Catalysis with Intermetallic Compounds through the Prism of their Chemical Properties

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The chemical process is a "competition" between different possible pathways, each with own thermodynamic and kinetic parameters. To drive the favourable process, the development of catalysts with the optimum adsorption properties is a key task for industry and scientific community. These adsorption properties are defined by the electronic state of the active element, atomic interactions with other components, morphology of the catalyst, etc. The immense experimental and computational efforts over the last decades were granted by disclosure of certain correlations between inherent catalyst properties and catalytic performance, e.g. the Sabatier principle, *d*-band theory, scaling relations, etc. However, considering the process complexity (temperature, gas ratios, pressure, etc.), the state of the catalyst under real reaction conditions becomes a decisive issue. Intermetallic compounds (IMCs) combine well-defined crystal structure, special features of electronic structure and chemical bonding, allowing (i) the knowledge-based search for catalysts with desired adsorption properties, (ii) understanding of their chemical properties and transformations under reaction conditions and/or (iii) gives new ideas about the chemical nature of active sites, reaction mechanism and, as a result, insight into possible routes for upscaling and further catalyst development. Since 2006, the Department of *Chemical Metals Science* was dealing with those and many other aspects on intermetallic compounds in heterogeneous catalysis and electrocatalysis.

Knowledge-based "quest" for efficient catalysts

On one hand, use of intermetallic compounds as catalysts allow to overcome the obstacles in catalysis research related to the complexity of supported catalysts represented by a poorly defined nature of active species, changes of the catalyst as a result of metal-support interactions, inhomogeneity of particle distribution over support, etc. On the other hand, intermetallic compounds have well-defined crystal structures, meaning definite atomic coordination of the active component. Considering the sensibility of ***semi-hydrogenation of acetylene*** ($C_2H_2 + H_2 \rightarrow C_2H_4$) to isolated active sites, the systematic study of the **Pd-Ga** system was carried out [1]. The reduced number of Pd neighbors in Pd_3Ga_7, PdGa and Pd_2Ga (compared to elemental Pd) and the covalent nature of chemical bonding lead to the improved selectivity and stability of these catalysts compared to the conventional Al_2O_3-supported Pd and Pd-Ag ones [2, 3]. Numerous *in situ* characterization studies (XRD, FTIR, XPS, EXAFS) clearly reveal the stability of Pd-Ga compounds under reaction conditions on different scales which allows to imply features of their crystal structures for realization of the so-called "*site isolation*" concept. To verify the influence of the electronic state of the Pd atoms on the selectivity towards ethylene, different compositions of the solid solution $Ga_{1-x}Sn_xPd_2$ ($0 \leq x \leq 1$) were studied [4]. Replacement of Ga by Sn leads to disorder only on Ga site, allowing to preserve the idea of site isolation with simultaneous modification of the electronic state of Pd. For the whole series, the values of selectivity towards ethylene were over 85 %, but the maximum of specific activity was observed for a nominal composition $Ga_{0.72}Sn_{0.28}Pd_2$, corresponding to 4.0 at.% Sn in the near-surface region. The intrinsic reasons for catalytic activity variation were explained by interesting features of electronic structure and chemical bonding in $Ga_{1-x}Sn_xPd_2$ [5]. Exploring the applicability of the "*site isolation"* concept and implementing our own expertise in chemical bonding analysis, the cheap and very selective semi-hydrogenation catalyst **Fe_4Al_{13}** was discovered and extensively studied [6]. Pd-Ga compounds as well as $Al_{13}Fe_4$ are excellent examples of rational knowledge-based search for new catalysts.

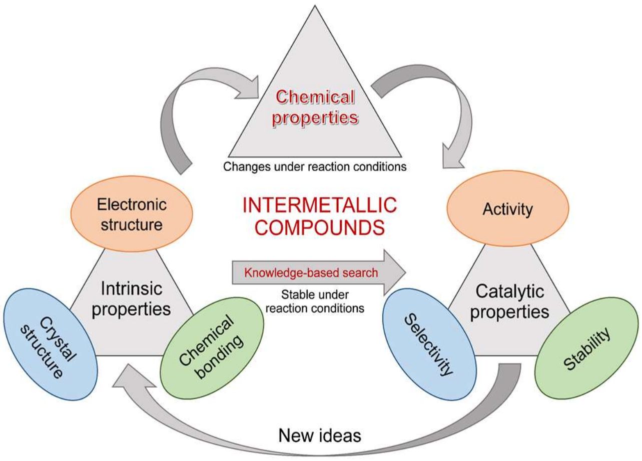

Fig. 1: Chemical properties of IMCs as a bridge between the intrinsic characteristics and catalysis.

Chemical properties for insights in catalysis

Only a limited number of catalytic processes provide the conditions under which intermetallic compounds do not undergo changes at least on the surface. Since a catalytic reaction takes place on the surface, it is vital to track and understand the state of the catalyst before and after the course of reaction for reliable catalytic data interpretation. In other words, exploring the area of IMC's application as catalysts makes stability one of the key issues. Therefore, knowledge about their chemical properties becomes essential. Scarce available information about the chemical properties of IMCs as well as the dynamics of the catalyst state under reaction conditions frequently leads to misleading results on their catalytic performance. A few prominent examples of how information about crystal structure and chemical bonding of IMCs guide an understanding of their behavior under oxidation conditions and interpretation of the catalytic data are presented below.

Methanol steam reforming (MSR; $CH_3OH + H_2O \rightarrow 3H_2 + CO_2$) is one of the important processes of hydrogen production. The similarity of the ZnPd electronic structure with that one of Cu, which is an industrially applied catalyst for MSR, was the driving force for an extensive study of **ZnPd** as MSR catalyst [7]. Interestingly, varying the composition of ZnPd within the broad homogeneity range (from 41 up to 53 at.% Zn) allows to modify the CO_2 selectivity towards ethylene from 10% up to 96%, respectively. CO_2 selectivity is governed by the *in situ*-state of the surface, favorably composed of the intermetallic compound ZnPd and ZnO for the most efficient "team work" in MSR process. This is an excellent example how a small difference in composition within the homogeneity range, i.e. preserving the same crystal structure, can lead to a catalyst with either high performance or extremely poor one.

Another case study on chemical properties of IMCs as a guide for the interpretation of catalytic results are **Ca-Ag** catalysts for ***ethylene epoxidation***. Ethylene epoxidation is a thermodynamically unfavorable process ($2C_2H_4 + O_2 \rightarrow 2C_2H_4O$, $\Delta H = -104.6$ kJ/mol) compared to its full combustion ($C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$, $\Delta H = -1422.6$ kJ/mol), making the search of the catalyst selectivity-driven. Two compounds, $CaAg_2$ (KHg_2-type, *Imma*) and CaAg (*α*-TlI-type, *Cmcm*), were investigated as heterogeneous catalysts for ethylene epoxidation in detail [4]. In case of $CaAg_2$, after the induction phase selectivity values reach 60–65% and remain unchanged over 500 h of the ethylene epoxidation experiment. The detailed characterization of the catalyst material reveals the oxidation of $CaAg_2$ with formation of Ag particles, which are embedded in a complex and dynamic support of CaO, $Ca(OH)_2$ and $CaCO_3$, that is in line with obtained catalytic data. Importantly, comparison of such an *in situ* formed catalyst with Ag@CaO, prepared via the conventional impregnation approach, clearly highlights the beneficial effect of $CaAg_2$ as catalyst precursor. Contrary to $CaAg_2$, binary CaAg possesses lower selectivity (32–34 %), but they don't change with time and variation of ethyl chloride (promoter) amount in the gas feed. And even more impressive, the particles of CaAg remain almost unchanged after 600 h on stream. Based on detailed chemical bonding analysis as well as adsorption energy calculations, the stability of CaAg can be explained by the formation of a dense and highly ordered CaO-overlayer on the (010) surface, which is also the favored cleavage surface upon sample crushing. A strong adsorption of the desired ethylene oxide as well as intermediate acetaldehyde on CaO@CaAg confirming the low values of ethylene conversion in case of CaAg catalyst. This passivating CaO-layer on CaAg (010) prevents its further bulk oxidation and provides the stable selectivity values during epoxidation. This study emphasizes that even if compounds have close compositions and are composed of the same elements, they can have different arrangements of atoms and structural motifs. This determines the chemical bonding and chemical properties of compounds and as a result, their catalytic performance.

Just like heterogeneous catalysis, electrocatalysis faces similar difficulties with the electrocatalyst characterization and interpretation of the catalytic data due to the complexity of the used electrode assemblies (composed of electrocatalyst, binders, additives, etc.), impact of electrolyte nature and its concentration, applied potential, etc. The consideration of the electrocatalyst as a part of the system under dynamic operational conditions is of extreme importance for advancing the electrocatalyst development. Given the above-mentioned prominent features of IMCs and the recent tremendous interest of human society in the chemical conversion and storage of energy, ***water electrolysis*** ($2H_2O \rightarrow 2H_2 + O_2$) as a promising way to produce "green" hydrogen was chosen for complementary studies. Without regard to the type of electrolysis (proton-exchange membrane (PEM) or alkaline electrolysis (AEL)), the sluggish kinetics of the oxygen evolution reaction on the anode side limits the large-scale application of this process. The optimum OER activity and stability under harsh oxidative conditions of PEM electrolysis is known for IrO_x electrocatalysts. The research in this field is focused on optimization of IrO_x catalysts as well as attempts to reduce the amount of, or completely replace, scarce Ir. Can Ir dissolution be controlled by the strength of the atomic interactions within IMC? Can OER activity be tailored by formation of IMC? Indeed, an electrochemical study of ternary **$Hf_2B_{2-2\delta}Ir_{5+\delta}$ compound** as anode for ***PEM electrolysis*** in combination with chemical bonding analysis clearly highlight this. The orthorhombic structure of the ternary compound $Hf_2B_{2-2\delta}Ir_{5+\delta}$ has cage-like character with the anionic covalently bonded Ir-B framework and hafnium cations occupying B-Ir cages. These features of chemical bonding are obviously reflected in the chemical behavior of $Hf_2B_{2-2\delta}Ir_{5+\delta}$ under OER conditions and have influence on the OER activity of this material. The prominent initial OER activity of $Hf_2B_{2-2\delta}Ir_{5+\delta}$ is accompanied with the suppressed dissolution of Ir (compared with an Ir anode), revealing the enhancement of the material’s stability in case of IMC. The long-term operation (246 h) at current densities of 100 mA cm^{-2} reveals the continuous improvement of OER activity with time, which can be explained by the “team” OER activity of Ir-terminated surface of $Hf_2B_{2-2\delta}Ir_{5+\delta}$ and *in situ*-formed $IrO_x(OH)_y(SO_4)_z$ particles as a catalyst of 2nd generation. In summary, the covalent bonding in the Ir-B framework hinders the massive Ir dissolution and leads to the long-term bulk stability of $Hf_2B_{2-2\delta}Ir_{5+\delta}$ [8].

Looking for Ir-free OER electrocatalysts, elemental platinum was considered as alternative with pronounced stability against dissolution compared to other noble metals. However, the OER activity of Pt is one of the lowest. The idea to modify the electronic state of Pt atoms to simultaneously improve OER activity and to preserve the stability of Pt against dissolution under anodic operation was verified by investigation of **Al-Pt intermetallic compounds**. Considering the crystal structures, Al-Pt intermetallic compounds can be divided into three groups: (i) Al-rich compounds (Al_4Pt and $Al_{21}Pt_8$) with their own structures based on icosahedral environment of Pt; (ii) the compounds Al_2Pt, Al_3Pt_2 and AlPt as derivatives of the close packing of Pt atoms; and (iii) Pt-rich phases (Al_3Pt_5 and Al_3Pt) with structures similar to elemental Pt. Study on these compounds as OER electrocatalysts clearly reveals: (i) the instability and noticeable leaching of Al in case of Al_4Pt and $Al_{21}Pt_8$; (ii) enhanced (compared to elemental Pt) OER activity of Al_2Pt and Al_3Pt_2 compounds with obvious activation after electrochemical pre-treatments, (iii) OER activity of Al_3Pt and Al_3Pt_5 comparable with elemental Pt [9]. Possessing a moderate OER activity and stability, the compound Al_2Pt was studied at elevated current density of 90 mA cm^{-2} for prolonged time (19 days) [8]. Considering the harsh oxidative conditions of OER, Al-Pt compounds do not maintain their structural and electronic properties on the surface and near-surface region due to the Al leaching and surface rearrangement. However, *in situ*-formed catalytically active and dynamic surfaces, containing the remnant of intermetallic compounds, Pt-rich Al_xPt_{1-x} phase and Pt oxides, possess comparable, or even better, OER activity (compared to *fcc* Pt). Depending on the composition and crystal structure, the depth of structural changes is different. Tracking the changes of the catalyst during the reaction using different spectroscopy techniques requires the use of reference values, which are rare for intermetallic compounds. Systematic HAXPES study on Al-Pt compounds brought thought-provoking results, showing the increasing shift of Pt 4*f* core levels towards higher binding energies with increasing Al content. At the same time, quantum chemical calculations reveal increasing absolute values of Pt negative charges. Based on the classical “chemical shift” idea, the core level shifts are expected in the opposite direction. To shed a light into this issue, extensive computational analysis points out that higher negative charges of Pt atoms are accompanied by reduced occupancy of Pt 5*d* orbitals, leading to the restricted screening of the 4*f* core hole by these electrons which can explain the experimentally observed shifts of the Pt 4*f* core levels towards higher binding energies (Figure 2) [10]. To the best of our knowledge, this is the first systematic case study, investigating the correlation between the experimental spectroscopic data (HAXPES) and computational data on electronic structure and chemical bonding analysis [10], **COLL_03_Antonyshyn_Altendorf**, **CMS_04_Wagner**.

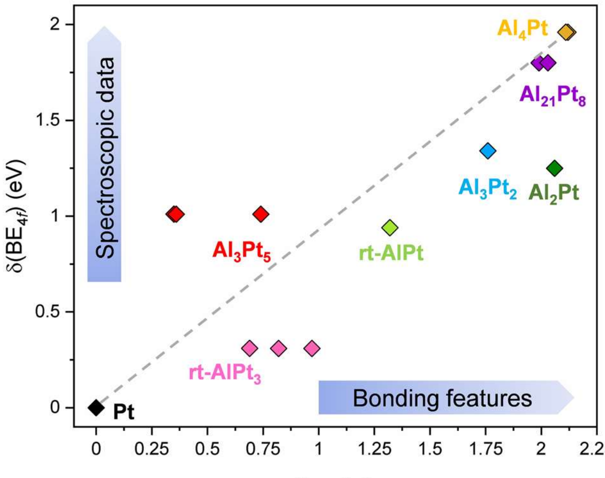

Fig. 2: The experimental Pt 4f core level shifts versus computed deviations in 5d occupancy in Al-Pt compounds.

Since Al_2Pt combines a sufficient OER activity and stability under oxidative conditions, the chemistry was explored via the replacement of Al by other main group elements (M = Ga, In, Sn), keeping the same crystal structure for $\boldsymbol{M_2}$**Pt** while modifying the electronic state of Pt [11]. The decrease of OER activity ($In_2Pt > Ga_2Pt > Al_2Pt$) is governed by the chemical nature of the counterpart elements M and their leaching rates under OER conditions. The improved OER activity is due to the roughening of the surface as well as a result of the enhanced reactivity of modified Pt. The inactivity of Sn_2Pt is due to the formation of a passiveting SnO_2 layer with poor electrical conductivity.

A high polarity of the heteroatomic bonds in $MoNi_4$ in combination with the negative charge of Ni atoms explain the corrosion behavior of **Mo-Ni HER catalysts**, and, additionally, illustrate the importance of such complementary studies [12].

From lab scale to industrially-relevant level

Remarkable advantages of unsupported single-phase catalysts as model systems for knowledge-based search and study of catalysts becomes a hindrance for large-scale application due to the small active surface areas and limited activity. Therefore, new intelligent ways for synthesis/production of high-surface area catalysts are of tremendous importance. To obtain the highly selective acetylene hydrogenation Pd-Ga catalysts in nanoparticulated state, top-down methods like milling and etching, as well as bottom-up synthesis routes were proposed and successfully employed [13]. For synthesis of ZnPd nanoparticles (promising MSR catalyst), three different approaches were applied with success: (i) co-reduction of Zn^{2+} and Pd^{2+}, (ii) the use of ZnH_2 as a reducing agent for Pd^{2+} and (iii) electroless plating of Zn nanoparticles [14].

The chemistry of borides is impressively rich in terms of structural motifs, characterized by strong covalent boron-boron and boron-metal interactions, leading to interesting chemical and physical properties of these compounds. Therefore, transition metal (*TM*) borides attract considerable attention as electrocatalysts, particularly **Ni-B electrocatalysts** for OER in alkaline media. The synthesis of borides is still a challenge, despite the large number of possible methods. The main disadvantage of the known synthesis processes is the contamination of the formed borides either by the components of the reaction process or by the used equipment. Therefore, a novel crucible-free synthesis route was investigated. This heterogeneous reaction between a solid metal M and a gaseous boron halide $BHal_3$ allows to obtain non-contaminated borides under quite moderate conditions (see equation).

$$(x+z)\ M\ (s) + y\ BHal_3\ (g) \rightarrow M_zB_y\ (s) + x\ MHal_{3y/x}\ (g)$$

The experimental setup for heterophase boronization is based on the hot wire method of *van Arkel* and *de Boer*, which includes heating of the metal wire in an atmosphere containing $BHal_3$ to form a corresponding metal boride and volatile metal halide that condenses in colder parts of the apparatus. Continuous removal of the halide is not only helpful for obtaining pure borides, but also facilitates its formation according to the *Le Chatelier's* principle. Heating of the metal substrate can be either conductive, using a direct current flow (suitable for wires or rods [15–17]) or inductive, using a high frequency furnace (applicable for geometrically complex objects such as nets, gauzes, foams, etc. [18]). By controlling the reaction conditions, in particular temperature, partial pressures of $BHal_3$ and reaction time, contaminant-free borides of different compositions can be obtained either as bulk materials or in the form of thin films. As an example, boronization of Ni foam (2.5 mm thick, 800 µm) with BBr_3 leads to the formation of a Ni_3B layer, which has a beneficial effect on the OER activity (Figure 3). The heterophase boronization has an enormous potential for future design of new electrocatalysts. On one hand, the library of the substrates can be explored towards other metals, binary and ternary IMCs, steels, etc., and, on the other hand, the spectrum of application can be widened towards other electrochemical processes.

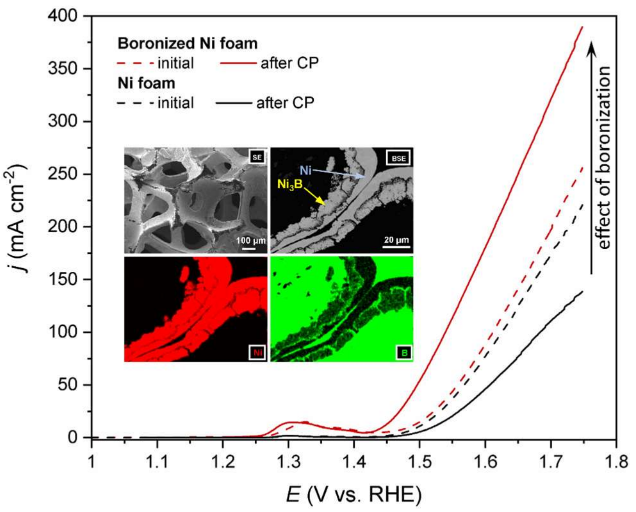

Fig. 3: OER activities of boronized and non-boronized Ni foams (inset: SEM images of boronized Ni foam (top view and cross section) with elemental mapping).

External Cooperation Partners

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