Nanocatalysis I: Synthesis of Metal and Bimetallic Nanoparticles and Porous Oxides and Their Catalytic Reaction Studies

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Abstract In recent heterogeneous catalysis, much effort has been made in understanding how the size, shape, and composition of nanoparticles and oxide-metal interfaces affect catalytic performance at the molecular level. Recent advances in colloidal synthetic techniques enable preparing diverse metallic or bimetallic nanoparticles with well-defined size, shape, and composition and porous oxides as a high surface support. As nanoparticles become smaller, new chemical, physical, and catalytic properties emerge. Geometrically, as the smaller the nanoparticle the greater the relative number of edge and corner sites per unit surface of the nanoparticle. When the nanoparticles are smaller than a critical size (2.7 nm), finite-size effects such as a change of adsorption strength or oxidation state are revealed by changes in their electronic structures. By alloying two metals, the formation of heteroatom bonds and geometric effects such as strain due to the change of metal–metal bond lengths cause new electronic structures to appear in bimetallic nanoparticles. Ceaseless catalytic reaction studies have been discovered that the highest reaction yields, product selectivity, and process stability were achieved by determining the critical size, shape, and composition of nanoparticles and by choosing the appropriate oxide support. Depending on the pore size, various kinds of micro-, meso-, and macro-porous materials are fabricated by the aid of structure-directing agents or hard-templates. Recent achievements for the preparation of

versatile core/shell nanostructures composing mesoporous oxides, zeolites, and metal organic frameworks provide new insights toward nanocatalysis with novel ideas.

Keywords Nanocatalysis · Mesoporous · Bimetallic · Core/shell · Strong-metal support interaction · Selectivity

1 Introduction

Nanotechnology is making huge strides, and its discoveries are affecting catalysis in gigantic ways. Colloidal synthesis has made great progress by controlling the size, shape, and composition of nanoparticles [1–4]. An ultimate goal of industrial catalysis is to achieve the highest catalytic activity and selectivity toward only one desired product, while maintaining high stability against deactivation. For this purpose, noble nanoparticle catalysts are developed by colloidal synthetic techniques and many reaction studies exhibit enhancement of reaction rates and change of selectivities with the optimum nanoparticle size and shape. Bimetallic nanoparticle catalysts, by alloying two metals, create new chemical and catalytic properties, which cannot be achieved by their parent single metal nanoparticles [5, 6]. High surface porous materials have also been developed as a support as well as a catalyst [7, 8]. As catalytic behaviors can also be altered at oxide-metal interfaces, support materials with high surfaces and ordered pore structures become increasingly important for supported catalysts.

In this review article, we classify nanoparticle catalysts. Through synthetic nanotechnology, we explain how metal and bimetallic nanoparticles are generated with well-defined size, shape, and composition. By means of versatile and elaborative synthetic approaches, various kinds of

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core/shell nanostructures are introduced with specific functions for catalysis as well. As a support, porous oxide materials are classified into three categories depending on their pore size which are micro-, meso-, and macro-porous materials. The synthetic strategies and several examples are provided for the preparation of microporous (zeolite), mesoporous, and macroporous materials with ordered pore structures.

In addition to nanoparticle catalysts, we account for the latest model catalytic reactions to show how the designed nanocatalysts impact catalytic properties and what are the major molecular factors to change the surface chemistry. With much progress on in situ surface characterization techniques, we can monitor working catalysts under real catalytic conditions and identify molecular information during the reaction [9, 10]. In a separate review article, an in-depth study for in situ surface characterization techniques will be given. Instead, here we will focus more on the correlation between specific nanoparticle catalysts and catalytic properties. We hope to provide basic knowledge of state-of-the-art nanoparticle catalysts for readers. Furthermore, we expect to provide an understanding of how the designed nanoparticle catalysts influence catalytic properties through the latest catalytic reaction studies.

2 Synthesis of Nanoparticles

2.1 Metal Nanoparticles with Controlled Size and Shape

The colloidal synthetic approach provides versatile tools to control the size and shape of nanoparticles. In order to get monodisperse nanoparticles, separation of burst nucleation from controlled growth is of key importance for a homogenous nucleation [11]. Many of the metal nanoparticles with a narrow size distribution have been synthesized mainly by either alcohol reduction or thermal decomposition of metal precursors in the presence of organic surfactants [1–4]. Noble metal nanoparticles including Pt, Pd, Rh, Ru, Au, and Ag are produced by the alcohol reduction, in which polyalcohols such as ethylene glycol and diethylene glycol serve both as a solvent by dissolving metal salts and as a reducing agent by generating zero-valent metal nanoparticles. Poly(vinylpyrrolidone) (PVP), alkylammonium halides, oleyl amine, and oleic acid are chosen as surfactants which have both hydrophobic hydrocarbon chains and hydrophilic functional groups, which stabilize nanoparticle surfaces in colloidal solution. Typical Pt nanoparticles are synthesized using dihydrogen hexachloroplatinate (H_2PtCl_6) or $\text{Pt}(\text{acac})_2$ (acac denotes acetylacetonate) in the presence of PVP and alcohols at 200–240 °C. The size of Pt nanoparticles is controlled with

a size range of 1.5–7 nm by the type of solvents such as methanol, ethanol, ethylene glycol, and diethylene glycol and by different reaction time and temperature (Fig. 1a). Transition metal nanoparticles including Co and Fe can be obtained through thermal decomposition by injection of organometallic precursors such as dicobalt octacarbonyl and iron pentacarbonyl into the surfactant solution at an elevated temperature [11]. The size of Co nanoparticles can be varied from 3 to 10 nm by the temperature of the oleic acid solution, when the Co precursor is injected rapidly [12]. In order to synthesize small nanoclusters less than 1 nm, a dendrimer which is a macromolecule with a central core surrounded by hyper-branched repeating units can be used as a template as well as a stabilizing agent [13]. Polyamidoamine (PAMAM) and poly(propylene imine) (PPI) dendrimers are used for the preparation of dendrimer-encapsulated metal nanoclusters, of which the degree of generations of the dendrimers, precursor concentrations, and reducing agents determine the size of the clusters. For example, in the presence of the fourth generation PAMAM dendrimers, Pt nanoclusters with average diameters of 0.8 and 1.0 nm were synthesized upon reduction (Fig. 1b). Recently, a photoreduction method was also developed for the synthesis of Pt nanoclusters in the presence of PVP or PAMAM dendrimers [14, 15]. Borodko et al. controlled the size of Pt nanoclusters (Pt_n , $n = 5\text{--}30$) under different UV irradiation time in the solution phase. They observed a transition from disordered Pt aggregates by forming an agglomeration of weakly bound Pt clusters, into Pt nanocrystals by high-resolution transmission electron microscopy (HRTEM) [14, 15].

By rational selection of surfactants, reducing agents, and additional foreign metal ions, nucleation and growth kinetics are further regulated to produce nanoparticles with different sizes and shapes [3]. For example, Pt nanocubes were selectively produced when an alkylammonium salt was introduced in the presence of PVP [16]. As shown in Fig. 1c, Pt nanoparticles with various shapes including cubes, cuboctahedra, and octahedra can be generated selectively by adding silver ions, because the crystal growth rate along $\langle 100 \rangle$ was determined by the amount of silver ions present during the reaction [17]. When small nanoclusters were introduced as a seed to the precursor solution, various nanoparticles with controlled shapes can be produced by seed mediated growth [18].

2.2 Bimetallic Nanoparticles

Bimetallic nanoparticles enable optimizing catalytic properties by tuning electronic states and modulating the charge transfer of the metals [5]. By adjusting the ratio of two metal precursors, the composition of bimetallic nanoparticles can be controlled. Figure 2 shows several bimetallic

Fig. 1 Schematics showing synthetic strategies of Pt nanoparticles with controlled size and shape. **a** TEM images of size-controlled Pt nanoparticles by the polyol reduction method. **b** A dendrimer-templating strategy for the synthesis of Pt nanoclusters. **c** High-

resolution TEM images of Pt nanoparticles with shapes of cubes, cuboctahedra, and octahedra by adding Ag ions as a structure directing agent (reproduced with permission from [13, 17], copyright 2008 and 2005 American Chemical Society)

Fig. 2 Scanning transmission electron microscopy/energy-dispersive spectroscopy (STEM–EDS) images of bimetallic nanoparticles: **a** Pt₉₀Rh₁₀, **b** PtCo, and **c**, **d** CoCu (reproduced with permission from [20, 22], copyright 2013, 2011 Springer, [23], copyright 2013 American Chemical Society). The *color points* represent distribution

of metals in the nanoparticles. STEM/EDS images of as-synthesized CoCu bimetallic nanoparticles show their Cu-rich core/Co-rich shell nature (**c**). When a redox cycle was applied in H₂/O₂ at 350 °C, the bimetallic CoCu nanoparticles suffered an intraparticle phase segregation of Co and Cu to form contact dimer particles (**d**)

nanoparticles synthesized by the polyol reduction. For example, PtFe bimetallic nanoparticles were synthesized with tunable compositions by reduction of Pt(acac)₂ and Fe(acac)₃ with PVP in ethylene glycol [19]. By adjusting the concentration ratio of two metal precursors, Pt₃Fe,

PtFe, and PtFe₃ nanoparticles were produced in a controlled manner. PtRh bimetallic nanoparticles with the ratios of 9:1 and 8:2 were also produced by different ratios of Pt(acac)₂ and Rh(acac)₃ with PVP in triethylene glycol [20]. In order to characterize atomic distributions, energy

dispersive spectroscopy (EDS) combined with scanning transmission electron microscopy (STEM) and elemental mapping using the electron energy loss spectroscopy (EELS) are widely used. Figure 2a shows STEM-EDS images of 6.5 nm Pt₉₀Rh₁₀ bimetallic nanoparticles with a homogeneous distribution of metals, in which the red points represent the Pt L-line and the green points represent the Rh L-line.

Recently, oxidation states and compositions of nanoparticle surfaces have been investigated through synchrotron-based in situ techniques such as ambient pressure X-ray photoelectron spectroscopy (APXPS) and near edge and extended X-ray absorption fine structure (NEXAFS/EXAFS) spectroscopies [9, 10]. From many investigations, it has been proven that bimetallic nanoparticles suffer profound structural and chemical changes in response to various gaseous environments. For example, RhPd bimetallic nanoparticles exhibited reversible changes in composition under alternating oxidizing or reducing conditions [21]. Pd, with a lower surface energy than Rh, migrated to the surface when reduced, while stable RhO_x formed on the surface under oxidizing conditions. Similarly, CoPt bimetallic nanoparticles synthesized by the polyol reduction of Pt(acac)₂ and Co(acac)₂ precursor mixtures were identified as having Pt-rich surfaces by atomic diffusion during exposure to 0.1 Torr of H₂ (Fig. 2b) [22]. Alayoglu et al. also reported that as-prepared CoCu bimetallic nanoparticles were identified as Cu-rich core/Co-rich shell nanoparticles by STEM/EDS phase maps [23]. In O₂ conditions, both metals were oxidized and Cu segregates to the surface having the Cu⁺ state, while the segregation was reversed in H₂, having reduced Co and fully reduced Cu on the surface (Fig. 2c, d).

2.3 Core/Shell Nanoparticles

Core/shell nanoparticles have been designed for a stable catalyst against coalescence and sintering during catalytic reactions by encapsulating the core nanoparticles with porous shells [24]. Joo et al. developed a Pt/SiO₂ core/shell as a thermally stable catalyst, in which mesoporous silica shells encaged Pt cores and the Pt nanoparticles maintained their structure up to 750 °C in air without aggregation (Fig. 3a) [25]. In order to allow access of reactants to the core metals, inorganic porous materials are selected as a protecting shell. The shells overgrown on the surface of core nanoparticles become porous during the calcinations by removing organic surfactants. Recently, an alternative strategy was developed to control the porosity of the shells systematically by a surface-protected etching process [24, 26]. The coated oxide shells resulted in porous layers by removing organic capping ligands in the shells by an appropriate etching agent. Pt/SiO₂ core/shell structures

surrounded by silica shells with a controlled porosity can be prepared by the surface-protected etching process. Mesoporous silica shells have been utilized as an excellent inorganic protecting layer, due to their high thermal stability and simple sol-gel synthetic chemistry. However, preparation of non-siliceous porous oxide shells is still challenging, because the calcination process for crystallization causes the loss of porosity. For the creation of high crystalline oxide shells, an alternative method was developed by silica-protected calcinations [24, 27]. Figure 3b shows Pt/TiO₂ core/shell structures synthesized by the growth of a TiO₂ layer on top of the given Pt/SiO₂ core/shells. The sacrificial silica layers protected core Pt nanoparticles during calcinations, enabling a phase transformation of amorphous TiO₂ to the anatase phase. The intermediate silica was removed by etching, then mesoporous anatase TiO₂ shells were formed, remaining on the core Pt nanoparticles. Another type of core/shell nanoparticles were produced by using silica microspheres [28]. When silica spheres with an average diameter of 200 nm were used as a core, Pt nanoparticles can be deposited on the surface of the silica. After coating by either silica or titania and subsequent calcination, SiO₂/Pt/oxides core/shell structures with mesoporous outer shells were generated (Fig. 3c). Recently, an inorganic micelle structure which has a hydrophilic cavity and a hydrophobic surface was fabricated to utilize different media in catalysis [29]. Au/resin core/shell nanoparticles prepared through polymerization over Au nanoparticles, were coated with mesoporous silica shells to produce hydrophobic Au/SiO₂ micelles with hydrophilic insides by surface modification. Recently, core/shell or yolk/shell nanoparticles with metal-organic frameworks (MOFs) were developed. Tsung group reported Pd/ZIF-8 yolk/shell nanoparticles by coating Pd nanoparticle cores with Cu₂O and polycrystalline zeolitic imidazolate framework 8 (ZIF-8) layers [30]. In this process, the Cu₂O layer as a sacrificial template in the middle of the structure assisted the formation of the ZIF-8 coating layer and was etched off to create a cavity as shown in Fig. 3d. They also created Pd/ZIF-8 core/shell structures composed of a single Pd nanoparticle coated by ZIF-8 shells with a specific lattice alignment (Fig. 3e) [31]. For these structures, self-assembled cetyltrimethylammonium bromide (CTAB) molecules were used to control interfaces in the core-shell, which consisted of a metal nanoparticle core and a MOF shell. Multiple core/shell structures were also developed by epitaxial growth. Sneed et al. designed Pd/Ni/Pt core/sandwich/shell nanoparticles using cubic and octahedral Pd nanoparticle seeds [32]. In their article, Pd nanocubes determined the final shape of nanoparticles and catalyzed the oriented overgrowth of Ni shells. Pt ions were added again over the Ni surfaces by a layer-by-layer epitaxial growth in solution (Fig. 3f). They also produced

Fig. 3 TEM images and corresponding synthetic strategies of various kinds of core/shell nanostructures: **a** Pt/SiO₂, **b** Pt/TiO₂, **c** SiO₂/Pt/SiO₂, **d** Pd/ZIF-8, **e** Pd/ZIF-8, and **f** Pd/Ni/Pt (modified with

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ternary and quaternary multilayered metal nanoparticles with controlled shape, size, and layer thickness.

2.4 Hybrid Nanoparticles

In this section, nanoarchitectures with novel catalytic functionalities are introduced. The Tsung group synthesized Pd-Rh nanoboxes and Rh nanoframeworks by the heating of Pd-Rh core/shell intermediates under either reductive or oxidative environments [33]. Figure 4a shows the structural evolution from a Pd nanocube to Rh nanoframeworks, in which the core-island-shell nanocubes undergo transformation to either bimetallic PdRh nanoboxes or Rh nanoframeworks through alternate pathways involving migration and oxidative etching of the Pd cubic core. They also fabricated metal nanoparticles overgrown with second metal islands by an iodide-mediated epitaxial overgrowth [34]. Figure 4b shows Pd nanocubes and

nanooctahedra deposited with Rh nanoparticles on the surfaces. The iodide-mediated epitaxial overgrowth can be extended to different sizes, morphologies, and identities of metal substrates. Several catalytic reactions are also utilized to characterize surface structures and strain effects of the epitaxially grown bimetallic nanoparticles [34]. Chen et al. reported structural evolution of PtNi bimetallic nanoparticles [35]. The crystalline PtNi₃ polyhedra as a starting material transformed to Pt₃Ni nanoframes in solution by interior erosion (Fig. 4c). Interestingly, the edges of the Pt-rich PtNi₃ polyhedra were maintained in the final Pt₃Ni nanoframes which enhanced catalytic oxygen reduction reaction (ORR) activity due to their unique interior and exterior surfaces of the open-framework structure. Recently, dumbbell-shaped Pt–CdSe–Pt nanostructures with metal nanoparticle-semiconductor junctions were designed as hybrid nanocatalysts, facilitating catalytic reaction rates by the charge carrier [36]. Figure 4d shows a

Fig. 4 TEM images and corresponding synthetic strategies of hybrid nanoparticles: **a** Pd nanocubes, PdRh core/shell intermediates, PdRh bimetallic hollow nanoboxes, and Rh nanoboxes, **b** Pd nanocubes and nanooctahedra deposited with Rh nanoparticles on the surfaces, **c** shape evolution from PtNi₃ polyhedra to Pt₃Ni nanoframes, and

d dumbbell-shaped Pt–CdSe–Pt hybrid nanoparticles (modified with permission from [33, 34, 36], copyright 2013, 2012, 2013 American Chemical Society, [35], copyright 2014 American Association for the Advancement of Science)

HRTEM image of Pt–CdSe–Pt nanodumbbells synthesized by the selective growth of Pt tips onto the CdSe nanorods. Collective and synergetic catalytic properties of nanostructured hybrid catalysts will be discussed in the following two sections: composition-dependent catalytic properties and oxide-metal interactions.

3 Synthesis of Porous Oxides

High surface porous materials have been widely utilized as a support by loading metal nanoparticles [7, 8]. Porous materials can be classified mainly into three kinds based on their pore diameter, which are micro-, meso-, and macroporous materials. According to IUPAC notation, microporous materials have pore diameters of less than 2 nm and macroporous materials have pore diameters of greater than 50 nm. The mesoporous category thus lies in the middle. In this section, several strategies for the preparation of three basic porous materials and advanced porous oxides with

two different porosities are described. In order to prepare for supported nanoparticle catalysts, as-prepared nanoparticles are incorporated into the pores of oxide supports by sonication-induced inclusion [16]. By repeated washing and calcination, organic capping molecules stabilizing the nanoparticle surface can be easily removed.

3.1 Mesoporous Oxides

A representative support in the field of heterogeneous catalysis is a mesoporous oxide due to its high surface area, ordered pore structure, and large pore volume [7]. Owing to the versatile sol–gel chemistry using silicates, a large number of mesoporous silicas have been discovered with well-defined mesostructures and controlled pore dimensions. Specifically, appropriate pore sizes (2–50 nm) of mesoporous silicas are attractive for incorporation of metallic nanoparticles. There are two general synthetic methods for ordered mesoporous oxides which are soft-templating (cooperative assembly) and hard-templating

Fig. 5 Preparation of Pt nanoparticle catalysts supported on mesoporous Co_3O_4 . The schematic illustration shows the hard-templating (nanocasting) approach for the preparation of mesoporous oxides by using mesoporous silica KIT-6. **a**, **b** TEM images of **a** the mesoporous

silica, KIT-6 as a template and **b** the resulting mesoporous Co_3O_4 . **c**–**e** TEM, EDS phase mapping, HRTEM image of Pt/ Co_3O_4 catalysts (reproduced with permission from [40], copyright 2013 American Chemical Society)

(nanocasting) [3]. Since mesoporous silicates of the M41S family were first discovered by Mobil researchers in 1992, the cooperative assembly of inorganic precursors and organic structure-directing agents combined with sol–gel processes have been utilized to create ordered mesoporous materials as a main synthetic route [37]. By selection of a proper structure-directing agent as a soft template which includes cationic, anionic, and nonionic species, various kinds of mesostructures such as hexagonal, cubic, and bi-continuous cubic can be created by having periodic arrangements, large surface areas, and controlled pore diameters. MCM-41, SBA-15 and MCF-17 are representative mesoporous silica supports used for loading metal nanoparticles into their inner pores. The SBA-15 with a hexagonal channel structure has average pore diameters of 6–15 nm, while MCF-17 with mesocellular frameworks has much bigger pores (20–50 nm) which afford to incorporate nanoparticles with a size bigger than 10 nm. While the soft-templating method provides versatile ways for the synthesis of mesoporous silica materials by the sol–gel process, preparation of non-siliceous mesostructured materials is still challenging, because the hydrolysis and polymerization of

transition-metal alkoxides are more difficult to control unlike silicon alkoxides. As an alternative route, nanocasting using a template offers a great possibility for the preparation of various mesoporous materials [8]. Nanocasting is a synthetic process using a mold with relevant structures which is filled with another material, and the initial mold is afterwards removed to give a remaining inverse replicas. Mesoporous silica frameworks, polymer latex or silica spheres can be used as a hard template as well as a mold [38]. The first mesoporous materials synthesized via the nanocasting method were reported by Ryoo's group. They synthesized highly ordered mesoporous carbon (CMK-1) which was produced by the replication of MCM-48 silicas [39]. The Schüth group developed the preparation of mesoporous oxides using KIT-6, mesoporous silica with cubic $1a3d$ symmetry [8]. When KIT-6 with a bi-continuous pore structure was used as a hard template, metal nitrates as metal oxide precursors were impregnated completely into the silica templates and were converted to the desired crystalline oxides after calcinations [40]. Because the mesoporous silica was easily removed in NaOH solution, highly crystalline oxide replicas with ordered mesostructures including Cr_2O_3 ,

Fig. 6 TEM images of **a** mesoporous zeolites with framework types of BEA and MFI and **b** macroporous-mesoporous aluminas synthesized via the hard-template approach using polystyrene beads

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Mn_xO_y , Fe_2O_3 , Co_3O_4 , NiO , CuO , WO_3 , and CeO_2 were readily produced. Figure 5 illustrates an entire preparation scheme for Pt nanoparticle catalysts supported on mesoporous Co_3O_4 , from the KIT-6 hard-template.

3.2 Mesoporous Zeolites

Zeolite, a crystalline aluminosilicate with micropores ($0 < \text{diameter} < 2 \text{ nm}$), is the most widely used catalyst as well as support in current chemical industries [41, 42]. Zeolites have their own catalytic activity due to the strong acidity originating from their distinct aluminosilicate frameworks. In addition, zeolite pores can isolate molecules selectively depending on their size and shape as a molecular sieve, which add one more function of the zeolite for pore size- or shape-selective separation. By supporting metal clusters into zeolite micropores, they are utilized as a bifunctional catalyst. However, relatively small micropores of zeolites have been an obstacle for loading metal nanoparticles with well-defined size and shape. In recent years, successful synthesis of zeolites with mesoporous frameworks has been achieved by creating mesopores in zeolites or by constructing mesoporous structures crystallized into zeolites without destroying the mesoporosity [41, 42]. These so-called mesoporous zeolites have many advantages due to the secondary mesopores beyond existing micropores. For example, the created mesopores improve molecular diffusion, resulting in enhancement of catalytic lifetime, and they allow direct access of bulky molecules to the acidic center which cannot be achieved by micropores. Moreover, they enable nanoparticle incorporation for bifunctional nanoparticle catalysts, providing enough surface area and pore size. For these purposes, mesoporous zeolites with framework types of BEA (zeolite beta polymorph A) and MFI (zeolite Socony Mobile—five) were recently prepared by using specially designed structure directing agents (Fig. 6a) [42]. In order to set aside enough

porosity, a cyclic diammonium-type organic molecule or a di-quaternary ammonium-containing organic surfactant were used for mesoporous BEA and MFI, respectively [43, 44]. The diammonium head group of the structure directing agent directs the MFI zeolite nanosheet framework, while long alkyl tails are responsible for the mesostructure. The surfactants are aligned along the straight channel of the MFI framework and di-quaternary ammonium head groups are embedded inside the zeolite framework [45]. By simple loading of metal nanoparticles into hierarchically nanoporous zeolites with mesopores, supported zeolite catalysts can be designed for bifunctional nanoparticle catalysts. While the strength and concentration of acidity are controlled by the framework composition, the nature of the surface can also be tailored from hydrophobic to hydrophilic depending on the Si/Al ratios. Supported zeolite catalysts promise many catalytic applications due to a variety of functions.

3.3 Macroporous Mesoporous Oxides

By employing colloidal crystals composed of silica microspheres or polymer beads as hard templates, periodic porous oxides can be generated [38]. For this process, the sphere templates should be removed without destroying the solid product. Monodisperse silica spheres synthesized by the Stöber method [46], polymethylmethacrylate or polystyrene spheres via emulsion polymerization, are packed to form three-dimensional or sometimes two-dimensional arrays. Dissolved or liquid metal alkoxides, typical sol-gel precursors, fill the interstitial space of the close-packed templates and are solidified by the condensation. The silica and polymer spheres are easily removed by strong base and calcinations, respectively. The solids result in inverse replicas of the template or inverse opals with highly ordered arrays of spherical voids. Because hard template spheres were formed in a micrometer size ($\sim 100 \text{ nm}$), the

resulting solids have macropores in general [47]. By applying the microspheres to the synthetic method of mesoporous materials, bimodal porous materials incorporating two distinct pore networks can be generated [48, 49]. For example, when Pluronic P123 organic surfactant as a soft-template and polystyrene beads as a hard-template were used together, hierarchical macroporous-mesoporous oxides were produced with high surface area and high crystallinity (Fig. 6b). Hierarchical macroporous-mesoporous oxides are useful not only in diffusion characteristics, separation, and catalysis, but also for the preparation of supported nanoparticle catalysts with high metal loading.

4 Catalytic Reaction Studies Using Nanoparticle Catalysts

4.1 Size- and Shape-Dependent Catalytic Properties

Metal nanoparticles with controlled size and shape via the colloidal synthetic route, enable the study of how their structures affect catalytic performances in catalytic reactions. Scheme 1 illustrates several model reactions which exhibit changes in catalytic activity and selectivity depending on the structure of the metal nanoparticles. In 1969, Boudart first mentioned structure-sensitive and structure-insensitive reactions catalyzed by supported metal catalysts for a classification of heterogeneous catalytic reactions [50]. When the reaction rate depends on the particle size of the active metal, we regard it as a structure-sensitive reaction. In order to define structure-sensitive or structure-insensitive reactions, we should determine the surface active site of the metal and consider the possibility of interaction between the metal and support. Many efforts in the field of catalysis have been devoted to identify structure-sensitive or structure-insensitive reactions on supported metal catalysts with different sizes, surface structures, and metal dispersions [1–4]. With emerging synthetic nanotechnology, now uniform-sized metal nanoparticles with tunable size ranges from 1 to 5 nm have been exploited to clarify the sensitivities of specific reaction rates to particle size. In 1975, Basset et al. reported that turnover rate in benzene hydrogenation over various Pt supported alumina catalysts did not depend on the particle size distribution, concluding benzene hydrogenation was a structure-insensitive reaction [51]. They prepared supported Pt nanoparticles based on the incipient wetness method, in which metal salts were dissolved in solution and impregnated into the support, followed by thermal reduction to form metal nanoparticles. As shown in Fig. 7a, the particle size distributions are too broad to determine an average size. In the recent report, benzene and toluene

hydrogenation reactions were strongly size-dependent of Pt nanoparticles with 1.5–5.2 nm size ranges evidenced by changes in their turnover rate (Fig. 7b, c) [52]. In particular, as shown in Fig. 7c, the 2.4–3.1 nm Pt nanoparticles exhibited the highest turnover rate for both reactions (at 90 °C using 48 Torr benzene and 174 Torr H₂ for benzene hydrogenation and 40 Torr toluene and 176 Torr H₂ for toluene hydrogenation). In order to determine the availability of surface sites of Pt, they used ethylene hydrogenation, a known structure-insensitive reaction on Pt which enabled not only calculating surface sites on the surface of the catalyst, but also confirming a site blocking or hindered area by residual organic capping molecules. Along with the development of nanotechnology, catalytic reactions regarded as structure-insensitive using nanoparticles with broad size distribution, turned out to become structure-sensitive reaction with well-defined nanoparticles. Recently, monodisperse Co nanoparticles with sizes ranging from 3 to 10 nm showed size-dependent activity enhancement of CO₂ hydrogenation which was an analogous reaction of Co catalyzed Fischer–Tropsch reaction [12]. The turnover frequency of CO₂ hydrogenation was significantly higher on the larger Co nanoparticles, which was in good agreement with the values reported for an incipient wetness impregnation prepared catalyst.

The size of nanoparticles influences not only the reaction rate but also the product selectivity. Many hydrogenation reactions of small molecules including pyrrole [53], furan [54], crotonaldehyde [55], butadiene [56], furfural [57], methylcyclopentane [58], cyclohexene [59], and *n*-hexane [60] have been proven to change their selectivity by Pt nanoparticle size or shape. For example, in 1,3-butadiene hydrogenation, 0.9 and 1.8 nm Pt nanoparticles increased the production of *n*-butane by full hydrogenation, whereas 4.6 and 6.7 nm Pt catalysts favored 1-butene by partial hydrogenation [56]. From the study of calculated intermediate structures, the 0.9 and 1.8 nm Pt nanoparticles provided low coordination adsorption sites facilitating H-insertion at the internal carbon as well as terminal carbon, while larger Pt catalysts favored H-insertion only at the terminal carbon as observed on Pt bulk materials. The product selectivity was greatly changed as well in furfural hydrogenation. Pushkarev et al. investigated the change of catalytic activity and selectivity in furfural hydrogenation by using supported Pt nanoparticles with different sizes and shapes [57]. For example, as the Pt size was increased from 1.5 to 7.1 nm, the selectivity toward furfuryl alcohol increased from 1 to 66 % and turnover rates of the furfuryl alcohol production remarkably increased from 1×10^{-3} to $7.6 \times 10^{-2} \text{ s}^{-1}$, while activation energies decreased gradually. In an oxidation reaction of methanol, the Pt size-dependent selectivity change was exhibited for the production of either formaldehyde or carbon dioxide, by the

Scheme 1 Model catalytic reactions for understating catalytic activity and selectivity depending on the structures of nanoparticles and the oxide-metal interactions

Fig. 7 Size distribution histograms of supported Pt nanoparticle catalysts prepared by **a** the impregnation and **b** the polyol reduction method. **c** Turnover frequencies in benzene and toluene hydrogenation reactions over supported Pt nanoparticle catalysts synthesized by

the polyol reduction, exhibiting the structure-sensitive feature (modified with permission from [51, 52], copyright 1975, 2012 Published by Elsevier B.V.)

partial or full oxidation, respectively [61]. While the 2, 4, and 6 nm Pt nanoparticles showed similar catalytic activity and selectivity, the 1 nm Pt nanoparticles exhibited a significantly higher selectivity toward formaldehyde, but a lower total turnover frequency due to the strong oxidation tendency of small nanoclusters.

In order to learn how the size of nanoparticles affects catalytic performance and what size causes the most dramatic effect in catalysis, several factors need to be considered. Generally, 0.8 nm Pt nanoparticles with a simple

cuboctahedral shape reach 92 % surface atoms, then the surface to volume ratios are abruptly decreased to 45 and 35 % for 3 and 4 nm, respectively. From the cube-octahedron model, the relative number of edge and corner sites can be calculated as a function of the particle size [60, 62]. As the size of nanoparticles become smaller, the number of highly active edge and corner sites is increased per mass unit of catalyst (Fig. 8a). Through model catalytic experiments on single crystal surfaces with well-defined step, kink, and terrace sites under ultrahigh vacuum conditions,

Fig. 8 **a** A plot of the fraction of surface sites versus size obtained from the modified cubooctahedron cluster model. **b** Charge redistribution upon oxygen adsorption seen from the top (*upper*) and the side (*lower*). Blue/red contours exhibit areas of accumulated/depleted electron density. **c** XPS of Pt nanoparticles with sizes of 0.8 and

1.5 nm. The 0.8 nm Pt nanoparticles were highly oxidized, whereas the 1.5 nm Pt nanoparticles have a metallic nature (modified with permission from [60, 63], copyright 2012, 2011 Springer and [13], copyright 2008 American Chemical Society)

catalytic behaviors were changed by the surface structures of the single crystal. Therefore, depending on the relative amount of active sites on nanoparticles of specific sizes and shapes, accompanied by their surface to volume ratio, catalytic activity and selectivity can be altered.

In another point of view, the small size maximizes surface active sites of the catalyst and changes greatly their electronic structure which becomes discrete as in a molecule, as opposed to the continuous spectrum of bulk metals. In order to find at what size regime the finite-size effect is generated, Kleis and their coworkers calculated adsorption energies for CO and O₂ on gold nanoparticles ranging from 13 to 1,415 atoms, regarding the gold nanoparticles formed as a closed-shell cubooctahedra [63]. Figure 8b shows charge redistribution upon oxygen adsorption, where blue and red contours denote areas of accumulated and depleted electron density, respectively. They concluded that clusters smaller than 561 atoms which correspond to 2.7 nm, showed clear finite-size effects, having stronger adsorption,

while bulk surface properties were obtained for clusters above that critical size. One of the factors inducing size-dependent catalytic properties is the oxidation state of metals. When nanoparticles are smaller, their oxidation becomes greater. Pt 4f signals of XPS in Fig. 8c clearly show 13 and 0.16 of Pt^{x+}/Pt^0 ratio for Pt₂₀ and Pt₄₀ clusters which correspond to 0.8 and 1.5 nm in size, respectively.

In studies of surface science using single-crystal model surfaces, structure sensitivity was also probed by comparing catalytic reactivity on single crystals by exposing surfaces with different orientations. Knowledge obtained from catalytic reaction studies based on the single crystals with specific planes now corresponds to those of differently shaped nanoparticles. For example, in benzene hydrogenation over single-crystalline Pt surfaces, cyclohexane and cyclohexene were produced on Pt (111) surface, while only cyclohexene was obtained on the (100) surface [64]. When benzene hydrogenation was conducted over Pt nanoparticles with shapes of cube and cuboctahedron, a similar trend

was observed, in which (100) faceted cuboctahedral Pt nanoparticles tended toward two products, whereas cubic Pt nanoparticles produced only benzene, which is in accordance with the single crystal studies [65].

4.2 Composition-Dependent Catalytic Properties

Bimetallic nanoparticle catalysts have shown distinct electronic, chemical, and catalytic properties which are different from the parent metals. The new electronic structures of bimetallic systems are formed by the formation of heteroatom bonds which change the electronic environment of the metal surface [5]. The geometry of the bimetallic structures is also changed from either of the parent metal surfaces. For example, changed average metal–metal bond lengths by bimetallic alloying result in the strain effect which modifies the electronic structure of the metal by orbital overlap [66]. Bimetallic catalysts have attracted much attention as excellent industrial reforming catalysts in the oil refining process in the 1960s, because they exhibited high activity, stability, and resistance against deactivation in the catalytic reforming reaction [5]. The industrial reforming catalysts for hydrocarbon conversion toward high octane gasoline normally consist of Pt alloyed with small amounts of promoter metals (such as Rh, Ir, Re and Sn) and an acidic support. While Pt atoms isomerize the reactants, the second metal promoters provide C–C and C–H bond breaking activity. Recently, size and composition of PtRh bimetallic nanoparticles supported on mesoporous silicas were investigated for the catalytic reforming of *n*-hexane [20]. Monometallic Rh nanoparticles exhibited high turnover frequency in *n*-hexane reforming, however they yielded cracking with 90 % selectivity. By considering the overall TOF and the percent selectivity of desired isomer products, Pt₉₀Rh₁₀ bimetallic nanoparticles were chosen by maximizing high isomer production (Fig. 9a). The composition effect of bimetallic PtFe nanoparticles was elucidated on catalytic hydrogenation of ethylene and hexane [19]. As compared to single Pt nanoparticles, 2 nm PtFe bimetallic nanoparticles accelerated reaction rates in the hydrogenation of ethylene, because incorporation of Fe into the Pt nanoparticle catalysts weakens the adsorption of inactive spectator species on the nanoparticle surface (Fig. 9b). The reaction rate was also changed by adding Sn into Pt nanoparticles in CO oxidation, because the strongly adsorbed CO on Pt catalysts hindered CO₂ formation by inhibiting O₂ adsorption [67]. As shown in Fig. 9c, PtSn bimetallic nanoparticles have a higher reaction rate than Pt nanoparticles in CO oxidation, because they provide an active site for O₂ adsorption that is important when Pt is covered with CO. As discussed previously, recent advances of in situ characterization techniques enable real time monitoring of

different segregation of two metals onto the surface under catalytically relevant reaction conditions. Through in situ APXPS, the negative effect of bimetallic CoPt nanoparticles was recently found in the reaction of CO₂ hydrogenation. Beaumont et al. reported mixed Pt and Co nanoparticles supported on mesoporous silica showed a greater CO₂ methanation rate than bimetallic CoPt nanoparticles [68]. In Fig. 9d, TOFs of bimetallic CoPt nanoparticles were negligible for the production of methane, compared to those of Co nanoparticles and their mixture with Pt nanoparticles in silica. It was attributed that Pt atoms in bimetallic CoPt nanoparticles were segregated to the surface in reducing conditions and blocked the active site of Co for CO₂ hydrogenation.

4.3 Oxide-Metal Interactions

The catalytic reactivity and selectivity of metallic nanoparticles supported on an oxide support can be altered by charge transfer. In the 1960s, Schwab discovered that there was a active site at the oxide-metal interface [69]. In the methane oxidation reaction, he found out that Ag supported on ZnO catalysts had a much higher activity toward CO₂ than Ag or ZnO catalysts due to the catalytic promoter effect by an electron exchange between support and catalyst (Fig. 10a). Later, Tauster et al. mentioned the strong metal-support interaction (SMSI) in 1978 to describe the drastic change in chemisorption properties of Group VIII metals such as Fe, Ni, Rh, Pt, Pd, and Ir, when they were supported on certain oxides (TiO_x, TaO_x, CeO_x, and NbO_x) [70, 71].

The interaction between the active metal and the oxide support induces charge transfer, resulting in enhancement of catalytic reaction rates. Boffa et al. used various oxides deposited on rhodium foils and observed a great enhancement of turnover rates, when TiO_x, NbO_x, and TaO_x were used in CO₂ hydrogenation (Fig. 10b) [72]. A similar SMSI effect was found on Pt nanoparticles supported in mesoporous oxide catalysts. When mesoporous Co₃O₄, NiO, MnO₂, Fe₂O₃, and CeO₂ were used as supports, turnover frequencies of the Pt/metal oxide systems were orders of magnitude greater than those of the pure oxides or the silica-supported Pt nanoparticles, due to the charge transfer (Fig. 10c) [40]. The SMSI affects not only catalytic activity but also selectivity. Baker et al. investigated furfural hydrogenation by comparing TiO₂ and SiO₂ films with deposited Pt nanoparticles [73]. While the SiO₂ film did not contribute to the catalytic properties of Pt, the TiO₂ facilitated the enhancement of activity along with a selectivity change. Charge transfer from TiO₂ on the Pt/TiO₂ catalyst lead to a fivefold increase of reaction rate and a 50-fold enhancement of selectivity towards furfuryl alcohol by the acid–base interaction (Fig. 10d). A similar

Fig. 9 Catalytic reaction rates of bimetallic nanoparticles depending on their composition. **a** Isomer TOFs of PtRh metallic nanoparticles with different compositions in *n*-hexane reforming. **b** TOFs and activation energies of PtFe bimetallic nanoparticles with different compositions in methanol oxidation. **c** CO oxidation rates of PtSn and Pt nanoparticles. **d** TOFs of Co, CoPt, and mixed Co and Pt nanoparticles in CO₂ hydrogenation (reproduced with permission from [20], copyright 2014 Springer, [67], copyright 2014 Published by Elsevier B.V., and [19, 68], copyright 2013, 2014 American Chemical Society)

trend was confirmed in crotonaldehyde hydrogenation, in which the activity of a Pt/TiO₂ catalyst was increased fourfold and over 50 % alcohol products were obtained selectively, compared to those of Pt/SiO₂ [74]. Recently, *n*-hexane reforming was carried out over various kinds of porous oxides including Al₂O₃, TiO₂, Nb₂O₅, Ta₂O₅, and ZrO₂ to investigate support-dependent catalytic selectivity toward branched C₆ isomers which are desired products for high-octane gasoline in the oil refining process [49]. In Fig. 10e, when Pt nanoparticles were supported in either porous Nb₂O₅ or Ta₂O₅, the production of C₆ isomers was increased selectively up to 97 % by the SMSI (See Scheme 1f for the reaction pathway). Zeolites also influence catalytic selectivity due to their unique acidic sites and interaction with metal nanoparticles. In methylcyclopentane hydrogenation as a model reforming reaction of hydrocarbons, mesoporous zeolites, BEA and MFI, exhibited totally different selectivity when they were used as pure acid catalysts or as supports for loading Pt nanoparticles [75]. The mesoporous zeolites BEA and MFI produced predominantly methylcyclopentene by dehydrogenation and C₆ isomers by ring-opening with isomerization (See Scheme 1g). On the other hand, when Pt nanoparticles were loaded on mesoporous zeolites, BEA and MFI, cyclohexane and benzene were obtained by ring-enlargement and subsequent hydro/dehydrogenation, in which the cyclohexene intermediate was identified at interfaces between Pt nanoparticles and acidic zeolites (Fig. 10f). A MOF influences the selectivity change by encapsulating the core metal catalyst, because it has a

controlled cavity to block large-molecules. For example, Pd@ZIF-8 yolk-shell nanostructures exhibited interesting molecular-size selectivity originating from the ZIF-8 shell in ethylene hydrogenation versus cyclooctene hydrogenation [31]. Recent studies have demonstrated that electronic excitation in exothermic reactions involves the hot electron flow at oxide-metal interfaces [1, 2]. Recently, Pt–CdSe–Pt nanodumbbells as a hybrid nanocatalyst induced enhancement of CO oxidation rates during light irradiation of energy higher than the bandgap of CdSe [36]. The repeating on- and off-light experiments demonstrated that the hot electrons were generated on the CdSe nanorods by the absorption of photons, and transferred to the Pt nanoparticles, resulting in the activity enhancement in CO oxidation. Because the hot electron flow is another big field in catalysis with a long history and lots of interesting phenomena, it will be reviewed in a separated article.

5 Conclusions and Outlook

Colloidal nanotechnology for the synthesis of nanoparticles attains a completeness of artistic achievement. Now, we can control the size of nanoparticles to the atomic cluster level, preserving a narrow size distribution. Through polyol reduction and dendrimer-templating approaches, noble metal nanoparticles size ranges can be reduced to less than one nanometer. By controlling nucleation and growth kinetics or by introducing foreign ions, nanoparticles with various shapes including sphere, cube, tetrahedron,

Fig. 10 Catalytic activity and selectivity changes, depending on the type of oxide supports, by the strong metal-support interaction. **a** Temperature dependence of CO₂ formation over Ag, ZnO, and Ag/ZnO catalysts in methane oxidation. **b** Activity enhancement of CO₂ hydrogenation over oxide-supported Rh catalysts. **c** TOFs of Pt nanoparticles supported on mesoporous oxide catalysts in CO oxidation. **d** Selectivity changes in furfural hydrogenation over Pt nanoparticles supported on either TiO₂ or SiO₂. **e** Product selectivities

in *n*-hexane reforming over 2.7 nm Pt nanoparticles supported on different kinds of oxide supports. **f** Product selectivities over mesoporous zeolites and Pt nanoparticle-supported zeolite catalysts in hydrogenative methylcyclopentane reforming (modified with permission from [69], copyright 1967 Wiley-VCH, [72], copyright 1994 Springer and [40, 49, 73, 75], copyright 2013, 2012, 2014, 2014 American Chemical Society)

octahedron, and cuboctahedron can be produced. By extending the knowledge of colloidal synthetic techniques, a variety of nanoarchitectures such as bimetallic, core/shell, and hybrid nanostructures are attained as novel

nanocatalysts. Beyond conventional porous materials which are classified as micro-, meso-, and macro-porous structures, advanced porous oxides such as mesoporous zeolites and macro-mesoporous oxides have been developed as

novel supports by using organic structure directing agents and inorganic hard-templates. By protecting a catalyst metal core and by providing functional properties, elaborate core/shell nanoparticles have also been designed, having various kinds of shells including mesoporous oxides, multiple metal layers, and MOFs. The functional nanoparticle catalysts provide unique surface structures and interfaces in many catalytic reactions. From our current model reaction studies, we found out that turnover rates and selectivity of reactions were strongly influenced by the size, shape, and composition of nanoparticles and strong oxide-metal interactions, which are created by various metal-oxide interfaces. With the evolution of in situ characterization techniques, we discovered that several molecular factors influenced catalytic activity and selectivity including surface structure and composition of nanoparticles, reaction intermediates, adsorbates, and oxidation states in nanocatalysis. Now, our focus is aimed toward new catalytic insights. For example, tandem catalysis, a sequential reaction governed by a catalyst with two or more interfaces, attracts much attention for researchers. Comparisons of two interfaces such as solid/liquid and solid/gas interfaces are intriguing. Homogenized heterogeneous catalysis and enzyme kinetics based on heterogeneous catalysts are also interesting themes in nanocatalysis. The utilization of elaborately designed nanoparticle catalysts, advanced in situ characterizations, and reaction studies in various environments opens new possibilities for understanding interesting catalytic phenomena and for developing ideal catalysts and efficient catalytic processes exhibiting 100 % selectivity, maximal activity, and long-term stability.

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