Heterogeneous catalysis for green chemistry based on nanocrystals

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ABSTRACT

Modern society has an ever-increasing demand for environmentally friendly catalytic processes. Catalysis research is working towards a solution through the development of effective heterogeneous catalysts for environment-related applications. Nanotechnologies have provided effective strategies for the preparation of nanocrystals (NCs) with well-defined sizes, shapes and compositions. Precise control of these NCs provides an important foundation for the studies of structure-performance relationships in catalysis, which is critical to the design of NCs with optimized catalytic performances for practical applications. We focus on recent advances in the development of bottom-up strategies to control NCs structures for some key catalytic applications, including CO oxidation, selective oxidation of alcohols, semihydrogenation of alkenes, and selective hydrogenation of unsaturated aldehydes and nitrobenzene. These key applications have been a popular research focus because of their significance in green chemistry. Herein we also discuss the scientific understandings of the active species and active structures of these systems to gain an insight for rational design of efficient catalytic systems for these catalytic reactions.

Keywords: nanocrystals, heterogeneous catalysis, green chemistry, CO oxidation, alcohol oxidation, selective hydrogenation

INTRODUCTION

Heterogeneous catalysts are vital to many industries including chemical manufacturing, energy-related applications and environmental remediation [1]. Nanocrystals (NCs) finely dispersed on high-surface-area oxides are the most widely used heterogeneous catalysts, with catalytic activity and selectivity of the supported NCs strongly dependent on their size and shape, and surface and local composition [1]. The fundamental aim of heterogeneous catalysis research is to understand mechanisms at the molecular level, and then to design and synthesize catalysts with desired active sites [2]. Heterogeneous catalysis occurs when the reactant molecules are adsorbed to the surface of the catalyst. In surface science, well-defined single-crystal surfaces are studied by applying physical techniques under ultralow pressure conditions. However, these model systems differ appreciably from real catalytic conditions, both with regard to the nature of the catalyst surface and the applied pressure range [3].

Owing to the high surface area to volume ratio, NCs with a well-defined structure are ideal materials to investigate mechanisms under real working conditions [4,5].

Significant progress in nanotechnology over the last 20 years has made it possible to open up the synthetic route to produce NCs with a uniform size, morphology, composition and moreover, with a core-shell, branched, alloy and hybrid nanoarchitecture [6–8]. New materials and novel approaches based on nanostructures can revolutionize the technology used in modern heterogeneous catalysis [1,2,9,10]. For example, applying 'bottom-up' chemistry techniques, the monodisperse nickel, palladium and platinum NCs are colloidally synthesized with different sizes. They are supported on ceria, making them a potentially model catalyst for CO oxidation [11]. The results showed a direct linear relationship between CO conversion and ceria–metal interface length, further demonstrating that the use of size-selected NCs can successfully
Figure 1. Schematic illustrations and corresponding TEM images of the samples obtained at four representative stages during the evolution process from polyhedra to nanoframes. (A) Initial solid PtNi polyhedra. (B) PtNi intermediates. (C) Final hollow Pt$_3$Ni nanoframes. (D) Annealed Pt$_3$Ni nanoframes with Pt(111)-skin-like surfaces dispersed on high-surface area carbon. Adapted with permission from [15].

Identify catalytically active sites. Moreover, many studies have shown that the catalytic properties of NCs are not only sensitive to changes in size, but also to changes in morphology [2, 12–14]. These findings are significant for advanced heterogeneous catalysis research. Rational synthesis of catalysts might be achieved for desired activity and selectivity by exposing the acquired crystal facets. Morphologically controlled NCs are relatively simple systems compared with traditional catalysts, suggesting that they may be effective in bridging the gap between real and model catalyst. Furthermore, through manipulating both ‘bottom-up’ and ‘top-down’ strategies at the nanoscale, an extremely active and durable electrocatalyst was synthesized by interior erosion from PtNi$_3$ polyhedra (synthesized by ‘bottom-up’ strategy) into Pt$_3$Ni nanoframes (synthesized by inverse ‘top-down’ strategy) with surfaces that offer 3D molecular accessibility (Fig. 1) [15]. The ionic liquid-encapsulated Pt$_3$Ni nanoframes exhibited a factor of 22 enhancement of specific activity relative to the oxygen reduction reaction compared to conventional platinum/carbon catalysts, yet contain about 85% less precious metal. The approach presented here, to control the structural evolution at the atomic level, can be readily applied to other multimetallic nanoframes such as PtCo, PtCu, Pt/Rh-Ni and Pt/Pd-Ni.

It is widely accepted that the modern chemical industry requires alternative and environmentally friendly catalytic processes. This trend towards ‘green chemistry’ necessitates a paradigm shift from traditional concepts of process efficiency, that focuses largely on chemical yield, to one that assigns economic value to eliminating waste at the source and avoids the use of toxic and/or hazardous substances [16]. On the chemistry of fine chemical manufacturing, a primary cause of waste generation is the use of stoichiometric inorganic reagents. For example, stoichiometric reductions with metals (Na, Mg, Fe, Zn) and metal hydrides (LiAlH$_4$, NaBH$_4$), and oxidations with permanganate or chromium (VI) reagents. To develop processes based on H$_2$, O$_2$, H$_2$O$_2$, CO and CO$_2$ as the green sources, catalytic hydrogenation and oxidation are good examples of highly atom efficient and greener processes. The milder reaction conditions, e.g., low reaction temperature and pressure, of these green processes is also advantageous [16]. Fortunately, the rapid growth and improved understanding of nanoscience and nanotechnology has facilitated the precise control of NCs synthesis with variable sizes, shapes, chemical compositions and dispersity in nanoarchitecture, factors all of which affect the activity (higher activity afford lower reaction temperature and pressure) and selectivity (higher selectivity afford higher atom efficiency) in the nanocatalyst. Combining nanotechnology with green chemistry will be a key contributor to an environmentally sustainable future.

Examining the applications of nanotechnology into green chemistry is the main theme of this review and around which our discussion is organized. In this review, we first discuss the correlation between NC structure and catalytic performance, leading to identification of the active catalytic sites. Due to the explosion of publications in this field, this review will provide a summary only. Mindful of space restrictions, we will limit this review to four reaction
systems associated with green chemistry or environment protection: CO oxidation, selective gas-phase oxidation of alcohols to aldehydes/ketones, selective hydrogenation of aldehydes and nitrobenzene and semihydrogenation of alkenes.

**GROWTH MECHANISM OF NCs AND BACKGROUND ON CATALYTIC REACTIONS**

Before discussing the catalytic behavior of NCs in a heterogeneous catalysis, we provide here a summary of the most common well-defined structures of NCs and their potential advantages for catalytic applications.

A typical synthesis process can be generally divided into two distinct stages: nucleation and growth of seeds into NCs [17]. Nucleation is the first stage of any crystallization process. As the concentration of building blocks (atoms, ions or molecules) becomes sufficiently high, they aggregate into nuclei through homogeneous nucleation. With a continuous supply of the building blocks, these nuclei can serve as seeds for further growth to form larger structures. Morphology and the growth rate of the seeds are controlled by an interplay between growing thermodynamics and kinetics, which play major roles in determining the final shape of NCs. In recent years, significant progress has been made in the controllable synthesis of NCs with well-defined structures. It has been well documented that the size, component structure, morphology of NCs and support are important factors in determining their catalytic performance. In the following discussion, we survey some recent studies reporting on catalytic reactions promoted by NCs.

Controlling the size of NCs during their synthesis is crucial when preparing an active catalyst as the surface to volume ratio of the particles increases sharply below 5 nm. A higher surface to volume ratio results in an increase in the number of active sites and low-coordination sites, for example steps and corners, which often result in more active and/or selective catalyst materials [18]. Furthermore, the electronic properties of the particles can vary significantly with size, especially at diameters below a few nanometers. At this point metals may lose their metallic properties and develop discrete electronic levels or undergo other electronic changes as a result of quantum-mechanic constraints. The size effect on catalytic activity for oxidation reactions was first exhibited by Au catalyst—a metal that shows almost no activity in bulk, but seems to be active below 10 nm [19]. In regard to CO oxidation, the maximum activity displayed by Au NCs ranging from 2 to 3 nm in diameter was explained by a quantum effect [20]. Another interesting size effect on catalytic activity for hydrogenations reactions was identified over supported Pt catalyst. The Somorjai group tested the performance of Pt NCs with sizes ranging from 0.8 to 5.0 nm for the hydrogenation and hydrogenolysis of pyrrole [21,22]. They found that the selectivity shifted from almost exclusive n-butylamine formation (a hydrogenolysis product) over larger particles to the formation of significant quantities of pyrrolidine (the result of stopping at the hydrogenation steps) over smaller particles. Selectivity differences were believed to occur because the N of n-butylamine is more electron rich than its counterpart in pyrrolidine; the pyrrole can therefore form stronger adsorbate-surface interactions. These interactions became stronger over smaller NPs, which possess more unsaturated surface bonds.

In surface science, single-crystal surfaces of metals or metal oxides have been widely adopted to systematically study the effect of a surface/interface structure on catalytic reactions [23]. New synthetic procedures in connection with nanotechnology have made it possible to grow NCs with specific shapes. As these NCs may expose certain facets preferentially, the ability to synthesize them offers a unique opportunity to create catalysts with high-specific activity or selectivity on the basis of differences in reactivity with different types of surface sites. Our group developed a hydrothermal method to obtain Co$_3$O$_4$ nanobelts with exposed {011} planes, nanosheets with {112} planes and nanocubes with {001} planes (Fig. 2) [24]. For methane combustion, the corresponding specific rates of CH$_4$ were 2.72, 2.28 and 1.25 mmol/g s for nanosheets, nanobelts and nanocubes, respectively. The results showed that the unusually high-index {112} crystal planes of Co$_3$O$_4$ NCs were more reactive than the more common {001} and {011} planes in the catalytic combustion of methane. An additional example is the oxidation of styrene by Ag catalysts in colloidal solutions. The reaction rate over Ag nanocubes was measured to be over 14 times higher than that on Ag nanoplates and four times higher than that on near-spherical Ag NCs [25].

NCs often emerge with various architectures including alloyed structures, heterostructures, core-shell structures, crown-jewel structures, hollow structures and porous structures [26,27]. Notably, NCs consisting of two distinct metals (oxide) allow a more flexible design according to the activity/selectivity requirements, particularly for structure-sensitive reactions [28]. Integrating two different metal-oxide interfaces with catalytically active NCs, Yang and co-workers designed...
Figure 2. (a) SEM image of typical Co$_3$O$_4$ nanosheets. (b) HRTEM image and structural model of typical Co$_3$O$_4$ nanosheets. (c) TEM image of typical Co$_3$O$_4$ nanobelts. (d) HRTEM image and structural model of typical Co$_3$O$_4$ nanobelts. (e) TEM image of typical Co$_3$O$_4$ nanocubes. (f) HRTEM image and structural model of typical Co$_3$O$_4$ nanocubes. Adapted with permission from [24].

Figure 3. Ethylene hydroformylation with methanol over a tandem catalyst. (a) Propanal produced as a function of reaction time over CeO$_2$-Pt-SiO$_2$ and Pt-CeO$_2$-SiO$_2$ bilayers at 190 °C from ethylene and methanol. (b) Illustration of the CeO$_2$-Pt-SiO$_2$ tandem catalyst. Adapted with permission from [29].
catalytic performances of supported catalysts [35]. Many studies have assigned the origin of the catalytic activities of supported metal catalysts to the perimeter interfaces between the metal NCs and oxide support [36–38]. Similar to the case of metal–metal interface, charge transfer might also occur across the nanoscale interface, either from metal to oxide (e.g. Au–TiO$_2$ [36]) or from oxide to metal (e.g. Fe$_3$O$_4$–Pt [39]) to promote the catalysis. For example, by depositing ~3 nm Au NCs on various supports (i.e. TiO$_2$, Al$_2$O$_3$, ZrO$_2$ and ZnO) via a colloidal deposition method, Comotti et al. found that TiO$_2$ was the most effective support to make the Au NCs the most active in CO oxidation [40]. Further to the ‘metal-on-oxide’ structure, ‘oxide-on-metal’ is another structure type to study the SMSI effect at the nanoscale. Bao’s group successfully extended the oxide-on-metal interface studies from single crystal model systems to nanoscale systems [39]. Based on surface science measurements and density functional calculations, they first found that CO bonding energy at coordinatively unsaturated ferrous (CUF) sites on the FeO$_{1-x}$/Pt (111) interface was smaller than that on FeO$_x$-free Pt surface. Moreover, the interface confined CUF sites between Pt and nano-FeO$_{1-x}$ was found as the active center for the activation of O$_2$

The physical/chemical properties of a material may be quite different for their various phase structures. For example, the phase structure (including anatase, rutile and brookite) of TiO$_2$ is one of the important factors determining its photocatalytic performance [41]. However, currently only a limited number of physical and chemical methods have been developed to prepare the noble metal with different crystal phases (hcp, fcc, etc.). It is thus difficult to compare the catalytic performance between the noble-metal-based NCs with various crystal structures. Recently, the Zhang group successfully synthesized a series of ultrathin Au sheets that exhibit an unusual hcp (2H type) phase [42–44]. These special gold nanostructures with unique properties may provide promising applications in the field of heterogeneous catalysis.

**CO Oxidation**

CO emitted from industrial and transportation activities is harmful to the atmosphere and human health. Catalytic oxidation is one of the most effective pathways to eliminate the CO, in which the key factor is the availability of high-performance catalysts. Furthermore, CO oxidation is an ideal probing reaction to study the fundamental steps of heterogeneous catalysis. In the past years, various kinds of catalysts, including supported transition-metal oxides and noble metals, have been used for the complete oxidation of CO [45].

For metal oxide catalysts, it is generally accepted that CO is preferably adsorbed on metal cations, whereas on the defected crystalline surface, CO may simultaneously bond with both metal cations and a 2-fold coordinated oxygen via the Mars van Krevelen mechanism [46]. Recently, ceria nanorod samples with different types and distributions of oxygen vacancies were synthesized and discussed in detail [47]. A direct relationship between the concentration of the larger size oxygen vacancy clusters and the reducibility/reactivity of nanosized ceria was formed. Xie et al. reported that Co$_3$O$_4$ nanorods not only catalyze CO oxidation at temperatures as low as −77°C but also remained stable in a moist stream of normal feed gas, even in feed gases containing large amounts of H$_2$O and CO$_2$ at 200–400°C. High-resolution transmission electron microscopy (HRTEM) demonstrated that the as-synthesized Co$_3$O$_4$ nanorods predominantly expose {110} planes, at which the active Co$^{3+}$ species are formed favorably. The kinetic analyses indicated that the significantly higher reaction rate over the nanorod morphology, compared to the conventional Co$_3$O$_4$ is probably due to the surface richness of active Co$^{3+}$ sites [48].

To gain further insights into the shape-dependent mechanism, CO oxidation has been performed on Co$_3$O$_4$ nanobelts and nanocubes as model catalysts [49]. The Co$_3$O$_4$ nanobelts with dominant {011} planes are more active than Co$_3$O$_4$ nanocubes with {001} planes. The essence of the shape and crystal-plane effect was revealed by the fact that different locations of Co$^{3+}$ sites on {011} and {001} planes are expected to lead to a different activity. In addition, Co$_3$O$_4$ NCs with different shapes, including plate-, rod-, cubical- and spherical-like, were synthesized in aqueous solution by the hydrothermal reaction. Plate-like Co$_3$O$_4$ NCs mainly exposed {111} planes and exhibited the highest catalytic activity for CO oxidation under dry stream [50], demonstrating that the {111} planes may keep their active surfaces in dry reactant gas to give a high catalytic activity. Fe$_3$O$_4$ NCs with different structures have been fabricated through a hydrothermal procedure and subsequent calcinations treatment [51]. These different nanostructures exhibited different CO oxidation activities, in the order of nanorods > nanotubes > nanocubes, which was closely related to the occupancy of iron ions on the surface of the catalysts. Atomically thin SnO$_2$ sheets with an extremely large proportion of surface atoms, were prepared using an ethylenediamine-assisted approach [52]. The
0.66 nm SnO\textsubscript{2} sheets showed remarkably improved CO catalytic performances compared with 1.9 nm SnO\textsubscript{2} sheets, SnO\textsubscript{2} nanoparticles and bulk SnO\textsubscript{2}, with the apparent activation energy lowered to 59.2 kJ/mol from 121.1 kJ/mol. The calculated adsorption energies showed that the abundant four-coordinate surface Sn atoms favored CO adsorption, while the adsorbed CO molecule effectively reacted with the neighboring two-coordinate surface lattice oxygen atoms to form CO\textsubscript{2}. This simultaneously created an oxygen vacancy, which favored O\textsubscript{2} dissociation into highly reactive oxygen atoms.

CO oxidation over supported gold NCs has become one of the most extensively studied systems in heterogeneous catalysis \[53\]. Specifically, the catalytic activity of gold NCs can be influenced by their size, shape and electron state (Au\textsuperscript{0}, Au\textsuperscript{+} or Au\textsuperscript{2+}) \[54\]. Unfortunately, great debate is likely to continue owing to the sensitivity and complexity of the gold catalysis. Taking the size influence as an example, it has long been believed that gold NCs with a diameter of 2–5 nm are specifically active for CO oxidation. Recently, however, Hutchings and co-workers presented the excellent activity of gold clusters of about 0.5 nm supported on iron oxide \[55\]. Liu et al. \[56\] synthesized gold NCs of about 2 nm by the colloidal deposition method and supported on FeO\textsubscript{2}, giving rise to very high activity at low-temperature CO oxidation, thus arguing for the role of the bilayer structure of gold. Jia et al. \[57\] prepared Mg(OH)\textsubscript{2} and MgO supported gold catalysts, which exhibited very high activity for low temperature CO oxidation, even at \(-89^\circ\)C. The reactive oxygen species, supplied from the support, is suggested as the origin of this high activity; the depletion of the oxygen species with increasing temperature causes the negative apparent activation energy at intermediate temperatures. However, the exact nature of the oxygen species remains elusive in these cases. The intrinsic catalytic performance of CO oxidation becomes even more complicated for the real catalyst. Nevertheless, improved experimental techniques have made the detailed understanding of real catalysts possible. The dynamic morphological fluctuation of supported Au NCs in oxygen-rich conditions under room temperature was directly observed using an \textit{in situ} environmental TEM technique. By using the same technique, the reconstruction of crystalline facets of supported Au NCs induced by CO adsorption was also visualized \[58\].

Considering the existence of metal–support interactions, and the effect of support properties, the real challenge is to fabricate supported catalysts of equal size to the metal NCs, while loaded on different supports, to specifically investigate the influence of support properties. A recent work suggested that the atoms at the metal–support interfacial region are the active sites \[11\]. The turnover rate for CO oxidation is considered to be independent of the size of metal NCs, making this reaction ideal to probe the role of the metal-support interface by measuring changes in CO oxidation rates by varying the concentration of interfacial sites. Three NCs of Ni, Pd and Pt with monodisperse and tunable size were synthesized by a chemical colloidal method and then deposited on CeO\textsubscript{2}, resulting in a variation of the relative fraction of metal–CeO\textsubscript{2} interfacial sites. The experimental result showed direct linear relationships between the CO conversion and ceria–metal interface fraction, which demonstrates that the use of size-selected NCs can successfully identify the interfacial active sites (Fig. 4).

Precise design of nanoscaled metal–metal oxide interfaces in catalysts has been successfully achieved by controllably assembling metal and metal oxide NCs. Murray and his colleagues have adopted the liquid–air interface self-assembly technique to synthesize Au-FeO\textsubscript{x} superlattices consisting of Au and Fe\textsubscript{3}O\textsubscript{4} NCs of 6 and 16 nm, respectively \[59\]. The Au-FeO\textsubscript{x} superlattices exhibited good catalytic activity for CO oxidation and the reaction rate increased linearly with the number of Au-FeO\textsubscript{x} interfaces, identifying the interfacial active sites for CO oxidation. Noble-metal NCs tended to aggregate during the catalytic reaction process, resulting in a sharp decrease of the activity. Recently, our group developed a general emulsion-based bottom-up self-assembly approach to assemble various kinds of NCs (including metal and metal oxide) as building blocks into 3D mesoporous multicomponent nanocomposite colloidal spheres (MMNCs, Fig. 5) \[60,61\]. The building blocks included noble-metal NCs (Ag, Au, Pd, Pt, Ru, Rh, etc.) and metal oxide NCs (CeO\textsubscript{2}, TiO\textsubscript{2}, Co\textsubscript{3}O\textsubscript{4}, Mn\textsubscript{3}O\textsubscript{4}, Fe\textsubscript{3}O\textsubscript{4}, etc.). In MMNCs, noble-metal NCs are encaged within a mesoporous-structured shell composed of oxide NCs, which effectively prevent their aggregation and displacement.

Heterogeneous dumbbell-like NCs represent an important type of composites nanomaterial, which form dumbbell-shaped heterostructures with considerably improved catalytic performance \[62\]. Sun’s group reported a general approach to noble-metal–metal oxide dumbbells via organic solvothermal synthesis. Catalytic studies revealed that, for example, Au-Fe\textsubscript{3}O\textsubscript{4} and Pt-Fe\textsubscript{3}O\textsubscript{4} exhibit enhanced catalytic activity towards CO oxidation compared to their conventional counterparts \[63\]. In addition, growing Fe\textsubscript{3}O\textsubscript{4} (10–15 nm) on uniform AuPd colloids produced dumbbell composites with an epitaxial heterojunction that favored electron transfer between the two components and thus...
Figure 4. Calculated number of sites with a particular geometry (surface and perimeter or corner atoms in contact with the support) as a function of diameter and TOF at 80°C of the nine ceria-based samples. Adapted with permission from [11].

Figure 5. (a) Schematic representation of the MMNCSs as high-temperature model catalysts compared with traditional supported catalysts. (b) Typical TEM images of Ag–CeO$_2$ MMNCSs. Adapted with permission from [61].

Experimental results showed that the presence of the iron oxide domain in the dumbbells should have beneficial effects on the formation of more reactive monomer Pd sites. The Au$^{4+}$ sites also benefit, which, in addition to being active themselves in the CO oxidation, could provide further oxygen activation capability. Through assembling the pre-synthesized monodisperse Au colloids and uniform LaVO$_4$ NCs, our group designed and obtained Au/LaVO$_4$ catalysts with well-defined nanostructures [65]. Monodispersed Au colloids with tunable size and LaVO$_4$ NCs with well-defined shapes were pre-synthesized, assisted with oleic acid/amine. As sizes of gold particles were well defined before the immobilization process, the size effect of gold particles was easy to investigate. The results showed that 5 nm Au/LaVO$_4$ nanocomposite has the highest activity for CO oxidation. According to the previous report, the Pd (100) surface is catalytically more active than both Pd (110) and Pd (111) surfaces for the CO oxidation reaction. Jin et al. synthesized Pd NCs enclosed by {100} facets with controllable sizes in the range of 6–18 nm. They found that the activity of this catalytic system for CO oxidation showed a strong dependence on the NCs size [66]. When the size of the Pd NCs was reduced from 18 to 6 nm, the reaction rate was significantly enhanced by a factor of $\sim 10$ and the corresponding maximum conversion temperature was lowered by 80°C.
Noble-metal NCs, despite their immense and wide practical applications in the chemical industry, suffer from high synthetic costs and rarity. Therefore, there is an urgent need to develop substitutes for pure noble-metal NC catalysts. In recent years, nanoalloys have been of great experimental and theoretical interest due to their potential technological applications in catalysis [67]. From a basic science perspective, nanoalloys exhibit very complex structures and properties, which strongly depend not only on their size, but also on composition and atomic ordering. Recently, Zheng’s group synthesized Pt-transition-metal hydroxide hybrid nanoparticles with diameters below 5 nm, and showed that they are highly efficient for CO oxidation catalysis at room temperature [68]. The oxide-supported Pt-FeNi nanocatalyst rapidly and fully removed CO from humid air with no decline in activity for one month (Fig. 6). Characterized results revealed that the OH groups at the Fe$^{3+}$-OH-Pt interfaces readily react with CO adsorbed nearby to directly yield CO$_2$ and simultaneously produce coordinatively unsaturated Fe sites for O$_2$ activation. Ni$^{2+}$ incorporation dramatically enhanced the long-term catalyst stability by stabilizing the Fe$^{3+}$-OH-Pt interfaces during catalysis. For CO oxidation catalyzed by the nanoalloy-Pt–Ni–Co catalyst, the active sites were proposed at the neighboring heteroatoms, where CO adsorbs on Pt, and concurrently Ni/Co activates O$_2$. Importantly, the atomic-scale structure, in particular the degree of structural and chemical ordering, in the alloy nanoparticles can be significantly affected by support–nanoalloy interactions and further modified by controlled thermochemical treatment. The support–nanoalloy interaction is shown to influence structural and chemical ordering in the nanoparticles, leading to support-tunable active sites on the nanoalloys for oxygen activation in the catalytic oxidation of carbon monoxide [69].

SELECTIVE OXIDATION OF ALCOHOL TO ALDEHYDES/KETONES

Selective oxidation of alcohols to the corresponding aldehydes/ketones is one of the most important processes in organic chemistry and the chemical industry. Aldehydes/ketones are particularly useful in the production of flavors, fragrances and biologically active compounds [70,71]. Traditional processes employed a stoichiometric amount of toxic and expensive inorganic oxidants, such as chromium salts, oxalyl chloride or hypervalent iodines, and volatile organic solvents [70], but a fundamental shift to greener and more atom-efficient methods, that adopts recyclable catalysts and O$_2$ as an oxidant under solvent-free conditions, is needed.

The aerobic catalytic oxidation of alcohols can be performed in the liquid- or gas-phase, largely depending on the thermal stability and volatility of both reagents and products. Liquid-phase routes could be performed at temperatures of generally below 100 °C, which is suitable for the selective oxidation of complex alcohols with low thermal stability and volatility, these routes have been extensively investigated based on homogeneous catalysts [71–73] and supported noble-metals NCs [71,74]. However, the homogeneous process is limited in industrial-scale production due to problems related to corrosion and plating on the reactor wall, handling, and the reuse of the catalyst. Supported catalysts active in the liquid phase under mild
conditions have a much broader application range. Recently, supported gold-based NCs were shown to be extremely active catalysts for aerobic oxidation of alcohols, such as Au/ CeO$_2$ [75], Au/Al$_2$O$_3$ [76] and Au/Al$_2$O$_3$ [77]. In particular, the Au-Pd/TiO$_2$ catalyst was used in the selective oxidation of primary and secondary alcohols with high efficiency with up to 270 000 turnovers per hour for benzyl alcohol oxidation; this might be the highest value in the selective oxidation of alcohols [78]. The careful characterization results showed that the structure of the Au-Pd bimetallic nanoparticle had an Au-rich core surrounded with a Pd-rich shell on titania. These supported catalysts have been well reviewed and therefore not further discussed here [71,79,80].

From the industrial perspective, gas-phase oxidation of alcohols would be a promising route: catalyst separation is easy, the process is solvent-free and efficiency much higher, especially in the bulk production of aldehyde/ketones such as benzaldehyde [81,82]. In early studies, pure and alkali-metal-promoted metal oxides and bulk electrolytic silver were initially investigated as catalysts but exhibited low activity, even when operated at above 400°C [83,84]. Considering the high activity and selectivity of gold NCs for various reactions [79,80], silica-supported nano-gold catalyst Au/SiO$_2$ was firstly applied by Rossi and co-authors for the gas-phase oxidation of alcohols. In the range of 300–400°C, various alcohols could be catalytically oxidized with the conversion of 50–70% [81]. Subsequently, they promoted this catalyst (Au/SiO$_2$) by alloying copper into gold to form the bimetallic AuCu NPs; the as-alloyed catalyst AuCu/SiO$_2$ showed a much-enhanced performance [85]. For example, benzyl alcohol could be quantitatively converted to benzaldehyde with a selectivity of above 99% at a much lower temperature of 260°C.

Titania-supported copper catalyst promoted by potassium K-Cu/TiO$_2$ was reported by Fan and co-authors for the gas-phase oxidation of benzyl alcohol to benzaldehyde. At a very low temperature of 210°C (the boiling point of benzyl alcohol is 203°C), the benzyl alcohol could be effectively converted into benzaldehyde with conversion and selectivity at 99% and a weight hourly space velocity (WHSV) of 0.6 h$^{-1}$ [82]. The same group then developed a novel gold-based catalyst Au/OMM by supporting gold NCs into an ordered mesoporous material (OMM) [86]. The catalyst Au/OMM showed excellent catalytic activity/selectivity and especially stability. At 250°C and a much higher WHSV of 10 h$^{-1}$, benzyl alcohol conversion could be stabilized at 95% with benzaldehyde selectivity of 99% for at least 500 h, indicating promising industrial application.

Mao et al. synthesized bimetallic nanoalloys of noble and non-noble metals via coreduction of mixed metal ions in a liquid–solid-solution synthetic system [87]. The as-synthesized nanoalloy catalysts were applied for the selective transformation of benzyl alcohol to benzaldehyde, and the results showed that bimetallic nanoalloy exhibited higher catalytic activity compared to monometallic NCs. These NCs are significant in fabricating highly efficient and low-cost bimetallic nanocatalysts. In order to greenly recycle the used batteries, Mao et al. employed Mn$_3$O$_4$ from used batteries as a cheap and viable support to load silver NCs for the selective gas-phase oxidation of alcohols [88]. The as-prepared catalyst is highly active for the oxidation of acyclic, benzylic and polyalcohols. For example, cyclohexanol could be oxidized into cyclohexanone with an 86% conversion and 88% selectivity over Ag-9/Mn$_3$O$_4$. The employed strategy can be expanded to fabricate other catalysts with the reuse of spent batteries.

Because of the strong exothermicity of the gas-phase alcohol oxidation, the catalyst should endow with good heat conductivity for rapidly dissipating reaction heat from catalyst bed which is especially favorable for the large molecules to suppress the thermal cracking and over-oxidation of the alcohols. Recently, a new class of Au/Cu-fiber catalyst was prepared simply by dipping the Cu fiber into a HAuCl$_4$ aqueous solution. The catalyst exhibited a good combination of high catalytic activity and heat-transfer ability [89]. For benzyl alcohol oxidation, 87% conversion as well as 98% selectivity could be obtained at a very low reaction temperature of 220°C. The characterization results of the Au/Cu fiber catalyst indicated that the formation of AuCu(alloy)-Cu$_2$O nanostructures contributed to the catalytic activity in the selective oxidation of alcohols. However, the reported lifetime is only 50 h at 220°C with WHSV of 20 h$^{-1}$ because of the powdering of Cu fiber in the long time in stream. In order to improve catalyst stability, the same type of catalyst Au/Ni fiber was subsequently developed with the aid of the galvanic exchange reaction between HAuCl$_4$ and Ni microfiber [90,91]. The resulting Au/Ni-fiber catalysts were active, selective and stable for the gas-phase oxidation of alcohols under mild conditions, while showing high heat-transfer ability. The formation of the Au@NiO nanostructure (i.e. large gold Au particles partially covered by NiO segments) on the Ni fiber was clearly identified and contributed to the low-temperature activity.

**ALKYNES HYDROGENATION**

The catalytic reduction by partial hydrogenation of internal alkenes is an efficient method to produce olefins. This reaction, particularized in the case of...
the semihydrogenation of acetylene to ethylene, is applied, for instance, in the industrial polymerization of ethylene to polyethylene to purify the feedstock from acetylene, which would otherwise poison the polymerization catalyst. Thus, research examining the active component for the catalytic semihydrogenation of acetylene to ethylene is a subject of present industrial interest [92]. Over the past decades, many transition-metal heterogeneous catalysts have been extensively explored for this reaction, among which Pd has been identified as the most effective in terms of combined high catalytic activity and selectivity to the target alkene. This response has been attributed to a stronger adsorption of the C≡C group on the Pd surface.

Today, the semihydrogenation of alkynes is still problematic because the reaction is often accompanied by isomerization and/or overreduction of the alkenes. Commonly, palladium is employed by modifying it with a second metal to promote its activity, selectivity and stability. Recently, a series of single-phase Pd$_x$Ga$_y$ intermetallic NCs were found to be highly selective for the semihydrogenation of acetylene [93,94]. The as-obtained spherical NCs have a relatively narrow size distribution with 3 nm for PdGa and 7 nm for Pd$_2$Ga, and deliver high selectivity of 77 and 60%, and good stability for the semihydrogenation of acetylene. The overall activity, in comparison to ground bulk material, is enhanced by a factor of 90 in the case of Pd$_2$Ga and more than 180 in the case of PdGa (Fig. 7). The alteration of the Pd coordination in PdGa leads to a strong modification of the electronic structure around the Fermi-level compared to elemental Pd. Further to PdGa, many other Pd-based NCs including PdCo [95], PdAg [96], PdAu [97] and PdZn [98] have also been proved efficient for selective alkyne hydrogenation. Uniform nanoplates of the intermetallic compound RhBi, with a diameter of 60 nm, were synthesized by a microwave-assisted polyol process. The RhBi catalyst exhibited an excellent selectivity towards ethylene of 88% at a conversion of 93% and only slight deactivation during long-term acetylene hydrogenation compared to Pd/Al$_2$O$_3$. The high selectivity can be assigned to the active-site isolation in the crystallographic intermetallic compound RhBi with only isolated Rh atoms [99].

NiZn was also developed as a promising catalyst for the selective hydrogenation of acetylene by the Nørskov group, based on DFT calculations and experimental studies. It is noteworthy that this particular catalyst is less expensive and more readily available than PdAg catalyst, which is currently used industrially for the removal of trace amounts of acetylene from ethylene. Different NiZn catalysts have been compared with the well-established PdAg system, and the results revealed that the selectivity of the NiZn catalyst increased substantially as the amount of Zn was increased, and the NiZn catalyst containing 75% Zn exhibited higher selectivity than the best PdAg catalyst containing 75% Ag [100].

Morphology of the metal (oxide) NCs is among the structural features that have a greater impact on catalytic performance in alkyne hydrogenation. Kiwi-Minsker and co-workers recently studied the structure sensitivity of alkyne hydrogenation on a series of Pd NCs with well-defined shapes and sizes. They attributed the observed differences in performance to the presence of two types of active sites on these NCs: one located on planes and the other located on edges (Fig. 8). Semihydrogenation to 2-methyl-3-buten-2-ol was found to occur on both sites, but reactivity depended on the coordination number of the atoms. Edge atoms with 4-fold are less active in the semihydrogenation compared to the plane atoms. Overhydrogenation to corresponding alkane occurred solely on the edge atoms, presumably due to the increased adsorption strength of the alkene. Kinetic simulations indicated 3–5 nm cubic NCs as an optimal catalysts for the highest productivity of 2-methyl-3-buten-2-ol [101]. This finding is complemented by work from the Moon group who examined acetylene hydrogenation. Their results showed that Pd nanocubes with {100} facets exhibited higher acetylene hydrogenation activity and ethylene selectivity than the spherical particles with {111} facets. Li et al. found that the hydrogenation activity of the Pd nanowires was
significantly higher than those of the cuboctahedron catalyst. HRTEM images showed that the twisted Pd nanowires were composed of primary cuboctahedrons. Furthermore, lattice distortion was observed at interfacial regions, and the number of crystal boundaries increased with increasing length of the nanowires. The results indicated that the defect sites at crystal boundaries are more active owing to the exposure of larger numbers of Pd atoms [102].

Usually, the incorporation of stabilizing agents, surfactants and polymers during the preparation process is required to stabilize the inherently thermodynamically and kinetically unstable solutions of NCs subsequently used for catalysis [103]. The presence of PVP as a stabilizer for Pd had been associated with improved alkene selectivity because of the electronic modifications of Pd induced by N-containing species. UV-ozone irradiation on PVP-capped Pd nanocubes appears to generate CO$_{ad}$ on the particle surface from the decomposition of PVP; no detectable N from PVP was found by XPS analysis. TOF increased 4-fold in the absence of PVP, suggesting that the stabilizing agent partially blocked the active sites over the NCs [104]. In the selective hydrogenation of alkynes, the competitive adsorption of reactants (alkyne and alkene) and capping agents on Pt-based catalysts determines the activity and selectivity. When the adsorption energy of capping agents is lower than that of desired alkene (1-octene), it did not promote the selectivity of hydrogenation of alkene to alkane at all [105].

Oxides are among the most commonly employed carriers for catalytic applications. The chemical and structural properties of these materials, for example, acid-base and redox properties, were found to influence the catalytic performance in alkene hydrogenation via metal-support interactions. Different materials supporting palladium could achieve this reductive transformation. For example, palladium supported on ZnO and formation of a PdZn alloy via in situ catalysis reaction, which have been used as catalyst in the gas-phase semihydrogenation of 1-pentyn, achieving suppression of the total hydrogenation to the corresponding alkane, contrary to silica-supported palladium as catalyst [98]. A metal-oxide@SiO$_2$ core-shell catalyst, in which a core of dual Pd and CuFe$_2$O$_4$ NCs was encapsulated within a silica-shell microsphere, showed excellent activity and selectivity for the hydrogenation of phenylacetylenes to related styrenes. The magnetic CuFe$_2$O$_4$ NCs in close contact with Pd NCs not only promote the catalytic reaction, but also act as magnets for easy separation of the catalyst [106].

Recently, low-loaded, organophilic Pd/graphite oxide (GO) nanocomposites were prepared using different complex precursors, which proved to be efficient catalysts for the reactions of lower alkynes [107]. GO-supported gold NCs have been used in a phenylacetylene hydrogenation and achieved a styrene selectivity of 99% and conversion of 99% at 60°C. Compared to Pd-based catalysts, the enhanced selectivity over Au/GO was interpreted by the absence of the subsurface dynamics of the metallic phase under reactive atmosphere and the preference for desorption of the partial hydrogenation product [108]. Despite being the most applicable catalyst in alkyne selective hydrogenation, palladium-based catalysts suffer fast deactivation due to the accumulated carbonaceous deposition and the delicate subsurface chemistry under hydrogenation conditions. Su and co-workers found that during the hydrogenation of acetylene, CNT-supported Pd was more stable than the traditional Pd/Al$_2$O$_3$ catalyst, which could be explained by the carbon concentration in PdC$_c$ (determined by the level of carbon diffusion). The open ends of the CNTs, and their straight walls and regular cavities permit the migration of coke deposition and regular exposure of saturated PdC$_c$. Similar to the case of Pd/Al$_2$O$_3$, due to the irregular porous structures with smaller diameters, deposited species encounter kinks and obstacles and accumulate into large surface oligomers/polymer [109].
SELECTIVE HYDROGENATION OF ALDEHYDES AND NITROBENZENE

Unsaturated alcohols and aromatic amines are important chemical intermediates for pharmaceuticals, polymers, dyes and urethanes. The selective hydrogenation of \(\alpha,\beta\)-unsaturated aldehydes \((R_1R_2C=CH-CH=O)\) to unsaturated alcohols \((R_1R_2C=CH-CH_2OH)\) and nitroarenes to anilines are important industrial processes [110]. From a thermodynamic point of view, it is well known that the formation of the saturated aldehyde is favored over that of the unsaturated alcohol. As a consequence, considerable efforts have been made in order to search for a catalytic system able to actively and selectively carry out the preferential hydrogenation of the \(C=O\) bond in the presence of a conjugated \(C=C\) bond [111]. The selectivity of the hydrogenation reactions depends on several parameters such as different kinds of metals, metal particle size, modification of active metals by a second inactive one and the nature of the support. Delbecq and Sautet [112] addressed the different unsaturated alcohol selectivities observed on different metals using theoretical calculations. These authors suggested that \(C=O\) adsorption is hindered by a more broad metal d band, the d band width decreases as follows: Os > Ir > Pt > Pd, in agreement with the experimental realization. Another discovery is low-coordination sites (such as corners, kinks and defective sites). They favor \(\pi\) interactions with \(\alpha,\beta\)-unsaturated aldehydes, which account for unselective products. The fraction of low-coordination sites decreases with the increase in the size of Pt NCs, thus accounting for the corresponding increase in the selectivity to the unsaturated alcohol [113].

Supported gold NCs are also very active and selective for the hydrogenation of \(\alpha,\beta\)-unsaturated aldehydes and nitroarenes. Baillie et al. [114] were the first to demonstrate that Au/ZrO\(_2\) and Au/ZnO catalysts are highly selective for the formation of crotyl alcohol through the hydrogenation of crotonaldehyde; conversions of 5–10% with selectivities up to 81% observed, indicating that hydrogenation of the \(C=O\) bond rather than the \(C=C\) bond is preferential over these supported gold NCs. Since then, supported gold catalysts have been applied to more complex hydrocarbon species, such as citral, benzen acitone and pent-3-en-2-one. Claus and co-workers designed catalysts comprising gold NCs with a size of 5 nm for the acrolein hydrogenation. They found that the support influences the morphology of the gold NCs. Moreover, the bimetallic Au-In/ZnO catalyst gives enhanced selectivity for \(C=O\) hydrogenation in acrolein [115]. This is an important example demonstrating that the selectivity of supported gold catalysts can be finely tuned by the addition of a second metal. Recently, Corma and Serna demonstrated the region-selective reduction of a nitro group in the presence of other reducible functions using gold NCs supported on TiO\(_2\) or Fe\(_2\)O\(_3\) [116–118]. Thus, they developed a new route for the synthesis of the industrially important cyclohexanone oxime from 1-nitro-1-cyclohexene. Thorough investigations have focused on these transformations, examining the size effects of gold NCs, support properties and gold-supports interactions. Understanding of catalytic mechanism was also studied in great detail.

Bimetallic nanocrystals (BNCs) catalysts are of great interest for the development of heterogeneous catalysts [119,120]. They often perform superiorly to the monometallic counterparts by creating hybrid sites or concerting the concomitant functionalities, which are referred to as ‘synergistic effects’. In addition, BNCs could reduce the cost of monometallic catalysts based on precious and scarce metals by alloying with abundant and inexpensive metals. Despite these attractive features of BNCs, few of them possess both high activity and high selectivity under mild reaction conditions, especially under ambient conditions. Recently, Li and co-workers synthesized concave Pt-Ni alloys via a controllable ‘top-down’ strategy with the coordination-assisted chemical-etching process [121]. The control experiment and DFT results showed that the formation of the concave structure was attributed to the different etching priorities on specific sites. Owing to highly exposed atomic steps and larger specific surface area, the concave Ptni alloys delivered superior activity to the octahedral counterparts for nitroarenes hydrogenation. The nitrobenzene could be completely converted with a selectivity of nearly 100% in 3 h under ambient conditions; the TOF over corroded PtNi\(_3\) was 7.9, 10.5 times higher than that over octahedral PtNi\(_3\) and Pt\(_3Ni\). This work could open the way to design special nanostructures and morphologies of BNCs, which would find various applications in heterogeneous catalysis.

Subsequently, Li and co-workers presented a series of Pt\(_x\)Ni\(_{1-x}\) \((0 < x < 1)\) BNCs with octahedral, truncated octahedral and cubic shapes uniformly controlled by varying crystal growth inhibition agents, including benzoic acid, aniline and carbon monoxide [122]. The structure-performance investigation clearly showed that the Pt\(_x\)Ni\(_{1-x}\) BNCs are more active than the monometallic counterparts, suggesting a synergistic effect between the two metals. In addition, it was found that the hydrogenation rate of benzalacetone, styrene and nitrobenzene were greatly dependent on the shape of the as-prepared BNCs (Fig. 9). For instance, octahedral...
Pt-Ni with the increased percentage of \{111\} facets showed higher activity than Pt-Ni-truncated octahedrons and cubes for benzalacetone hydrogenation, corresponding to the shape evolution from cube through truncated octahedron to octahedron. Very recently, Cai et al. successfully prepared a series of Rh\(_x\)Ni\(_y\) BNCs using the ‘noble metal induced reduction’ strategy [123]. The as-synthesized Rh\(_x\)Ni\(_y\) was applied for the nitroarenes hydrogenation, and was subsequently identified to be highly active and selective under ambient conditions, underscoring a remarkable synergistic effect of the two metals. For the selective hydrogenation of 4-nitrobenzaldehyde to 4-aminobenzaldehyde, pure Rh NCs showed good activity but low selectivity; Ni-rich Rh\(_x\)Ni\(_y\) BNCs were inactive. Interestingly, a steady improvement in both activity (>99%) and selectivity (>99%) was obtained with Rh\(_3\)Ni\(_1\) NCs. Further experiments demonstrated the high efficiency, selectivity and recyclability of Rh\(_3\)Ni\(_1\) catalyst for a range of nitroarene substrates.

The incorporation of a third metal into BNCs to form ternary metallic NPs has exhibited improved catalytic activity towards some reactions [124]. The fabrication of multifunctional and multi-center nanostructures with optimized catalytic performance is gaining increasing interest. Wu et al. presented a shape recovery phenomenon of Pt-Ni BNCs that is unequivocally attributed to the defect effects [125]. Experiments and theoretical results demonstrated that the defect-induced growth mechanism allows the site-selective nucleation of a third metal around the defects, achieving the sophisticated fabrication of Pt\(_3\)Ni\(_1@M\) core-shell nanostructures (M = Au, Ag, Cu, Rh; Fig. 10). Utilizing the nitrobenzene hydrogenation to aniline, they established a tandem reaction involving the decomposition of formic acid as a reductant source. Among the as-prepared Pt\(_3\)Ni\(_1@M\) core-shell nanostructures, Pt\(_3\)Ni\(_1@Au_{0.5}\) (containing 0.5 atom% Pt) exhibited the best catalytic activity and selectivity performance. These results showed the crucial role of the existence of atomic steps composed of Pt and Au in the catalytic behavior. It is a reasonable forecast that this synthesis strategy will greatly expand the rational fabrication of multicenter and multifunctional nanocatalysts at the atomic level.

**CONCLUSION AND OUTLOOK**

The ultimate goal of heterogeneous catalysis is to design and synthesize catalysts with defined active sites to achieve desired activity and selectivity, based on understanding the mechanism at a molecular level. The development of highly active and selective catalysts is also of great significance for green chemistry. Exploring well-defined NPs of various size, shape and composition is crucial to this goal. Our review suggests that well-defined NPs may be of great importance for the rational design of useful catalysts as well as understanding the catalytic mechanism. There are several critical issues when applying NPs in the field of catalysis.

Firstly, the stability of the metal NPs and the role of the capping agents (or named as surfactant used to maintain the specific nanostructure) under catalytic reaction conditions is the fundamental
issue. Most metal NCs have been obtained in the liquid phase and the size and shape maintained only in the synthesis system. When used for chemical reactions, however, the surface atomic configuration undergoes rearrangement or reconstruction induced by the temperature and the reaction media. In other words, the exposed crystal facets are only present under the specific conditions, and they can be easily transformed into thermodynamically stable spherical nanoparticles upon exposure to the reaction conditions. Moreover, the remaining surfactant that strongly adsorbs on the surface of the NCs may passivate the catalytic sites by blocking the reactive facets. Therefore, we need more efficient routes to prepare nanocatalysts with a stable size and shape without the surfactant, or a route to remove the surfactant easily while keeping the nanostructure.

Secondly, the development of novel strategies to precisely controlled synthesis of the NCs with a novel nanostructure is still of great importance, despite the significant progress made in the controllable synthesis of metal and oxide NCs. New synthetic methods will allow the preparation of NCs with required structures, which will bring new properties to existing and new catalytic reactions.

Furthermore, bimetallic or multimetallic alloys and intermetallic compounds are also most interesting. In these alloys, one metal can modify the catalytic properties of the other metal as a result of both electronic and geometry effects. The bimetallic or multimetallic NCs with well-defined size, structures, compositions and shapes should be used as excellent building blocks for fabricating highly active and selective catalysts. Ideally, the alloys could be synthesized through precisely controlling the structure and packing of the metal atoms. These alloys are regarded as ‘artificial atoms’. The as-obtained ‘artificial atoms’ can be expected to bring novel collective and cooperative properties. Undoubtedly, developing the precise synthesis for these ‘artificial atoms’ is the foundational issue for their future applications.

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