CO2 reduction on post-transition metals and their alloys: an industrial approach

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Post-transition metals: their characteristics and use in sustainable heterogeneous catalysis and electrocatalysis

2.1 Post-transition metals: general overview and electronic structure

Catalysis plays a tremendous role in industry, with approximately 85-90% of all chemical processes making use of catalytic steps. Catalytic processes are not only more efficient, but can be more environmentally sustainable due to the better use of atoms in molecules and avoidance of extra chemical reagents. Despite the fact that catalysts can be present in many forms, a preponderance of catalytic processes are based on heterogeneous catalysis, with transition metals making up the majority of the catalyst materials employed in the most relevant industrial processes.[1] It is obvious then that a great deal of knowledge and understanding in this field orbits around these metals, with important models, such as the d-band center model[2] able to describe reactivity trends and many studies on well-defined systems providing insights on structure and reactivity relationships. It is useful, then, to give a brief overview of post-transition metals in order to highlight their characteristics and to examine their role in heterogeneous catalysis and electrocatalysis.

When talking about p-block metals, we generally refer to a small number of elements included between the end of the d-block series and the semimetals. The elements included in this group are Al, Ga, In and Tl in group 13, Sn and Pb in group 14 and Bi in group 15. Out of these elements, Al is the only one not possessing d-orbitals in its electronic configuration, and therefore it is excluded from the somewhat similar classification of post-transition metals. This latter way of grouping elements can generate confusion due to the IUPAC definition of a transition metal as “an element whose atoms have an incomplete d sub-shell, or which can give rise to cations with an incomplete d sub-shell.”[3] This creates a somewhat uncertain border which brings different authors to classify group 12 elements in the d-block either as post-transition or transition metals. Elements that always fall under the classification of post-transition metals are Ga, In, Tl, Sn, Pb and Bi. In the following, when talking about post-transition metals, we will be referring to these elements.

The outer electronic configuration of post-transition metals is ns^2np^1 for Ga, In and Tl, ns^2np^2 for Sn and Pb and 6$s^2$6p^3 for Bi. The n*d* band is completely full in these metals and it is therefore a core level with little influence on their chemistry. This has an effect, for example, on the cohesive energy and the catalytic properties. In a simplified way, we can say that in transition metals the cohesive energy, which is related to the melting point, follows a parabolic trend from the left to the right of the series. As the highly localized d-band is filled up until the middle of the transition series (bonding section of the band) the cohesive energy increases, while further filling of the band (anti-bonding section) causes a decrease of cohesive energy. This explains why metals around the center of the transition series are the most refractory. Even more importantly to our purposes, the catalytic properties of transition metals are strongly influenced by their d-band. This sharp, localized band can bond with adsorbates allowing, for example, the breaking or rearrangement of internal molecular bonds.[1]

These effects are absent in post-transition metals, and their behavior is mostly influenced by their broad sp-band. Without the localized interaction of the d-electrons the cohesive energies are much smaller, resulting in lower melting points, and the interaction with molecules is mild due to the overlap of the orbitals of the molecule with the broad sp-band.[1] For this reason, post-transition metals cannot catalyze chemical reactions the same way transition metals do.

The elements in the first periods of groups 13, 14 and 15 are non-metals, due to the different overlap of s and p orbitals in different shells as well as relativistic effects. This is well illustrated in the case of group 14. Carbon, in its diamond allotropic form, adopts a tetrahedral, covalent coordination. With this geometry, two electronic bands are formed: these can be thought as a bonding and an anti-bonding band, separated by a large band gap. This is advantageous in the case of carbon because all the electrons can occupy the bonding band, giving rise to the very strong covalent bonds observed in diamond. If carbon adopted the close packed structure typical of metals, the overlap of the orbitals of the atoms in the crystal would give rise to a half full continuous band, in which some electrons would have a non-bonding character. As we go down the group, the smaller overlap of the s and p orbitals in progressively more external shells gives rise to a smaller band gap when the diamond structure is adopted. For this reason, Si and Ge are semiconductors (their band gap is much smaller) and Sn shows a mixed behavior: the band splitting when Sn forms a diamond structure is very small, so that the advantage of adopting the diamond or the metallic structure is not clear-cut. At room temperature, the most stable phase is β-Sn, metallic, with a body-centered tetragonal structure, while below 13°C it transitions into α-Sn with a diamond structure. Note that β-Sn, despite its metallic character, does not have a typical close-packed structure. This is due to the fact that even in its metallic state the bonds in the crystal show a partially directional, covalent character. Pb is fully metallic with an fcc structure, due to relativistic effect making the *s*-electrons of Pb behave like core electrons.[4]

The thermal and electronic conductivities of post-transition metals are about one order of magnitude lower than those of transition metals and as mentioned above, they show low melting points, the highest one being Pb at 327 °C and the lowest one being Ga at approximately 30 °C. With the exception of Pb and Tl that are somehow more metallic due to relativistic effects keeping their s valence electrons more tightly bound (see, for example, the +2 chemistry of Pb and the +1 chemistry of Tl), the crystal structures of these elements diverge from the more typical close-packed structures of metals. This is due to the partial directionality and covalency of the bonds, caused by the not fully metallic character. Moreover, these metals tend to have poor mechanical properties, being very soft or brittle (in the case of Bi) and to oxidize easily, being moderately electropositive.

Post-transition metals have relatively negative standard redox potentials and tend to oxidize easily when exposed to the atmosphere. The hybridization of the p orbitals of oxygen with the sp-orbitals of these elements in their oxides yields wide band gap semiconductors. The oxides are amphoteric materials and react with both acids and bases.

2.2 Use of post-transition metals in heterogeneous catalysis

In the following section, we will discuss some proposed applications of post-transition metals in heterogeneous catalysis, especially focusing on those processes that can be advantageous from an environmental point of view. Thallium will be excluded from the discussion due to its extreme toxicity.

2.2.1 Gallium. The introduction of bio-based molecules, such as sugar derivatives from lignocellulosic biomass, as building blocks in the chemical industry can be an advantageous strategy to promote the needed shift from oil-based raw materials.[5] One interesting route to make use of these bio-based compounds is the conversion of furanics (sugar derivatives) into BTEX (benzene, toluene, ethylbenzene and xylenes) or the catalytic fast pyrolisis of raw biomass into bio-oil on zeolite catalysts.[6,7] In this way, a drop-in strategy can be adopted, that is, the substitution of building blocks usually obtained from fossil sources with the same building blocks obtained from sustainable sources, so that the pre-existing industrial infrastructure can undergo minimal processing changes.[5] In this context, it has been shown that addition of Ga to zeolites can improve the BTEX yield of both the aromatization of furanics and catalytic fast pyrolysis of sawdust.[8] Moreover, Ga-promoted zeolites are known for their ability to convert several feeds, such as alkanes, alkenes and methanol to aromatic compounds.[9,10]

A possible use of Ga in catalysis, relevant to the general topic of CO_2 utilization and green chemistry, is the conversion of primary amines, CO_2 and alcohols to carbamates on Ga_2O_3 catalysts. Carbamates are chemicals relevant to a wide variety of applications, from polymer production to drug synthesis, but are currently produced with the use of toxic phosgene and isocyanate so that switching to a benign and environmentally friendly process while making use of CO_2 would present many advantages.[11]

Other known uses of Ga-based catalysts are, for example, the conversion of NO_x to N_2 using alkanes,[12,13]and the dehydrogenation of alkanes in the presence of CO_2.[14,15]

2.2.2 Indium. An attractive approach to the utilization of CO_2 can be its catalytic conversion to methanol. This chemical is a fundamental building block in industry and can be used as a sustainable energy carrier if methods for its production from the hydrogenation of waste CO_2 with sustainable hydrogen are developed.[16,17] At the moment, methanol is produced industrially from syngas (derived from steam reforming of fossil fuels) with low amounts of CO_2 present in the stream over a Cu-ZnO-Al_2O_3 catalyst. This catalyst, though, is not able to effectively promote the formation of methanol when CO_2 is the only carbon source, due to low activity, selectivity and stability of the catalyst.[18–21]For the direct hydrogenation of CO_2, In_2O_3 catalysts stand out due to their superior selectivity and stability in industrially relevant conditions[22–24]and their performance can be ulteriorly enhanced by promoting the activity with Pd.[25]

Another use of In in heterogeneous catalysis, analogous to Ga, is the dehydrogenation of propane in the presence of CO_2 on In_2O_3. This reaction yields propylene from the propane and CO from the CO_2, with good potential for CO_2 utilization.[26]

2.2.3 Tin. Sn is an attractive catalyst in the general field of biomass conversions. As mentioned above, the conversion of biomass, especially the non-edible kind such as lignocellulosic material, is an attractive strategy for the production of platform molecules to be further converted to fuels and materials by the chemical industry. One attractive platform molecule that can be easily derived from cellulosic feedstocks is levulinic acid[27] and its conversion to γ-valerolactone, a high-quality solvent and fuel additive, is one of its most important uses.[28,29] In this regard, SnO_2 modified silica catalysts can be used for the reaction as an active, stable and recyclable alternative to precious metal catalysts.[30] Other uses of Sn-based heterogeneous catalysts for the conversion of sugar-related compounds are, for example, the isomerization of glucose to fructose,[31] the conversion of 1,3-dihydroxyacetone or sugars to lactatic acid and its ethyl and methyl esthers[32,33] and the conversion of carbohydrates to 5-hydroxymethylfurfural,[34] another important bio-based platform chemical.[35]

Sn catalysts are not only relevant for the conversion of carbohydrate-derived biomass, but find application also for the processing of fatty fractions. The production of biodiesel is one such example. Fatty acid methyl and ethyl esthers are potential renewable alternatives to oil-derived diesel.[36,37]At present, though, the majority of the biodiesel is produced using expensive edible vegetable oils through a transesterification reaction catalyzed homogeneously by a base. If a cheaper oil, richer in free fatty acids is used, a pre-esterification step in acid is required, to avoid saponification in the basic environment. These problems increase the cost and the effluent production deriving from biodiesel plants.[38,39] The use of heterogeneous catalysts is desirable to lower the cost of the process, for example by enabling the use of waste oil instead of high-quality vegetable oil, and decrease effluent production by avoiding the use of large quantities of acids and bases.[40] Moreover, heterogeneous catalysts can be easily filtered and reused. Sulfated tin oxide catalysts have emerged as promising candidates for the production of biodiesel from low grade vegetable oils.[41,42]

2.2.4 Lead. The role of Pb in sustainable heterogeneous catalysis seems to be marginal, possibly because of concerns due to its toxicity. Pb is frequently mentioned as a poison to several catalysts[43–46] . It is used in the synthesis of the Lindlar catalyst for the semi-hydrogenation of alkynes to alkenes.[47]

2.2.5 Bismuth. Like Pb, Bi does not find many uses in heterogeneous catalysis, especially not in sustainable processes. Mentioned uses are, in combination with Mo, as a catalyst for the selective oxidation or ammoxidation of propylene to acrolein or acrylonitrile[48,49] and in combination with Cu as a substitute for Hg for the hydrochlorination of acetylene to vinyl chloride.[50]

Ga, In and Sn based catalysts are predominantly employed in their oxide form (variously supported or modified), and, in the majority of cases, catalytic mechanisms involving heterogeneous acid-base reactions are proposed (see above references). As mentioned above, these oxides are wide band gap semiconductors. Without electronic density at the fermi level, it makes sense that their catalytic properties will depend mostly on mechanisms such as, for example, Brønsted/Lewis acidity/basicity. An exception is the In_2O_3 catalyst for methanol production. In this case, it is thought that hydrogen molecules are activated by heterolytic splitting on surface sites with oxygen vacancies, initiating the reaction.[23]

2.3 Use of post-transition metals in electrocatalysis

Post-transition metals can hardly be regarded as attractive electrode materials by conventional means. By themselves, they are mechanically and chemically unstable, have low melting points, low electrical conductivities and usually exhibit high overpotentials for electrochemical reactions. Nevertheless, their high selectivity towards otherwise unachievable electrochemical conversions makes them interesting candidates for the scale-up of certain electrochemical technologies. This is often due to their very high HER overpotential, that allows this parasitic reaction to be avoided in aqueous electrochemical reactions when these metals are used. In this section, we will discuss some of the promising applications of post-transition metals and their alloys in electrocatalysis.

2.3.1 CO_2 reduction. The selectivity of post-transition metals for the electrochemical reduction of CO_2 towards formate in aqueous media (with the exception of Ga, a CO selective metal) is possibly one of their most renowned characteristics in the field of electrocatalysis.[51] These metals are practically the only ones able to achieve and retain high selectivity towards formate when operating at industrially relevant current densities.[52,53] Formate is an interesting target molecule due to its possible use as a hydrogen carrier for fuel cell applications, enabling the use of CO_2 for energy storage[54] and its existing market as preservative for animal feeds and for leather production. Formate can also be converted to C_2 products such as oxalic and glycolic acid,[55–57] which can be used, for example, for the synthesis of sustainable polymers.[58] The most evident disadvantage of employing post-transition metals for the production of formate from CO_2, as mentioned above, is the particularly high overpotential they show for electrochemical reactions, which results in lower energy efficiencies. This efficiency problem, from a practical perspective, can be minimized by proper cell design and by coupling the cathodic CO_2 reduction with a remunerative anodic reaction, possibly with less positive equilibrium potential and overpotential than oxygen evolution. One such reaction, for example, is the oxidation of 5-hydroxymethilfurfural to 2,5-furandicarboxylic acid, a valuable chemical usable for the production of polymers. By using this reaction instead of oxygen evolution not only a higher value product is produced from a biomass derived feedstock, but the cell voltage can be lowered by about 0.2V compared to oxygen evolution at the same current density.[59,60]

CO_2 has a thermodynamical stability similar to that of water,[61] but post-transition metals proceed with the reduction towards formate only at about 1V overpotential.[51] Interestingly, it has been shown that on post-transition metals the overpotential for the electrochemical reduction of CO_2 to formate in CO_2-saturated, 0.1M $KHCO_3$ at pH 6.8 is similar to the overpotential for hydrogen evolution in a N_2-saturated phosphate buffer at the same pH.[62] This suggests that CO_2 reduction to formate is not intrinsically difficult, but that post-transition metals are, generally, “bad” electrocatalysts, despite their appealing selectivity. The overpotential for CO_2 reduction is well correlated with the heat of fusion of the metals, which is particularly low on post-transition metals.[62] The metals with the lowest heats of fusion have the highest overpotentials for CO_2 reduction. This is due, as mentioned above, to the absence of d-orbitals in the valence shell of post-transition metals. The d-electrons, in fact, contribute to the cohesive energy of transition metal crystals (which translates to a higher heat of fusion) as well as to their catalytic properties (intermediate adsorption), due to their localized nature. A low heat of fusion is a sign of the absence of the contribution of d-orbitals to the valence shell, which in turn affects the catalytic properties negatively.[51,62] Due to these unfavorable conditions hindering intermediate adsorption, CO_2 reduction is thought to occur on these metals through an outer sphere electron transfer, leading to a CO_2^- radical anion free in solution, which rapidly reacts with water to acquire a proton on the C atom (which is calculated to carry the majority of the negative charge when the radical anion is not bound to a surface) and then is further reduced to formate.[51] The high overpotential derives from the extremely negative standard equilibrium potential of this first electron transfer (-1.9V vs NHE). This is particularly true for Pb, Tl and Bi, while in the case of In and Sn a slightly lower overpotential is observed, possibly due to a weak coordination of the CO_2^- intermediate on these metals.[51] Indeed, it has been reported that while In and Sn form a carbonate intermediate by reaction of CO_2 with residual, metastable surface oxides during reduction, Pb and Bi reduce CO_2 without observable surface intermediates.[63]

In this context, Pd deserves to be mentioned despite not belonging to the group of post-transition metals due to its exceptional ability to "electro-hydrogenate" CO_2 to formate with very high selectivity at potentials close to the equilibrium. This is thought to happen through the insertion of CO_2 in the Pd-H bond of electrochemically generated hydrides.[64] Unfortunately, its applicability for a more energy efficient scale up of this reaction is currently hindered by the very fast poisoning of the metal's surface by CO. In fact, while Pd is very selective to formate at low overpotentials, CO is produced as a byproduct and remains tightly bound to the surface, lowering reactivity.[64]

CO_2 reduction can be carried out in organic solvents, such as propylene carbonate or acetonitrile with tetra-alkylammonium salts electrolytes. The advantages of this approach are the suppression of hydrogen evolution when aprotic, anhydrous solvents are used, the significantly higher solubility of CO_2 which increases the limiting current density without employing complex electrode architectures, and the different products that can be obtained. Notable is the capability of Pb and Tl to selectively electro-reduce CO_2 to oxalate, which could be advantageous over the sequential reduction to formate followed by thermal coupling. The obvious disadvantages of this approach are the high cost and low sustainability of the organic solvents employed. In and Sn electrodes yield mainly CO in organic solvents.[51]

2.3.2 Nitrate reduction. Sn electrodes are known to be interesting candidates for the electrochemical reduction of NO_3^- ions, which are known water pollutants from overfertilization. This electrochemical reaction can yield several products, many of which would carry their own environmental problems, such as ammonia, nitrite, hydroxylamine and others. Sn electrodes can selectively electro-reduce NO_3^- to N_2 with obvious environmental advantages. The reaction, though, happens at very negative cathodic potentials (-2.8V vs Ag/AgCl) so that the Sn cathodes start undergoing cathodic corrosion (or disintegration).[65,66,67] The problem can be solved by using Bi cathodes. In this case the reaction is still selective to N_2, but it happens at more positive potentials, avoiding the degradation of the electrode and the accumulation of metal in the electrolyte, which would constitute a source of pollution.[66,68] The combination of Bi and Sn in bimetallic nanoparticles seems to have a synergistic effect increasing activity and selectivity of the reaction toward N_2.[69] Pb cathodes yield mostly ammonium cations from the electrochemical reduction of nitrate.[70]

2.3.3 Organic electrosynthesis. In the field of organic electrosynthesis, Pb assumes an important role, especially for its high hydrogen evolution overpotential, which enables organic reactions to prevail over hydrogen evolution in aqueous solvent.[71] Pb cathodes can be used for the selective reduction of oxalic acid, a molecule that can be derived from CO_2, to glyoxylic acid.[71,72] Moreover, the addition of the CO_2^- radical to butadiene in anhydrous acetonitrile on a Pb cathode to give carboxylic acids has been investigated.[73] Pb electrodes are used also for the dimerization of acrylonitrile to adiponitrile, an important and large scale industrial process, and the hydrogenation of pyridine to piperidine.[74]

2.4 Intermetallic compounds with transition metals

An interesting property of post-transition metals that has especially attracted attention not only in the field of material science, but also in catalysis and electrocatalysis,[75–80] is the formation of intermetallic compounds with transition metals. As the name suggests, intermetallic compounds comprise two or more metallic elements. Differently from substitutional and interstitial alloys, though, these compounds exhibit stoichiometric compositions and crystal structures that differ from those of the single elements that compose them. Indeed, often their crystal structures are more complex than the fcc, hcp and bcc structures usually displayed by transition metals.[76,79,80] This, of course, has important consequences on the properties of the resulting materials for several reasons. To start, the geometry of the elements in the crystal is altered, leading, at least from a catalytic point of view, to a redistribution or isolation of active sites. Of course, the alteration of the geometry has repercussions on the electronic structure, since this is determined not only by the nature of the elements, but by their distribution in space. For this reason, elements in intermetallic compounds can show electronic structures different from those in their pure state. Even more modifications to the electronic structure are caused by the covalent interaction between the elements forming the intermetallic compounds.[76] For example, the formation of the intermetallic compound PdGa causes a shift of the Pd 4d states to lower energy due to the covalent bonding, inducing a higher degree of electronic filling of this band and the acquisition of a partial negative charge of the Pd atoms. Moreover, the geometrical isolation of the Pd atoms in the crystal causes a narrowing the 4d band.[79] The formation of strong bonds in intermetallic compounds is reflected by their markedly exothermic formation enthalpies[76], which also contributes to their stability. In fact, the formation of a covalent network can contribute to a site preference caused by the directionality of the bonds, a situation not encountered in random alloys, in which the absence of a strong site preference can induce an easier occurrence of segregation.[76,80] Like metals and random alloys, intermetallic compounds are electronic conductors, even though to a lesser degree, due to the interference of ionic and covalent interactions.[76,80] Moreover, with thousands of structures known, they can provide an incredible diversity of possible candidates for many applications, especially when the tailoring of the geometry or electronic structure of a material is a relevant optimization strategy, like for example in the field of catalysis.

2.4.1 Heterogeneous catalysis. As mentioned above, the study of intermetallic compounds applications in heterogeneous catalysis is growing rapidly in recent years,[80] and these catalysts are being proposed to enhance performance in many important fields of catalysis. In this case, usually, transition metals are the main active phase, the activity of which is modified or modulated by the presence of the post-transition metals. In this section, we will discuss some applications of bimetallic transition-post transition catalysts, whether a confirmed intermetallic phase has been reported or not.

Intermetallic compounds of Ga in combination with Pd or Ni, such as Pd_2Ga, PdGa and Ni_3Ga are known as effective catalysts for the semi-hydrogenation of acetylene.[79,81] Liquid, Ga-rich alloys with Pd have been successfully used for the dehydrogenation of alkanes, with high coke resistance.[82] Even more interestingly, Pd-Ga,[83] Cu-Ga[84] and Ni-Ga[85] bimetallic catalysts are emerging as catalysts for the direct hydrogenation of CO_2 to methanol. In particular, the Ni-Ga intermetallic compound Ni_5Ga_3, discovered through a computational screening and then tested experimentally, is active and selective towards methanol production from CO_2 at ambient pressure, in contrast with the usual high-pressure conditions employed. This offers operational as well as environmental advantages.[85]

Similarly to the Pd-Ga intermetallic compounds, Pd-In intermetallics have been described to be good catalysts for the direct CO_2 hydrogenation to methanol and alkane dehydrogenation,[86,87] but also for the hydrogenation of CO_2 to CO using different CO_2/H_2 ratios and operating at atmospheric pressure.[88] Another interesting use of these bimetallic catalysts is for the catalytic reduction of NO_3^- to N_2 and water using molecular hydrogen.[89,90] Nitrate contamination of water, deriving from fertilizers in agriculture, wastewaters and landfill contaminant leaching, is a cause of concern because of the negative effects this anion and its reduction product nitrite can have on human health. The catalytic decomposition can be an appealing alternative (or be integrated as a final step to) ion exchange or reverse osmosis, due to the fact that they produce streams of highly concentrated salts, an expensive waste product. Moreover, it could substitute microbial denitrification, which suffers from long startup times.[89] Ni-In intermetallics can find application in the dry reforming of methane with CO_2, a process capable of transforming these two greenhouse gases to syngas usable as a feedstock for Fischer-Tropsch to produce liquid fuels.[91] They can also be used for the selective hydrogenation of α,β-unsaturated aldehydes to unsaturated alcohols, which could be relevant to the transformation of bio-derived platform molecules such as furfural.[92] The selective catalytic hydrogenation of α,β-unsaturated aldehydes to allylic alcohols is a fundamental step in the production of fine chemicals, but monometallic catalysts such as Ni, Ru and Pt tend to catalyze the undesired hydrogenation of the C=C bonds.[76] Cu-In and Ni-In intermetallics in which the Cu_2In and Ni_2In phases are predominant were found to be good catalysts for the hydrogenation of volatile fatty acids, a class of biomass-derived compounds, to their relative alcohols. In particular, the reduction of acetic acid to ethanol and octanoic acid to octanol was investigated.[93] Volatile fatty acids are short chain, mono-carboxylic acids, very useful in industry. Not only they can be used as substrate for the production of aldehydes, alcohols, esthers and alkanes, but they are known precursors for the production of methane and hydrogen, as well as biopolymers, such as polyhydroxyalkanoates (PHA).[94] In a biorefinery approach, volatile fatty acids can be produced, for example, by the microbial fermentation of food waste[95,96] as well as agricultural wastewater and municipal sludge.[97]

The proposed applications of the bimetallic compounds of Sn in heterogeneous catalysis, especially with Ni, Pt and Pd, are very broad. In the field related to biomass conversions, for example, Ni-Sn catalysts are studied for the aqueous phase reforming of renewable oxygenated organic molecules derived from biomass to produce hydrogen. Target molecules are, for example, sorbitol, which can be obtained from the hydrogenation of glucose (a process that can be also catalyzed by Raney-type Ni-Sn catalysts),[98] glycerol, a byproduct of biodiesel production, and ethylene glycol. In these catalysts, Sn has the role of promoting the selectivity against the side reactions forming alkanes and the stability of the Ni catalyst.[99–101] Ni-Sn catalysts where Sn has a similar role have been investigated for the upgrading of ethanol, obtainable from the fermentation of biomass, into higher alcohols (C4+)[102] and liquid hydrocarbons (up to C17).[103] The separation of ethanol from the aqueous medium of the fermentation can be challenging, so that converting it directly into products with lower water solubility can be advantageous. Moreover, the higher energy density and lower hygroscopicity of these longer chain products can help in their drop-in into existing transport technology.[102,103] Ni-Sn catalysts can be used for the direct conversion of cellulose (biomass not competing with food) to ethylene glycol or 1,2-propylene glycol, which can be used, for example, for the production of sustainable polyesters.[104,105] Another possible use of these catalysts is for the upgrading of biogas to syngas via dry reforming. Biogas is one possible product from the fermentation of waste (typically municipal and agricultural waste and sewage sludge) and its main components are CH_4 and CO_2. Rather than using it for combustion, it may be advantageous to convert it to a mixture of CO and H_2 and further convert it to liquid fuels.[106,107] Pd-Sn catalysts have been proposed for the direct synthesis of H_2O_2 from O_2 and H_2, a process that would hold environmental advantages over the conventional anthraquinone process, that uses large amounts of toxic compounds.[108,109] Pt-Sn and Ru-Sn bimetallic materials can be used for the hydrogenation of several bio-derived molecules such as furfural to furfuryl alcohol,[110] oleic acid to unsaturated alcohols[111] and butyric acid to butanol.[112]

Bimetallic catalytic systems containing Pb for sustainable and environmental purposes do not seem to be mentioned frequently in the literature, with a few applications in combination with Pd for the oxidation of glycerol with H_2O_2[113] and glyoxal[114] and in combination with Pt for the oxidation of furfural to furoic acid.[115] On the other hand, Bi-containing catalytic systems have received much more attention, even though there seems to be a partial overlap with Pb in the use, in combination with Pd and Pt, as a catalyst for the partial oxidation of small organic molecules, such as glycerol,[116–119] glucose[120–122] and glyoxal.[123] An especially creative catalytic system that makes use of Bi as a component is the one for the pyrolysis of methane. In this process, methane is decomposed to hydrogen and carbon, avoiding the production of CO_2. If conventional catalysts are used, the resulting coking can hinder the catalytic activity. Liquid alloys of Bi with Ni and Cu can be used as the catalyst. In this type of system, methane bubbles are converted to hydrogen and carbon as they rise through the liquid alloy, always being in contact with a clean (i.e. not coked) catalyst. The carbon byproduct, then, remains floating on the liquid alloy and can be easily skimmed.[124,125] Liquid Bi has been studied as a promotor for Fe based catalysts for the Fischer-Tropsch reaction of syngas to light olefins, able to increase its reaction rate by 5-10 times and the selectivity by 50%.[126] Pt-Bi catalysts are being studied for the upgrading of bio-oil derived from the fast pyrolysis of biomass. Bio-oil is a very complex mixture of many compounds and one of the problems associated with it is its high oxygen content compared to fossil oil, which can limit its use as a substitute. Usually, guaiacol (2-methoxyphenol) is used as a model molecule to study the catalytic deoxygenation of bio-oil. This reaction can be carried out with H_2 or, to address problems related to hydrogen cost and problematic transport, with CH_4. The reaction products when using methane are various deoxygenated derivatives of guaiacol and ethane and Bi has the role of promoter, significantly extending the lifetime of the Pt catalyst.[127,128]

2.4.2 CO_2 electroreduction. The use of post-transition in combination with transition metals yields bimetallic catalysts that can be highly selective or have other advantages, such as lower overpotential for CO_2 reduction. None of these catalysts, though, is reported to be operated at industrially relevant current. Intermetallic compounds of Ni and Ga such as NiGa, Ni_3Ga_5 and Ni_3Ga in the form of thin films yield hydrocarbons as CO_2 reduction products[129] (a characteristic usually only associated with Cu), although with total faradaic yields lower than 5%, the rest being hydrogen. Cu-In intermetallics such as $Cu_{11}In_9$

nanoparticles and 3D porous In catalysts the surface of which is covered by Pd atoms by galvanic displacement are selective to CO[130,131] and Sn intermetallics with Ag and Pd, both in the form of nanoparticles, are reported to be selective to formate.[132,133]

2.4.3 Energy production and storage. In the field of electrochemical energy conversion, bimetallic catalysts, especially comprising Pt and Pd, in combination with post transition metals are frequently mentioned in the literature for application in several of the relevant reactions in this area of study. Among the advantages are performance improvement due to their electronic and geometrical characteristics of intermetallics as well as reduced utilization of precious metals, which are frequently employed as electrocatalysts for these reactions.

Pt-Bi intermetallics have been reported as effective and durable electrocatalysts for the hydrogen evolution reaction,[134] while Pt-Sn compounds show enhanced activity for the hydrogen oxidation reaction, while also being more resilient to CO poisoning, an advantage given the fact that CO is a common impurity in hydrogen streams.[135,136] AuSn and PdSn also show enhanced poisoning resistance, but are not as good catalysts as PtSn.[137]

As illustrated above, it is possible to convert CO_2 to several products by means of heterogeneous catalysis and electrocatalysis. Aside from the use in the chemical industry, some of the molecules obtainable from CO_2 can be considered as energy carriers, alternative to hydrogen. This way, liquid and gaseous fuels can be produced that are easier to handle, transport and store.[138,139] Of course, the full oxidation of these molecules to extract the stored energy will ultimately yield CO_2, but if particular attention is used, these systems can be used as CO_2 neutral power generators. In the previous sections we introduced the direct hydrogenation of CO_2 to methanol on In_2O_3 and the electrochemical reduction to formic acid on post-transition metals. A consolidated industrial method for the production of methanol is the reduction of syngas on Cu-ZnO-Al_2O_3, which could be an environmentally appealing process if renewable energy and syngas produced from CO_2 and water are used. Moreover, it is possible to efficiently convert CO_2 to methane on Ni catalysts, which would have the added advantage of the pre-existing infrastructure for the distribution of this molecule.[137] In this context, it is desirable to develop reliable fuel cell technologies, which are significantly more efficient than traditional combustion in using the energy stored in the fuel molecules.[140] Fuel cells relying on the anodic oxidation of methanol, formic acid and methane are known in the literature.[141–143] Also in this field, the addition of post-transition metals to base transition metal catalysts is frequently investigated. In the case of formic acid and methanol oxidation, CO can be produced in the oxidative pathways and is prone to poison the surface of pure Pt catalysts, so that active catalysts with improved resistance to poisonous species are warranted.[144,145] The intermetallic compound PtBi has been found to perform better than Pt for the electrochemical oxidation of formic acid, while also being resistant to CO poisoning.[146] An improved performance both in activity and resistance to CO and sulfur poisoning compared to Pt, Pd and Pt-Ru was found on the ordered intermetallic compound PtPb.[147] Similar results have been obtained in the case of the methanol oxidation reaction where it is found that intermetallic compounds of Pt-In, Pt-Bi and Pt-Pb offer not only improved activity, but also longer durability thanks to their enhanced CO poisoning resistance.[148–151]

While methanol and formic acid fuel cells can be grouped into the category of proton exchange membrane fuel cells, operated at relatively low temperature, the case is different for methane fuel cells, which usually make use of the solid oxide technology, usually operated at 600-800 °C.[141–143] The use of Ni-Sn catalysts in these solid oxide fuel cells can suppress the formation of carbon residues commonly observed on the mostly used Ni anodes.[152,153]

2.5 The formation of Zintl phases

Another remarkable characteristic of post-transition metals is their ability to form Zintl phases. These phases can be described as a transition between ionic and intermetallic compounds and are named after the German scientist Eduard Zintl, for his fundamental contribution to their study. Practically speaking, Zintl phases are formed between electropositive elements such as alkaline and alkaline-earth metals and more electronegative p-block metals and semi-metals. The compounds are composed of polyanions formed by negatively charged clusters of p-block elements, the negative charge of which is usually counterbalanced by the alkaline or alkaline-earth cations.[154]

The first evidences of what we now call Zintl phases came from studies of the reaction of Na in liquid ammonia with different metals. In particular, the reaction with Pb gave a solution of an intense green color, which was demonstrated to be an electrolyte, with the green color associated with the anion, some kind of negatively charged Pb cluster.[155] Since then, ethylenediamine and dimethylformamide have been identified as suitable solvents alternative to liquid ammonia.[156] Today, we know that a large variety of structures (soluble or insoluble) can be formed, such as isolated homoatomic cluster anions (e.g. $[Sn/Pb_4]^{4-}$, $[Sn/Pb_9]^{4-}$, $[Bi_2]^{2-}$, $[Bi_4]^{2-}$)[156], as well as more complex ones, such as Rb_2In_3, in which the anion structure is formed by a network of In_6 octahedra interconnected to form quasi-infinite sheets.[157] Isolated and network structures based on heteroatomic cluster anions are also known (e.g. $[Sn_2Bi_2]^{2-}$ or the more complex $Eu_7Ga_6Sb_8$ in which polymeric chains of $[Ga_6Sb_8]^{14-}$ are present).[155,158] Despite this rich variety of structures, Zintl phases are usually chemically unstable when exposed to oxygen and moisture and need to be handled in a protected environment.[155,156,159]

Zintl anions, due to their chemical reactivity and particular polyhedral structures, can be used as intermediates for the synthesis of materials, for example for the bottom-up synthesis of nanostructured semiconductors. The anionic subunits of Zintl phases, whether isolated or in the form of 2D or 3D networks, can act as molecular building blocks from which materials can be derived via oxidative polymerization (in the case of isolated cluster anions) or simply by oxidation of the pre-existing anionic 2D or 3D structures. This method has been used to produce meso-porous Ge.[159] The formation of polymeric super-structures such as sheets, spheres or nanotubes based on repeating units derived from Zintl anions has been predicted to be thermodynamically stable.[156] The oxidation of the insoluble Zintl compounds KSi has been used to synthesize Si nanoparticles.[156]

In general, Zintl phases can be prepared not only by dissolution of p-block metals in liquid ammonia in the presence of alkali metals, but also by heating stoichiometric amounts of the elements of interest in an inert atmosphere[159] and, in the case of Sn and Pb, they can be prepared electrochemically when these elements are used as cathode materials.[156,160]

2.6 Summary

Post-transition metals are extremely interesting elements with a rich and unusual chemistry. While lacking the mechanical and thermal resilience, as well as the very high conductivity of their d-block neighbors, they can find a broad range of applications due to their physical and chemical properties. Their low melting points, for example, makes them excellent candidate for soldering materials, but also for creative catalytic systems employing liquid metal alloys, as illustrated above.

The formation of Zintl phases opens the possibility to synthesize materials with interesting structural properties and possibly with high atom efficiencies, due to the fact that pre-formed Zintl clusters can be simply oxidized to their metal or semi-metal equivalents. Their interaction with transition metals to form intermetallic compounds or, more in general, bimetallic systems, allows for the modulation of the catalytic properties of these widely used materials, to provide improved catalysts for the chemical industry.

In addition to this, post-transition metals are proposed in several fields of sustainable catalysis as promising materials, able to catalyze reactions of economical as well as environmental relevance, both alone and in combination with zeolites and transition metals. This is of capital importance nowadays, as with hopes that global fossil fuel use peaked in 2019 and is bound to fall,[161] the time is coming to provide effective, reliable, environmentally friendly and big-scale processes for a sustainable future.

In the following chapters, we will see examples of the use of post-transition metals, both alone and in combination with transition metals, for the electrochemical reduction of CO_2. In addition to this, we will discuss a possible mechanism for the cathodic disintegration of Sn and Pb mediated by the formation of Zintl phases.

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