Evolving Generation of Intermetallic Catalysis

B. Viswanathan

National Centre for Catalysis Research

Indian Institute of Technology Madras

Chennai 600 036

1. **Introduction**

Intermetallic appears to evolve as a new-class materials for catalysing reactions [1-4] and for energy storage applications. In some literature, intermetallic and alloys are employed interchangeably. This means that one has to clearly see the difference between intermetallic and alloys. It is well known for long time that melting two or more metals together followed by cooling to re-solidify leads to the formation of new materials with properties mostly distinct from that of the constituent metals. For example, bronze consisting of 88% Cu and 12% Sn was found to be harder than that of the constituent metals and suited for making tools and weaponry than pure Cu [5]. Among the various alloys, steel ranks on the top.

Hydrogen storage is another application wherein intermetallic are exploited in recent times. The three generic systems namely AB, AB2 and AB5 type of intermetallic systems have been examined for hydrogen storage applications, though so far these systems showed storage capacity only up to 3 weight percent while the required storage is around 6 weight percent. There are many attempts to modify these generic systems so that the storage capacity can be improved. However, these attempts have not yielded the desired result. The possible reasons for this situation can be as follows: (1) The number of possible accommodating void space may be related to the number of metal atoms in a unit cell. (2) Hydrogen storage may take place either associatively or and there can be mixed absorption mode depending on the experimental conditions employed. (3) The sites for dissociation and the subsequent migration of dissociated hydrogen on the surface may be activated processes and hence the preparation procedures employed should take care of surmounting these energy barriers encountered.

However, at the current level of understanding, the hydrogen storage in intermetallic systems cannot reach the levels specified, namely around 6 weight percent, which is the lowest limit required to substitute fossil fuels as energy sources for transport applications.

Apart from hydrogen storage applications, intermetallic is also examined for use as heterogeneous catalysts in recent times. This may evolve as a new-generation catalyst systems and it is necessary to examine the possibility of this new development in this field. There are various aspects of these systems need careful consideration. As usual, in catalysis, the nature of active sites has to be preciously identified and coded. The geometric arrangement of the active sites has to be elucidated and documented. Another aspect is how the activity of the sites are changed or altered by the presence of another element in the neighbourhood. Many of these aspects have been raised even by the founding fathers of catalysis like G M Schwab in the early investigations involving multicomponent systems. However, at that time, they were not able to dissect the active sites since the appropriate techniques were not available.

The surface topography of the intermetallic can now be deciphered to atomic level with the modern surface analytical tools. These types of studies have been carried out routinely these days and they have revealed the nature, electronic and geometric environment of the active sites in a precise manner. By the selection of the constituent metals in an intermetallic system, it is possible to vary the chemical potential of the active metal site withing a broad range. For example, Pd an active element for catalytic reactions can vary its oxidation state between 0 and +2 if a suitable anion environment is adopted. However, by choosing more electropositive elements like Ga will impart negative charge in Pd in GaPd intermetallic system as has been shown by quantum chemical calculations [2,6].

In general, intermetallic systems are appealing as the geometric active site can be deciphered clearly by the surface analytical tools. This has paved the way to precisely define the concept of active sites in catalysis. In addition, the resulting ligand effect and the extent of this effect could be assessed in general and also realize the changes that take place on the active sites.

However, catalysis by intermetallic systems have not yet received the attention this field deserves. At present, there are only limited studies reported on catalysis by intermetallic systems. This presentation therefore, is to briefly assess this field so that further progress can be channelized.Many times, the systems studied though identified as intermetallic, they may turn out to be consisting of more than one metal (like alloy or solid solutions) where the atom arrangements are random and not as regularly ordered in an intermetallic system. This situation warrants that we differentiate intermetallic systems from other alloys.

1. **Difference between alloys and Intermetallic**

An intermetallic is a solid phase containing at least two metal atoms having a well-defined crystal structure with fixed and specific atom positions and site occupancies leading to long range ordering. This can also be identified as definite ligand environment. An alloy is a random substituted solid solution of at least two metals where the atomic site distribution of the constituent elements is not fixed or can be random. Figure 1 represents the geometrical arrangement of metals in an intermetallic and an (random arrangement) alloy.



Fig.1. (a) the geometric arrangement of an intermetallic and (b) that of an alloy. One can recognise the ordering of atoms in (a) with a specific crystallographic space group (with distinct lattice positions and random distribution in (b) an alloy

The reason for the well-defined periodicity of intermetallic is the strong ionic/electronic interaction between the constituents. These interactions possibly promote formation of unique and complex crystal structures different from either of the parent metals, whereas in an alloy the crystal structure of the more abundant parent material (solvent) can be expected to be retained.

Hume-Rothery has postulated that the crystal structure of most of the intermetallic systems are determined by the **valence electron concentration** (vec), which is defined as the number of valence electrons/atom in a unit cell. Valence electron charge is based only on the number of valence s and p electrons. For the value of vec = 1.5, the structure is bcc, for vec = 1.61 it is γ-brass and for vec = 1.75 the structure is hcp. Many intermetallic systems follow these guidelines and are called Hume-Rothery phases. The stability of Hume-Rothery phases arise from the electronic density of state (DOS) of the specific systems. However, the necessary conditions for Hume-Rothery phases are not fully understood. A detailed discussion on the origin of the stability of Hume-Rothery phases is presented elsewhere [6, 7]. It may be remarked that the conditions for Hume-Rothery phases need not be strictly adhered to. The concept of electronic factor in catalysis is a well- accepted concept and most intermetallic catalysts used to date are Hume-Rothery phases.

The systematic application of alloys in catalysis possibly dates back to the work of Schwab and his co-workers. Alloying can affect the catalytic properties of a material by modifying both the active site morphology (geometric effect) and electronic structure as these two concepts are often discussed in the field of catalysis. The geometric effect of alloying essentially stems from the fact that many commercially important reactions are either structure sensitive at an atomistic level or requires a certain chemical environment at the gas-solid interface for better performance. It is therefore intuitive that a suitable bi-metallic (or multi-metallic) alloy may have significant catalytic applications due to geometric or ensemble effect.

Apart from geometric effects (i.e., crystallographic site isolation or ensemble), change in electronic structure (due to charge transfer and hybridization effect as a result of different coordination environment) during alloying can also affect the interaction of the surface with the reactants which may in turn influence catalytic properties. It is possible to postulate that geometric effect may predominate in catalysis by intermetallic systems though it is not general concept.

Typically, both geometric and electronic effects occur simultaneously as a result of alloying. The primary concern was electronic effects can alter interaction of the surface with the reactants, but they cannot provide positive correlations between adsorption energy of desired and undesired intermediates which is the main cause of non-selectivity in catalysis. However, geometric effects can break such correlations and have a stronger impact on selectivity.

It is even more advantageous to use an intermetallic than an alloy because the unique crystal structure and long-range atomic ordering in an intermetallic system ensures homogenous and reproducible active site morphology and allows greater control on catalyst design. This essential difference between the two types of phases of pure bi (multi)-metallics is the motivation for specifically calling intermetallic as model catalysts. At this point it is worth highlighting that the surface composition may vary with respect to the bulk and the long-range periodic order in the crystal lattice may be perturbed at the surface depending on reaction temperature and chemical atmosphere. The exact relationship between bulk and surface (active site) configurations in intermetallic has not been well studied in detail and is likely difficult to achieve as the surface morphology can be altered even in the presence of a few ppm of an impurity such as oxygen.

In any muti-component system, the surface composition can be different from that of the bulk due to the phenomenon known as segregation effect. In any bimetallic systems, the free energy differences between the atoms will decide which atoms will segregate to the surface. This effect may be predominant on alloy systems due to random distribution of the components. In intermetallic systems, the surface segregation though may take place, it will be governed by the geometric arrangement of the constituent metals. It is therefore, necessary to precisely elucidate the surface composition and morphology of intermetallic systems in order to understand their surface properties including catalysis.

In addition to greater atomic ordering, intermetallic can also form unique crystal structures, which are not commonly demonstrated by alloys and may be advantageous to catalysis due to favorable geometric or electronic effects. For example, the γ- brass phase seen in many transition metal phase diagrams has a distinct crystal structure leading to unique coordination geometries and hence active site morphology.

It was shown [8] two Cu0.6 Pd0.4 catalysts were tested with Pd being considered to be the “active element”. Despite having identical compositions, one bimetallic was a disordered alloy (prepared by heating at 1023 K) with an FCC structure (similar to the solvent, Cu) while the other crystallized (heated at 473 K) into an ordered CsCl structure (intermetallic). The intermetallic had a higher Pd-Pd separation (0.29624 nm compared to 0.26436 nm) resulting in greater extent of site isolation and higher ethylene selectivity (90% versus 75% at ~90% acetylene conversion).

Such direct comparison between alloy and intermetallic of same composition is rare and it is common to compare alloy/intermetallic systems with their pure constituent elements. Interestingly, a certain intermetallic may have identical DOS as a third catalytic metal and may be used as a direct replacement for catalysing relevant chemistries. For example, the performance of PdZn and PdCd for methanol steam reforming is exactly similar to that of pure Cu (due to similarity in the DOS of the three materials) and distinctly different from that of Pd. It can be stated at this stage that the DOS of Pt catalytic systems may resemble to that of carbides of Mo and W and hence these systems can be considered as replacement to noble metal Pt in many of the electrode applications.

An additional advantage of intermetallic is their well-defined periodic arrangement and this makes them tenable for treatment by density functional theory (DFT) calculations. In fact, intermetallic systems have also been used as quasi-crystal models and approximants, because of the ease of computing associated with their long-range order.

Intermetallic systems are typically mechanically hard and brittle, have properties distinct from the parent metals. Over the past four decades, intermetallic systems have been used in a wide variety of mechanical, electrical and thermal applications with the most common chemical application being hydrogen storage [9] and corrosion resistance. There was a feverish interest in employing intermetallic systems for hydrogen storage application after the three generic systems namely AB (FeTi), AB2 (Mg2Ni) and AB5 (LaNi5) have been identified as hydrogen storage materials. There has been a spate of publications aiming to achieve the desired storage levels of nearly 6.25 weight percent but this figure has not yet been achieved in intermetallic systems [10]. There are various reasons for this situation and they have to be carefully examined. Among the various possible reasons, the state of stored hydrogen (depends on the experimental conditions employed) molecular or atomic, the possible number of void spaces that can be available for storing hydrogen in intermetallic systems and the thermodynamic limitations like room temperature hydrogen absorption, and desorption temperature should not be high are some of the limitations that are encountered while attempting to make intermetallic systems for hydrogen storage application. In spite of this situation, there continues to be great interest to exploit intermetallic systems for this application. The limitations mentioned need careful and concerted consideration to decide whether these systems will evolve as suitable materials for hydrogen storage for mobile or transport applications.

In recent times, intermetallic have enjoyed exponentially increasing popularity as catalysts in academia and industry. Table 1 summarizes a number of intermetallic compounds and the relevant chemistries they catalyse better than the respective traditional catalysts [10].

**Table 1.** Examples of intermetallic catalysts and potential advantage

over constituent metals. [2,4]

|  |  |  |  |
| --- | --- | --- | --- |
| Reaction | Intermetallic systems tried | Conventional catalyst systems | Remarks |
| Hydrogenation of acetylene | PdZn, PdIn, Pd2Ga PdGa, Ga7Pd3, Ni5Zn, Pd3Ga, Al13 Fe4 | Pd, Ni | Higher selectivity and yield of ethylene |
| Butadiene to butene | PdSn, PdPb, Pt3Ge | Pd | Selectivity advantage |
| CH4 + CO2🡪2CO +2H2 | NiSc | Ni | Activity and selectivity improved |
| CO2 + H2🡪C1+C2 | NiGa, Ni3Ga | Cu | Higher activity |
| CO2 + H2 🡪CH3OH | NI5CA3 | Cu/ZnO | Low pressure reaction |
| CH3OH + H2O🡪 CO2 + 3H2 | PdZn | Cu/ZnO | CO2 selectivity |
| HCOOH 🡪 CO2 + H2 | PdZn, PtBi | Pt | CO2 selectivity |
| C6H12🡪 C6H6 + 3H2 | Pt3Sn, PtGe | Pt | Higher selectivity |
| C4H10 🡪 C4H8 + H2 | Pt3Sn, PtGe | Pt | Higher selectivity |
| Steam reforming of methanol | PdZn, PtZn, NiZn, PdCd | Cu/ZnO | CO­­­2 selectivity |
| C4H6 + H2 → C4H8 | PdSn PdPb, Pt3Ge | Pd | Selectivity improved |
| CH4+CO2→2CO+2H2 | Co2Hf, NiSc | Ni | Activity increased selectivity decreased |
| C6H5CCH+H2→C6H5CHCH2 | Ni5Ga3, Ni3Ga, NiGa | Pd and Ni | Higher selectivity, higher stability |

1. **Synthesis of Intermetallic Compounds**

The synthesis of metallic catalysis by wet or dry methods are known in the literature. But however, the synthesis of intermetallic systems has not received similar kind of attention. The methods available are only applicable for a given set of elements and these methods cannot be adopted more generally for preparing similar intermetallic systems for all the elements which can form similar stoichiometric intermetallic compositions.

Conventionally, high temperature solid state reaction involving diffusion limitations is adopted and this procedure most often results in thermodynamically stable phases with high purity. Since, heating and cooling cycles have to be chosen for phase pure generation of the intermetallic compositions. Because of the high temperature treatments are involved in the preparation, the obtained samples have low surface area and hence find application for catalytic activity in limited cases.

Miura et al [11] adapted this method of high temperature diffusion method to synthesize supported Pt-Zn NPs. A Pt/Vulcan material and a lump of zinc mole ratio 1;1 physically separated in a tube furnace were heated to 500oCfor 8 hours in an inert atmosphere of nitrogen. By the consumption of the entire amount of Zn. The intermetallic PtZn nano particles were obtained with particle size less than 15 nm. The procedure has only limited applicability since it could not be extended to metals like Bi, Pb or Tl because of their lower vapour pressures even at temperatures nearing 800oC.

Shao et al.,[12] mixed together stoichiometric amounts of Ni and MP nanoparticles originally formed by arc melting and heated to 623 K under hydrogen atmosphere for 2 hours leading to the formation of Mg2NiH4 which can be dehydrogenated to obtain phase pure Mg2Ni with particle sizes in the range of 30-50 nm by evacuation at 623 K for 45 mins.

Li et al.,[13] employed an in situ reduction of layered double hydroxide precursor and found that the starting composition as well as the reduction temperature had an effect on the synthesized Ni:Ga intermetallic phase and also its particle size. Zhou et al., synthesized Ni-Ga intermetallic by calcining and reducing a Pd/ZnO material [14]. A similar method was also useful in synthesizing NiZn/ZnO nanoparticles [15]. These are some (only) typical high temperature (calcination) procedures employed for preparing intermetallic systems.

Onda et al., [16] used chemical vapour deposition of a tin complex on Ni/SiO2 to prepare a number of phase pure Ni:Sn supported catalysts. Milanova et al., used a template approach to synthesize Cu:Sn and Ni:Sn nanoparticles using a porous Carbon foam support [17]. Solvothermal methodology have been applied by Sarkar et al., [18]to synthesize Pd2Ga. Other possible techniques include electro-deposition [19] and mechanical attrition methods and so on.

Several techniques have also been applied to meta stable intermetallic structures (those which cannot be obtained by high temperature bulk synthesis) but however, phase purity is often an issue due to the presence of residual pure metals or oxides [21-23]. Wet chemical methods have also been adopted for the synthesis of mano-metallic nanoparticles to intermetallic. Cable and Schaak synthesized a number of M-Zn intermetallic systems through a solution synthesis method starting with zero-valent organometallic Zn Source [24]. Among them is Cu5Zn8 gamma brass phase since the preparation of this phase nanoparticle is difficult due tolarge and complex but symmetric crystal structure. A modified polyol method has been reported by Cable and Schaak for the synthesis of M-Sn and Pt-M intermetallic with particle sizes in the range 10-100 nm [25]. Other similar solution-based techniques are also reported [26-30]. Brian et al., [31] synthesized ternary intermetallic Au-Cu-Sn and Au-Ni-Sn phases through polyol method.

A major drawback of these techniques is that no rational guideline as to which starting composition is required to achieve a desired intermetallic. Secondly in many of the solution-based techniques, precise particle size control is not possible [24,25]. It is known that Zn can form a large number of intermetallic compounds. However, a potential drawback of Zn containing intermetallic is the ubiquitous presence of ZnO which may reflect in the resultant catalytic activity [32,33]. This has been circumvented by using LiOH (at 200oC) [this being a reducing agent] to prepare PdZn. In recent times significant effort has been focused on synthesizing hybrid intermetallic pure metal/alloy catalysts with specific core-shell configuration though various de-alloying methods. Examples are where either the core or the shell or even both may be intermetallic [35-39] These materials find application in catalysing electrochemical half reactions commonly taking place in fuel cells.

1. **Intermetallic in Catalysis**

Schwab was the first to recognize anomalous activation barriers in case of unsupported alloy and intermetallic catalysts compared to their pure metal constituents [40] and studied the effect of compositional variation within the same phase as well as between different crystallographic phases for formic acid dehydrogenation as early as 1946. Since the late 1980s the interest in intermetallic catalysts has garnered significantly more attention and efforts with increased commercial incentive of synthesizing low cost and high performing catalysts.

*Formic acid dehydrogenation:* Formic acid dehydrogenation is a popular model reaction because of the simple nature of the substrate as well as its practical importance in modern fuel cell operation. Schwab et al. initially studied the activation barrier for this model system (on a large number of Ag-M and Au-M’ catalysts) and determined different Hume-Rothery phases had markedly different activation energies. It was determined to be an electronic effect (establishing the applicability of Hume-Rothery’s *vec* concept in catalysis) as the barrier was strongly correlated with intrinsic properties commonly associated with the valence shell electronic configuration of metals, such as electrical resistivity and hardness [40]. More recently, it has been found that the selectivity of formic acid dehydrogenation is also an important consideration since the formation of CO (as by-product) can poison typical fuel cell catalysts such as Pt. This has prompted the development of intermetallic catalysts which are less susceptible to CO poisoning than Pt. PtBi is suggested to be a suitable alternative demonstrating high activity (due to electronic effects) and low CO adsorption energies (increased Pt-Pt distance compared to pure Pt). [41,42] Similar results were also observed for Pt-Zn and Pt-Pb intermetallic [43 44,45]. This reaction is one of the test reactions to establish the selectivity of a catalyst system since the reaction free energy for both the routes namely dehydrogenation and dehydration are almost similar magnitude in the temperature range of the catalytic reaction.

*Selective Alkyne Semi-hydrogenation:* Selective semi-hydrogenation of alkyne in an alkene rich stream is a commercially important and widely studied chemistry. Alkynes are typically present in trace amounts in alkene feeds destined for polymerization (a multi-hundred-billion-dollar industry) [46]. However, alkynes are poisonous to the polymerization catalyst and must be reduced to ppm level. Ideally, only the alkyne should be selectively semi-hydrogenated to decrease its concentration and enhance the alkene feed stream. However, typical hydrogenation catalysts either lead to total hydrogenation of all unsaturated C-C bonds to (low value) alkane (Pd) or forms oligomers and green oil (Ni).

The geometric (and possibly also the electronic) effects of alloying is seen to impart suitable catalytic properties for this reaction to a large number of intermetallic compounds. In this case, the primary design concept is limiting Pd cluster size to just a few atoms as alkyne semi-hydrogenation requires fewer number of Pd atoms than any of the competing steps [47,48]. It is important to note that reducing the number of Pd atoms per active site (by adding inactive metals as spacers) to increase selectivity is always associated with a loss in activity and identifying the best catalyst is essentially an optimization challenge, balancing the gain in selectivity with the loss in activity [49].

Of all alkyne semi-hydrogenation reactions, acetylene semi-hydrogenation is considered to be the most challenging (in terms of selectivity) because of the small molecular size and very strong interaction of reaction intermediates with transition metal surfaces (particularly Pd).[50] Several intermetallic systems such as Pd-In,[26] Pd-Zn [51] and Pd-Ga [52-54] have shown high selectivity (sometimes even >90%) for this reaction.

The current focus in this field is replacing Pd with cheaper base metals. Spanjers et al. [55] studied the Ni-Zn phase diagram and found that only the γ-brass phase has a sufficiently high selectivity (~65%), almost 3 times higher than any other Ni-Zn alloy. This was attributed to the high degree of site isolation of Ni in Zn due to the unique crystal structure of this phase. In fact, it was concluded that the γ-brass phase had effectively single atom Ni sites [56] which led to high ethylene selectivity by minimizing oligomerization. Liu et al. [57] has demonstrated high acetylene semi-hydrogenation selectivity on Ni3Ga and Ni3Sn2. Another highly selective Al-Fe catalyst having a unit cell of more than 100 atoms has been reported by Armbruster and co-workers [58]. It was found that neither of the pure components under experimental conditions was able to catalyse the reaction. The catalytic activity was therefore attributed to the small but apparently significant change in DOS due to alloying. Further, reduction of Fe-Fe coordination was also hypothesized to be an important factor for reducing oligomerization.

Intermetallic compounds have been found to be effective for semi-hydrogenation of higher molecular weight alkynes as well. For example, Ni-Ga intermetallic was found to be selective for phenylacetylene semi-hydrogenation [57] while Pd3Pb is selective for hydrogenating functionalized alkynes (aldehyde, ketone, carboxylic acid and ester) to alkenes [59].

*Steam Reforming of Methanol: The reaction under consideration is* CH3OH + H2O → CO2 + 3H2. Steam reforming of methanol is gaining popularity in the field of fuel cell development because methanol can act as a relatively safe, high yield and easy to handle liquid source of hydrogen. However, parallel CO formation pathways must be suppressed to ensure the success of any methanol-based hydrogen storage approach. Pure Pd and Pt are exclusively selective to CO and is therefore not suitable. On the other hand, near-surface intermetallic such as Pd-Zn, Pd-Ga and Pd-In which are generated *in situ* from Pd/MOx materials under reactive or pre-treatment conditions are found to be highly selective towards the desired products (CO2 +H2 ). The high selectivity is attributed to the different preferred configurations of HCHO (which is a key intermediate) on intermetallic versus pure metal surfaces possibly due to differences in electronic structure.[60]. Of these PdZn is perhaps the most widely studied; Armbruster et al. has published a detailed review of this chemistry on PdZn catalysts.[61]. The near-surface composition plays a huge role in the selectivity of PdZn catalysts for this chemistry. Rameshan et al. reported that if the intermetallic existed to a depth of at least 5 layers below the surface (including the top exposed surface) the catalyst is selective towards CO2 but if there is only a surface monolayer of the intermetallic on a Pd substrate then the pathway for CO production is favoured.[62]. The thickness (number of layers from the surface) of PdZn near-surface intermetallic is a function of temperature and becomes effectively a monolayer (on a Pd substrate) above 623K thereby reversing the CO/CO2 selectivity.

Another interesting development within using intermetallic compounds to gain deep insight into catalysis is testing Heusler compounds for their catalytic properties. Heusler compounds are typically ternary *X*2*YZ* intermetallic compounds, where *X* is a group 8–12 transition metal, *Y* a group 3–8 transition metal and *Z* is a main group metal from groups 13–15. The structural scaffold of the class of Heusler compounds allows for extensive substitution of the constituting elements, thus enabling to test for electronic influences in different reactions. Up to now, this approach has been applied to the magnetic properties as well as in the selective hydrogenation and methanol steam reforming.

*Low Temperature Electrocatalytic Oxygen Reduction:* The electrocatalytic reduction of oxygen is the typical cathode half reaction for low temperature (polymer-electrolyte-membrane, phosphoric acid, direct alcohol etc.) fuel cells. The preferred pure metal catalyst for this reaction is Pt. However, the high cost of Pt is detrimental to the commercialization of this clean energy technology and there is considerable focus on increasing the intrinsic activity (on a per mole Pt basis) through alloying with base metals and introducing beneficial active site ensemble effects [63-65]. The key descriptor for activity is the adsorption energy of oxygenated species (most importantly OH) on the catalyst surface. Reduction in the OH bond strength is positively correlated with catalyst activity.[66] Alloying of Pt with suitable and cheaper transition metals (Fe[67-69], Cr[70,71], Co[72], Ni[73]) leads to a Pt d-band downshift which weakens this surface-OH interaction, thus increasing activity.[74] Further, it is seen that the specific activity of intermetallic Pt-M phases are always higher than that of alloys of similar composition.[75] Even though the exact reason behind this observation is not yet known, one possibility certainly may be that the disorder in random alloys only results in a fraction of the active sites to have the desired ensemble morphology (as determined by stoichiometry) whereas in the ordered intermetallic the desired ensemble morphology is guaranteed in the entire catalyst bed. In recent times several research groups have focused on strategic design of hybrid core- shell intermetallic catalysts which show some of the highest oxygen reduction activity and time- on-stream stability reported to date [36-38].

*Other examples:* Several other chemistries have also been successfully tested on different intermetallic materials. For example, Ni-Ga intermetallic are reported to be highly active and selective catalysts for CO2 reduction to methanol [49] and even to alkanes and alkenes.[48] Pt- Ge, Al-Cu and Pd-Zn intermetallic catalysts were found to be selective for butadiene semi-hydrogenation [46]. Pd-Zr and Co-Hf intermetallic compounds are seen to be more active for dry reforming of methane compared to the constituent pure metals [47]. Takeshita et al. has reported a number of transition metal-rare earth metal intermetallics to be highly active for ammonia synthesis [76]. Pd-Zn catalysts have been found to be effective for a variety of reactions (beyond those mentioned above) including partial methanol oxidation, methanol dehydrogenation and ester hydrogenation [77].

**References**

[1] A.P.Tsai, S.Kameoka, K.Nozawa, M.Shimoda and Y.Ishii, Acc.Chem.Res., 50,2879 (2017)

[2] Marc Armbruster, Science and Technology of Advanced Materials, 21, 303 (2020)

[3] Marc Armbruster, Robert Schlogl and Yuri Grin, Science and Technology of Advanced Materials, 15, 1, (2014).

[4] Anish Dasgupta and Robert M Rioux, Catalysis Today, 330, 2 (2019). [5] G. Gleig, Encylopaedia Britannica, Wentworth Press 2016.

[6] Armbrüster, M.; Kovnir, K.; Behrens, M.; Teschner, D.; Grin, Y.; Schlögl, R.,Pd-Ga Intermetallic Compounds as Highly Selective Semi-hydrogenation Catalysts, Journal of the American Chemical Society 2010, 132, 14745-14747.   
[6] R. Evans, P. Lloyd, M. Rahman, On the origin of the Hume-Rothery rules for phase stability in α and β brasses, Journal of Physics F: Metal Physics, 9 (1979) 1939.  
[7] V.F. Degtyareva, O. Degtyareva, M.K. Sakharov, N.I. Novokhatskaya, P. Dera, H.K. Mao, R.J. Hemley, Stability of Hume-Rothery phases in Cu–Zn alloys at pressures up to 50 GPa, Journal of Physics: Condensed Matter, 17 (2005) 7955. [8] M. Friedrich, S. Villaseca, L. Szentmiklósi, D. Teschner, M. Armbrüster, Order-Induced Selectivity Increase of Cu60Pd40 in the Semi-Hydrogenation of Acetylene, Materials, 6 (2013) 2958.  
[9] P.Selvam, B.Viswanathan, C.S.Swamy and V.Srinivasan, Int .J. Hydrogen Energy,11,169 (1986). [10] M.V.C.Sastri, B.Viswanathan and S.Srinivasamurthy, Metal Hydrides, Fundamentals and applications, Narosa Pulishing House (1998). [11] A. Miura, H. Wang, B.M. Leonard, H.D. Abruña, F.J. DiSalvo, Synthesis of Intermetallic PtZn Nanoparticles by Reaction of Pt Nanoparticles with Zn Vapor and Their Application as Fuel Cell Catalysts, Chemistry of Materials, 21 (2009) 2661-2667. [12] H.Y. Shao, H.R. Xu, Y.T. Wang, X.G. Li, Preparation and hydrogen storage properties of Mg2Ni intermetallic nanoparticles, Nanotechnology, 15 (2004) 269-274. [13] C. Li, Y. Chen, S. Zhang, J. Zhou, F. Wang, S. He, M. Wei, D.G. Evans, X. Duan, Nickel-Gallium intermetallic nanocrystal catalysts in the semi-hydrogenation of phenylacetylene, ChemCatChem, 6 (2014) 824--831.  
[14] H. Zhou, X. Yang, L. Li, X. Liu, Y. Huang, X. Pan, A. Wang, J. Li, T. Zhang, PdZn Intermetallic Nanostructure with Pd-Zn-Pd ensembles for Highly Active and Chemo-selective Semi-hydrogenation of Acetylene, ACS Catalysis, (2015) 1054--1061. [15] C.S. Spanjers, R.S. Sim, N.P. Sturgis, B. Kabius, R.M. Rioux, In Situ Spectroscopic Characterization of Ni1– x Znx ZnO Catalysts and Their Selectivity for Acetylene Semi-hydrogenation in Excess Ethylene, ACS Catalysis, 5 (2015) 3304--3315.  
[16] A. Onda, T. Komatsu, T. Yashima, Preparation and Catalytic Properties of Single-Phase Ni–Sn Intermetallic Compound Particles by CVD of Sn(CH3)4 onto Ni/Silica, Journal of Catalysis, 201 (2001) 13- 21.   
[17] V. Milanova, T. Petrov, I. Denev, I. Markova, Nanocomposites based on intermetallic nanoparticles template synthesized using different supports, J Chem Techn Metall, 48 (2013).  
[18] S. Sarkar, R. Jana, Suchitra, U.V. Waghmare, B. Kuppan, S. Sampath, S.C. Peter, Ordered Pd2Ge Intermetallic Nanoparticles as Highly Efficient and Robust Catalyst for Ethanol Oxidation, Chemistry of Materials, 27 (2015) 7459-7467.  
[19] M. Martin-Gonzalez, A.L. Prieto, M.S. Knox, R. Gronsky, T. Sands, A.M. Stacy, Ele[24ctrodeposition of Bi1-xSbx films and 200-nm wire arrays from a nonaqueous solvent, Chemistry of Materials, 15 (2003) 1676-1681.  
[20] C.C. Koch, J.D. Whittenberger, Mechanical milling/alloying of intermetallics, Intermetallics, 4 (1996) 339-355.  
[21] Y. Vasquez, Z. Luo, R.E. Schaak, Low-Temperature Solution Synthesis of the Non-Equilibrium Ordered Intermetallic Compounds Au3Fe, Au3Co, and Au3Ni as Nanocrystals, Journal of the American Chemical Society, 130 (2008) 11866-11867.  
[22] K. Takanashi, S. Mitani, M. Sano, H. Fujimori, H. Nakajima, A. Osawa, Artificial Fabrication of an L1(0)-type Ordered FeAu Alloy by Alternate Monatomic Deposition, Applied Physics Letters, 67 (1995) 1016-1018.  
[23] K. Sato, B. Bian, Y. Hirotsu, L1(0) type ordered phase formation in Fe-Au nanoparticles, Jpn. J. Appl. Phys. Part 2 - Lett., 41 (2002) L1-L3.  
[24] R.E. Cable, R.E. Schaak, Solution Synthesis of Nanocrystalline M−Zn (M = Pd, Au, Cu) Intermetallic Compounds via Chemical Conversion of Metal Nanoparticle Precursors, Chemistry of Materials, 19 (2007) 4098-4104.

[25] R.E. Cable, R.E. Schaak, Low-Temperature Solution Synthesis of Nanocrystalline Binary Intermetallic Compounds Using the Polyol Process, Chemistry of Materials, 17 (2005) 6835-6841.  
[26] N. Cinca, C.R.C. Lima, J.M. Guilemany, An overview of intermetallics research and application: Status of thermal spray coatings, Journal of Materials Research and Technology, 2 (2013) 75-86.

[27] D.O. Downing, Z. Liu, B.W. Eichhorn, Synthesis of PtSn4 and Ir3Sn7 intermetallic nanoparticles from bimetallic Zintl cluster precursors, Polyhedron, 103, Part A (2016) 66-70.  
[28] A. Yakymovych, H. Ipser, Synthesis and Characterization of Pure Ni and Ni-Sn Intermetallic Nanoparticles, Nanoscale Research Letters, 12 (2017) 142.

[29] V. Milanova, T. Petrov, O. Chauvet, I. Markova, Study of carbon-based nanocomposites with intermetallic (Co-Sn, Ni-Sn) nanoparticles, Rev Adv Mater Sci, 37 (2014).  
[30] A. Ota, M. Armbrüster, M. Behrens, D. Rosenthal, M. Friedrich, I. Kasatkin, F. Girgsdies, W. Zhang, R. Wagner, R. Schlögl, Intermetallic Compound Pd2Ga as a Selective Catalyst for the Semi-Hydrogenation of Acetylene: From Model to High Performance Systems, The Journal of Physical Chemistry C, 115 (2011) 1368--1374.  
[31] B.M. Leonard, N.S.P. Bhuvanesh, R.E. Schaak, Low-Temperature Polyol Synthesis of AuCuSn2 and AuNiSn2: Using Solution Chemistry to Access Ternary Intermetallic Compounds as Nanocrystals, Journal of the American Chemical Society, 127 (2005) 7326-7327.

[32] S. Jana, J.W. Chang, R.M. Rioux, Synthesis and Modeling of Hollow Intermetallic Ni–Zn Nanoparticles Formed by the Kirkendall Effect, Nano Letters, 13 (2013) 3618-3625.

[33] C.S. Spanjers, R.S. Sim, N.P. Sturgis, B. Kabius, R.M. Rioux, In Situ Spectroscopic Characterization of Ni1– x Znx ZnO Catalysts and Their Selectivity for Acetylene Semi-hydrogenation in Excess Ethylene, ACS Catalysis, 5 (2015) 3304--3315.   
[34] H.M. Barkholtz, J.R. Gallagher, T. Li, Y. Liu, R.E. Winans, J.T. Miller, D.-J. Liu, T. Xu, Lithium Assisted “Dissolution–Alloying” Synthesis of Nanoalloys from Individual Bulk Metals, Chemistry of Materials, 28 (2016) 2267-2277.  
[35] J.S. Sun, Z. Wen, L.P. Han, Z.W. Chen, X.Y. Lang, Q. Jiang, Nonprecious Intermetallic Al7Cu4Ni Nanocrystals Seamlessly Integrated in Freestanding Bimodal Nanoporous Copper for Efficient Hydrogen Evolution Catalysis, Advanced Functional Materials, 28 (2018) 1706127.  
[36] X.Y. Lang, G.F. Han, B.B. Xiao, L. Gu, Z.Z. Yang, Z. Wen, Y.F. Zhu, M. Zhao, J.C. Li, Q. Jiang, Mesostructured Intermetallic Compounds of Platinum and Non-Transition Metals for Enhanced Electrocatalysis of Oxygen Reduction Reaction, Advanced Functional Materials, 25 (2015) 230-237.  
[37] D. Wang, H.L. Xin, R. Hovden, H. Wang, Y. Yu, D.A. Muller, F.J. DiSalvo, H.D. Abruña, Structurally ordered intermetallic platinum–cobalt core–shell nanoparticles with enhanced activity and stability as oxygen reduction electrocatalysts, Nature Materials, 12 (2012) 81.  
[38] T. Cheng, X.-Y. Lang, G.-F. Han, R.-Q. Yao, Z. Wen, Q. Jiang, Nanoporous (Pt1-xFex)3Al intermetallic compounds for greatly enhanced oxygen electroreduction catalysis, Journal of Materials Chemistry A, 4 (2016) 18878-18884.  
[39] G.-F. Han, L. Gu, X.-Y. Lang, B.-B. Xiao, Z.-Z. Yang, Z. Wen, Q. Jiang, Scalable Nanoporous (Pt1– xNix)3Al Intermetallic Compounds as Highly Active and Stable Catalysts for Oxygen Electroreduction, ACS Applied Materials & Interfaces, 8 (2016) 32910-32917.

[40] Schwab, G. M. Metal electrons and Catalysis Trans. Faraday Soc. **1946**, 42, 689– 697 DOI: 10.1039/tf9464200689; Schwab, G. M.; Pesmatjoglou, S. Metal electrons and alloy catalysis J. Phys. Colloid Chem. **1948**, 52, 1046– 1053 DOI: 10.1021/j150462a014. [41] Casado-Rivera, Z. Gál, A.C.D. Angelo, C. Lind, F.J. DiSalvo, H.D. Abruña, Electrocatalytic Oxidation of Formic Acid at an Ordered Intermetallic PtBi Surface, ChemPhysChem, 4 (2003) 193-199. [42] X. Ji, K.T. Lee, R. Holden, L. Zhang, J. Zhang, G.A. Botton, M. Couillard, L.F. Nazar, Nanocrystalline intermetallics on mesoporous carbon for direct formic acid fuel cell anodes, Nature Chemistry, 2 (2010) 286. [43]] A. Miura, H. Wang, B.M. Leonard, H.D. Abruña, F.J. DiSalvo, Synthesis of Intermetallic PtZn Nanoparticles by Reaction of Pt Nanoparticles with Zn Vapor and Their Application as Fuel Cell Catalysts, Chemistry of Materials, 21 (2009) 2661-2667.  
[44] L.J. Zhang, Z.Y. Wang, D.G. Xia, Bimetallic PtPb for formic acid electro-oxidation, Journal of Alloys and Compounds, 426 (2006) 268-271. [45] L.R. Alden, D.K. Han, F. Matsumoto, H.D. Abruña, F.J. DiSalvo, Intermetallic PtPb Nanoparticles Prepared by Sodium Naphthalide Reduction of Metal-Organic Precursors: Electrocatalytic Oxidation of Formic Acid, Chemistry of Materials, 18 (2006) 5591-5596. [46] Global Demand of Polyethylene to reach 99.6 million tons in 2018, Pipeline & Gas Journal, 241 (2014). [47] J. Margitfalvi, L. Guczi, Reactions of acetylene during hydrogenation on Pd black catalyst, Journal of Catalysis, 72 (1981) 185-198.  
[48] E. Vignola, S.N. Steinmann, A. Al Farra, B. Vandegehuchte, D. Curulla, P. Sautet, Evaluating the Risk of C-C Bond Formation during Selective Hydrogenation of Acetylene on Palladium, ACS Catalysis, (2018). [49] F. Studt, F. Abild-Pedersen, T. Bligaard, R.Z. Srensen, C.H. Christensen, J.K. Norskov, Identification of non-precious metal alloy catalysts for selective hydrogenation of acetylene., Science (New York, N.Y.), 320 (2008) 1320--1322.  
[50] A. Molnar, A. Sarkany, M. Varga, Hydrogenation of carbon-carbon multiple bonds: chemo-, regio- and stereo-selectivity, Journal of Molecular Catalysis A-Chemical, 173 (2001) 185-221. [51] H. Zhou, X. Yang, L. Li, X. Liu, Y. Huang, X. Pan, A. Wang, J. Li, T. Zhang, PdZn Intermetallic Nanostructure with Pd-Zn-Pd ensembles for Highly Active and Chemoselective Semi-hydrogenation of Acetylene, ACS Catalysis, (2015) 1054--1061. [52] A. Ota, M. Armbrüster, M. Behrens, D. Rosenthal, M. Friedrich, I. Kasatkin, F. Girgsdies, W. Zhang, R. Wagner, R. Schlögl, Intermetallic Compound Pd2Ga as a Selective Catalyst for the Semi-Hydrogenation of Acetylene: From Model to High Performance Systems, The Journal of Physical Chemistry C, 115 (2011) 1368-1374. [53] M. Armbrüster, K. Kovnir, M. Behrens, D. Teschner, Y. Grin, R. Schlögl, Pd−Ga Intermetallic Compounds as Highly Selective Semihydrogenation Catalysts, Journal of the American Chemical Society, 132 (2010) 14745-14747.   
[54] J. Osswald, K. Kovnir, M. Armbrüster, R. Giedigkeit, R.E. Jentoft, U. Wild, Y. Grin, R. Schlögl, Palladium–gallium intermetallic compounds for the selective hydrogenation of acetylene: Part II: Surface characterization and catalytic performance, Journal of Catalysis, 258 (2008) 219-227. [55] C.S. Spanjers, J.T. Held, M.J. Jones, D.D. Stanley, R.S. Sim, M.J. Janik, R.M. Rioux, Zinc inclusion to heterogeneous nickel catalysts reduces oligomerization during the semi-hydrogenation of acetylene, Journal of Catalysis, 316 (2014) 164-173. [56] C.S. Spanjers, A. Dasgupta, M. Kirkham, B.A. Burger, G. Kumar, M.J. Janik, R.M. Rioux, Determination of Bulk and Surface Atomic Arrangement in Ni–Zn γ-Brass Phase at Different Ni to Zn Ratios, Chemistry of Materials, 29 (2017) 504-512. [57] Y. Liu, X. Liu, Q. Feng, D. He, L. Zhang, C. Lian, R. Shen, G. Zhao, Y. Ji, D. Wang, G. Zhou, Y. Li, Intermetallic NixMy (M = Ga and Sn) Nanocrystals: A Non-precious Metal Catalyst for Semi- Hydrogenation of Alkynes, Advanced Materials, 28 (2016) 4747-4754. [58] M. Armbruster, K. Kovnir, M. Friedrich, D. Teschner, G. Wowsnick, M. Hahne, P. Gille, L. Szentmiklsi, M. Feuerbacher, M. Heggen, F. Girgsdies, D. Rosenthal, R. Schlogl, Y. Grin, Al13Fe4 as a low-cost alternative for palladium in heterogeneous hydrogenation, Nature Materials, 11 (2012) 690--693. [59] S. Furukawa, T. Komatsu, Selective Hydrogenation of Functionalized Alkynes to (E)-Alkenes, Using Ordered Alloys as Catalysts, ACS Catalysis, 6 (2016) 2121-2125. [60] N. Iwasa, N. Takezawa, New Supported Pd and Pt Alloy Catalysts for Steam Reforming and Dehydrogenation of Methanol, Topics in Catalysis, 22 (2003) 215-224. [61] M. Armbrüster, M. Behrens, K. Föttinger, M. Friedrich, É. Gaudry, S.K. Matam, H.R. Sharma, The Intermetallic Compound ZnPd and Its Role in Methanol Steam Reforming, Catalysis Reviews, 55 (2013) 289-367. [62] G. Weirum, M. Kratzer, H.P. Koch, A. Tamtögl, J. Killmann, I. Bako, A. Winkler, S. Surnev, F.P. Netzer, R. Schennach, Growth and Desorption Kinetics of Ultrathin Zn Layers on Pd(111), The Journal of Physical Chemistry C, 113 (2009) 9788-9796. [63] Y.-J. Wang, N. Zhao, B. Fang, H. Li, X.T. Bi, H. Wang, Carbon-Supported Pt-Based Alloy Electrocatalysts for the Oxygen Reduction Reaction in Polymer Electrolyte Membrane Fuel Cells: Particle Size, Shape, and Composition Manipulation and Their Impact to Activity, Chemical Reviews, 115 (2015) 3433-3467. [64] S. Mukerjee, S. Srinivasan, M.P. Soriaga, Role of Structural and Electronic Properties of Pt and Pt Alloys on Electrocatalysis of Oxygen Reduction J. Electrochem. Soc, 142 (1995) 1409-1422.  
[65] M. Shao, Q. Chang, J.-P. Dodelet, R. Chenitz, Recent Advances in Electrocatalysts for Oxygen Reduction Reaction, Chemical Reviews, 116 (2016) 3594-3657. [66] E. Antolini, J.R.C. Salgado, M.J. Giz, E.R. Gonzalez, Effects of geometric and electronic factors on ORR activity of carbon supported Pt–Co electrocatalysts in PEM fuel cells, International Journal of Hydrogen Energy, 30 (2005) 1213-1220.  
[67] D.Y. Chung, S.W. Jun, G. Yoon, S.G. Kwon, D.Y. Shin, P. Seo, J.M. Yoo, H. Shin, Y.-H. Chung, H. Kim, B.S. Mun, K.-S. Lee, N.-S. Lee, S.J. Yoo, D.-H. Lim, K. Kang, Y.-E. Sung, T. Hyeon, Highly Durable and Active PtFe Nanocatalyst for Electrochemical Oxygen Reduction Reaction, Journal of the American Chemical Society, 137 (2015) 15478-15485. [68] Q. Li, L. Wu, G. Wu, D. Su, H. Lv, S. Zhang, W. Zhu, A. Casimir, H. Zhu, A. Mendoza-Garcia, S. Sun, New Approach to Fully Ordered fct-FePt Nanoparticles for Much Enhanced Electrocatalysis in Acid, Nano Letters, 15 (2015) 2468-2473.  
[69] L. Chen, C. Bock, P.H.J. Mercier, B.R. MacDougall, Ordered alloy formation for Pt3Fe/C, PtFe/C and Pt5.75Fe5.75Cuy/CO2-reduction electro-catalysts, Electrochimica Acta, 77 (2012) 212-224.  
[70] Z. Cui, H. Chen, W. Zhou, M. Zhao, F.J. DiSalvo, Structurally Ordered Pt3Cr as Oxygen Reduction Electrocatalyst: Ordering Control and Origin of Enhanced Stability, Chemistry of Materials, 27 (2015) 7538-7545.  
[71] L. Zou, J. Li, T. Yuan, Y. Zhou, X. Li, H. Yang, Structural transformation of carbon-supported Pt3Cr nanoparticles from a disordered to an ordered phase as a durable oxygen reduction electrocatalyst, Nanoscale, 6 (2014) 10686-10692.  
[72] H. Schulenburg, E. Müller, G. Khelashvili, T. Roser, H. Bönnemann, A. Wokaun, G.G. Scherer, Heat- Treated PtCo3 Nanoparticles as Oxygen Reduction Catalysts, The Journal of Physical Chemistry C, 113 (2009) 4069-4077.  
[73] L. Zou, J. Fan, Y. Zhou, C. Wang, J. Li, Z. Zou, H. Yang, Conversion of PtNi alloy from disordered to ordered for enhanced activity and durability in methanol-tolerant oxygen reduction reactions, Nano Research, 8 (2015) 2777-2788.  
[74] A. Nilsson, L.G.M. Pettersson, B. Hammer, T. Bligaard, C.H. Christensen, J.K. Nørskov, The electronic structure effect in heterogeneous catalysis, Catalysis Letters, 100 (2005) 111-114.  
[75] E. Antolini, Alloy vs. intermetallic compounds: Effect of the ordering on the electrocatalytic activity for oxygen reduction and the stability of low temperature fuel cell catalysts, Applied Catalysis B: Environmental, 217 (2017) 201-213. [76] T. Takeshita, W.E. Wallace, R.S. Craig, Rare earth intermetallics as synthetic ammonia catalysts, Journal of Catalysis, 44 (1976) 236-243.  
[77] B.E. Green, C.S. Sass, L.T. Germinario, P.S. Wehner, B.L. Gustafson, Ester Hydrogenation over Pd- Zn/SiO2, Journal of Catalysis, 140 (1993) 406-417.