preparation of supported intermetallic compounds via reactive metal-support interaction. In addition, the complexity of such systems is highlighted also addressing structural and catalytic aspects in selected examples. Cross-correlation to unsupported intermetallic compounds are attempted whenever applicable to highlight the differences and common features.

## 2. Overview about the formation of intermetallic compounds

To highlight the widespread presence of intermetallic compounds, Table 1 gives a compact overview of up-to-now known combinations of transition metals and oxides, for which after a high-temperature treatment in hydrogen the formation of intermetallic compounds has been reported. By far the most data are found for the classical catalytically active noble metal particles Pt, Rh and Pd, much less data for Ni, Cu, Ru and Au. The examples include only supported nanoparticulate systems, either as classical impregnated catalysts or thin film model systems. A particular note should be added to the stability of the discussed intermetallic phases discussed below: the TEM work contains exclusively *ex situ* obtained data. This poses the general stability question if the formed intermetallic compounds are exposed to air and cross-correlations to catalytic data are established. Although *in situ* or better still, operando characterization would be highly desireable, these data are not availbale so far. However, most of the intermetallic compounds need very harsh re-oxidation temperatures for decomposition (T  $\geq 673$  K; see section 3.1.3.). An obvious exception concerns intermetallic compounds with a bi-functional synergism being prevalent in the working state of the catalyst

between the support and the intermetallic compound particles, but even in these cases, the working state is sometimes preserved upon transfer (e.g. ZnPd on ZnO<sup>[111]</sup>).

#### 2.1. Platinum

For the systems including Pt particles, formation of intermetallic compounds is a quite common feature, both on easy reducible and hard-to-reduce oxides. On CeO<sub>2</sub>, only two distinct intermetallic compounds were observed, CePt<sub>3</sub> <sup>[13,14]</sup> and CePt<sub>5</sub> <sup>[11,20,44,45,91]</sup>. Whereas the former has only been observed in thin film systems after reduction in hydrogen at 873 K  $^{[13,14]}$ , the latter is more frequently reported  $^{[11,20,44,45,91]}$ . As a common feature, CePt<sub>5</sub> is only observed at reduction temperatures of 1173 K and higher. CePt<sub>5</sub> is also reported for Tb-doped Pt/CeO<sub>2</sub> systems <sup>[91]</sup>. Ce-Pt compound formation has also been reported at and above 750 K in thin film Pt samples <sup>[92]</sup> and has been held responsible for catalyst deactivation upon reduction in hydrogen between 473 K and 773 K<sup>[93]</sup>. For Pt on Ga<sub>2</sub>O<sub>3</sub>, reduction at 773 K on an impregnated catalyst yielded the intermetallic compounds  $Ga_3Pt_5$  and  $Ga_{5,4}Pt_{10,6}$  <sup>[3,6]</sup>. The system Pt/ZnO is a very interesting one, as different intermetallic compounds are observed, in case different Zn-containing supports are used. On Pt/ZnO, only the intermetallic compound ZnPt is encountered, typically after high-temperature reduction between 473 K and 773 K [3,6,48,49,76,119,121,132,137,141,150]. For Pt particles supported on an Al-Zn spinel, both ZnPt and ZnPt<sub>3</sub> have been observed <sup>[18,94]</sup>, depending on the reduction/annealing temperature. ZnPt is found after reduction at 830-850 K in hydrogen, whereas treatments at lower temperatures or oxidative regeneration led to the formation of the Pt-rich  $ZnPt_3$  phase <sup>[18,94]</sup>. Using SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> as support for metal particles, strong metal-support interaction for the first time involves hard-to-reduce oxides. Reduction at high temperatures (773-1173 K), led to the formation of the intermetallic compounds PtSi, Pt<sub>2</sub>Si, cubic and monoclinic Pt<sub>3</sub>Si as well as Pt<sub>12</sub>Si<sub>5</sub> <sup>[13-15,29,39,40,47]</sup>. Similar to SiO<sub>2</sub>, intermetallic compound or alloy formation with participation of Al<sub>2</sub>O<sub>3</sub> needs very harsh reduction conditions at and above 773 K. Al-Pt alloys,

as well as the intermetallic compound AlPt<sub>3</sub> were reported<sup>[13-14,25,31,33,161]</sup>. Reduction of Pt/SnO<sub>2</sub> and Pt/In<sub>2</sub>O<sub>3</sub> catalysts at 673 K and 523 K caused the formation of the intermetallic compounds SnPt, Sn<sub>2</sub>Pt, Sn<sub>4</sub>Pt and In<sub>2</sub>Pt, respectively<sup>[3,6,95,144]</sup>. On Pt/V<sub>2</sub>O<sub>3</sub> catalysts, the ordering of the intermetallic compound Pt<sub>3</sub>V, prepared by reduction at 773 K, could be triggered by pre-oxidation treatments prior to reduction<sup>[96]</sup>. Also using TiO<sub>2</sub> as support, electron microscopy revealed the formation of TiPt intermetallic compounds after high-temperature reduction <sup>[97]</sup>, as well as a TiPt<sub>3</sub> phase after reduction at 823 K <sup>[116]</sup>. TiPt<sub>3</sub> has also been observed by Beard et al. after reduction at 973 K <sup>[117]</sup>. Direct Pt-Ti interactions were also reported by Belton et al. after reduction at 773 K <sup>[98]</sup>.

## 2.2. Rhodium

Compared to oxide-supported Pt and Pd particles, the formation of intermetallic compounds in Rh-containing systems is relatively scarcely investigated. Only for four oxides, that is,  $CeO_2$ ,  $SiO_2$ ,  $TiO_2$  and  $V_2O_3$ , intermetallic formation after high-temperature reduction is reported. CeRh<sub>3</sub> particles were obtained after reduction at 773 K on a Rh/CeO<sub>2</sub> thin film catalyst <sup>[49]</sup>, Rh<sub>2</sub>Si <sup>[26]</sup> and Rh<sub>3</sub>Si particles <sup>[21]</sup> on powder samples after reduction at 1223 K and 850 K. EXAFS measurements were used to identify not only direct Rh-Ti interactions after reduction at 773 K <sup>[99]</sup>, but also distinct TiRh<sub>3</sub> and TiRh intermetallic compounds at 623 K <sup>[30]</sup>. Using V<sub>2</sub>O<sub>3</sub> as support, Rh<sub>3</sub>V, RhV<sub>3</sub> and Rh<sub>5</sub>V<sub>3</sub> intermetallic compounds have been reported at temperatures of 673 K and higher <sup>[54,55,76]</sup>.

# 2.3. Palladium

A closer look in the literature reveals that for oxide-supported Pd particles, by far the most data are available<sup>[3-6,12,24,36,37,50-52,54-65,85-90,96,100-102,118,120,122-129,131,133,136,138-140,143,145-149,151-157,159,160]</sup>. This refers both to the number of different intermetallic compounds formed and to the fact, that the Pd/ZnO system has been particularly scrutinized from a structural, electronic

<sup>140,143,145-149,151-157,159,160]</sup>. It is by far the experimentally and theoretically most studied system. Intermetallic compound formation has been observed with participation of easily reducible transition metal oxides (e.g.  $V_2O_3$  or  $V_2O_5$ <sup>[96]</sup>), refractory oxides (e.g. SiO<sub>2</sub> <sup>[24,27,36,37]</sup>, Al<sub>2</sub>O<sub>3</sub> <sup>[57]</sup> or GeO<sub>2</sub> <sup>[12]</sup>) or with oxides giving rise to special catalytic applications (e.g. methanol steam reforming and selective hydrogenation of acetylene –  $Ga_2O_3$  <sup>[3-6,50,51,58,59,64,74,75,103,140]</sup>, ZnO [3-6,56,60-63,86-89,100-102,118,120,122-129,131,134,135,143,145-149,151-157,159,160], In<sub>2</sub>O<sub>3</sub> [3-6,110,140] or SnO<sub>2</sub>  $^{[12]}$  as well as the reverse water-gas shift reaction – ZnO  $^{[138,139]}$ ). More or less well-ordered Pd<sub>3</sub>V is obtained after high-temperature reduction treatments in hydrogen at and above 773 K<sup>[96]</sup>. Pd/SiO<sub>2</sub> systems are particularly well studied with respect to metal-support interaction at high temperatures. Moss et al. explained the decrease in specific activity for benzene hydrogenation for a Pd/SiO<sub>2</sub> catalyst upon raising the reduction temperature to 873 K by the formation of an intermetallic compound <sup>[35]</sup>. Metal-support interaction and Pd<sub>2</sub>Si intermetallic compound formation was also reported by Lamber et al. <sup>[104]</sup> and Penner et al. <sup>[56]</sup> after reduction at 873 K. In the former case, microdiffraction showed an oriented growth of the Pd<sub>2</sub>Si compound with respect to the Pd matrix. A variety of different Pd-silicides (notably Pd<sub>3</sub>Si, Pd<sub>4</sub>Si and Pd<sub>5</sub>Si) in strongly reduced Pd/SiO<sub>2</sub> samples, showing different catalytic properties, were also detected by XRD and TEM <sup>[24,36,37,104]</sup>. Equally, the interaction of Pd particles with reduced Al<sub>2</sub>O<sub>3</sub> supports yielded the intermetallic compounds AlPd and Al<sub>3</sub>Pd<sub>4</sub> <sup>[41,57,105]</sup>. Recent interest in preparing CO<sub>2</sub>-selective methanol steam reforming catalysts resulted in the formation of a number of Pd-based intermetallic compounds on "unusual" oxide supports, namely ZnO, Ga<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub> and GeO<sub>2</sub>. Whereas the intermetallic compound formation, at least at low reduction temperatures (that is, 573 K) for ZnO and GeO<sub>2</sub>, is relatively simple and gives rise to ZnPd <sup>[3-6,56,60-63,86-89,100-102,118,120,122-129,131,133,136,138-</sup>  $^{140,143,145-149,151-157,159,160]}$  and GePd<sub>2</sub> <sup>[12]</sup>, the situation is more complex for the other oxides. Over Ga<sub>2</sub>O<sub>3</sub>, a large variety of different intermetallic compounds with compositions from GaPd<sub>2</sub> and Ga<sub>2</sub>Pd<sub>5</sub> over GaPd to Ga<sub>5</sub>Pd have all been reported on thin film and impregnated Pd/Ga<sub>2</sub>O<sub>3</sub> systems <sup>[3-6,50,51,58,59,64,85,103]</sup> after reduction at and above 523 K. Particularly wellstudied is the supported intermetallic compound GaPd2 [50,51,58,59,64,103], which can also be prepared by decomposition of hydrotalcite precursors <sup>[74,75]</sup>. In this respect, the formation of the intermetallic compound was also structurally and catalytically studied over different polymorphic forms of Ga<sub>2</sub>O<sub>3</sub><sup>[64,103]</sup>. The intermetallic compound InPd was obtained after heating thin films and impregnated Pd/In<sub>2</sub>O<sub>3</sub> samples at 523 K in hydrogen <sup>[3-6,102]</sup>. In<sub>3</sub>Pd<sub>2</sub> was only obtained on the impregnated system after reduction at 773 K, followed by In<sub>3</sub>Pd <sup>[102]</sup>. In general, intermetallic formation over Pd/In<sub>2</sub>O<sub>3</sub> is heavily influenced by the reducibility of single-phase In<sub>2</sub>O<sub>3</sub> to the metallic In state. For the thin film sample, InPd formation occurs already upon preparation before the actual reduction treatment <sup>[102]</sup>. Reduction of Pd/SnO<sub>2</sub> samples induces formation of an array of Pd-Sn intermetallic compounds, including Pd<sub>2</sub>Sn, PdSn and Pd<sub>3</sub>Sn<sub>2</sub> <sup>[12,41]</sup>. As with Pd/Ga<sub>2</sub>O<sub>3</sub>, intermetallic compound formation in the impregnated Pd/GeO<sub>2</sub> system offers the advantage of conveniently studying the influence of the structure and chemical state of the oxide support. In fact, GePd<sub>2</sub> formation using Pd particles on tetragonal GeO<sub>2</sub> yielded only GePd<sub>2</sub>, but those on hexagonal GeO<sub>2</sub> a mixture of GePd<sub>2</sub> and GePd. This was tentatively explained by the higher solubility of hexagonal GeO<sub>2</sub> in water, giving rise to an enhanced metal-support contact area upon catalyst preparation and it turn, more efficient intermetallic compound formation <sup>[12]</sup>. The properties of the prototypical intermetallic-oxide system that has evolved in the last decade, Pd/ZnO (and ZnPd/ZnO after reduction), should not be discussed in detail at this point, since comprehensive reviews for almost all aspects of its chemical and electronic structure, as well as its catalytic properties, already exist <sup>[86,100,101,106]</sup>. However, also mixtures of ZnPd, Zn<sub>3</sub>Pd<sub>2</sub> and ZnPd<sub>2</sub> have been obtained by interaction between Pd and ZnO, depending on the synthesis conditions  $^{[1,79]}$ . The Pd/CeO<sub>2</sub> system has been scrutinized in detail under comparable reducing conditions, but no signs of a well-defined intermetallic compound have been observed up to 1180 K (and 20 h) neither by X-ray diffraction (XRD), Selcted area electron diffraction (SAED) nor High-resolution transmission electron microscopy (HRTEM). A solid solution of Ce in the Pd structure was proposed instead<sup>[59]</sup>. Similarly, Kepinski et al. discuss a substitutional alloy Ce-Pd exhibiting an fcc structure with a slightly larger lattice constant as compared to Pd metal, forming at 773 K and above. Interestingly, the authors infer the influence of a suppressed metal-support interface, being due to increased crystallite size of both Pd and CeO<sub>2</sub> at higher reduction temperatures <sup>[114,115]</sup>. A Pd-Cr alloy phase has been observed after a methanol decomposition reaction by XRD <sup>[130]</sup>.

#### 2.4. Nickel

Information on the metal-support interaction and intermetallic compound formation in Nioxide systems is up to now limited to the Ni-CeO<sub>2</sub>, Ni-TiO<sub>2</sub> and Ni-SiO<sub>2</sub> systems. CeNi and CeNi<sub>2</sub> are observed after the hydrogenation of benzene at temperatures of about 500 K <sup>[8]</sup>. In addition, Ni<sub>3</sub>Si was observed on a Ni/SiO<sub>2</sub> catalyst after heating in hydrogen at 850 K <sup>[23]</sup>. Martin et al. interpreted the decrease in hydrogenation and hydrogenolysis activity at 1120 K by formation of Ni-silicide species <sup>[107]</sup>. Praliaud and Martin inferred the presence of a Ni<sub>79</sub>Si<sub>11</sub> compound from magnetic measurements at 1180 K <sup>[22]</sup>. Ni/TiO<sub>2</sub> reported by Chettibi et al. represents a complex system: whereas radiation-treated catalysts show the presence of Ni<sub>2</sub>Ti and Ni<sub>3</sub>Ti phases, in the simple calcined and H<sub>2</sub>-reduced sample, a Ni<sub>5</sub>TiO<sub>7</sub> compound was found. This was attributed to contribution of the persisting NiO phase during reduction. A higher cyclohexane selectivity in benzene hydrogenation for the radiation-treated catalyst in turn resulted <sup>[158]</sup>.

# 2.5. Copper

Formation of a  $Cu_{0.61}Si_{0.39}$  intermetallic compound was observed after the decomposition of methanol over a Cu/ZnO catalyst <sup>[9]</sup>. A copper silicide with unknown composition was

postulated by van den Otelaar after a thermal treatment of a  $Cu/SiO_2$  catalyst under ultra-high vacuum conditions at 873 K<sup>[25]</sup>.

# 2.6. Gold

The single formation of an Au-Cu bimetallic phase has been observed for complex Au/CuO/TiO<sub>2</sub> catalysts, which were formed by first activation in air at 573 K and subsequent reduction in hydrogen at 573 K <sup>[16]</sup>. A recent report by Liu et al. for the first time indicates reactive metal-support interaction in nanorod Au/ZnO systems, that is, after reduction at 573 K in hydrogen, XPS and EXAFS measurements indicate the formation of an Au-Zn alloy phase <sup>[108]</sup>.

#### 2.7. Ruthenium

Studies on the catalytic combustion of ethyl acetate over  $Ru/SnO_2$  catalysts revealed the formation of a  $Sn_7Ru_3$  intermetallic compound after pre-reduction at 673 K (for 0.5 h) in hydrogen as evidenced by XRD, XPS and HRTEM. Interestingly, the large  $Sn_7Ru_3$  particles are present in a characteristic core-shell structure, with a well-crystallized intermetallic compound core and an amorphous Sn-enriched shell. The core shell structure is proposed to arise from a phase separation of the catalyst after contact to air <sup>[142]</sup>.

<u>**Table 1:**</u> Overview of intermetallic compounds occurring during reactive metal-support interaction

	Pt	Rh	Pd	Ni	Cu	Au	Ru
CeO <sub>2</sub>	CePt <sub>5</sub> [11,44,45,91] CePt <sub>3</sub> <sup>[13,14]</sup>	CeRh <sub>3</sub> [53]		CeNi, CeNi <sub>2</sub> <sup>[8]</sup>			

Ga <sub>2</sub> O <sub>3</sub>	Ga <sub>3</sub> Pt <sub>5</sub> <sup>[3,6]</sup>		GaPd <sup>[58,59]</sup> , GaPd <sub>2</sub> [50,51,58,59,103,140]				
	Ga <sub>5.4</sub> Pt <sub>10.6</sub>		Ga <sub>2</sub> Pd <sub>5</sub> <sup>[58,59]</sup> , Ga <sub>5</sub> Pd <sup>[3,6]</sup>				
GeO <sub>2</sub>	GePt, Ge₂Pt [ <sup>7]</sup>		GePd <sub>2</sub> , GePd <sup>[12]</sup>				
ZnO	<b>ZnPt</b> [3,6,48,49,76,119,121 ,132,137,141,150]		ZnPd, Zn <sub>3</sub> Pd <sub>2</sub> , ZnPd <sub>2</sub> [3-6, 58,59,64,85,103, 118,120,122-129, 131,133,136,138-140,143,145-		Cu <sub>0.61</sub> Zn <sub>0.39</sub> <sup>[98]</sup> Cu-Silicide	<b>ZnAu</b> [108]	
			149,151-157,159,100]				
SiO <sub>2</sub>	Pt <sub>3</sub> Si (cub, mon) , Pt <sub>2</sub> Si, Pt <sub>12</sub> Si <sub>5</sub> [15,29,39,47,40]	Rh <sub>3</sub> Si, Rh <sub>2</sub> Si <sup>[21,26]</sup>	Pd <sub>3</sub> Si, Pd <sub>2</sub> Si,Pd <sub>4</sub> Si, Pd <sub>5</sub> Si <sup>[24,27,56,104]</sup>	Ni <sub>3</sub> Si,Ni <sub>79</sub> Si 11			
Al <sub>2</sub> O <sub>3</sub>	AIPt3 <sup>[13,14,162]</sup> , AI-Pt alloy <sup>[17]</sup>		AIPd, Al <sub>3</sub> Pd <sub>4</sub> <sup>[57]</sup>				
SnO₂	SnPt <sup>[144]</sup> , Sn₂Pt, Sn₄Pt <sup>[10]</sup>		SnPd <sub>2</sub> , SnPd, Sn <sub>2</sub> Pd <sub>3</sub> <sup>[12]</sup>				Sn <sub>7</sub> Ru <sub>3</sub> [142]
In <sub>2</sub> O <sub>3</sub>	In <sub>2</sub> Pt <sup>[3,6]</sup>		InPd, In <sub>3</sub> Pd <sub>2</sub> , In <sub>3</sub> Pd <sup>[102]</sup>				
V <sub>2</sub> O <sub>3</sub>	Pt <sub>3</sub> V <sup>[102]</sup>	Rh <sub>3</sub> V, RhV <sub>3</sub> , Rh <sub>5</sub> V <sub>3</sub> [54,55]	Pd <sub>3</sub> V <sup>[96]</sup>				
CuO						<b>Au-Cu</b> [16]	
TiO <sub>2</sub>	PtTi	RhTi,		Ni₂Ti, Ni₃Ti			

#### 3. Structural and catalytic aspects in selected examples

# 3.1. Structural aspects

# 3.1.1. Influence of the oxide's reducibility on the formation of intermetallic compounds

The discussion about the influence of the oxide's reducibility on the formation of intermetallic compounds represents one of the core topics in reactive and strong metal-support interaction. In the early days, "strong" metal-support interaction was solely assigned to easily reducible transition metal oxides, such as TiO<sub>2</sub> or CeO<sub>2</sub>, capable of forming sub-stoichiometric oxide species <sup>[163]</sup>. Hard-to-reduce oxides, such as (as extreme cases) SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>, were excluded from entering a state of strong metal-support interaction. Recent studies, however, showed that this mutual discrimination is no longer valid. Even SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>, albeit at higher reduction temperatures, were found to enter the state of reactive metal-support interaction. Here, these comparably harsh reduction treatments did not lead to a collapse of the original structures of both metal and support. Even more, the metal species is sometimes needed for epitaxial growth of the intermetallic compound (for details, see section 3.1.2.). TEM analysis of thin film Pt/SiO<sub>2</sub> and Pt/Al<sub>2</sub>O<sub>3</sub> samples after entering the intermetallic compound state directly revealed the structural stability of especially the support<sup>[13,14]</sup>. Combinations, where this concept has been explicitly proven, include e.g. Pt and Pd, both on SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> <sup>[13-</sup> <sup>15,24,27,29,35-37,39,40,56,162]</sup>. Although this of course already implies that the reducibility of the corresponding oxides does have an influence on the formation of intermetallic compounds, a more catchy example include Pd particles on  $In_2O_3$  <sup>[102]</sup> (Figure 3). Driven by the abilities of the intermetallic compound InPd to selectively catalyze the methanol steam reforming reaction towards CO<sub>2</sub>, the formation of InPd is heavily influenced on the one hand by the reduction behavior of In<sub>2</sub>O<sub>3</sub>, on the other hand by the special preparation pathway. In due course, Pd particles conventionally prepared by incipient wetness impregnation on In<sub>2</sub>O<sub>3</sub> (TEM image, Figure 3, panel A) enter a state of reactive metal-support interaction at around 573 K and InPd is thereby formed (TEM image, Figure 3, panel B; the corresponding XRD diffraction patterns are highlighted in panel C). InPd is subsequently transformed into In<sub>3</sub>Pd<sub>2</sub> at higher reduction temperatures. In contrast, if InPd is formed via a thin film model system, prepared by growing epitaxial Pd particles on NaCl(001) and subsequent embedding in a nm-thick film of In<sub>2</sub>O<sub>3</sub> at 573 K (TEM image, Figure 3, panel D), compound formation occurs already during the preparation process (compare the SAED pattern, Figure 3, panel E). The reason for this rather peculiar feature is the outspokenly well-pronounced reducibility of single-phase In<sub>2</sub>O<sub>3</sub>, where In metal species are even formed at 573 K in hydrogen <sup>[110]</sup> (Figure 3, panel F). Together with the extended metal-oxide interface being prevalent for these thin film systems, this leads to effective loss of reactive oxygen, In metal species and InPd formation even in the only slightly reducing conditions of a high vacuum in the absence of hydrogen <sup>[96,110]</sup>.



**Figure 3:** Structural characterization of the  $Pd/In_2O_3$  powder catalyst (panels A-C) and of the  $Pd/In_2O_3$  thin film system (panel D and E). Panels A and B represent TEM micrographs of the as-prepared catalyst and after reduction in hydrogen at 573 K. The corresponding XRD diffraction patterns are shown in panel C. A TEM overview micrograph and the corresponding SAED pattern of the thin film are shown in panels D and E. The reduction of pure  $In_2O_3$  to In metal by hydrogen reduction is highlighted in panel F. Partially adapted from ref. <sup>[96,110]</sup>. Copyright ACS 2010, Elsevier 2010.

#### 3.1.2. Stabilization of unusual particle morphologies and crystallographic aspects

The discussion of both topics goes well beyond the simple formation of the intermetallic compound itself. Although reported for a number of systems, triggering special particle morphologies and directed exploitation of crystallographic relations in the formation of intermetallic formation by reactive metal-support interaction usually requires special model systems. Special particle morphologies have been reported for CePt<sub>5</sub> (starting from a 4% Pt/CeO<sub>2</sub> powder catalyst) <sup>[44,91]</sup>, Pt<sub>3</sub>V <sup>[96]</sup>, Pd<sub>3</sub>V <sup>[96]</sup>, Pt<sub>3</sub>Si <sup>[15]</sup>, Pt<sub>3</sub>Al <sup>[13,14]</sup> and CePt<sub>3</sub> <sup>[13,14]</sup> (starting from Pt/V<sub>2</sub>O<sub>3</sub>, Pd/V<sub>2</sub>O<sub>3</sub>, Pt/SiO<sub>2</sub>, Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/CeO<sub>2</sub> thin film catalysts). As a representative example, Figure 4 shows two well-facetted CePt<sub>5</sub> particles in the [010] zone axis obtained by Bernal et al. starting from a 4% Pt/CeO<sub>2</sub> catalyst, subsequently reduced in hydrogen at 1173 K. The intermetallic particles both show (100) and (001) lattice fringes and are attached to two larger CeO<sub>2</sub> grains. The presence of CePt<sub>5</sub> has also been confirmed by image simulation. The importance of the metal-oxide interface is further highlighted by the HRTEM image shown in Figure 5. Epitaxy of (100) CePt<sub>5</sub> // (002) CeO<sub>2</sub> and (001) CePt<sub>5</sub> // (002)CeO<sub>2</sub> has been observed in the image and thus in the corresponding FFT pattern. This is due to the high degree of structural match of the cubic CeO<sub>2</sub> and hexagonal CePt<sub>5</sub> structures [44]

Special growth orientations have also been reported to account for the formation of welloriented CePt<sub>3</sub> particles starting from Pt/CeO<sub>2</sub> thin film catalysts (Figure 6). Due to the epitaxial growth of Pt on NaCl(001) and the subsequent embedding in the CeO<sub>2</sub> matrix [TEM image and SAED pattern shown in panel A) and C)], a large metal-oxide interface is created. In consequence, well-facetted and reconstructed CePt<sub>3</sub> particles are formed at comparatively low temperatures of 773 K [TEM image and SAED pattern shown in panel B) and D)]. CeO<sub>2</sub> itself appears in the SAED pattern as a set of ring reflections, Pt exhibits discrete spots – due to its crystallite size and epitaxial growth on NaCl(001). It is worth noting, that Pt and CePt<sub>3</sub> are well-oriented with respect to each other, a consequence of the close match of the fcc Pt and simple cubic CePt<sub>3</sub> structures (lattice parameter mismatch about 8% <sup>[13,14]</sup>). Hence, the Pt(200) and CePt<sub>3</sub> (100) spots are found in the same azimuthal orientation in the SAED patterns.



**Figure 4:** Two examples of high-resolution TEM images of  $CePt_5$  particles obtained after reduction of a 4% Pt/CeO<sub>2</sub> catalyst reduced in hydrogen at 1173 K. Adapted with permission from ref. <sup>[44]</sup>. Copyright Elsevier 1997.



**Figure 5:** High-resolution TEM micrograph of a CePt<sub>5</sub> particle (left) and corresponding FFT of the CePt<sub>5</sub>/CeO<sub>2</sub> interface, revealing the crystallographic match of both structures and the resulting high ordering. Adapted with permission from ref. <sup>[44]</sup>. Copyright Elsevier 1997.



**Figure 6:** TEM overview images of a Pt/CeO<sub>2</sub> thin film catalyst in the as-grown state (panel A) and after reduction at 573 K in hydrogen (panel B). The corresponding SAED patterns are shown in panels C and D, respectively.

Special crystallographic relations between metal, oxide support and intermetallic compound may give rise to a much larger number of well-oriented intermetallic compounds. These have been obtained in all of the above including ZnPd <sup>[3-6,56,60-63,86-89,100-102]</sup>, Ga<sub>5</sub>Pd<sub>2</sub> <sup>[58,59]</sup>, Ni<sub>3</sub>Si <sup>[23]</sup>, Pd<sub>2</sub>Si <sup>[104]</sup>, ZnPt <sup>[18]</sup> and Pt<sub>3</sub>Si <sup>[47]</sup>. The explanation for both phenomena must include the complex interaction of the reducing agent (hydrogen) with the metal surface at higher temperatures, as well as topotactic growth or melting and recrystallization. Regarding the former, and most obvious also for the particles of Figure 6 and  $MPt_3$  (M = Ce, Al, Si) intermetallic compound particles in general, it is clear that the first step of intermetallic compound formation must involve the dissociative adsorption of hydrogen on the Pt surface. In due course, it is for long known, that particle shapes may be altered by exposure to a specific gas atmosphere at elevated temperatures. In that respect, a transformation of drop-like Pt particles into particles with cubic morphology has been reported both by Wang et al. <sup>[168]</sup> and by Shi and Masel<sup>[170,171]</sup> upon exposure to hydrogen at 900 K. However, nevertheless of the high importance for the subsequent intermetallic compound formation and the stabilization of unusual particle morphologies, the authors give different explanations. Wang et al. ascribed the behavior to the initial presence of impurities (e.g. carbon or oxygen), which are subsequently removed upon treatment in hydrogen, but stay intact if other gases are used (e.g. nitrogen)<sup>[168]</sup>. This implies that the cubic outlines represent the equilibrium crystal shape of the clean Pt particles, whereas the rounded ones are associated with those of the adsorbatecovered Pt particles. In contrast, Shi and Masel argued that the adsorption of hydrogen on different crystal facets might specifically lower the surface free energy of certain facets. As a result, those facets might grow in the presence of an adgas. This has been also focused upon by McCabe and Schmidt, who concluded that the activation energy of hydrogen adsorption significantly varies with the crystal facet <sup>[172]</sup>. In that respect, Pt(110) facets bind hydrogen more strongly, followed by Pt(210) and Pt(211). In contrast, Pt(110) and Pt(111) bind hydrogen most weakly. Accordingly, the Pt(110) surface should fill up with hydrogen first, is stabilized and grows in the presence of hydrogen, whereas the Pt(111) facets are expected to shrink. Similar shape transformations for Pt particles have also been observed in H<sub>2</sub>Scontaining mixtures <sup>[173,174]</sup>. It should be however noted, that some authors did not observe these shape transformations upon treatment in hydrogen or hydrogen-containing mixtures <sup>[175-</sup> <sup>182]</sup>. At least it can be expected that some crystallographic relation between Pt and the substrate may be responsible for the peculiar cubic morphology of the intermetallic compounds observed, because the transformation into cubes was almost always observed on planar thin-film model catalysts. Similar arguments also hold for the corresponding AlPt<sub>3</sub> and CePt<sub>3</sub> systems  $^{[13,14]}$ . As discussed in the preceding section on the reaction mechanism, the next steps in the intermetallic compound formation process are the penetration of the metal surface by atomic hydrogen and the reduction of  $SiO_2$  (or any other oxide) followed by the migration of the Si atoms into the Pt particles and a topotactic growth of Pt<sub>3</sub>Si at the interface of the Pt particles. This crystallographic match can be derived from high-resolution TEM images and electron diffraction patterns, showing cubic Pt<sub>3</sub>Si with the Cu<sub>3</sub>Au-type crystal structure (Figure 7A) and slightly distorted monoclinic Pt<sub>3</sub>Si (Figure 7B) on their simplest zone axes, i.e. the [100] zone axis for Pt and cubic Pt<sub>3</sub>Si and the [100], [010] or [001] zone axes for monoclinic Pt<sub>3</sub>Si. The corresponding electron diffraction patterns show spots of cubic Pt<sub>3</sub>Si in the same azimuthal orientation as those of Pt<sup>[15]</sup>. Figure 7C shows a HRTEM image of an irregular Pt<sub>12</sub>Si<sub>5</sub> particle without pronounced crystallographic relation to the former Pt lattice. It is worth noting, that intermetallic compound formation in the Pt-SiO<sub>2</sub> system has been revealed by dark-field imaging to include a flattening of particles due to increased metalsupport interaction <sup>[15]</sup>. Similar observation have also been made by Lamber et al. during the formation of the intermetallic compounds Pt<sub>3</sub>Si and Pt<sub>2</sub>Si<sup>[39]</sup>.

Figure 8 highlights a corresponding well-facetted ZnPt particle, obtained by reduction of Pt particles on a  $ZnAl_2O_4$  spinel matrix at 773 K. The 3-fold outline of the particle can be clearly seen <sup>[18]</sup>. This is a clear indication, that also on complex oxide systems, metal-support interaction effects may stabilize well-outlined intermetallic particle morphologies.



**Figure 7:** High-resolution TEM images of various Pt-Si intermetallic compounds, obtained after reduction at 873 K starting from a Pt/SiO<sub>2</sub> thin film catalyst. Panel A: cubic Pt<sub>3</sub>Si, panel B: monoclinic Pt<sub>3</sub>Si, C: monoclinic Pt<sub>12</sub>Si<sub>5</sub>. Adapted from reference <sup>[15]</sup>, Copyright Elsevier 2003.

An instructive example encompassing both particle morphologies and crystallographic aspects are  $Pt_3V$  and  $Pd_3V$  intermetallic compounds, which are both formed after a treatment in

hydrogen at 673-773 K, starting from the corresponding  $Pt/V_2O_3$  and  $Pd/V_2O_3$  systems. Due to the epitaxial ordering between the Pt/Pd structures and the  $V_2O_3$  support, well-ordered and cube-like particles of tetragonal  $Pt_3V$  and  $Pd_3V$  are obtained (Figures 9A and B). In contrast, if the epitaxy between Pt/Pd and  $V_2O_3$  is lifted by a simple oxidation procedure (at 673 K, transforming the catalysts into  $Pt/V_2O_5$  and  $Pd/V_2O_5$ ) before the actual reduction steps, the same  $Pt_3V$  and  $Pd_3V$  intermetallic compounds are obtained, but without ordering and without distinct cube morphology<sup>[96]</sup> (Figure 9C). This is a clear indication that the crystallographic match between the metal particles and the forming intermetallic compound steers the morphology that is subsequently formed and stabilized.



**Figure 8:** Well-facetted ZnPt intermetallic compound particle obtained by reactive metalsupport interaction of Pt particles on a  $ZnAl_2O_4$  spinel after reduction at 773 K in hydrogen. Adapted with permission from ref. <sup>[18]</sup>. Copyright Elsevier 2001.



**Figure 9:** TEM overview images of a  $Pt/V_2O_3$  thin film catalyst after reduction at 773 K (panel A) and after reduction at 773 K with oxidation pretreatment at 673 K (panel B). Panel C highlights the reduction of  $Pd/V_2O_3$  at 773 K. The corresponding SAED patterns are shown as insets, respectively. Partly adapted from ref. <sup>[96]</sup>. Copyright Springer 2014.

It should be noted, that the morphology and crystallographic match can explain the formation of a number of especially well-ordered intermetallic compounds, but not those of typically higher "non-noble metal" content. This has been in detail discussed for the formation of Pt<sub>12</sub>Si<sub>5</sub> (starting from Pt/SiO<sub>2</sub>)<sup>[15,40]</sup>, Pd<sub>3</sub>Si (starting from Pd/SiO<sub>2</sub>)<sup>[24]</sup>, V<sub>3</sub>Rh and VRh (both starting from Rh/V2O3) [54,55], GaPd (starting from Pd/Ga2O3) [58], GePd (starting from Pd/GeO<sub>2</sub>) <sup>[12]</sup>, Pd<sub>3</sub>Sn<sub>2</sub> (starting from Pd/SnO<sub>2</sub>) <sup>[12]</sup> and In<sub>3</sub>Pd<sub>2</sub>/In<sub>3</sub>Pd (starting from Pd/In<sub>2</sub>O<sub>3</sub>) <sup>[102]</sup>. The formation of all these noble-metal poorer intermetallic compounds is sometimes believed to proceed via the correspondingly noble-metal-richer intermetallic compounds by diffusion and stepwise incorporation of the other atom into the noble metal phase. This has explicitly discussed for  $Pt_{12}Si_5$  (proceeding via the initial cubic  $Pt_3Si$  phase) <sup>[15]</sup>. A similar mechanism was suggested by Juszczyk et al. to explain the presence of Pd-depleted phases in the Pd/SiO<sub>2</sub> system <sup>[24]</sup>. In particular, the stepwise formation of the Pd-depleted Pd<sub>3</sub>Si compound should proceed via the Pd-richer Pd<sub>4</sub>Si compound and was stated to involve the incorporation of Si into the intermetallic compound <sup>[24]</sup>. However, as e.g. the Pt-depleted phases do not show any crystallographic relationship with Pt or the Pt<sub>3</sub>Si compound, the exact mechanism remains unclear. For the corresponding V-richer intermetallic compounds, the penetration of metallic V from the Rh-VO<sub>x</sub> interface into the Rh bulk was found to depend on both the concentration gradient and the reduction temperature. One therefore might anticipate a V-richer shell around the particle perimeter at lower reduction temperature, whereas at higher temperatures the V-gradient to the particle core is gradually levelled and V-richer intermetallic compounds are formed, but not primarily influenced by crystallographic orientations<sup>[54,55]</sup>.

However, even coalescence of neighboring particles, overlapping of different phases, melting and recrystallization phenomena must be taken into account to fully appreciate the pathway of intermetallic compound formation and the resulting morphology. This scenario is clearly visible in the high-temperature reduction of Pt/SiO<sub>2</sub>. Curved edges, grain boundaries, truncated corners and other features of high atom diffusitivity are all present on and in the particles and accordingly visible in the corresponding high-resolution transmission electron micrographs. This also includes flattening of the particles upon silicide formation <sup>[15]</sup>.

#### 3.1.3. Reversibility of intermetallic compound formation

The potential decomposition and (full) structural reversal of intermetallic compound formation represents one of the core topics in not only the full understanding of the structural and catalytic action of intermetallic compounds, but also in the judgment of metal-support interaction itself <sup>[91,163]</sup>. As already outlined in the Introduction, the full structural reversal to the state before entering the intermetallic state is a prerequisite for an interaction to be classified as "strong" metal-support interaction <sup>[163]</sup>. Nevertheless, the general inability for an intermetallic system, formed after reduction in hydrogen, to return to this initial state, ultimately led to the introduction of the new term "reactive" metal-support interaction <sup>[11]</sup>. Usually, the decomposition of the intermetallic compound is achieved via high-temperature oxidation in either oxygen or air. This oxidation treatment, however, does typically not reverse morphological and structural changes and metal particle re-dispersion after sintering is only partially restored.

There are only a few cases in literature, where these issues are in detail discussed, directly via monitoring by structure-determining methods or indirectly via changes in the catalytic profiles. Jusczuyk et al. <sup>[24]</sup> investigated the transformation from Pd<sub>2</sub>Si to Pd metal and SiO<sub>2</sub> after a high-temperature oxidation treatment and revealed a final state of partial coverage of the metal by SiO<sub>2</sub> species. This was proven on the basis of catalytic measurements in n-pentane isomerization <sup>[24]</sup> and is schematically depicted in Figure 10. It shows the complex interplay of metal, intermetallic compound and support upon different reduction and oxidation treatments and gives hints towards a partial coverage of the metal particles by re-oxidized SiO<sub>2</sub> <sup>[24]</sup>. However, no direct structural proof has been provided. Similar observations have been made by Hippe et al. for the oxidative decomposition of Pt<sub>3</sub>Si/Pt<sub>12</sub>Si<sub>5</sub> mixtures <sup>[40]</sup>, who

concluded the partial decoration of the metal particles by SiO<sub>2</sub> to account for the insufficient CO chemisorption capability upon re-oxidation (Figure 11, dashed spectrum E). Pakhomov et al. reported the transformation of  $\delta$ -ZnPt to ZnPt<sub>3</sub>, the initial supporting spinel and ZnO after a treatment in air at 823 K for 30 min<sup>[94]</sup>. Zawadski et al. reported decomposition of the ZnPt compound upon treatment in air at 1073 K<sup>[18]</sup>, as did Ren-Yuan et al. for Al-Pt alloys<sup>[17]</sup>. Sadi et al. reported that very high temperatures are necessary to invert Rh<sub>2</sub>Si intermetallic compound formation by H<sub>2</sub>O titration <sup>[26]</sup>. Similar arguments were also stressed by Bernal et al. for the stability of CePt<sub>5</sub> compound particles. Even after re-oxidation at 773 K, no decomposition was observed <sup>[45]</sup>. A Pd/Ga<sub>2</sub>O<sub>3</sub> catalyst shows the same behavior, although in this special case, the formation of the covering oxide layer after re-oxidation seems to be dependent on the initial degree of intermetallic compound formation. Thus, a catalyst prereduced at 523 K (with the presence of Ga<sub>2</sub>Pd<sub>5</sub>) is fully transformed to a Pd/PdO mixture after re-oxidation in oxygen at 673 K, whereas deeper reduction at 673 K causes the formation of a core-shell particle with a metallic Pd core and an amorphous Ga<sub>2</sub>O<sub>3</sub> shell after re-oxidation at 673 K<sup>[58]</sup>. A similar shell of In<sub>2</sub>O<sub>3</sub> around a Pd metal particle has been observed upon oxidative decomposition of InPd<sup>[102]</sup>. In contrast, there are also some reports, where the decomposition of the intermetallic compound does not lead to encapsulated metal particles, but rather to a mixture of metal particles and oxide. This has been proven directly by electron microscopy for the decomposition of Pt<sub>3</sub>V, Pd<sub>3</sub>V and Rh-V intermetallic compounds <sup>[54,96]</sup>. and for the latter additionally by changes in the selectivity patterns in CO hydrogenation<sup>[55]</sup>.



**Figure 10:** Schematic model of reactive metal-support interaction between Pd and  $SiO_2$  upon high-temperature reduction including potential regeneration of the catalyst system by oxidation, as by Jusczyk et al. Adapted with permission from ref. <sup>[24]</sup>. Copyright Elsevier 1989.



**Figure 11:** Pt-Si intermetallic compound formation and reversibility on Pt/SiO<sub>2</sub> studied by FT-IR spectroscopy and CO chemisorption. Reduction has been carried out in hydrogen at 773 K (A), 823 K (B), 873 K (C) and 923 K (D), re-oxidation in oxygen at 623 K after reduction at 923 K (E) and subsequent reduction at 773 K (F). Adapted with permission from reference <sup>[40]</sup>. Copyright Elsevier 1997.

#### 3.1.4. Single- and multiphase intermetallic compound formation

The discussion in this section is very much connected to the preceding section about the reaction mechanism and the stabilization of unusual particle morphologies or the influence of crystallographic aspects. It nevertheless is of high importance, especially regarding the potential technological or catalytic applications. Regarding the use in the latter cases, from both a fundamental scientific and a more application-oriented use, preparation and/or formation of single-phase intermetallic compounds would be highly desirable. Generally, the preparation pathway to intermetallic compounds via reactive metal-support interaction is not a very directed one and very often mixtures of several intermetallic compounds occur – this is due to a delicate interplay between thermodynamic stability of the intermetallic compound and the diffusion kinetics, which strongly depend upon the particle size. This is especially true if the compound is formed during the catalytic reaction. Some steering can be achieved via crystallographic relationships, as discussed earlier, but this usually applies only to a minor number of intermetallic compounds. As the occurrence of such compounds is a frequent phenomenon in catalytic science, getting some ideas about how to judge whether single- or multiphase intermetallic compounds can be expected, would be desirable. A valuable starting point are the corresponding phase diagrams and to subsequently search for phases with high melting points, indicating highly stable intermetallic compounds. An archetypical example is the Pd-Zn phase diagram (but also valid e.g. for the phase diagrams of Pd-Si and Ge-Pd, strongly dominated by Pd<sub>2</sub>Si and GePd<sub>2</sub>, respectively <sup>[183]</sup>), which exhibits one very pronounced intermetallic compound, namely ZnPd with tetragonal structure <sup>[101]</sup>. By additionally exploiting the crystallographic match between the Pd fcc and the ZnPd tetragonal structure, which is better than 92%, it is not only possible to prepare single-phase ZnPd particles, but also to structurally stabilize the particles over a wide temperature region up to 873 K<sup>[56]</sup>. This, however, is a rare example. It is by far more common that due to the diffusion kinetics mixtures of different intermetallic compounds are present. In addition, the kind of phases present as well as their ratios are not only strongly time dependent (diffusion kinetics), but also depend on the applied temperature (thermodynamic stability). At best, distinct temperature regions exist, where a single intermetallic compound prevails before it is further transformed. Focusing in detail on the individual intermetallic compounds that are reported in the literature to be formed upon reactive metal-support interaction, for the majority of systems some experimental procedures exist, which indeed allow to stabilize the compound within a well-defined temperature region. This is true for Rh<sub>3</sub>Si <sup>[21]</sup>, Rh<sub>2</sub>Si <sup>[26]</sup>, Pd<sub>2</sub>Si<sup>[104]</sup>, Pt<sub>3</sub>Al<sup>[13,14]</sup>, CePt<sub>3</sub><sup>[13,14]</sup>, Ni<sub>3</sub>Si<sup>[23]</sup> (in this special case, for smaller particles only Ni<sub>3</sub>Si is observed, but mixtures of Ni metal and Ni<sub>3</sub>Si for larger ones), ZnPt <sup>[3-6,48,49,83,94]</sup>, CePt<sub>5</sub><sup>[91]</sup>, monoclinic Pt<sub>3</sub>Si<sup>[47]</sup>, Pt<sub>12</sub>Si<sub>5</sub><sup>[15]</sup>, ZnPt<sub>3</sub><sup>[49,94]</sup>, ZnPd<sup>[3-6,56,60-63,86-89,100-102]</sup>, InPd<sup>[102]</sup>,  $In_{0.52}Pd_{0.48}$  <sup>[3-6]</sup>, GaPd <sup>[58,59]</sup>, Ga<sub>2</sub>Pd<sub>5</sub> <sup>[58,59]</sup>, In<sub>2</sub>Pt <sup>[3-6]</sup>, GePd<sub>2</sub> <sup>[12]</sup>, In<sub>3</sub>Pd<sub>2</sub> <sup>[102]</sup>, Pd<sub>2</sub>Sn <sup>[12]</sup>, Pd<sub>3</sub>Sn<sub>2</sub> <sup>[12]</sup> and PdSn <sup>[12]</sup>. In contrast, potential mixtures are reported for Rh<sub>3</sub>Ti/RhTi <sup>[30]</sup>, Ni<sub>2</sub>Ti/Ni<sub>3</sub>Ti Ga5Pd/Ga2Pd5 [3-6].

Summarizing the literature, the conclusion can be drawn that the higher the amount of the corresponding main group metal in the intermetallic compound, the higher the necessary reduction temperature.

#### 3.1.5. Influence of preparation artefacts on the formation of intermetallic compounds

A particular important topic, which is also connected to the general assignment of intermetallic compound formation to a true reactive metal-support interaction, is related to sometimes misleading preparation artefacts of supported metal catalysts. These artefacts are usually connected with an at least partial dissolution of the oxide support in the aqueous precursor solution upon catalyst impregnation<sup>[184]</sup>. Thus, an extended metal-oxide interface is artificially created, which may give rise to peculiar behavior upon heating in hydrogen at elevated temperatures. This effect is best highlighted in two examples, which on the one hand discusses the pre-intermetallic compound state, on the other hand the different extent of intermetallic compound formation, if separate oxide modifications with varying solubility in water are used. Bernal et al. report on the peculiar behavior of La<sub>2</sub>O<sub>3</sub>-supported Rh particles, which show encapsulation effects (i.e. reduced  $La_{2-x}O_{3-y}$  species decorating the Rh particles) at surprisingly low reduction temperatures (473 - 573 K), given the hard reducibility of La<sub>2</sub>O<sub>3</sub>. As an explanation, which is supported by HRTEM imaging, partial dissolution of La<sub>2</sub>O<sub>3</sub> in the aqueous Rh-nitrate solution is offered. In due course, the Rh particles are covered by oxidic La species, which, upon reduction, are converted to LaRhO<sub>3</sub> perovskite and La-oxycarbonate species <sup>[91]</sup> (Figure 12). Due to the intimate contact, this facilitates subsequent formation of La-Rh intermetallic compounds.



**Figure 12:** High-resolution TEM image of a La-oxycarbonate species obtained after reduction of a 10% Rh/La<sub>2</sub>O<sub>3</sub> catalyst at 473 K including corresponding FFT in the lower right corner. Metal-support interaction effects, manifesting itself as decoration of metal particles by La-suboxide species (reduction at 773 K, lower left corner). Adapted with permission from ref. <sup>[91]</sup>, Copyright Elsevier 2003.

Although not always directly correlated with intermetallic compound formation, these preparation artefacts have been directly linked to peculiar intermetallic compound formation of Pd/GeO<sub>2</sub> catalysts. For the latter, Pd particles have been impregnated on the tetragonal and hexagonal modifications of GeO<sub>2</sub>. The former is insoluble in water, but the latter slightly soluble. This different chemical behavior causes formation of GePd<sub>2</sub> on Pd/GeO<sub>2</sub> (tetr.) at 673 K and GePd at 723 K (Figure 13, panel A). In contrast, GePd<sub>2</sub> formation starts already at 473 K and GePd at 573 K, if Pd particles are supported on hexagonal GeO<sub>2</sub> <sup>[12]</sup> (Figure 13, panel B). The shift in onset temperature to lower temperatures in the latter case exactly reflects the more intimate contact between Pd and GeO<sub>2</sub>, which is established by partial dissolution of hexagonal GeO<sub>2</sub> during catalyst preparation. In summary, these two examples highlight the importance of the extent of metal-oxide contact area for efficient intermetallic compound formation, also in view of the reaction mechanism discussed in the preceding section.



**Figure 13:** Comparative X-ray diffraction patterns obtained during reactive metal-support interaction on Pd/GeO<sub>2</sub> (tetragonal – panel A) and Pd/GeO<sub>2</sub> (hexagonal – panel B) catalysts in hydrogen at various temperatures. Obtained phases have been marked by legends, the reflections from the sample holder by an arrow. Adapted in part from ref. <sup>[12]</sup>, copyright Elsevier 2010.

# 3.1.6. Particle size effects during the preparation of intermetallic compounds by reactive metal-support interaction

The kinetically motivated discussion about possible particle size effects during the preparation of oxide-supported intermetallic compounds is very much connected to the general importance and influence of the (inter)metallic-oxide interface on catalytic behavior and the formation of the intermetallic compounds in general. However, detailed studies on the particle size effects are very limited and only available for a few selected systems. Lamber and Romanowski linked the dispersion of Pt particles on SiO<sub>2</sub> upon oxidation and reduction directly to an enhanced strong metal-support interaction <sup>[39]</sup>. Lamber et al. found that the extent of Ni-Si intermetallic compound formation can be directly correlated to the Ni particle size in accordance with the increase in time needed for compound formation due to the longer diffusion paths. In due course, smaller Ni crystallites (< 5 nm) were exclusively found to be fully converted to Ni<sub>3</sub>Si, but larger ones (> 10 nm) only partially, that is, they contained both Ni metal and Ni<sub>3</sub>Si<sup>[23]</sup>. Similar observations have been also made by Karim et al. in the Zn-Pd system. In this case, the particle size was also directly correlated to the CO<sub>2</sub>-selectivity in MSR. High-temperature treatment led to complete transformation of Pd into ZnPd, but the CO<sub>2</sub>-selectivity did not increase monotonically with the extent of intermetallic compound formation. Both fully transformed particles and mixed particles showed the same CO<sub>2</sub> selectivity. However, smaller particles showed generally a lower CO<sub>2</sub>-selectivity. It was hence concluded, that an increase in ZnPd particle size had no detrimental impact on the catalyst reactivity<sup>[89,122,151]</sup>. A very similar particle size effect for ZnPd particles has been observed in the reverse water-gas shift reaction: the results indicated that the turnover frequency increases as the ZnPd crystallite size decreases <sup>[138]</sup>. Also in the Pd-Ga<sub>2</sub>O<sub>3</sub> system, a particle size effect was observed. Thus, higher reduction temperatures caused the formation of larger Ga<sub>2</sub>Pd<sub>5</sub> particles and a generally deeper reduction of former Pd particles. However, the extent of intermetallic compound formation was not directly linked to CO<sub>2</sub>-selectivity in MSR<sup>[58]</sup>.

#### 3.2. Catalytic aspects

# 3.2.1. Overview of catalytic aspects

Table 2 gives an overview of the intermetallic compounds that are encountered upon reactive metal-support interaction and the respective catalytic reactions. The vast majority of intermetallic compounds are thus observed upon reductive pretreatments and only a few during the catalytic reaction itself <sup>[7-11]</sup>. Regarding the former, the view on the use of intermetallic compounds for specific catalytic reactions has been changed in the last view years in favor of the directed preparation of specific intermetallic compounds, which have been found to selectively catalyze the methanol steam reforming reaction towards CO<sub>2</sub> <sup>[3-6]</sup> or the selective hydrogenation of acetylene <sup>[185]</sup>. This directed approach has been fuelled by better understanding of their structural, bonding and electronic properties in the last decade <sup>[11]</sup>.

In view of Table 2, the formation of intermetallic compounds by reactive metal-support interaction is reported to have both a beneficial or detrimental effect, whereby upon deliberate preparation by pre-reduction, the vast majority of samples show beneficial effects. This has been especially reported for the selective dehydrogenation of methanol to methyl formate over ZnPd<sup>[4]</sup> (Figure 14, upper two panels), the increase of the isomerization selectivity (n-pentane<sup>[24]</sup> and n-heptane<sup>[17,105]</sup>) over Pd<sub>3</sub>Si and AlPt catalysts or the increase in the CO methanation activity upon formation of ZnPt<sup>[83]</sup>. Exemplarily, Figure 15 shows how the n-heptane isomerization selectivity is drastically increased on AlPt from about 0% before entering the intermetallic state to almost 20% after reduction at 873 K. ZnPt has been also in detail shown to be a promising catalyst for selective hydrogenation of crotonaldehyde to crotyl alcohol<sup>[48,49,186]</sup>. Rh-V intermetallic compounds (especially V<sub>3</sub>Rh<sub>5</sub>) have been shown to increase the methane selectivity in CO hydrogenation<sup>[54,55]</sup>. Nevertheless, most data are nowadays available for a series of Pd-based intermetallic compounds, whose presence have

been shown to steer the selectivity of methanol steam reforming towards  $CO_2$  <sup>[3-6,12,50,51,56,58-63,86-89,100-103,113,122-126,128,134,135,139,145,149,151,152,154,156]</sup> (Figure 14). It should be noted that a series of comprehensive review articles especially for the archetypical ZnPd exist, which highlight almost every structural and catalytic aspect in detail <sup>[2,86,100,101,106]</sup>.



**Figure 14:** Methanol dehydrogenation and steam reforming over Pd/ZnO catalysts. Upper panel: Selectivity to methylformate during methanol dehydrogenation as well as methanol conversion as a function of pre-reduction temperature (reaction temperature 473 K). Lower panel: CO<sub>2</sub>-selectivity in methanol steam reforming over Pd/ZnO (filled circles) and Pd/ZrO<sub>2</sub> (open circles) as a function of the pre-reduction temperature. In both reactions, the selectivity

changes are accompanied by reactive metal-support interaction and the formation of ZnPd. Adapted with permission from ref.<sup>[4]</sup> and <sup>[3]</sup>, copyright Elsevier 1995 and Springer 2003.

Detrimental effects upon intermetallic compound formation have been only reported for benzene dehydrogenation over so far compositionally unspecified Pd-Si phases (decrease in specific activity)<sup>[35]</sup> and n-heptane conversion over ZnPt<sub>3</sub> and ZnPt supported on Al-Zn spinels (catalyst deactivation)<sup>[18]</sup>.

However, although the experimental catalytic results are in most cases very clear, explanations for the behavior are in most cases not given or based on speculation. This is generally owed to the high structural and morphological complexity of the obtained systems, which very often hamper a clear addressing of the catalytic active site. This is even true for the most scrutinized Pd-based intermetallic systems in methanol steam reforming. Although the general presence of the intermetallic compounds for selective steam reforming of methanol are a widely accepted fact, the structural details of the catalytically active site are by far less clear and most probably involve interaction of the intermetallic compound with its (reduced) oxidic support <sup>[111,112]</sup>.



**Figure 15:** Selectivity for cracking and isomerization of n-heptane as a function of prereduction temperature of  $Pt(1 \text{ wt\%})/Al_2O_3$  catalysts. At the highest temperatures, formation of AlPt is proposed. Adapted with permission from ref.<sup>[17]</sup>. Copyright Elsevier 1981.

# 3.2.2. Influence of the supporting oxide and the intermetallic-oxide interface

For a full understanding of the catalytic properties, the material has to be considered in whole. Although clear from a materials point of view, the fact that the resulting intermetallic compound is supported on a more or less reduced oxidic phase has been less in the focus of discussion for most of the catalytic materials containing intermetallic compounds. Revisiting Pd-based systems again, Coq et al. discussed the presence of a not fully reduced Pd promoter in active mixed sites ensembles of various catalytic reactions. This species is referred to as "Pd-M  $^{\delta+}$ " and may lead to synergistic effects, e.g. in liquid-phase hydrogenation of  $\alpha,\beta$ unsaturated aldehydes via activation of the C=O bond  $^{[187]}$ . Even in this case, it has to be emphasized that the so created mixed sites are closely related to those typically encountered upon reactive metal-support interaction and the associated presence of adlineation, i.e. metaloxide phase boundary, effects. Without revisiting the structural prerequisites and effects of metal-support interaction, it is clear that the picture of the active mixed-site ensemble infers that the potentially active mixed site, e.g. in the case of Pd/SiO<sub>2</sub>, is composed of structural ensembles of some type Pd- $(SiO_x)^{\delta^+}$ , if only the formation of migrated reduced oxide species is considered. Likewise, the presence of intermetallic compounds in contact with a reduced oxide species gives rise to mixed sites, best characterized as "Pd<sub>2</sub>Si-(SiO<sub>x</sub>)<sup> $\delta+$ </sup>" or, with increasing complexity, "Pd/Pd<sub>2</sub>Si-(SiO<sub>x</sub>)<sup> $\delta$ +</sup>". As a consequence, not only the metal-metal or metal-support interface, but also the intermetallic compound-oxide support interface is extremely variable and intermetallic – oxide interaction can no longer be neglected and hence must be considered for a full catalytic understanding of the catalytic ensemble. Taking this idea even further, this necessarily implies that not only the intermetallic, but also the oxide itself may be structurally, morphologically or catalytically altered. Typical manifestations include creation of surface and/or bulk defects, partial surface reduction including chemical or compositional changes. Summarizing, the actual catalytically active and selective state of such entities appears to be a composition of different potentially active sites, which go far beyond the simple picture of an isolated intermetallic compound. Such a state would necessarily include intermetallic compounds, the intermetallic compound-oxide interface and a more or less reduced state of the oxide itself.

Unfortunately, for the overwhelming majority of the systems, where structural and catalytic functions of intermetallic compounds formed by reactive metal-support interaction are cooperatively discussed, the role of the oxide is largely neglected and the catalytic properties are almost solely discussed on the basis of the pure intermetallic compound. This is surprising given that the metal-support interface is for long suspected to be important for catalytic activity. It is worth noting, that the mutual discrimination between a facilitated exchange of reactants at the interface and newly created interfacial sites is not important to highlight the general importance of the intermetallic-oxide interface. For the Pd/SiO<sub>2</sub> system, Jusczyk et al. indicate the potential importance of this interface in n-pentane isomerization (cf. Figure 6 of ref.<sup>[24]</sup>), but it is again the Pd-based intermetallic compound system, where this influence of the interface is best appreciated and the historical transformation of understanding of this class of catalyst systems from a quite simple picture to a very complex one, including the establishment of an intermetallic-oxide bifunctional synergism, can be best seen. In this respect, Iwasa et al., in the course of discovering the peculiar properties of the Pd-Zn, Ga-Pd, In-Pd, Pt-Zn, Ga-Pt and In-Pt intermetallic compounds in methanol steam reforming, argued over specifically on the intermetallic surface adsorbed formyl species, which subsequently selectively decomposes to  $CO_2^{[3]}$ . This led to the electronic picture of resembling the electronic structure of copper (in the industrially used Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst) by the strongly altered electronic structure of ZnPd compared to the constituting metals<sup>[188]</sup>. This match of electronic structure has in due course been verified by a number of experimental methods, including *in situ* X-ray photoelectron spectroscopy<sup>[189,190]</sup>. However, whereas the presence of the corresponding intermetallic compound is a prerequisite for CO<sub>2</sub>-selective steam reforming, a number of studies showed that water activation, which is of crucial importance for high CO<sub>2</sub> selectivity, cannot efficiently proceed on the intermetallic surface and thus must involve the oxide support in some way <sup>[112,113,189,191]</sup>. Especially for the Pd/ZnO and Pd/Ga<sub>2</sub>O<sub>3</sub> systems, this has been verified by structural, spectroscopic and catalytic methods <sup>[111-113,192]</sup>. For the outstanding Pd/ZnO system, evidence has been collected by aberration-corrected electron microscopy that the simple ZnPd intermetallic compound supported on ZnO is not CO<sub>2</sub>-selective, but only a state with reaction-induced extended ZnPd-ZnO interface, formed via ZnO surface segregation from the ZnPd particles and subsequent oxidation (Figure 16) <sup>[111]</sup>. Similar observations have also been made on a number of unsupported ZnPd samples <sup>[113,189]</sup>



**Figure 16:** High-resolution electron micrograph of the CO<sub>2</sub>-selective working state of a ZnPd/ZnO catalyst. The active interface between the intermetallic ZnPd particle and the ZnO patches on its surface is clearly visible. Adapted with permission from ref. <sup>[111]</sup>. Copyright Wiley-VCH 2013.

<u>**Table 2:**</u> Overview of the intermetallic compounds present after reactive metal-support interaction with additional correlation to the corresponding catalytic reactions.

Catalyst	Intermetallic compound	Reaction
Au/ZnO	ZnAu <sup>[108]</sup>	CO oxidation
Pd/SiO₂	Pd-Si (unspecified) <sup>[35]</sup> Pd <sub>3</sub> Si <sup>[24]</sup>	Benzene hydrogenation n-pentane isomerization
Pt/ZnO	ZnPt <sup>[83]</sup> ZnPt <sup>[3-6,48,49]</sup>	CO methanation Methanol decomposition and dehydrogenation, Crotonaldehyde dehydrogenation
Pt/Al <sub>2</sub> O <sub>3</sub>	Al-Pt (unspecified) <sup>[17,105]</sup>	n-Heptane conversion
Pt/ZnAl₂O₄	δ-ZnPt <sup>[94]</sup>	n-Butane dehydrogenation
Pd/ZnO	ZnPd <sup>[3-5,12,24,36,37,50-52,54-65,85-90, 122, 126,128,134,135,139,143,145-149,151,152,154,156,157]</sup>	Methanol dehydrogenation and steam reforming, Oxidative Steam Reforming, Partial oxidation of Methanol, Crotonaldehyde dehydrogenation, 2-methyl-3- butyn-2-ol hydrogenation, reverse water-gas shift reaction, methanol synthesis, ethanol steam reforming, Dimethylether steam reforming, butene/isoprene hydrogenation
Pd/In <sub>2</sub> O <sub>3</sub>	In <sub>0.52</sub> Pd <sub>0.48</sub> <sup>[3-6]</sup> InPd <sup>[102]</sup>	Methanol dehydrogenation and steam reforming

Pd/Ga₂O₃	Ga₅Pd/Ga₂Pd₅ <sup>[3-6]</sup>	Methanol dehydrogenation and steam reforming
	Ga <sub>2</sub> Pd <sub>5</sub> , GaPd <sub>2</sub> <sup>[50,51,58,59,74,75]</sup>	Methanol dehydrogenation and steam reforming
		Selective hydrogenation of acetylene
	GaPd <sup>[58,59]</sup>	Methanol dehydrogenation and steam reforming
Pt/In <sub>2</sub> O <sub>3</sub>	In <sub>2</sub> Pt <sup>[3,6]</sup>	Methanol dehydrogenation and steam reforming
Pt/Ga <sub>2</sub> O <sub>3</sub>	Ga <sub>3</sub> Pt <sub>5</sub> /Ga <sub>5.4</sub> Pt <sub>10.6</sub> <sup>[3,6]</sup>	Methanol dehydrogenation and steam reforming
Pd/SnO₂	Sn <sub>2</sub> Pd <sub>3</sub> <sup>[12]</sup>	Methanol dehydrogenation and steam reforming
	SnPd <sub>2</sub> <sup>[12]</sup>	Methanol dehydrogenation and steam reforming
Pd/GeO₂	GePd <sub>2</sub> <sup>[12]</sup>	Methanol dehydrogenation and steam reforming
Pt/CeO <sub>2</sub>	CePt <sub>5</sub> <sup>[11]</sup>	Hydrogenation of α,β- unsaturated aldehydes
PtGeO <sub>2</sub>	GePt/Ge <sub>2</sub> Pt <sup>[7]</sup>	Hydrogenation of α,β- unsaturated aldehydes
Ni/CeO <sub>2</sub>	CeNi/CeNi <sup>2<sup>[8]</sup></sup>	Benzene hydrogenation
	Ni <sub>2</sub> Ti/Ni <sub>3</sub> Ti <sup>[158]</sup>	
Cu/ZnO	Cu <sub>0.61</sub> Zn <sub>0.48</sub> <sup>[9]</sup>	Methanol dehydrogenation
Pt/SnO₂	Sn <sub>2</sub> Pt/Sn <sub>4</sub> Pt <sup>[10]</sup>	Water synthesis

### 4. Conclusion

Reviewing the published studies involving the formation of intermetallic compounds by reactive metal-support interactions and the impact on the catalytic properties leads to the following conclusions. First of all, the RMSI occurs in a large number of catalytically interesting and rather relevant systems. The RMSI is very specific for each system, i.e. the temperature upon which intermetallic compounds or alloys are formed during reduction depends not only on the combination of noble-metal and supporting oxide, but also upon the size of the supported noble-metals and the oxide modification as well as the pretreatment of the latter. In addition, the delicate interplay of thermodynamic stability of the compounds and diffusion kinetics of the second component further complicates the resulting phase composition after reduction. Taking the large amount of available data into account, the phenomenological effects of the RMSI are well defined. This applies to both structural and catalytic effects. Regarding the latter, unintended reactive metal-support interaction usually has a largely detrimental effect on the catalytic activity, while the selectivity towards thermodynamically less stable products increases. For potential beneficial effects, a systematic approach of exploring noble-metal/oxide combinations with focus on the aforementioned parameters is needed. This, however, has not been attempted yet. The outcome of such studies would be the possibility for optimized, i.e. single-phase and as small intermetallic particles as possible, synthesis allowing exploring the full beneficial potential of intermetallic compounds in catalysis.

To finally revisit the definition of a "strong" metal-support interaction, it is likely that all reports of intermetallic compound formation starting from oxide-supported metal particles by partial reduction of the support are most likely no "strong" metal-support interaction in the strict definition of the term. This is always due to violation of the prerequisite "full reversibility of the phenomenon by re-oxidation followed by mild reduction".

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