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Morphology-Dependent Catalysis of CeO₂-Based Nanocrystal Model Catalysts

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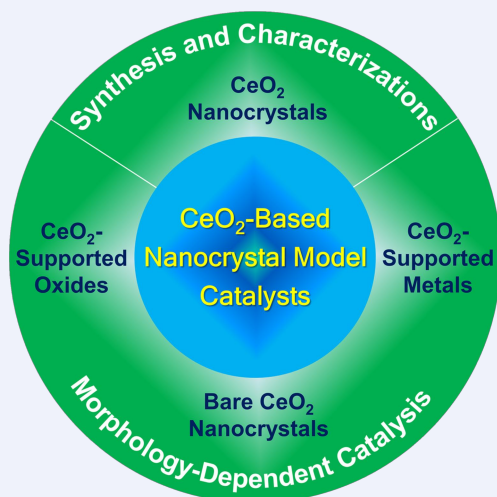
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Comprehensive Summary

Recent progress in colloidal synthesis has realized the preparations of uniform nanocrystal (NC) model catalysts with rich and well-controlled morphologies that were employed to explore structure-activity relationships of powder catalysts, similar to single-crystal-based model catalysts under ultrahigh vacuum conditions but can work at the same conditions as powder catalysts without the “materials gap” and “pressure gap”. In this perspective, the CeO₂-based NC model catalysts with various morphologies are included and their relevant progresses are critically reviewed. The detailed descriptions of morphology-controlled synthesis and characterizations of uniform CeO₂ NCs, and morphology-dependent catalysis of CeO₂-based NC model catalysts containing pure CeO₂ NCs, CeO₂-supported oxide catalysts, and CeO₂-supported metal catalysts, provide us a comprehensive cognition in CeO₂-involved catalytic reactions and also open up a new approach for the fundamental studies of complex heterogeneous catalysis. Finally, a concept of oxide-based NC model catalysts and outlook of oxide NCs acting not only as model catalysts for the fundamental study but also as the support in tailoring structures and optimizing performance of oxide-involved catalysts are discussed.



Keywords

CeO₂ nanocrystals | Model catalysts | Surface chemistry | Heterogeneous catalysis | Structure-activity relationships

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Top, Left to Right: Yang Wen and Qiuyu Huang;
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1. Introduction

Catalysis plays an extremely crucial role in modern chemical industry, energy development, and environmental remediation.^[1–2] The core of a catalytic reaction is the catalyst, which can either accelerate a reaction to reach the chemical equilibrium (catalyst activity), or selectively accelerate a reaction to the desirable product from a competing reaction network (catalyst selectivity), nevertheless, its structure remains unchanged before and after the reaction (catalyst stability). The urgent issue of green chemical process demands the catalysts to be not only active but also highly selective and stable. Therefore, it is of importance to identify the key role of a catalyst in governing the catalytic reaction, *i.e.*, understanding structure-activity relationships, so as to guide the structural design and controlled synthesis of efficient catalysts.

The catalytic properties of solid catalysts are determined by the surface composition and structure.^[3] However, it is difficult to realize the precise identification of the active sites in a catalytic reaction due to the structural complexity of powder catalyst surface. With this regard, single-crystal-based materials with unique exposed surface have been extensively used as model catalysts for the study of surface structure-catalytic property relationships,^[4–9] but they are limited by the existences of so-called “ma-

terials gap” and “pressure gap” compared to corresponding powder catalysts. As a result, the conclusions drawn from single-crystal-based model catalysts sometimes cannot be simply extended to working powder catalysts. Fortunately, recent progress in colloidal synthesis has realized the preparations of uniform nanocrystal (NC) model catalysts with exclusive surface composition and structure.^[10–15] These NC model catalysts not only fulfill the structural requirements of single-crystal-based model catalysts, but also can be studied under the same conditions as powder catalysts. It is thus being regarded as a novel type of model catalyst to explore the structure-activity relationships of powder catalysts.^[16–24]

Oxides have been extensively used as catalysts and catalyst supports in heterogeneous catalysis. Their surface composition and structure are more plentiful and complex than those of metals due to both cations and anions exposure on the surface. The exposed crystal planes on oxide catalysts determine not only the surface composition, but also the surface geometric structure, and thus strongly affect their catalytic properties. However, the crystal-plane effects on oxide catalysts are less explored because of the difficulty in synthesizing oxide NC model catalysts exposing one or two types of crystal planes, less microscopic information acquired from oxide catalysts with semiconductors or insulators unsuitable for surface science techniques involving electrons, and facile restructuring to minimize the surface energy on the polar surfaces of oxide catalysts.

Benefiting from the great advancement in nanotechnology, the oxide-based NC model catalysts with uniform sizes and well-controlled morphologies can be successfully prepared.^[25–29] According to the Wulff's rule,^[30] the morphology of a solid crystallite determines the exposed crystal plane, and thus the surface composition and structure. This provides an excellent candidate to realize the study of structure-activity relationships by employing oxide-based NC model catalysts with one or two types of crystal planes exposed. In the past several years, increasing number of examples of morphology-dependent catalytic properties of uniform oxide-based NCs, such as Cu₂O,^[31–36] Co₃O₄,^[37] TiO₂,^[38–39] ZnO,^[40–41] and Fe₂O₃^[42–43] have been comprehensively explored, also including several nice reviews published on this topic.^[16–24,44–52]

As one of the most extensively investigated oxides, CeO₂ has

been frequently applied in heterogeneous catalysis, either as the catalyst or as the catalyst support.^[53] Preparations of uniform CeO₂ NCs with different morphologies and corresponding explorations of the structure-activity relationships using CeO₂-based NC model catalysts have been realized in previous literature,^[54–62] including ours.^[63–65] In this perspective, we focus on the summarization of CeO₂-based NC model catalysts to realize the fundamental understanding of surface composition and structure-catalytic performance relationships in CeO₂-involved catalysts. Firstly, morphology-controlled synthesis and characterizations of uniform CeO₂ NCs and their surface composition and structure are introduced. Then, morphology-dependent catalysis of CeO₂-based NC model catalysts, including pure CeO₂ NCs, CeO₂-supported oxide catalysts, and CeO₂-supported metal catalysts, are reviewed. Finally, conclusions and outlook are given.

2. Synthesis and Characterizations of CeO₂ NCs

2.1. Morphology-controlled synthesis of uniform CeO₂ NCs

CeO₂ is a fluorite structure (space group O^5_H-Fm3m) with a unit cell length of 5.41 Å and the structure consists of an fcc unit cell of cations with the octahedral interstitial sites occupied by anions (Figure 1A). In the bulk CeO₂, the cerium cations are eight-fold-coordinated with each cerium cation bonded with eight neighboring oxygen anions, while the oxygen anions are four-fold-coordinated with each oxygen anion bonded with four neighboring cerium cations. Previously, various CeO₂ morphologies from one-dimensional (1D) nanostructures such as nanowires, nanorods (r-CeO₂), and nanotubes,^[66–72] to 2D/3D nanostructures such as nanoplates, nanodisks, nanosheets, nanocubes (c-CeO₂), nanooctahedra, and nanopolyhedra,^[27,73–84] have been successfully prepared via the wet-chemistry methods. The preparation process of CeO₂ NCs with different morphologies employed either organic/inorganic additives-assisted strategies or the template-free hydrothermal/solvothermal synthesis. The use of organic/inorganic additives as capping agents could affect the nucleation and growth of CeO₂ NPs by selectively blocking the growth of the crystal in one specific direction.^[76–77,80] Typically, Zhang *et al.*^[77] have employed the decanoic acid as capping agents to tune the morphology of the resulting CeO₂ NCs. Due to the decanoic acid preferentially interacting with the CeO₂{100} facets, the crystal growth in the [100] direction reduces while it can increase the growth rate in the [111] direction. The increased {100} facets lead to the formation of a cube-like morphology. As a further increase of the capping agent, all the surface growing directions are blocked to lead to the formation of truncated octahedra of smaller dimensions. Additionally, the additions of chloride and nitrate ions can also selectively interact with the {111} and {100} facets,

respectively, which can change the surface free energies and thus control the growth rate of different CeO₂ facets. With this regard, the presence of chloride ions is favorable for the formation of elongated 1D structures like nanowires and nanorods, while nanoparticles or nanocubes are easily formed in the presence of nitrate ions.^[84]

For the template-free hydrothermal/solvothermal synthesis approach, it has been verified that the size and morphology of the resulting CeO₂ NCs are sensitively dependent on the balance among adopted Ce precursor content, pH, temperature and time that determine the processes of nucleation and growth (Figure 1B).^[27,78–80,82] For instance, Mai *et al.*^[27] developed a hydrothermal method with a dissolution/recrystallization mechanism to synthesize CeO₂ nanopolyhedra (p-CeO₂), r-CeO₂, and c-CeO₂ by changing the reaction temperature and OH[−] concentrations, in which a low dissolution/recrystallization process with the synthesis condition of 100 °C and low OH[−] concentration ($C_{NaOH} < 1$ mol/L) is beneficial to the formation of p-CeO₂ NCs enclosed with {111} and {100} crystal planes. With the acceleration of dissolution/recrystallization rate, r-CeO₂ NCs enclosed with {110} and {100} crystal planes were produced under high OH[−] concentration ($C_{NaOH} > 6$ mol/L) and c-CeO₂ NCs enclosed with {100} crystal planes were produced when the hydrothermal temperature further rose to 180 °C.

Due to its high surface energy, CeO₂{100} surface is less stable than CeO₂{111} surface to bring about a great challenge in producing high quality cubic NCs in terms of uniformly small size, well-defined crystal morphology, and ease of fabrication. To address this issue, a simple and rapid approach using organic-ligand-assisted supercritical water as the medium was developed to produce c-CeO₂ NCs, which can realize the size less than 10 nm.^[77] This could be ascribed to the chemical bonds between the NC surface and the organic-ligand molecule that limit the crystal growth and inhibit the agglomeration, ultimately lead to the fabrication of small and well-dispersed c-CeO₂ NCs. Notably, the morphology and correspondingly exposed facets of as-prepared CeO₂ NCs were significantly affected by the thermal treatments.^[71,81,83,85–86] It was widely reported that c-CeO₂ and r-CeO₂ NCs are respectively enclosed with {100} and {110} + {100} crystal planes when the thermal treatment was conducted at 500 °C.^[86–87] With the rise of thermal treatment temperature, the extent of truncations at the corners and edges of the cubes takes place at 600 °C, which results in the {111} faceting of the {100} flat surface.^[83] Furthermore, the truncated corners/edges and irregular truncated cuboctahedron were formed via c-CeO₂ NCs induced by a thermal treatment at 900 °C.^[81] Similar results were also observed on r-CeO₂ NCs. A calcination temperature increasing from 500 °C to 700 °C can induce the dominantly exposed facets on r-CeO₂ NCs changing from the {100} and {110} facets to the {111} facets.^[71,86] Moreover, the exposed facets on c-CeO₂ NCs were also dependent on the cerium precursors,^[70] rod diameters and a high density of crystallographic defects.^[88]

2.2. Surface composition and structure of various CeO₂ NCs

CeO₂ NCs with controlled morphologies of rods, cubes, and octahedra (o-CeO₂) were prepared following the previously reported recipes,^[27] and p-CeO₂ was purchased commercially. As shown the TEM and HRTEM images in Figure 2, c-CeO₂ and o-CeO₂ NCs with highly symmetric morphologies are dominantly enclosed with {100} (Figure 2 A1 and A2) and {111} (Figure 2 B1 and B2) crystal planes, respectively, while p-CeO₂ is irregular and predominantly enclosed with {111} facets (Figure 2 C1 and C2), and the crystal planes exposed on less symmetric r-CeO₂ NCs are not unambiguously determined and are dependent on the calcination temperature. Agreeing with previous results,^[71,86] the HRTEM images identify the dominant lattice fringe of {110} in the parallel direction with the side crystal planes of as-synthesized

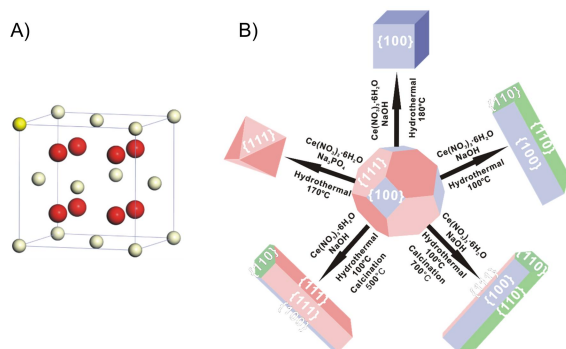


Figure 1 (A) The structure of CeO₂ units cell; (B) Polyhedral morphology of CeO₂ and the synthesis approach of other uniform morphologies. Reprinted with permission from Ref. 19, Copyright 2019, Elsevier.

r-CeO₂ calcined at 500 °C (r-CeO₂-500) (Figure 2 D1 and D2) but of {111} in the parallel direction with the side crystal planes of r-CeO₂ calcined at 700 °C (r-CeO₂-700) (Figure 2 E1 and E2). In addition, the {110} facets still exist on top and bottom of the rods over r-CeO₂-700 (inset in Figure 2E2). In the optimized surface structures (Figure 2 F–H), the CeO₂(110) surface exhibits 3-fold coordinated O (O_{3C}) and 6-fold coordinated Ce (Ce_{6C}) on the topmost layer. The CeO₂(100) surface exhibits 2-fold coordinated O (O_{2C}) on the topmost layer and Ce_{6C} on the second layer. The CeO₂(111) surface exhibits O_{3C} on the topmost layer and 7-fold coordinated Ce (Ce_{7C}) on the second layer.

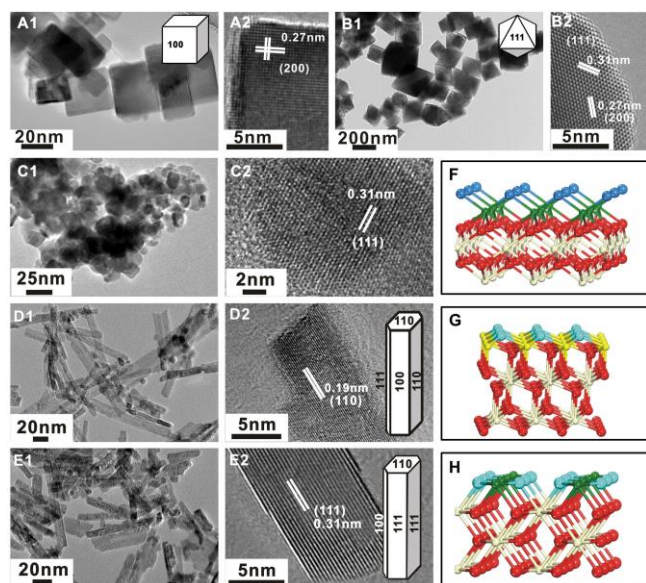


Figure 2 Representative TEM and HRTEM images of (A1, A2) c-CeO₂, (B1, B2) o-CeO₂, (C1, C2) p-CeO₂, (D1, D2) r-CeO₂-500, and (E1, E2) r-CeO₂-700 (Insets schematically illustrate the crystal planes exposed on the CeO₂ cubes, octahedral, and rods.); Surface structures of (F) CeO₂(100) with relaxation, (G) CeO₂(111), and (H) CeO₂(110) crystal planes. Red, blue, cyan, white, yellow, and green represent O_{4C}, O_{2C}, O_{3C}, Ce_{6C}, Ce_{7C}, and Ce_{6C} atoms, respectively. Reprinted with permission from Ref. 86, Copyright 2016, American Chemical Society.

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of CO and CO₂ chemisorption was used to probe the surface composition and structure of various CeO₂ NCs.^[86] The results reveal that the crystal planes exposed on the CeO₂ NCs are characteristic for CO chemisorption (Figure 3 A and B) but not for CO₂ chemisorption (Figure 3 C and D). CO molecules chemisorbed at Ce(IV) sites were observed on all CeO₂ NCs, whereas adsorbed CO at Ce(III) sites was not observed on o-CeO₂, which is associated with crystal plane-dependent location of oxygen vacancies that exist on the surfaces of CeO₂(110) and CeO₂(100) but dominantly locate in the subsurface/bulk regions of CeO₂(111).^[17–19] The formation of carbonate species arising from CO chemisorption can probe the different surface structures of the crystal planes exposed on various CeO₂ NCs. o-CeO₂ enclosed with {111} crystal plane exposes adjacent O_{3C} atoms on the topmost layer connected by the same Ce_{7C} atom on the second layer, thus, only bidentate carbonate species (1296 and 1579 cm^{−1}) can form but not for the bridged carbonate species. c-CeO₂ enclosed with {100} crystal plane exposes adjacent O_{2C} atoms on the topmost layer connected by the same Ce_{6C} atom on the second layer or not, these are both present. Thus, both bidentate (1292 and 1572 cm^{−1}) and bridged carbonate (1218 and 1395 cm^{−1}) species can form. Moreover, the carbonite species (1277 cm^{−1}) is formed with the presence of surface oxygen vacancies on the

{100} crystal plane. For r-CeO₂ NCs, the exposed crystal planes vary with the calcination temperature during the synthesis. The *in situ* DRIFTS results upon CO chemisorption reveal that increasing the calcination temperature of r-CeO₂ can result in the quick increase and dominance of bicarbonate (1600–1609 cm^{−1}) and carbonite (1277–1279 cm^{−1}) species on the surface but the decrease and vanishing of bridged carbonate species (1218 and 1385–1410 cm^{−1}). Comparing the dominant surface species formed on CeO₂(111) and CeO₂(100) surfaces, on the CeO₂(110) surface, bidentate carbonate and carbonite species form but bridged carbonate species do not. Thus the bridged carbonate species are characteristic for CO chemisorption on the CeO₂(100) surface. The above CO chemisorption results suggest that the fraction of {100} crystal planes exposed on r-CeO₂ should decrease with the calcination temperature increase.

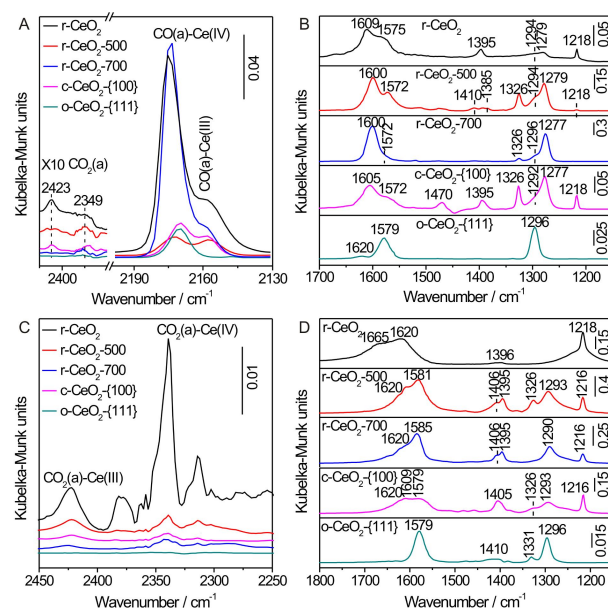


Figure 3 *In situ* DRIFTS spectra of CO chemisorption on various CeO₂ NCs at 173 K and $p_{\text{CO}} = 250$ Pa: (A) CO and CO₂ regions and (B) C–O vibration region; *In situ* DRIFTS spectra of CO₂ chemisorption on various CeO₂ NCs at room temperature and $p_{\text{CO}_2} = 300$ Pa: (C) CO₂ region and (D) C–O vibrations region. Reprinted with permission from Ref. 86, Copyright 2016, American Chemical Society.

3. Morphology-Dependent Catalysis of CeO₂-Based NC Model Catalysts

3.1. Morphology-dependent catalysis of pure CeO₂ NCs

CeO₂ has wide and important applications in heterogeneous catalysis.^[53,89–91] The typical feature of CeO₂ is attributed to the nonstoichiometric composition accompanied by the oxygen vacancies that makes it a widely-used catalyst in heterogeneous catalysis.^[92–93] Previous experimental results of the Raman spectroscopy and positron annihilation lifetime spectroscopy (PALS) of CeO₂ NCs^[94–95] coupling with surface oxidation reactivity and surface hydroxyl reactivity of reduced CeO₂ NCs^[87] demonstrate the morphology-dependent oxygen vacancy concentrations and structures of various CeO₂ NCs. The oxygen vacancy concentrations of r-CeO₂ and c-CeO₂ are much higher than that of o-CeO₂, and oxygen vacancies are mainly located on the surfaces of r-CeO₂ and c-CeO₂ but in the subsurface of o-CeO₂.^[17–19]

Various CeO₂ NCs were used to a diversity of catalytic reactions, whose activities^[54–56,66,70,85,96–103] have been verified to strongly depend on the CeO₂ morphology. Typical examples in

morphology-dependent catalytic activity of CeO₂ NCs were observed in CO oxidation reaction,^[66,96,98] as it was also the first observed catalytic reaction that demonstrated the morphology-dependent catalysis of CeO₂ NCs. It has been proposed that CO oxidation catalyzed by CeO₂ follows the Mars-van Krevelen (MvK) mechanism, by which CO can firstly react with the surface lattice oxygen of CeO₂ to generate CO₂ and oxygen vacancy, and subsequently O₂ is activated on the oxygen vacancy.^[89] Thus, the catalytic activity of various CeO₂ NCs in CO oxidation is dominantly determined by concentration/structure of oxygen vacancies in CeO₂. As a result, the oxygen vacancies are more clustered on r-CeO₂ than on c-CeO₂ and o&p-CeO₂, which results in the best activity in catalyzing CO oxidation emerging on r-CeO₂ and that of o&p-CeO₂ is always poorest (Figure 4A).^[98] Very interestingly, the morphology-dependence of various CeO₂ NCs in catalyzing selective hydrogenation reaction of C₂H₂ to C₂H₄ presents an opposite trend.^[100] CeO₂ octahedron-like nanoparticles enclosed with {111} crystal planes show higher activity in C₂H₂ hydrogenation (Figure 4B). This could be ascribed to the key role of oxygen on low-vacancy CeO₂{111} surface that contributes to the stabilization of reactive intermediates and subsequently favors C₂H₂ hydrogenation.

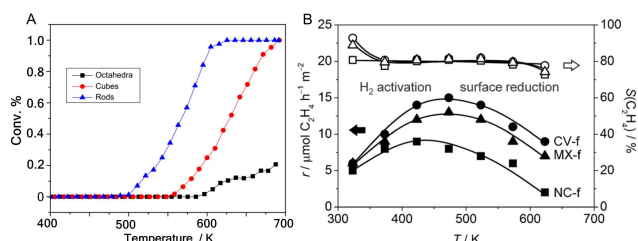


Figure 4 (A) Light-off curves for CO oxidation over ceria rods, cubes, and octahedra; (B) Reaction rate (solid symbols) and selectivity to ethylene (open symbols) of the ceria catalysts in C₂H₂ hydrogenation at variable temperature. CV: conventional nanoparticles; NC: nanocubes; MX: mixed morphology of both nanoparticles and nanocubes. Reprinted with permission from Refs. 98 and 100, Copyright 2012 and 2014, Elsevier and Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

In addition to the activity, morphology-dependent selectivity and stability of pure CeO₂ NCs were also observed.^[64,103–106] We previously reported a metal-free CeO₂ catalyst for gas-phase hydrogenation of crotonaldehyde to crotyl alcohol.^[64] As shown in Figure 5, compared to c-CeO₂ and p-CeO₂, r-CeO₂ exhibits considerably catalytic efficiency and an unprecedented high crotyl alcohol selectivity of 93.2% at 50 °C. The combined *in situ* characterization and DFT calculation results demonstrate that the density of surface oxygen vacancies plays a key role in determining the catalytic performance of gas-phase selective hydrogenation of crotonaldehyde. A relatively high density of surface oxygen vacancies on r-CeO₂ can construct the solid frustrated Lewis pair sites that enhance the heterolytic dissociation of H₂ to produce H[−] species at the surface oxygen vacancy site and another OH[−] group. The formed H[−] species at the surface oxygen vacancy site suppresses the formation of crotonaldehyde adsorption via the C=C bond on the CeO₂, resulting in the dominant crotonaldehyde adsorption via the C=O bond and subsequently high selectivity toward crotyl alcohol. However, both the catalytic activity and the crotyl alcohol selectivity decline after a further reduction of r-CeO₂ by H₂ (r-CeO₂-R) due to the presence of extra vacant surface oxygen vacancy site that leads to the emergence of crotonaldehyde adsorption via the C=C bond. Li *et al.*^[106] reported that besides the catalytic activity, the stability of CeO₂ NCs in the catalyzed HCl oxidation reaction was also morphology-dependent. Under harsh reaction conditions (Ar : HCl : O₂ = 6 : 2 : 2), r-CeO₂ NCs are very

stable without the destroy of surface structures, while c-CeO₂ and o-CeO₂ NCs are both instable due to the formation of hydrated CeCl₃ during reaction.

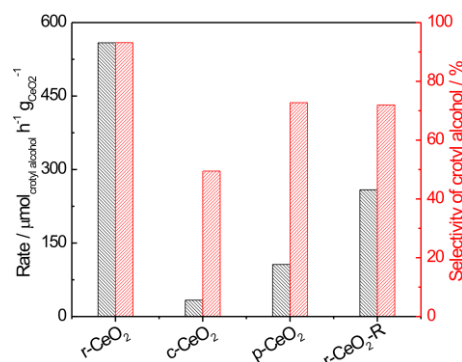


Figure 5 Formation rate (μmol_{crotyl alcohol} h^{−1} g_{CeO₂}^{−1}) and catalytic selectivity (%) of crotyl alcohol for the gas-phase selective hydrogenation of crotonaldehyde catalyzed by r-CeO₂, c-CeO₂, p-CeO₂, and r-CeO₂-R at 323 K. The data were acquired after a 30-min reaction. Reprinted with permission from Ref. 64, Copyright 2020, American Chemical Society.

3.2. Morphology-dependent catalysis of CeO₂-supported oxide catalysts

CeO₂ is also widely used as catalyst support in heterogeneous catalysis.^[107] The oxygen vacancies in CeO₂ were found to play a critical role in tailoring the metal/oxide-CeO₂ interactions, which is an important factor to affect structure and catalytic performance of the resulting catalyst. It is therefore regarded as an effective strategy to optimize the metal/oxide-CeO₂ interactions, and thus the structure and catalytic performance of CeO₂-supported metal/oxide catalysts via the morphology engineering strategy of CeO₂ NCs. Previously, the morphology effect of CeO₂ support on the metal/oxide-CeO₂ interactions, structure and catalytic performance of the resulting CeO₂-supported metal/oxide catalysts has been successfully demonstrated and widely reported. The following will introduce them in detail, respectively.

For CeO₂-supported oxide catalysts, different oxides including VO_x,^[57,108] NbO_x,^[109] Fe₂O₃,^[58,110] WO_x,^[111] and CuO_x,^[63,112–116] interacting with CeO₂, and their structures and catalytic performance have been confirmed to be ceria morphology-dependent. Liu *et al.*^[109] presented a comprehensive study of morphology-controlled CeO₂ NCs supported NbO_x catalysts (NbO_x/CeO₂) prepared by conventional wetness incipient impregnation method. The precursor Nb⁵⁺-CeO₂ interaction was proven to affect the surface structures of the resulting NbO_x/CeO₂ catalysts. The monomeric Nb⁵⁺ species interacting with Ce³⁺ (oxygen vacancies) on the CeO₂ surface are reduced to form monomeric Nb⁴⁺ species at low Nb loading, and Nb⁵⁺ then generally grows at the expense of Nb⁴⁺ with the evolution from the monomeric Nb species to the polymeric Nb species and the CeNbO₄ species with the increase of Nb loadings (Figure 6 A and B). For various CeO₂ NCs, the formed monomeric Nb species are most abundant on r-CeO₂-500, while c-CeO₂ is favorable for the formation of monomeric Nb⁴⁺ species. Moreover, the loading of NbO_x suppresses the surface reduction of c-CeO₂ and r-CeO₂-500 but promotes the surface reduction of r-CeO₂-700 (Figure 6 C–E). These results clearly demonstrate morphology-dependent NbO_x-CeO₂ interaction over NbO_x/CeO₂ catalysts. Various CeO₂ and NbO_x/CeO₂ catalysts were evaluated in the oxidative dehydrogenation of propane reaction (ODHP). Bare r-CeO₂-500 and r-CeO₂-700 exhibit similar C₃H₈ conversion and C₃H₆ selectivity, whereas the catalytic activity of c-CeO₂ is negligible. This implies that the CeO₂(110) facets present on both r-CeO₂-500 and r-CeO₂-700 should be the active facets on cata-

lyzing the ODHP reaction. Due to the smallest oxygen vacancy formation energy of CeO₂(110) surface verified previously,^[17-19] the ODHP reaction catalyzed by CeO₂ at low temperatures is suggested to process via the MvK mechanism, in which the oxidation of propane by surface lattice oxygen of CeO₂ is the rate-determining step. After Nb being loaded, the formation of highly dispersive monomeric Nb⁴⁺ species accompanied by the refilling of surface oxygen vacancies likely enhances the activity of neighboring surface lattice oxygen in CeO₂ for the ODHP reaction to facilitate C₃H₆ formation, whereas the formation of other NbO_x species likely decreases the available surface lattice oxygen in CeO₂ for the ODHP reaction. With this regard, a loading of 0.6 Nb/nm² on r-CeO₂-500 can enhance the C₃H₈ conversion at 200 °C quite much.

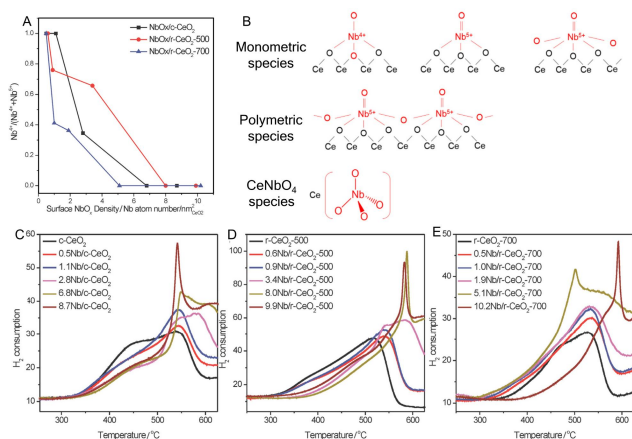


Figure 6 (A) The percentage of Nb⁴⁺ in Nb species (Nb⁴⁺/(Nb⁴⁺ + Nb⁵⁺)) calculated from the integrating Nb⁴⁺ and Nb⁵⁺ XPS peak areas as a function of the Nb loading for the NbO_x/c-CeO₂, NbO_x/r-CeO₂-500 and NbO_x/r-CeO₂-700 catalysts; (B) Proposed NbO_x species on CeO₂. “O” and “O” represent oxygen atoms in CeO₂ and NbO_x, respectively; H₂-TPR profiles of (C) c-CeO₂ and NbO_x/c-CeO₂, (D) r-CeO₂-500 and NbO_x/r-CeO₂-500 and (E) r-CeO₂-700 and NbO_x/r-CeO₂-700 catalysts. Reprinted with permission from Ref. 109, Copyright 2016, Elsevier.

CuO_x/CeO₂ catalyst is a superb candidate in catalyzing the oxidation of CO,^[117-119] in which the catalytic performance has been demonstrated to sensitively depend on the CeO₂ morphology.^[63,112-114] Wang *et al.*^[112] reported that sub-nanometer CuO_x clusters supported on CeO₂{111} facets were more active in catalyzing CO oxidation than those supported on CeO₂{110} facets due to a weakly bound Cu-[O_x]-Ce structure on CeO₂{111} facets. Another typical example is to employ CuO/CeO₂ catalysts with a ~7.5% Cu loading and different CeO₂ morphologies (rods, cubes and polyhedra) to investigate the CeO₂ morphology effect on the structure and catalytic performance in CO oxidation of CuO/CeO₂ catalysts.^[113] The results exhibited the highest catalytic activity emerging on CuO/r-CeO₂ catalyst, which could be ascribed to its abundance of weakly bound oxygen species, relative abundance of defects and oxygen vacancies, and relative population of Cu(I)/Ce(III) redox pairs.

We have also systematically explored the morphology-dependent CuO_x-CeO₂ interaction and catalysis in CO oxidation using CuO_x/CeO₂ catalysts with Cu loadings ranging from 0.025% wt. to 5% wt. and different CeO₂ morphologies (rods, cubes and polyhedra) prepared by the incipient wetness impregnation method.^[63] The results demonstrated that both the Cu loading and the CeO₂ morphology affect the structural evolution of CuO_x species over CuO_x/CeO₂ catalysts (Figure 7A). As the Cu loading increases, isolated Cu ions are formed preferentially on the surface defect of CeO₂ and then aggregate and grow, accompanied by the sequen-

tial formations of the CuO_x clusters strongly/weakly interacting with the CeO₂ support, highly dispersed CuO nanoparticles, and large CuO nanoparticles (Figure 7 A and B). For various CeO₂ morphologies, the CuO_x clusters-CeO₂ interaction depends on the CeO₂ surfaces and follows an order of CeO₂{110} > CeO₂{111} > CeO₂{100}. Moreover, in view of the O-terminated {100} facets exclusively exposed on c-CeO₂ NCs, the isolated Cu ions and CuO_x clusters weakly interacting with the CeO₂ support are mainly formed on CuO_x/c-CeO₂ catalysts. As such, the Cu(I) species in CuO_x/c-CeO₂ catalysts are better stabilized during CO reduction processes than those in CuO_x/r-CeO₂ and CuO_x/p-CeO₂ catalysts.

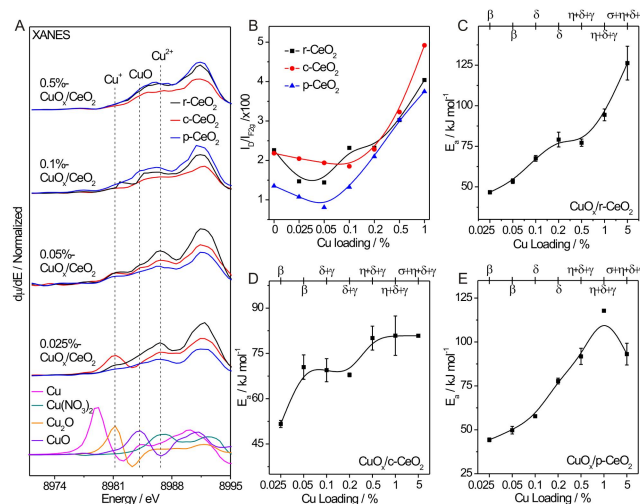


Figure 7 (A) The differentiated spectra of various CuO_x/CeO₂ catalysts derived from the Cu K-edge XANES; (B) The relevance of the I₀/I₂₃ ratio to Cu loading on various CeO₂ and CuO_x/CeO₂ catalysts; The relevance of the calculated E_a value in CO oxidation and Cu loading/structure of CuO_x species on (C) CuO_x/r-CeO₂, (D) CuO_x/c-CeO₂, and (E) CuO_x/p-CeO₂ catalysts. Reprinted with permission from Ref. 63, Copyright 2020, Elsevier.

Catalytic performance of the CuO_x/CeO₂ catalysts in CO oxidation varies with both the structure of CuO_x species and the CeO₂ morphology (Figure 7 C–E). The CO oxidation catalyzed by the CuO_x-CeO₂ interface is determined by the formation of CO₂ by the reaction of CO adsorbed on the Cu(I) sites with the surface lattice oxygen of CeO₂, *i.e.*, the reducibility of CeO₂. With the increase of Cu loading, the density of CuO_x-CeO₂ interface reasonably increases that contributes to the enhancement of catalytic performance, whereas the observably increased E_a values suggest that the intrinsic reactivity of surface lattice oxygen of CeO₂ should be suppressed by CuO_x loaded. It is noteworthy that such a suppressing effect not only depends on the nature of the CuO_x species that presents an order of CuO nanoparticles > CuO_x clusters > isolated Cu ions, but also varies with the morphology of CeO₂ NCs. These results comprehensively elucidate the morphology-dependent CuO_x-CeO₂ interaction and structure-activity relationships of the CuO_x/CeO₂ catalysts in CO oxidation.

3.3. Morphology-dependent catalysis of CeO₂-supported metal catalysts

For CeO₂-supported metal catalysts, the morphology effect of CeO₂ support on the metal-CeO₂ interaction, structure and catalytic performance has been extensively observed on the Au/CeO₂,^[59,120-124] Ag/CeO₂,^[94] Pt/CeO₂,^[95,125-126] Pd/CeO₂,^[60,65,127-129] Ru/CeO₂,^[61,130-132] and Ni/CeO₂^[133-134] catalysts. Zhang *et al.*^[133] prepared a series of Ni/CeO₂ catalysts with controlled CeO₂ morphologies, including c-CeO₂, p-CeO₂, r-CeO₂-500, and r-CeO₂-700,

by the wet impregnation method, which in catalyzing propane oxidation reactions are not only ceria structure-dependent, but also reaction-sensitive. It has been observed that both C_3H_8 combustion and ODHP reactions at low temperatures catalyzed by CeO_2 -involved catalysts follow the MvK mechanism, in which the rate-determining step is generally considered as the oxidation of propane by surface lattice oxygen of CeO_2 .^[135] $r-CeO_2$ -500 exhibits the highest catalytic activity for both reactions that could be attributed to the largest specific surface area and the smallest oxygen vacancy formation energy of CeO_2 (110) surface dominantly exposed.^[17–19] However, the Ni/CeO_2 catalysts in catalyzing the propane oxidation reactions are reaction-sensitive. $Ni/r-CeO_2$ -500 is the most active in catalyzing C_3H_8 combustion, while the most active catalyst in catalyzing ODHP reaction is $Ni/c-CeO_2$. These indicate that the C_3H_8 combustion and ODHP reactions catalyzed by the Ni/CeO_2 catalysts should be associated with different oxygen species.

In H_2 -TPR results (Figure 8 A1–A4), the added Ni particles can greatly promote the reducibility of the resulting Ni/CeO_2 catalysts, on which different Ni species (Ni^{2+} dissolved in CeO_2 , highly dispersive NiO , and NiO aggregate) and oxygen species (strongly/medially/weakly activated oxygen species) were observed. Among various Ni/CeO_2 catalysts, $Ni/c-CeO_2$ catalysts exhibit the strongest $Ni-CeO_2$ interactions. Furthermore, through analyzing the catalytic reaction rate and the amount of oxygen species from H_2 -TPR peak fitting (Figure 8 B1 and B2), it can conclude that the $Ni/r-CeO_2$ -500 catalyst is the most catalytic active in the propane combustion reaction due to the largest strongly activated oxygen species ($\alpha_1 + \alpha_2$), while the $Ni/c-CeO_2$ catalyst exhibits the best catalytic performance in the ODHP reaction due to the largest amount of weakly activated oxygen species (γ and $(\gamma + \gamma')$).

Ceria morphology-dependent Pd- CeO_2 interaction and catalysis in CO_2 hydrogenation into formate have been investigated in our previous literature.^[65] Various Pd/ CeO_2 catalysts with three CeO_2 morphologies (rods, cubes, and polyhedra) and Pd loading of ca. 2% wt. were prepared via a deposition-precipitation method. The Pd- CeO_2 interaction is determined by the oxygen vacancy concentrations, which follow an order of rods > cubes > polyhedra either in CeO_2 or in Pd/ CeO_2 catalysts (Figure 9 A1 and A2). As a result, $r-CeO_2$ with the highest concentration of oxygen vacancy

resulted in the formation of smaller Pd particles (Figure 9 B1–B3) and more positively-charged Pd species in the Pd/ $r-CeO_2$ catalysts (Figure 9C). Various Pd/ CeO_2 catalysts were applied to CO_2 hydrogenation into formate. *In situ* DRIFTS results show that the surface species of bidentate carbonate and bicarbonate are two key intermediates of CO_2 hydrogenation into formate, whose hydrogenation process affected by the electronic structure of Pd species is regarded as the rate-determining step. Metallic Pd species is favorable for the activation and reactivity of H_2 and thus contributes to the enhanced production rate of formate. Consequently, Pd/p- CeO_2 catalyst with the highest content of metallic Pd species exhibits the best performance in formate production, giving a turnover frequency of $746\ h^{-1}$ at $40\ ^\circ C$ (Figure 9D).

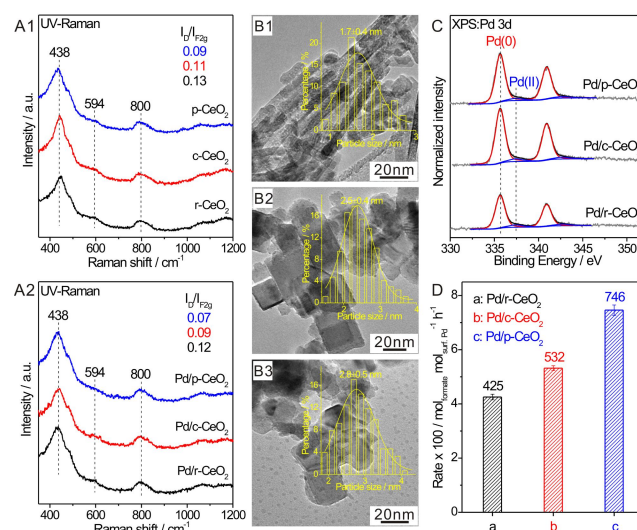


Figure 9 UV-Raman spectra of various (A1) CeO_2 and (A2) Pd/ CeO_2 catalysts; TEM images with corresponding insets of Pd particle size distributions of (B1) Pd/ $r-CeO_2$, (B2) Pd/ $c-CeO_2$, and (B3) Pd/ $p-CeO_2$ catalysts; (C) Pd 3d XPS spectra of various Pd/ CeO_2 catalysts; (D) The formation rate of formate ($mol_{formate} \cdot mol_{surf}^{-1} \cdot h^{-1}$) from CO_2 hydrogenation over various Pd/ CeO_2 catalysts. Reprinted with permission from Ref. 65, Copyright 2021, Elsevier.

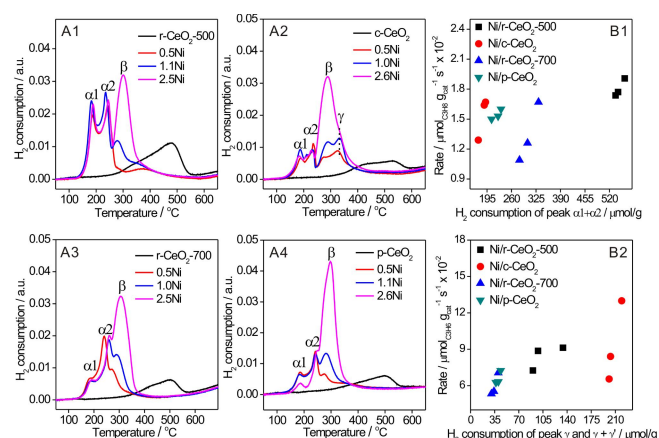


Figure 8 H_2 -TPR profiles of (A1) $r-CeO_2$ -500 and $Ni/r-CeO_2$ -500, (A1) $c-CeO_2$ and $Ni/c-CeO_2$, (A3) $r-CeO_2$ -700, and $Ni/r-CeO_2$ -700, and (A4) $p-CeO_2$ and $Ni/p-CeO_2$ catalysts; (B1) Relationship between the propane oxidation rate at $250\ ^\circ C$ in the propane combustion reaction and the H_2 -consumption values of $(\alpha_1 + \alpha_2)$ peak for various Ni/CeO_2 catalysts; (B2) Relationship between the propene formation rate in the ODHP reaction at $300\ ^\circ C$ and the H_2 -consumption values of γ and $(\gamma + \gamma')$ peaks for various Ni/CeO_2 catalysts. Reprinted with permission from Ref. 133, Copyright 2017, American Chemical Society.

Based on the above results on CeO_2 -supported metal/oxide catalysts, it is well concluded that the oxygen vacancy concentrations and structures of starting CeO_2 support strongly affect the metal/oxide- CeO_2 interactions, and structures and catalytic performance of the resulting oxide/ CeO_2 or metal/ CeO_2 catalysts. On the contrary, the resulting oxide/ CeO_2 or metal/ CeO_2 catalyst structures can also change the oxygen vacancy concentrations and structures of CeO_2 supports. For instance, our previous results clearly demonstrated that the oxygen vacancy concentrations dramatically vary with the supported CuO_x structures over the CuO_x/CeO_2 catalysts.^[63] With the increase of Cu loading (Figure 7B), the oxygen vacancy concentrations slightly decrease when isolated Cu ions are produced at low Cu loadings, whereas the loading of CuO species formed at high Cu loadings could create more defects. Therefore, this is proven to be a facile strategy of fundamental understanding and structural optimization to tune catalytic properties of CeO_2 -based NC model catalysts by the morphology engineering of oxide NCs.

4. Conclusions and Perspectives

In summary, uniform CeO_2 NCs exhibit distinctly morphology-dependent catalysis that is well correlated to their exposed crystal planes and the subsequent surface composition/structure and defect structure/concentration. Through a comprehensive study

in the structure-property relationships of CeO₂-based NC model catalysts, it can be concluded that the oxygen vacancy in the CeO₂ NCs plays a key role in determining not only the catalysis of pure CeO₂ catalysts but also the metal/oxide-CeO₂ interactions, and structure and catalytic performance of the resulting CeO₂-supported catalysts. Moreover, the active structure for a catalytic reaction acquired from the morphology-effect study also subsequently guides diverse morphology-controlled syntheses of CeO₂-involved catalysts with high-performance crystal planes exposed or high-quality metal/oxide-CeO₂ interfaces to tune the catalytic activity and selectivity. These results adequately exemplify the prevailing concept of morphology-dependent catalysis of oxide NCs that become both fundamental and efficient in heterogeneous catalysis.

However, it still should be paid attentions to that the morphology-controlled synthesis of oxide NCs notices not only the regularity of crystal growth but also the size, the complexity of surface composition, and the stability of surface structure. Endeavor of controlling the sizes to small values can easily be understood to increase the active sites, while, to the deeper knowing of active sites, different structures including the terrace, edge, and corner sites, anyway, are all changing dynamically. Some of unsaturated-coordinated sites including edge and corner sites may be favor of catalytic reactivity accompanied by surface defects formation, and thus the morphology-effect study will be ambiguous. Meanwhile, as-synthesized oxide NCs are always containing hydroxyl groups and carbonate species on the surface via the wet-chemistry method, leading to complexity of surface chemistry and catalytic process. In addition, the oxide NCs are facile to undergo surface restructuring under catalytic reaction conditions including oxidative or reductive reactant and exothermic effect, in demand of tracking the surface composition and structure of oxide-based NC mode catalysts before and after catalytic reactions or better conducted with *in situ* study.

With these in mind, oxide NCs as model catalysts are becoming a promising approach in the fundamental understanding of working catalysts at the molecular level. Furthermore, as more and more requirements of selective catalysis, oxide-based NC catalysts exposing a single type of active sites specifically catalyzing the target reaction are an emerging frontier that will be a promising method to realize the structural design and controlled synthesis of novel efficient oxide-based catalysts in the future.

Acknowledgement

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