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Controllable Catalysis with Nanoparticles: Bimetallic Alloy Systems and Surface Adsorbates

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ABSTRACT: Transition metal nanoparticles are privileged materials in catalysis due to their high specific surface areas and abundance of active catalytic sites. While many of these catalysts are quite useful, we are only beginning to understand the underlying catalytic mechanisms. Opening the “black box” of nanoparticle catalysis is essential to achieve the ultimate goal of catalysis by design. In this Perspective we highlight recent work addressing the topic of controlled catalysis with bimetallic alloy and “designer” adsorbate-stabilized metal nanoparticles.

KEYWORDS: bimetallic alloy, nanoparticle, ligand, gold, platinum, selectivity, controllable catalysis

1. INTRODUCTION

Transition metal nanoparticles (NPs) are uniquely suited for applications in heterogeneous catalysis due to their extremely high specific surface areas and strong correspondence between particle structures and surface chemistries.^{1–7} Small nanoparticles that are typically most catalytically active are also most disposed to aggregation. Thus, a variety of solid support strategies, including (meso)porous materials,⁸ simple oxide supports,⁹ graphene¹⁰ and other carbon nanomaterials,^{10–11} have been utilized in practical catalytic systems for the stabilization and recycling/reuse of nanoparticulate catalysts.

While significant strides towards atomically precise synthesis of metal NPs have been made in recent years,^{12–14} the catalytic mechanisms operational at NP surfaces are not yet entirely understood. It is commonly accepted that clean/pristine NP surfaces are preferable in well-behaved catalysts.^{15–16} At the same time, the supporting materials have been shown to strongly affect the catalytic properties of NPs, sometimes acting as synergistic co-catalysts.^{17–21} Small particle size is often a prerequisite of their high catalytic competency; however, the optimal size cannot be predicted *a priori*.^{7,22–26} NP catalysts are extremely useful, yet in many cases they remain *Dinge an sich*. Strategies for the rational design of NP catalysts and better mechanistic understanding of the underlying reaction mechanisms are highly desirable.

The two prevalent and sometimes interrelated approaches to achieving control in metal-complex catalysis are the modulation of electronic properties of the operational metal sites, and changing the steric environment around these sites. While the same approaches should be just as applicable to nanoscale catalysts, the synthetic and analytical techniques are considerably more challenging for these systems in comparison to small molecules. In this Perspective, we highlight some of the recent work addressing the broad topic of catalysis-by-design with metal NPs. Recent reviews on the subject targeted phosphine ligands/Ru,^{27–28} stabilizers/Rh,^{29–30} and thiolate ligands/Pd or Pt.³¹ We specifically focus on the emerging fields of catalysis with bimetallic alloy NPs and “designer”

adsorbate-stabilized NPs.

Bimetallic NPs with controllable morphology and composition have been intensively investigated over the last few decades due to their unique catalytic properties.^{32–40} The combination of properties associated with two distinct metals sometimes has a synergistic effect on catalytic competence. Ligands and polymers with high affinity for specific metals have been employed to control the growth and aggregation of bimetallic NPs.^{34,38,41–42} Meanwhile, solvents, such as glycerol,^{43–44} deep eutectic solvent⁴⁵ and ionic liquid,^{46–48} play a central role in the dispersion of bimetallic NPs and can modulate the catalytic properties.

There are three different types of bimetallic NPs in terms of the mixing pattern,^{32–33,35,37} corresponding to heterostructures (two different NPs sharing an interface), core-shell structures, and alloyed/intermetallic structures (almost homogeneous on the atomic level). Among these bimetallic structures, alloyed NPs exhibit unique and more flexible surface structures compared to monometallic NPs.^{36,39,49–50} These surface structures can be useful for tailoring the affinity with surface adsorbates and substrates, leading to superior and efficient catalysts.

2. CONTROL OF THE CATALYTIC PROPERTIES OF BIMETALLIC ALLOY NANOPARTICLES THROUGH COMPOSITION

Catalysis with bimetallic NPs is a topic of considerable current interest.^{32–33,37,49–52} One of the reasons these materials are so attractive is cost: the incorporation of a non-precious metal in the composition can make for a dramatically cheaper catalyst. Core-shell nanoparticles with non-precious metal cores have been used extensively for this reason. Furthermore, the incorporation of a second metal as an alloy/intermetallic compound can be used to control the surface composition, the geometry of the adsorption sites, and the electronic properties of the catalyst. The combination of these factors is traditionally referred to as the “ensemble effect”.

The AuPd alloy is one of the most widely studied bimetallic systems because of its easy accessibility and broad catalytic

scope.^{37,50,53-55} The catalytic properties of AuPd NPs are closely correlated with alloy composition. For example, the Pd-Pd distance on the catalytic surface is an extremely important parameter for the synthesis of vinyl acetate from acetic acid and ethylene (Figure 1).⁵⁶ The closer distance of a monomer Pd pair on the Au(100) surface is near optimal and has been shown to function better than the Pd pair on the Au(111) surface. Goodman and coworkers exploited this to create an exceptionally active and selective catalyst for the production of vinyl acetate. Recently, Zhang and coworkers demonstrated that the ion-exchange resin-supported AuPd NPs could switch the pathways of aerobic oxidative coupling of alcohols and amines by tuning the molar ratio of the alloy.⁵⁷

Figure 1. Proposed mechanism of vinyl acetate synthesis from acetic acid and ethylene over Pd atoms on the surface of Au. The optimized distance for this reaction is 3.3 Å. This reaction is possible via a Pd monomer pair on the surface of Au(100), but impossible on the surface of Au(111). Reprinted with permission from ref 56. Copyright 2005 American Association for the Advancement of Science.

Bimetallic alloy NPs containing nickel, including CuNi,⁵⁸ RhNi,⁵⁹ PdNi,⁶⁰ and PtNi,⁶¹ have also attracted considerable attention. Medlin and coworkers reported that the catalytic activity of furfural hydrogenation over Cu₄Ni alloy was increased by at least 30 %, and selectivity only slightly reduced in comparison with pure Cu (Figure 2).⁶² Further modification of the NPs with an octadecanethiol self-assembled monolayer (SAM) improved the stability of Cu on the surface, maintaining a high selectivity for furfuryl alcohol, and likely retaining small amounts of surface Ni to assist with hydrogen splitting.

Figure 2. Combined selectivity for furfuryl alcohol and methylfuran, and the turnover frequency of furfural hydrogenation over uncoated

and C18-coated Cu₄Ni catalysts. Reprinted with permission from ref 62. Copyright 2014 American Chemical Society.

Similarly, the composition of the PtSn alloy capped with dodecylamine displayed some influence on the selective hydrogenation of acetylene toward ethylene.⁶³ The most selective catalyst was the PtSn catalyst with a molar ratio of 1:1. Increasing the Sn content led to a decrease in the activity, whereas the catalytic selectivity was reduced with increasing Pt content. Michaelis and coworkers exploited the composition effect on the chemoselectivity of nitroarene reduction catalyzed by bimetallic RuCo NPs.⁶⁴

3. CONTROL OF THE CATALYTIC PROPERTIES OF NANOPARTICLES WITH SURFACE ADSORBATES

Metal NPs and nanoclusters are commonly solubilized and stabilized by a variety of surface adsorbates, which are often indispensable for achieving solubility and control over nanomaterial size.^{16,65-66} A variety of such adsorbates have been utilized, including small molecules with a high affinity towards transition metals (thiols, amines, and heterocycles⁴⁴), surfactants, and polymers.^{16,31,52} The surface accessibility of NPs stabilized with these methods is usually impaired; additionally the strongly-binding ligands, such as thiols, are classic catalytic poisons. Thus, a variety of surface treatment protocols for the removal of adsorbates have been developed to yield pristine NP surfaces for catalytic applications.^{15-16,67-70}

However, the “naked” NPs are not always optimal catalysts. The influence of adsorbates on the catalytic properties of NPs can be salutary, resulting in improved or modified chemoselectivities and increased reaction rates.^{31,52} In this section, we shall summarize some of the recent publications utilizing adsorbates for controlling the catalytic chemistry of metal NPs.

The effects of adsorbates can be arranged into the broad categories of active site selection/selective poisoning, steric effects, electronic effects, specific molecular recognition, and competitive adsorption. More than one effect could be operational in any given scenario.

Figure 3. (A) The chemical structures of *n*-octadecanethiol (**1a**) and mercaptoacetic acid (**1b**). (B) The aerobic oxidation reaction of benzyl alcohol (**1c**). (C) The hydrogenation reaction of ketopantolactone (**1e**).

3.1. Active Site Selection. High surface coverage by strongly-bound capping ligands, such as thiols, phosphines, or amines typi-

cally results in the poisoning of a metal-NP catalyst.^{15-16,31,52} However, catalytic reactions in the presence of limited amounts of such catalytic poisons can result in a beneficial change of catalytic selectivity towards more desirable reaction products. Often, a catalytic poison can be chosen to selectively block active sites related to undesirable processes, improving the selectivity and overall usefulness of the catalytic process. An archetypal example of such site selection is the Lindlar catalyst.⁷¹⁻⁷²

More recently, Baiker and co-workers investigated aerobic oxidation of **1c** (Figure 3B) and the hydrogenation of **1e** (Figure 3C), both reactions are catalyzed by Au NPs.⁷³ They found that the Au catalyst could be poisoned by thiols **1a** or **1b** (Figure 3A). The poisoning susceptibility of both reactions was independent of the type of support (CeO₂ and TiO₂) and the size of Au NPs (2.1 or 6.9 nm). Results showed that **1a** was a stronger poisoning agent in the aerobic oxidation, while **1b** was a stronger poisoning agent in hydrogenation. Both experiments and density functional theory (DFT) calculations indicated that **1a** tends to adsorb on large Au terraces, whereas **1b** tends to attach to defected sites, such as crystal edges and corners. Therefore, the active sites of the hydrogenation reaction are most likely these edges and corners that can be readily poisoned by **1b**, whereas the active sites of the oxidation reaction are probably the extended gold faces that can effectively be blocked by **1a**.

A striking example of thiolate-mediated selectivity control was provided by Tsukuda and co-workers.⁷⁴ They investigated the catalytic properties of immobilized and thiolate-protected Au₂₅ nanoclusters in the aerobic oxidation of **1c** (Figure 4). The coverage of dodecanethiolates (C12S) on the cluster surfaces decreased with increasing calcination temperature and period. When gold catalysts were completely protected with thiolate ligands, they were so heavily poisoned that no conversion was detected in the oxidation reaction. However, as the ligands were gradually removed, the conversion increased and the main product changed from benzaldehyde to benzoic acid. These results, as is common for the active site selection approach, indicate a trade-off between activity and selectivity. The suppression of the undesirable overoxidation of benzaldehyde to benzoic acid was ascribed by the authors to the electron-withdrawing effect of the thiolates; however, selective site poisoning cannot be ruled out.

Figure 4. Schematic illustration of thiolate-mediated selectivity control in aerobic alcohol oxidation over supported gold clusters. Reprinted with permission from ref 74. Copyright 2014 American Chemical Society.

3.2. Electronic Effects. Complex interactions between metal NPs and active supports, such as ceria and titania, often result in a significant change in the catalytic properties as compared to the free NPs in solution.^{18,21} Such a change in reactivity has often been ascribed to electron transfer between NPs and support materials. Similar interactions can be designed into the structure of the capping ligands.

P1: R = H **M_w** = 35,000 **P2:** R = Me **P3:** R = OMe **P4:** R = CF₃

Figure 5. Polymers with a variety of substituent groups used to stabilize RuCo NPs and control their catalytic activity.

Tsukuda and co-workers reported the first instance of negatively charged gold clusters with increased activity for aerobic oxidation of *p*-hydroxybenzyl alcohol due to electron donation from the capping ligand poly(*N*-vinyl-2-pyrrolidone).⁷⁵ Following that, Michaelis and co-workers confirmed that electronic interactions between NPs and polymers were responsible for catalytic performance and that the electronic properties of different polymers could tailor catalytic activity.⁶⁴ A variety of substituted polymers (Figure 5) containing electron-donating or electron-withdrawing functional groups were synthesized and used for the preparation of bimetallic (RuCo) NP catalysts. Protected by polymers containing electron-withdrawing functional groups (**P4**), these catalysts consumed the starting material rapidly. Consistently, catalysts protected with more electron-rich polymers (**P2**, **P3**, **P5**, **P6** and **P7**) led to slower catalysis.

3.3. Specific Molecular Recognition. Enzymes use specific molecular recognition of substrates to achieve unparalleled selectivity of catalytic transformations. Taking inspiration from Nature, several groups attempted to exploit non-covalent interactions between reaction substrates and adsorbates on the surface of metal NPs.

Figure 6. The hydrogenation pathway of cinnamaldehyde (**2a**).

Miki and coworkers reported an improved catalyst for alcohol hydrosilylation based on an ordered 2D array of alkanethiol-coated Au NPs.⁷⁶ The increased catalytic activity of the SAM-protected

NPs was attributed to hydrophobicity-driven encapsulation of the reactants by the monolayer alkyl chains.

Figure 7. (A) A molecule of **2a** lying flat on the uncoated surface of a platinum NP. (B) **2a** with an upright molecular orientation directed by the SAMs of 3-phenylpropanethiol (**3e**). (C) The chemical structures of thiolate ligands with conjugated tail moieties and different lengths of carbon chains between head and tail. Adapted with permission from ref 77. Copyright 2014 American Chemical Society.

A more specific mode of molecular recognition on the SAM-protected nanoparticle surface was reported by Medlin and coworkers.⁷⁷ In the hydrogenation of **2a** over platinum NPs (Figure 6), cinnamyl alcohol (**2c**) is the most industrially valuable of the three products. When naked Pt NPs are used as the catalyst, the chemoselectivity of **2c** is typically low (no more than 25 %). This has been attributed to the preferred “flat” mode of adsorption of **2a** on the platinum surface, which favors the hydrogenation of the C=C bond (Figure 7A). In contrast, when this catalyst was modified with 3-phenylpropanethiol (**3e**), the chemoselectivity for **2c** of over 95 % was attained. These results are attributed to the aromatic stacking interaction between **2a** and **3e** (Figure 7B), which strongly favors the “upright” adsorption mode for **2a**. In addition to the essential role of the phenyl moiety for the aromatic stacking interaction, the distance between phenyl groups and the platinum surface was also central for chemoselectivity. Longer or shorter modifiers (Figure 7C) can lower the chemoselectivity for the desired product. The higher prevalence of the “upright”-bound **2a** on phenyl-functionalized surfaces was further confirmed via polarization modulation-reflection absorption infrared spectroscopy when **3e** was used as the modifier.⁷⁸ This modifier, which has the same number of carbon atoms as **2a**, is the most effective modifier for the chemoselective conversion of the aldehyde moiety. The improved chemoselectivity was accompanied by significantly compromised activity. In addition, repeated recycling or aging in air of platinum NP catalysts modified with thiolate ligands occurred, and chemoselectivity decreased.⁷⁹ This observation was attributed to the increasing disorder of the thiolate monolayer after use or aging. Fortunately, the chemoselectivity of catalysts after the first use could be largely recovered by adding a fixed concentration of thiolate ligands to the reaction solution or by re-depositing a fresh thiolate SAM on the spent catalyst.

3.4. Steric Effects. Steric effects have been extensively investi-

gated and are well understood by organic chemists. Similar design principles have been successfully applied to nanoscale catalysts.^{16,31,52}

Recently, Fu and coworkers reported on amine-capped bimetallic PtCo NPs for the selective hydrogenation of **2a**, (Figure 8).⁸⁰ Taken together, experimental results and DFT calculations suggested that the presence of long-chain amines on the surfaces of NPs was responsible for the resultantly high chemoselectivity of **2c**. The steric effect created by long-chain amines helped to prevent **2a** from adsorbing in a flat mode on the surface of the metal. As a result, **2c** was the main product, and further hydrogenation into **2d** was prevented. Unlike Medlin catalyst (*vide supra*), the amine-capped PtCo NPs derive their selectivity only from the steric bulk of the SAM alkyl chains. The amine ligands with longer carbon chains increase chemoselectivity (Figure 8) at the expense of overall activity.

Figure 8. The influence of different amine-capped Pt₃Co catalysts on catalytic selectivity of the hydrogenation of **2a**. **2c** (white), cinnamyl alcohol (**2b**, cross-hatch), and hydrocinnamyl alcohol (**2d**, gray). Reprinted with permission from ref 80. Copyright 2012 Wiley-VCH Verlag GmbH & Co. KGaA.

A related paper by Bokhoven and coworkers reported on the change in chemoselectivity of a SAM-protected Pt NP catalyst for the reduction of nitrostyrene.⁸¹ The chemoselectivity was altered from 4-ethylnitrobenzene and 4-ethylaniline (on naked Pt) towards 4-aminostyrene. The change in selectivity was attributed to the SAM preventing flat adsorption of nitrostyrene on platinum surface. Similarly, bimetallic PtRu NPs confined in multiwalled carbon nanotubes (MWCNTs) exhibited higher catalytic selectivity in the hydrogenation of **2a** than unsupported ones due to the steric effect.⁸² Meanwhile, the confined catalysts showed higher activity, resulting from a higher local concentration of reactants and catalyst within MWCNTs.

Figure 9. A schematic illustration of the hydrogenation of **1a** via a bimetallic PtFe NP catalyst stabilized by fluoros ligands containing carboxylate groups that prefer binding to one of the metals (Fe). Reprinted with permission from ref 83. Copyright 2015 American Chemical Society.

To make more efficient use of precious metals, bimetallic FePt

NPs stabilized with carboxylate surface ligands were developed by Rodionov and coworkers for the chemoselective hydrogenation of **2a** under mild conditions.⁸³ Carboxylate surface ligands have a high affinity for Fe and almost none for Pt. Thus, the catalytic activity of Pt patches on the surfaces of bimetallic NPs is preserved. Compared with the parent platinum NP catalysts, bimetallic FePt NPs exhibited much higher activity and chemoselectivity. Surprisingly, FePt NPs stabilized by carboxylate surface ligands containing hydrocarbon chains were dramatically less active compared to that containing fluorocarbon chains. The chain length of the fluororous ligands displayed significant influences on the chemoselectivity of the FePt NP catalysts. Using fluororous carboxylic acid ligands containing longer carbon chains (Figure 9), both the chemoselectivity of **2c** and the reaction rate were simultaneously improved. Remarkably, the fluororous-stabilized catalysts were both more selective and more active than the parent Pt catalyst. These properties were attributed to the isolation/crowding of the Pt active sites by the monolayer formed by the rigid fluororous ligands. Additionally, this catalyst has excellent colloidal stability and could be easily recovered via a fluororous-biphasic recycling procedure.

3.5. Competitive Adsorption. The capping ligands of metal NPs can be replaced by other more active molecules in solution.^{65-66,84-85} This is true even for the strongest interaction between thiolate ligands and gold, which is commonly considered to be purely covalent. In general, the interaction between thiolate ligands and metal NPs is much stronger than the one between most practical reactants and metal NPs. However, when the affinity between reactant and NP surface is very close to that between the capping ligand and the metal NP, the activity and selectivity of catalytic reactions can be switched by using various capping ligands.

Figure 10. (A) The hydrogenation reaction of 4-octyne (**4a**) over Pt or CoPt NPs. (B) The chemical structures of 1-octylamine (**4d**), 3-hexyne (**4e**), 5-decyne (**4f**), and 1-octyne (**4g**).

Based on the competitive adsorption of the capping ligands and reactants, Jellinek and coworkers were able to control the catalytic selectivity of the hydrogenation reactions using ligated Pt and CoPt NPs.⁸⁶ In the hydrogenation reaction of **4a** (Figure 10A), platinum NPs with capped with **4d** ligands exhibited remarkably better selectivity for alkenes (Figure 11) without hindering its reactivity as compared to trioctylamine, oleic acid, trioctylphosphine (TOP), trioctylphosphine oxide (TOPO), or 1-dodecanethiol (DDT). Moreover, coverage of the amine ligands on platinum surfaces af-

fects selectivity, which was confirmed by analyzing the influence of **4d** concentrations. DFT calculations provided further insight into the excellent selectivity of alkene via platinum NPs protected with amines. With a high concentration of amines in the solution, primary alkylamines have a higher adsorption energy than alkenes, which can prevent further hydrogenation into alkanes. Compared with the reactants (**4a** and 4-octene (**4b**)), capping ligands with relatively high adsorption energies, such as trioctylphosphine and 1-dodecanethiol, were shown to dramatically reduced activity (Figure 11). Capping ligands with relatively low adsorption energies, such as trioctylphosphine oxide, oleic acid, and trioctylamine, led to poor selectivity (Figure 11). Similarly, high yields of alkene products were obtained through the hydrogenation of **4e** and **4f** (Figure 10B) due to the higher adsorption energy of **4d** than 5-decene or 3-hexene. However, the hydrogenation selectivity of **4g** (Figure 10B) was approximately 4% as a result of the higher adsorption energy of 1-octene.

Figure 11. Effects of various capping ligands on catalytic performance of Pt NPs (3.5 nm) in the hydrogenation reaction of **4a**. Reprinted with permission from ref 86. Copyright 2012 American Chemical Society.

4. CHIRAL LIGANDS AND MODIFIERS FOR ASYMMETRIC CATALYSIS

In recent years, considerable advances have been made towards practical asymmetric heterogeneous catalysts.⁸⁷⁻⁹² Such catalysts can be more useful than the traditional homogeneous asymmetric catalysts due to the advantages of easy separation, efficient recycling, and overall lower costs. For example, palladium NPs modified by chiral ligands has drawn much attention in the field of asymmetric catalysis⁹³⁻⁹⁶ (the in-depth discussion of these systems is outside the scope of this Perspective, as the discrimination between homogeneous and heterogeneous catalysis is often challenging for Pd catalysts). Heterogeneous asymmetric catalysts can be arranged into three categories: immobilized homogeneous catalysts, metals with chiral surfaces, and metals modified with chiral adsorbates.⁸⁹⁻⁹⁰ For the purposes of this discussion, we shall focus on the effects of chiral adsorbates.

The two most studied systems of this type are the tartaric acid-modified Ni catalyst for the hydrogenation of β -keto esters, and the cinchonidine-modified Pt catalyst for the hydrogenation of α -keto esters.⁸⁹⁻⁹⁰ It is important to note that tartaric acid only works well with Ni, whereas cinchonidine is the best modifier for Pt. For instance, high enantioselectivity (> 90 % enantiomeric excess (ee)) was achieved in the hydrogenation of ethyl pyruvate over Pt/Al₂O₃.

catalysts by using 10,11-dihydrocinchonidine as the chiral modifier.⁹⁷ Several mechanistic models have been proposed for the origin of the enantioselectivity in these reactions. The most widely accepted model considers direct interaction between the chiral modifier and the substrate on the surface of the metal. The results of scanning tunneling microscopy measurements and DFT calculations support the formation of chemisorbed modifier-substrate complexes on Pt(111).⁹⁸⁻⁹⁹

Figure 12. A schematic illustration of asymmetric catalysis of olefin cyclopropanation reaction using gold nanoclusters encapsulated in chiral SAM/mesoporous MCF-17 support. Reprinted with permission from ref 100. Copyright 2013 American Chemical Society.

Increasing catalytic selectivity is typically achieved at the expense of activity. To overcome the poisoning effect of strongly adsorbed chiral ligands on the surfaces of metals, Toste and Somorjai collaborated to develop a heterogeneous catalyst with gold clusters embedded in chiral SAMs (Figure 12).¹⁰⁰ The resulting catalyst exhibited up to 50% enantioselectivity with a high diastereoselectivity for olefin cyclopropanation reactions. The formation of a hydrogen-bonding network in the chiral SAMs that was unveiled by spectroscopic measurements was considered to be the origin of the improved enantioselectivity. Thus, reactant molecules prefer specific alignment to the active gold clusters when they approach through the chiral SAMs. Zaera and coworkers also reported a unique case where alkyl thiol SAMs improved both activity and selectivity significantly for the hydrogenation reaction of α -keto esters with cinchonidine as a chiral modifier over Pt/ Al_2O_3 catalysts.¹⁰¹ Additionally, platinum catalysts protected with cinchonidine-derivatized thiols were successfully developed and shown to perform reasonably well without cinchonidine in the reaction mixture. Very recently, Kunz and coworkers demonstrated that both the catalytic activity and selectivity were improved simultaneously using the hydrophilic chiral ligand L-proline.¹⁰² The resulting platinum catalyst was highly chemoselective toward the desirable aromatic alcohol with modest stereoselectivity (14% ee) in the hydrogenation reaction of acetophenone (Figure 13).

Figure 13. A schematic illustration of the catalytic hydrogenation of acetophenone. The desirable product is phenyl 1-ethanol. Reprinted with permission from ref 102. Copyright 2015 American Chemical Society.

Heterogeneous asymmetric catalysts with bimetallic NPs have also been successfully developed in recent years.⁹¹ Kobayashi and coworkers demonstrated that polymer-incarcerated chiral Rh/Ag NPs are effective for the asymmetric 1,4-addition reactions of arylboronic acids to α,β -unsaturated carbonyl compounds.¹⁰³⁻¹⁰⁴ The composition of the bimetallic Rh/Ag NP and the type of chiral ligand affected catalytic activity and the amount of metal leaching. Interestingly, a novel secondary amide-substituted chiral diene ligand was developed and acted as a bifunctional ligand that interacted with the surface of the metal and the substrate to facilitate reactions. High catalytic turnover and outstanding enantioselectivity (> 90 % ee) have been achieved for a wide range of substrates.

5. SUMMARY AND OUTLOOK

Significant progress has been made in recent years towards rational design of NP-based catalysts. The catalytic activity and selectivity can be controlled by utilizing bimetallic alloy NPs. "Naked" or supported nanoparticles are not *always* preferable: surface adsorbates can play multiple roles in controlling catalytic properties of metal NP catalysts. Active-site selection can be achieved through controlled blocking/poisoning of undesirable active sites. The steric effects of capping ligands can suppress the randomness in the geometry of the approaches to active site, resulting in a highly selective catalyst. The electronic/charge transfer effects of surface ligands can also be used to modulate catalytic activity or selectivity. A number of workers successfully exploited specific supramolecular interactions between NP surface adsorbates and substrates to direct the binding geometry around the active sites to achieve selectivity-by-design in heterogeneous catalysis. Last but not least, the competitive adsorption approach has been very promising for certain classes of substrates and surface adsorbates.

A number of challenges in the field of controllable catalysis with NPs remain unaddressed. One such challenge is creating catalysts that are both more active and selective. While a variety of surface- and site-blocking strategies have been extremely fruitful for developing selective catalysts, most existing systems trade catalytic prowess for selectivity. While the same can be said about many chemist-designed catalysts, we believe that adsorbate-stabilized NPs are one of the more promising platforms for mimicking enzymes, Nature's "perfect" catalysts. The size of practical NPs is enzyme-like, and the possibility of atomically-precise control of surface chemistry make these materials more tantalizing than ever. We believe that the coming years will see significant advances in the field, with a specific emphasis to asymmetric transformations.

The catalyst stability challenge is one that needs to be addressed. For adsorbate-stabilized NP catalysts, the resilience of the surface ligands is very important. For instance, alkanethiol based SAMs often suffer from oxidation of thiol groups in air,^{79,105} but this issue is yet to be addressed systematically. For the bimetallic NPs, the stability of surface composition of metals is of paramount importance. Because of the advances of ambient pressure techniques for surface analysis, surface reconstruction of bimetallic NPs during catalytic reactions has been extensively investigated.¹⁰⁶⁻¹⁰⁷ In practice, some pretreatments, such as thermal annealing,¹⁰⁸ acid washing,¹⁰⁹ phase transfer process¹¹⁰ and hydrogen absorption/desorption,¹¹¹ have been developed for transforming the surface composition of bimetallic NPs, resulting in enhanced activity and/or selectivity.¹¹²⁻¹¹³ In addition, to efficiently reuse the bimetallic NPs, the leaching/dissolution problem should be tackled.⁴¹ In particular, bimetallic NPs containing Pd commonly exhibited

leaching behavior in catalysis,¹¹⁴⁻¹¹⁵ which has also been intensively investigated and well documented in monometallic Pd NPs.¹¹⁶⁻¹¹⁷

Continued investigation into specific catalytic mechanisms on NP surfaces, especially in the presence of adsorbates, is another frontier. While mechanistic investigations of classic heterogeneous catalysts are routine, the “dirty” surfaces of adsorbate-stabilized NPs present are quite challenging for current *in situ* and *in operando* observation techniques. Reports of such studies are beginning to appear. The rapid development of spectroscopic techniques will certainly provide more mechanistic insights, enabling rational design of catalysts.¹¹⁸

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ABBREVIATIONS

NPs, nanoparticles; SAM, self-assembled monolayer; ee, enantiomeric excess; DFT, density-functional theory; MWCNTs, multiwalled carbon nanotubes.

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