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Irene Mustieles Marin, Juan M Asensio, Bruno Chaudret. Bimetallic Nanoparticles Associating Noble Metals and First-Row Transition Metals in Catalysis. *ACS Nano*, 2021, 15 (3), pp.3550-3556. 10.1021/acsnano.0c09744 . hal-03210862

HAL Id: hal-03210862

<https://hal.science/hal-03210862>

Submitted on 28 Apr 2021

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Bimetallic Nanoparticles Associating Noble Metals and First-Row Transition Metals in Catalysis

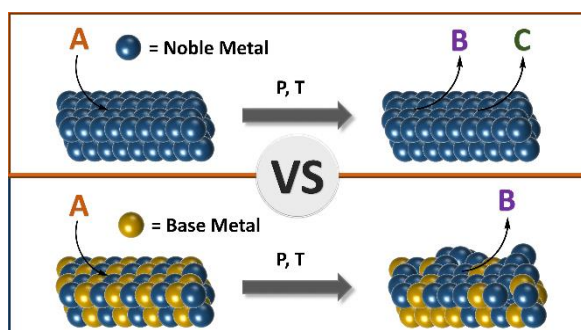
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Abstract

Bimetallic nanoparticles (NPs) are complex systems with properties that far exceed those of the individual constituents. In particular, association of a noble metal and a first-row transition metal are attracting increasing interest for applications in catalysis, electrocatalysis, and magnetism, among others. Such objects display a rich structural chemistry thanks to their ability to form intermetallic phases, random alloys, or core-shell species. However, under reaction conditions, the surface of these nanostructures may be modified due to migration, segregation, or isolation of single atoms, leading to the formation of original structures with enhanced catalytic activity. In this respect, Zakhtser *et al.* report in this issue of *ACS Nano* the synthesis and study of the chemical evolution of the surface of a series of PtZn nanostructured alloys. In this Perspective, we report some selected examples of bimetallic nanocatalysts and their increased activity compared to the corresponding pure noble metal, with a special focus on Pt-based systems. We also discuss the mobility of the species present on the catalyst surface and the electronic influence of one metal to the other.



Bimetallic nanocrystals, which comprise a noble metal (in particular, a platinum group metal) and a non-noble metal (in general, a first-row transition metal), are attracting a lot of interest because of

the important modifications to their properties (*e.g.*, chemical, mechanical, electrical, magnetic, *etc.*) that are induced by the presence of the two metals and their interactions with one another.¹ Alloys have been used since the beginning of metallurgy, when tin was employed to harden copper in the Bronze Age. One particularly interesting example is brass (alloy of copper and zinc) for which the preferential dealloying of zinc has been studied since the 19th century. Although the properties of bulk alloys have been known for a long time, the situation becomes more complex when reaching the nanoscale. Thus, for nanocrystals, the stoichiometry may be more difficult to control and the surface chemistry may be responsible for changes in stoichiometry, the most common effect being surface oxidation. These systems can give rise to disordered (or random) alloys or to ordered alloys, also known as intermetallics. Intermetallic compounds display an atomically ordered structure where the atoms occupy the lattice following a defined stoichiometry.¹

Pt-based catalysts are active for many reactions, including alkane dehydrogenation and CO oxidation, but are also electrocatalysts for the oxygen reduction reaction (ORR) and the methanol oxidation reaction (MOR). Furthermore, it has been observed in many cases that, when combined with another metal, their catalytic properties are enhanced. This enhancement enables spectacular transformations in catalysis, including a recent demonstration of the possibility to oxidize methane selectively into methanol.² However, precise knowledge of the composition or surface structure of the system is highly challenging because of the dynamics present in these nano-objects, which depend on external conditions. For instance, in this issue of *ACS Nano*, Zakhtser *et al.* report the synthesis and study of the chemical evolution of the surface of a series of PtZn nanostructured alloys.³ This research highlights the mobility of the surface atoms when exposed to different conditions. The authors found that zinc was preferentially oxidized when the particle was in contact with air, and that the Pt-Zn phase was not stable and showed a tendency to lose Zn. Depending on the zinc concentration, either ultrathin islands of ZnO or a thin shell of ZnO at the surface of the Pt particles resulted (Figure 1). Upon exposure to CO, the size of ZnO patches reduced due to a preferential binding of the CO molecule to the Pt surface. It turns out that ZnO islands play an important role in the catalytic oxidation of CO. This inverse oxide/metal configuration takes advantage of the promotion of the catalytic activity by incorporating nanostructures of base metal oxides at the surface of a catalyst.

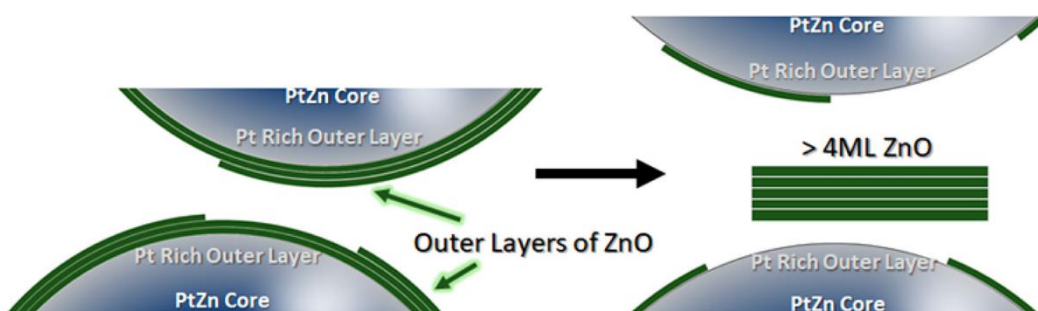


Figure 1. Exposition of Pt-Zn nanoparticles (NPs) under air leads to formation of ZnO sheets that leach from the NP surface. The PtZn NPs displaying a Pr-rich outer layer with ZnO nano-islands showed enhanced performance in catalysis. Reprinted from ref 3. Copyright 2020 American Chemical Society.

Furthermore, Zakhtser *et al.* also describe the leaching of zinc when PtZn nanoparticles (NPs) were left for several days at room temperature in non-degassed toluene, a phenomenon which leads to the formation of a Pt-enriched surface.³ These observations highlight the dynamic behavior of bimetallic nano-alloys that can eventually be segregated or can give rise to the isolation of one atom of an element at the surface of another, leading to a large complexity of situations, some aspects of which we will discuss here. Using selected recent examples, we will underscore the importance of such bimetallic compounds in catalysis and electrochemistry and give evidence for their atomic mobility and for the electronic influence of one metal on the other.

Structural and Electronic Considerations of Bimetallic Systems

Bimetallic NPs have been studied ever since nano-objects first aroused interest.⁴ The expected gains concern both physical and chemical properties and, hence, may include catalytic, magnetic, photophysical, and electronic properties. Thus, alloying between two metals leads to site isolation of specific atoms but also induces a change in the electronic structures of the resulting alloy due to the presence of neighboring atoms.⁵

Bimetallic PdCu NPs were reported in 1993 by J. S. Bradley in collaboration with our group⁶ and by Toshima, who has been a pioneer in the field.⁴ The NPs were prepared by an organometallic approach, and noted two interesting features. First, prior reduction of Pd induced the reduction of the Cu precursor, which was not otherwise reduced in the reaction conditions;⁶ this finding appears to be a general trend for the preparation of bimetallic NPs. Second, the atomic mobility within the NPs induced by surface chemistry. Under a CO atmosphere, the surface of the particles was enriched with Pd up to the point that only Pd-CO stretches were visible by infrared (IR) spectroscopy.

However, when the system was then placed under vacuum and CO was rapidly reintroduced, the main feature observed was the presence of a Cu–CO stretch. Reversible atom migration was then highlighted, with Pd and Cu being attracted in turn at the surface of the NPs. This point is important regarding the adaptation and migration of atoms within NPs.⁷ However, in most cases, migrations are induced by surface oxidation and thus are irreversible, as in the case of the PtZn alloy reported by Zakhtser *et al.*³

The field has grown tremendously since that time and the understanding of the chemistry of these species has made considerable progress thanks to theoretical approaches. For instance, Tsai *et al.* calculated that PdZn alloys exhibit valence electron densities of states similar to that of Cu and significant chemical shifts of Pd 3d states with respect to pure Pd.⁸ It is therefore reasonable to observe that the activity of PdZn in steam reforming of methanol is similar to that of Cu. This finding led the authors to the concept of pseudo-elements, which can be of interest for designing new intermetallic systems.⁸

As far as chemical properties are concerned, the first advantage of an association between a Pt metal and a main group element or a catalytically inactive species may be to induce site selectivity when the NPs can offer several tracks of reactivity. This selectivity was noted in early studies on MSn bimetallic nanocatalysts (M = Ru, Rh, Pt) prepared by surface organometallic chemistry for which researchers used techniques including NMR to elucidate the bonding and coordination environment on the surface.⁹ These systems were first used for the steric bulk induced by the presence of Sn which, when present on the surface of Ru NPs prevents the hydrogenation of phenyl rings during the reduction of acetophenone or styrene.¹⁰ Similar selectivity was also found for unsaturated aldehydes and ketones, the carbonyl group of which can be selectively hydrogenated on RhSn NPs.¹¹

Other systems associating a catalytic metal to an inert one are expected not only to lead to a partial deactivation of the surface but also to increase its selectivity. In this respect, FeRu NPs were shown to reduce the C=O bond of acetophenone selectively whereas Ru NPs of the same size would first reduce the phenyl ring.¹² This research was extended to benzylideneacetone and furfuralacetone, a platform molecule derived from biomass. In both cases, C=O and C=C bonds were selectively reduced and no reduction of the phenyl or furan rings was observed, in contrast to pure Ru NPs. Although this reactivity was expected, it was surprising to observe an enhancement of the catalytic activity of the bimetallic NPs compared to the pure Ru NPs. The explanation is not straightforward but has to do with the polarization of Ru induced by Fe or to the better coordination of oxygen species to partially oxidized surface Fe atoms.¹³ A somewhat similar effect can be found in the decarbonylation *versus*

hydrodeoxygenation (HDO) of hydroxymethyl furfural. Pino *et al.* observed the PdFe nanocatalysts were selective for HDO whereas Pd NPs of the same size and on the same support predominantly led to decarbonylation and the formation of furan (Figure 2). The reason given for this shift in selectivity is that the use of an alloying metal with a strong affinity for oxygen, such as Fe, enhances the selectivity toward C-O hydrogenolysis and disfavors other reaction pathways such as C-C cleavage.¹⁴

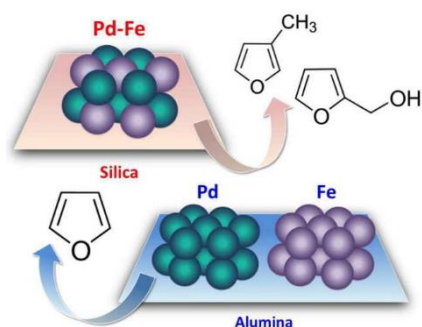


Figure 2. Pd-Fe nanoparticles (NPs) bind furan rings more weakly than do pure Pd NPs. Thus, ring hydrogenation and decarbonylation pathways are disfavored, enhancing the selectivity in the hydrodeoxygenation of biomass-derived platform molecules. Reprinted with permission from ref 14.

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Bimetallic NPs are complex systems with properties that far exceed those of the individual constituents,⁵ as illustrated by case studies of ordered intermetallics (PdZn, Pd₂Ga) and substitutional alloys (PdCu, PtCu). For both PdZn and PdGa, the active phase is created under reaction conditions by deposition of Pd and further reduction of the metal oxide support, which has become a typical route to access this family of alloys. This method not only leads to isolation of Pd sites but also induces electronic modification of Pd by the Zn or Ga neighbors. The stability of the active phase is an issue because partial decomposition of PdZn or Pd₂Ga produces Pd islands that reduce selectivity.

Selective Hydrogenation

A first application of these nanocatalysts is the use of their encumbered surface for selective hydrogenation reactions, which we will limit to two representative examples. In an early example, Bronstein *et al.* showed that the formation of a PdZn alloy enhances catalytic activity in the hydrogenation of dehydrolinalool. Introducing Zn in the Pd lattice induced a change in its electronic configuration and overall geometric structure. The authors ascribed the nature of the active centers on the particle surface as the main effect responsible for the increase in the catalytic activity. In other terms, the site isolation could enhance the catalytic activity.¹⁵

Zhou *et al.* reported a PdZn intermetallic catalyst presenting both high selectivity and activity in the semi-hydrogenation of acetylene. The Pd–Zn–Pd surface pattern displays a weak π -bonding pattern for ethylene adsorption, which prevents further hydrogenation and facilitates its desorption. This pattern is responsible for the high chemoselectivity for acetylene semi-hydrogenation, whereas the moderate σ -bonding mode for acetylene on the Pd sites was responsible for the high hydrogenation activity (Figure 3).¹⁶

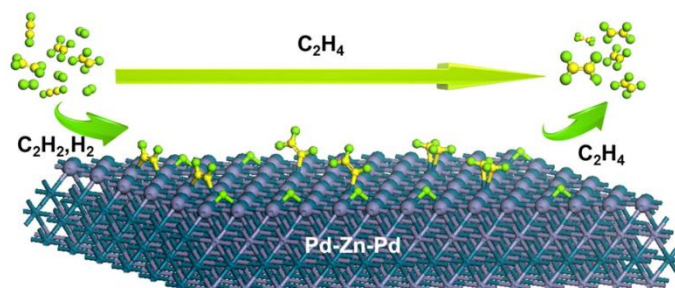


Figure 3. PdZn alloys selectively catalyze the semihydrogenation of acetylene into ethylene thanks to the easy desorption of the alkenes from the surface of the bimetallic catalyst. Reprinted from ref 16.

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Alkane Dehydrogenation

A more challenging application resulting from the same electronic effect is alkane dehydrogenation. Researchers have used modification of the Pt catalyst by main group elements to limit the isomerization and hydrogenolysis activities of the catalyst. In addition, the presence of these elements is reported to limit sintering and to facilitate coke elimination.¹⁷ Tin is the most-often employed promoter and it gives rise to the formation of a Pt-Sn alloy during catalysis. Platinum assists the reduction of Sn; the origin of the effect is both a limitation of the extension of the Pt surface and an electronic effect. Thus, alloyed metallic Sn or Sn^{2+} species in close contact with Pt are able to transfer electrons to the 5d band of platinum atoms, which will modify the adsorptive and catalytic properties of the metal.¹⁸

Other metals have been studied as promoters of Pt activity in the dehydrogenation of alkanes as well. Most notably, Zn prevents undesired side reactions such as coke formation and isomerization in a way similar to that of Sn.¹⁹ Thus, Zn-promoted Pt NPs have been shown to be efficient and selective catalysts for alkane dehydrogenation. Similar to the studies regarding alkyne hydrogenation but instead at high temperature, it has been proposed that Pt sites in PtZn alloys are more electron-rich than pure Pt, which would weaken the Pt–olefin bonds and promote olefin desorption, hence increasing the reaction rate.²⁰ Theoretical calculations of the partial d-orbital density of states (DOS)

suggested that the d band center of the Pt DOS on PtZn(111) is shifted toward lower energies respect to that of Pt(111).

In another work, Cybulskis *et al.* prepared Pt₁Zn₁ intermetallic NPs (iNPs) supported on SiO₂ with isolated Pt surface sites, leading to near 100% C₂H₄ selectivity in ethane dehydrogenation (EDH). In addition, PtZn showed a 6-fold higher turnover rate (TOR) per Pt surface at 600 °C with respect to monometallic Pt/SiO₂. As discussed above, density functional theory (DFT) studies reveal that the addition of Zn modifies the energy of Pt 5d electrons, promoting TOR, while incorporation of Zn into the catalyst surface explains the enhanced product selectivity (Figure 4).²¹

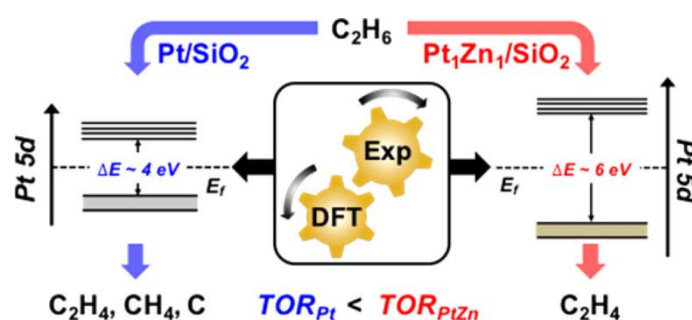


Figure 4. Intermetallic PtZn nanoparticles supported on SiO₂ display higher activities in ethane hydrogenation thanks to the modification of the d-band center. TOR, turnover rate. Reprinted from ref 21. Copyright 2017 American Chemical Society.

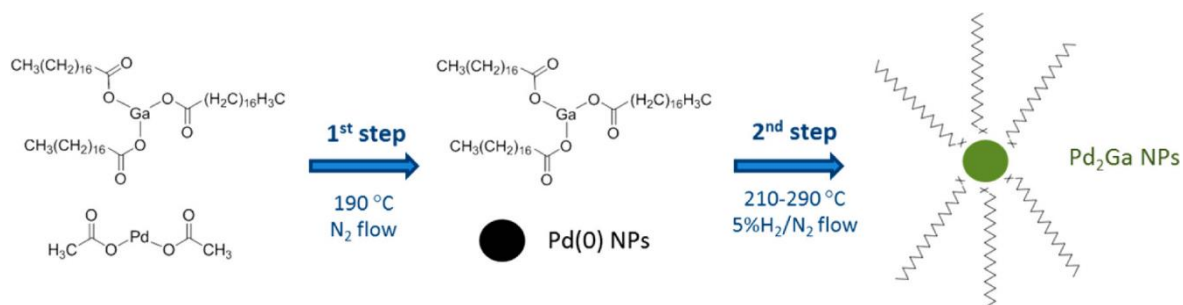
CO Oxidation

Naitabdi *et al.* reported that pure Pt and bimetallic PtZn NPs showed similar behaviors during catalytic CO oxidation reactions. Both types of NPs are prone to being encapsulated by the support whereas pure Zn NPs are not encapsulated.²²

For other oxides such as iron oxides, an interesting phenomenon could be evidenced: Pt NPs partially covered with FeOx nanopatches displayed higher activities in CO oxidation than neat Pt NPs, whereas those with a full Fe oxide shell at the surface showed much lower activity. Characterizations by X-ray diffraction, transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) suggested that Pt promoted the reduction of interfacial Fe oxide.²³

Carbon Oxides Hydrogenation

Hydrogenation mostly concerns PdGa alloys, which, like PdZn, can form intermetallic phases. García-Trenco *et al.* used these catalysts for the hydrogenation of CO₂ into methanol in a single step.²⁴ Interestingly, colloidal Pd₂Ga-based catalysts were shown to catalyze the hydrogenation of CO₂ into methanol efficiently in solution. The catalysts were synthesized by thermal decomposition of Pd(II) acetate and Ga(III) stearate, which generated Pd⁰ nanoparticles of *ca.* 3 nm (Scheme 1). The further reduction of Ga(III) species at 210–290 °C assisted by Pd afforded Pd₂Ga NPs that were used for hydrogenation of carbon dioxide into methanol in solution at 50 bar. Their catalytic activity was 2-fold higher than that observed for commercial Cu-ZnO-Al₂O₃. Characterizations indicated that the catalyst was composed of Pd₂Ga NPs associated with a network of amorphous Ga₂O₃. The authors found a correlation between the catalytic activity and the content of Ga₂O₃ surrounding the Pd₂Ga NPs and suggested that methanol was formed by a bifunctional mechanism involving both phases.²⁴



Scheme 1. Synthesis of Pd₂Ga nanoparticles (NPs) by reduction of Ga(III) stearate promoted by Pd NPs, which are obtained *in situ* by reduction of Pd(II) acetate at high temperatures. Reprinted from ref 24. Copyright 2017 American Chemical Society.

In another work, Gentzen *et al.* deposited well-defined NPs containing a Pd/Ga phase on Al₂O₃. The NPs were active catalysts for the syngas-to-dimethyl ether reaction. *In situ* X-ray absorption spectroscopy experiments carried out under catalytically relevant conditions (CO/H₂, 20 bar, 250 °C) showed some morphological changes of the NPs during the first hour of reaction, which the authors ascribed to the presence of some dealloying.²⁵

Electrochemistry

The preparation of bimetallic alloys can lead to significant enhancement of the efficiency of Pt electrodes through different effects as a result of the mobility and/or oxidation of one component, for example zinc. A first effect can be the induction of nanostructuring of a Pt electrode through the dealloying and oxidation of a PtZn alloy. For example, Huang *et al.* obtained a PtZn alloy by

electrodeposition of a Zn salt on a Pt electrode. Immersion in acidic ZnCl_2 -EMIC ionic liquid can provide a simple yet effective way to fabricate nanostructured Pt electrodes with high surface area.²⁶

Kang *et al.* showed that PtZn and Pt_3Zn NPs are active toward methanol oxidation. In this system, the spherical NPs exhibited higher activity than the cubic ones and the intermetallic Pt_3Zn showed better performance than the alloy phase PtZn. Although the PtZn NPs showed lower activity toward methanol oxidation than other comparable phases (PtMn, PtCo or PtCu), the PtZn NPs were advantageous in terms of poisoning tolerance and the low cost of Zn.²⁷

PtZn iNPs supported on multiwalled carbon nanotubes (MWNTs) are active catalysts toward formic acid and methanol electrooxidation (Figure 5).²⁸ Sub-4-nm PtZn iNPs, synthesized using a sacrificial mesoporous silica shell, exhibited *ca.* 10 times higher mass activity toward MOR in both acidic and basic solutions compared to larger PtZn iNPs synthesized on MWNT. Density functional theory calculations demonstrate that MOR on smaller PtZn iNPs is energetically more favorable than on larger iNPs, due to their high density of corner sites and the lower-lying energetic pathway. The calculations also predicted that PtZn systems follow a “non-CO” pathway for MOR because of the stabilization of the OH^* intermediate by Zn atoms, whereas pure Pt systems form highly stable COH^* and CO^* intermediates, leading to catalyst deactivation.²⁹

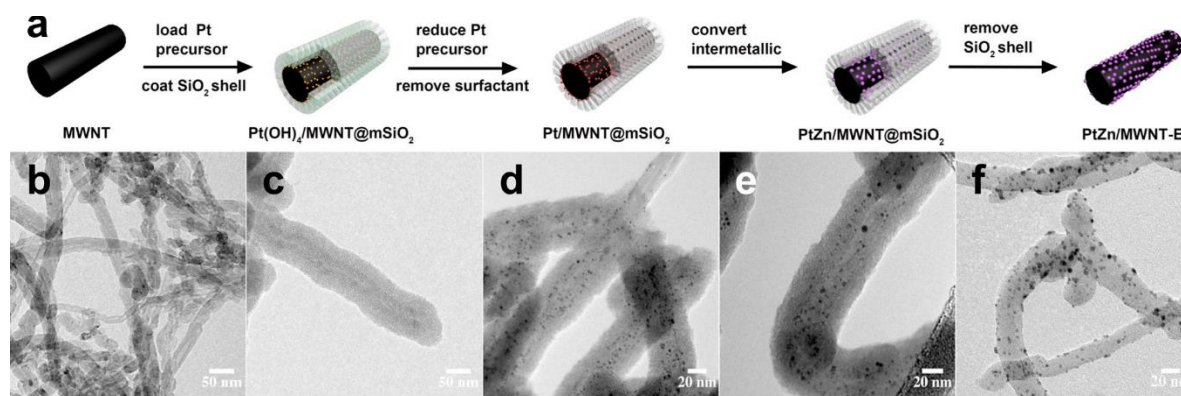


Figure 5. (a) Schematic representation of the synthesis of PdZn nanoparticles (NPs) supported on multiwalled carbon nanotubes. First, the Pt precursor is loaded and reduced to yield Pt NPs coated in a SiO_2 shell. Then, addition of the Zn precursor and removal of the SiO_2 shell led to the intermetallic system. MWNT, multiwalled carbon nanotubes. (b–f) Transmission electron microscopy micrographs for each step of the synthetic pathway. Reprinted from ref 29. Copyright 2009 American Chemical Society.

In addition to electronic modifications, the influence of the compressive strain induced by the formation of bimetallic NPs has been studied by Jia *et al.*³⁰ and Strasser *et al.*³¹ for PtCo and PtCu alloys, respectively, as electrocatalysts in ORR. The geometric effect in this case is generated by a mismatch between the Pt-enriched shell and the base-metal-enriched core that it coats. *In situ* measurements demonstrated that this configuration generates a compressive strain that modifies the Pt–Pt distance, depending on the alloy composition. Through calculations and experimental measurements, the authors demonstrated that this compressive strain induces a downshift of the d band center, which is translated in a weakening of the chemisorption of the oxygenated species leading to an increase in the catalytic activity.

Magnetic Properties

Bimetallic NPs comprising a platinum group metal and a first-row ferromagnetic metal may also display interesting physical properties. Such bimetallic compositions can give rise to new and interesting properties when preparing hard (FeRh, CoRh, CoPd, FePt, CoPt) or soft (CoRu) magnets. These magnetic materials are also dynamic and possess interesting applications in catalysis. For example, Wu *et al.* recently described monitoring the reactivity of CoPd alloy NPs under catalytic CO oxidation conditions using ambient pressure X-ray spectroscopy and TEM. As for the PtZn system, the catalysis process induces a reconstruction of the catalysts, leaving CoOx on the NP surface. The synergy between Pd and CoOx coexisting on the surface promotes the catalytic activity of the bimetallic catalysts.³²

In the case of magnetic properties, the chemical order within the particle is of utmost importance, perhaps even more so than in catalysis. Many studies have been devoted to FePt NPs and, specifically, to the formation of the fully ordered, face-centered tetragonal phase (fct). This phase exhibits a large coercivity and can therefore store magnetic information. However, the ordering occurs at high temperatures, which limits their applicability.³³ In the case of CoPt, the hardening of the magnetic properties depends on the concentration of Pt. Hence, for Co_xPt_y NPs of 1.0–1.5 nm diameter, coercive fields of 0.52, 1.76, and 2.06 T were found for Co₃Pt, CoPt, and CoPt₃ compositions, respectively.³⁴ In the case of CoRh NPs, a strong increase of magnetization of both cobalt and rhodium results from the alloying process for a series of 2 nm NPs of variable compositions.³⁵ Ordering has nevertheless been observed in solution in the case of FeCo NPs where we could evidence the formation of the ordered B2 phase under relatively mild conditions (Figure 6).³⁶

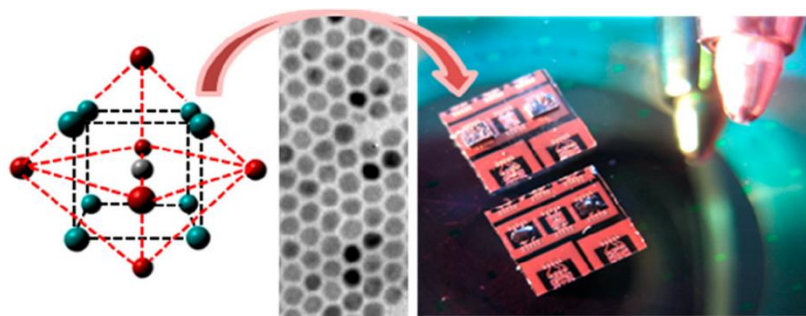


Figure 6. Formation of the ordered B2 phase in intermetallic FeCo nanoparticles (NPs) led to interesting magnetic properties that make these NPs suitable for applications in microelectronics (induction-based systems). Reprinted from ref 36. Copyright 2019 American Chemical Society.

Another aspect that we have not explored in this Perspective but that we expect will develop in the coming years is the possibility of combining physical and chemical properties in a single entity to address the onset of catalytic reactions by an external optical or magnetic stimulus. We are presently engineering $\text{FeC}_x\text{@Ru}$,³⁷ FeCo@C ,³⁸ and $\text{FeNi}_3\text{@Ni}$ NPs for CO_2 methanation,³⁹ methane dry reforming, or hydrodeoxygenation of biomass platform molecules in solution in mild conditions.⁴² Here, all the phenomena of alloying, dealloying, and oxidation that we have highlighted in this Perspective can be present and can participate in the catalysis under the magnetic stimulus.³⁷⁻⁴²

Conclusions and Perspectives

The development of reproducible and scalable synthetic methods for the preparation of controlled bimetallic NPs still remains a challenge. The synthesis of such objects can involve complex methodologies if one wants to control the composition and the surface of the NPs precisely. In addition, if we consider the few selected examples described here, the vision of a stable alloy is vanishing as the surfaces appear as dynamic entities subjected to the reaction conditions. Thus, *operando* techniques or *in situ* characterization under catalytically relevant conditions may arise as the most fruitful tools to understand this dynamic behavior. Dynamics can also lead to the formation of catalytically active single atoms such as isolated Pt, recently characterized at the surface of Cu NPs, which display a particularly high activity for the hydrogenolysis of glycerol.⁴³ Regarding this alloy formation as a consequence of the dynamic behavior, it has been evidenced that in some cases reduction of the support led to catalyst deconstruction and formation of oxide patches on the surface of the NPs, which have been shown to enhance the catalytic activity. Such phenomena have been known for a long time in heterogeneous catalysis but more examples are being reported that

profit from these mobilities to enhance activity and/or selectivity of the catalysts. Such is the case for Pt—the prototypical catalyst—which is as important for electrochemistry (electrolysis, fuel cells) as for oil refining (in particular, cracking and, now, biomass conversion). Modulation of its reactivity may require an additional metal to prevent drawbacks (*e.g.*, bimetallics for fuel cells: PtRu, PtZn, *etc.*) such as the poisoning of the catalyst by CO. Modification of the electronic properties of the nanocatalysts, which are now well-understood by modeling, in particular by DFT calculations, opens the door to a fine tuning of the electron density on the NP surface for specific reactions (*e.g.*, the alkane dehydrogenation or the selective hydrogenation reactions described hereabove). In addition, we have seen that the addition of a second metal not only prevents reaction drawbacks but in many cases enhances the catalytic activity because of the modification of the d-band center of the Pt DOS. Further complexifications will likely lead to novel polymetallic NPs that will be able to perform more complex reactions. Finally, the combination of the intrinsic physical properties of the nano-objects, whether optical or magnetic, and their chemical properties open new avenues to a rich catalysis based on complex but well-mastered nanostructures.

ACKNOWLEDGMENT

The authors thank funding from the European Research Council ERC-Advanced Grant MONACAT 2015-694159.

The authors declare no conflict of interest.

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