Engineering well-defined rare earth oxide-based nanostructures for catalyzing C1 chemical reactions

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C1 chemical reactions have attracted extensive attention in recent decades due to their significant roles in energy transfer and utilization and environmental protection. Among the various catalytic materials, rare earth oxide-based nanocatalysts exhibit superior performances in C1 chemical reactions because of their flexible electronic structures and abundant defect states. In this review, we summarize the nanostructural engineering and applications of rare earth oxide-based nanomaterials with well-defined compositions, crystal phases and shapes for efficiently catalyzing C1 chemical reactions. Initially, we introduce the structural features of rare earth oxides. Subsequently, we present common synthetic approaches and nanostructural engineering strategies toward the preparation of rare earth oxide nanomaterials with well-defined structures. Further, we discuss the structure–function correlation of well-defined rare earth oxide-based nanocatalysts in some important C1 chemical reactions including CO oxidation, water-gas shift reaction, CO₂ hydrogenation, methane oxidation and methanol oxidation. Finally, we prospect the challenges and future research trends in this promising field.

1. Introduction

As a type of important strategic resource, rare earth elements include 15 lanthanide elements (La–Lu) and two other elements, scandium and yttrium. They usually co-exist in minerals and have similar properties, which make their separation challenging.¹ Rare earth elements (except for Sc and Y) have partially unfilled 4f orbitals and abundant electronic energy level structures, thus they have flexible coordination numbers and outstanding catalytic properties for many reactions.²,³ Rare earth materials play a significant role in various applications such as agriculture, military, petrochemical industry, metallurgy, glass, and ceramics.⁴,⁵

Nanstructured rare earth oxides are the most common rare earth nanomaterials, which are also the most widely studied.⁶ They are cheap and easily obtained, and they have different oxidation states in various conditions. The earliest report of the synthesis of rare earth oxide nanocrystals with a well-defined architecture dates back to the work of Cao’s group,⁷ which involved the preparation of square Gd₄O₂ nano-plates via a colloidal approach. At almost the same time, Zhang and Yan’s group successively developed various methods for the synthesis of well-defined rare earth oxides with zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) nanostructures.⁸–¹¹ After development for more than 15 years, researchers have developed various synthetic strategies, and successfully prepared many rare earth oxide nanostructures with diverse well-defined morphologies.

Rare earth oxide nanostructures are broadly applied in catalysis, especially heterogeneous catalysis.¹²–¹⁵ On the one hand, rare earth oxide nanostructures by themselves are active for some catalytic reactions such as CO oxidation.¹² However, their activity is usually limited due to the weak adsorption of the reagent molecule. On the other hand, rare earth oxide nanostructures can act as supports or promotors to be combined with other metal or metal oxide catalysts.¹⁴ The catalytic properties of composite materials are significantly enhanced due to the synergistic effect between the support materials and loading elements. Further, they are used more widely in catalysis than single rare earth oxide nanostructures.

Among the catalytic reactions, C1 chemical reactions are crucial for addressing both energy and environmental problems faced by mankind in this century due to their important roles in producing essential chemicals (e.g. methane and methanol) and controlling pollution (e.g. CO and CO₂).¹⁶–¹⁹ Rare earth oxide-based catalysts are a vital class of catalytic nanomaterials for C1 chemical reactions.²⁰,²¹ Thus, the devel-
opment of high-performance rare earth oxide-based catalysts is urgent and significant. Engineering rare earth oxide-based catalysts with well-defined nanostructures is not only beneficial for enhancing their catalytic properties, but also facilitates the study of the relationship between catalytic properties and structure, which can provide guidance for designing catalysts with excellent performances since this is still unclear in many catalytic systems.

Due to the importance of rare earth-based nanomaterials, many groups have reviewed their synthesis and applications in catalysis. For example, Hussein6 published a thermal analysis and applied pyrolysis review about the formation, characterization, and catalytic activity of rare earth oxides. In addition, Zhan et al.3 mainly discussed the catalytic applications of rare earth materials in energy production and utilization, and environmental protection. Guo et al.5 commented on the recent progress on rare earth-based nanomaterials and their catalytic applications of CeO2 nanostructures. Besides, Huang et al.1 reviewed the synthetic routes and electrochemical applications of rare earth-based nanomaterials. Similarly, the review by Gao et al.4 also discussed and summarized the recent progress on rare earth-based nanocatalysts, but their key point was the incorporation of rare earth elements with transition metals. Although rare earth oxide-based nanostructures were a significant part introduced in the abovementioned reviews, few of them focused on the shape-control of well-defined rare earth nanostructures and their catalytic applications in C1 chemical reactions. Besides, most of the reported reviews about rare earth oxides mainly focused on the applications of CeO2 nanomaterials,22−30 and rarely discussed other rare earth oxides. Therefore, a review that systematically summarizes the morphological engineering of nanostructured rare earth oxides (not only CeO2) and highlights their structure−activity correlations in some important catalytic reactions is still necessary.

Thus, to meet this demand, in the present review, we focus on the shape-controlled synthesis of well-defined rare earth oxide nanostructures and their catalytic structure−activity correlations. Herein, we introduce the structure features of rare earth oxides and summarize the most common synthetic routes for the preparation of well-defined rare earth oxide nanostructures from the perspective of their morphologies. Moreover, we choose some typical C1 chemical reactions to summarize the relationship between the engineered nanostructures of the rare earth oxide-based nanomaterials and their catalytic properties.

2. Structural features of rare earth oxides

Generally, rare earth oxides can be divided into two categories, trivalent oxides and tetravalent oxides. Most of the stable rare earth oxides are trivalent except for CeO2, PrO2, and TbO2. The trivalent RE2O3 usually has three types of structures, which are denoted as A, B, and C (Fig. 1a–c, respectively). The A-type RE2O3 is hexagonal, with the P3m1 space group. The RE3+ is seven-coordinated with O, in which six O2− form an octa-

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hedron and the last $O^{2-}$ is located at one of the facets of the octahedron. The B-type RE$_2$O$_3$ is monoclinic, with the $C2/m$ space group. Similarly, the RE$^{3+}$ is also seven-coordinated and six $O^{2-}$ form an octahedron, but the last $O^{2-}$ is a little farther from the RE$^{3+}$. The C-type RE$_2$O$_3$ is cubic, with the $Ia3$ space group. The RE$^{3+}$ is six-coordinated, and the cell structure of C-type RE$_2$O$_3$ is similar to the cubic fluorite structure, in which only two $O^{2-}$ are removed regularly.

REO$_2$ has a cubic fluorite structure, with the $Fm3m$ space group, in which the RE$^{4+}$ is cubic close packing and coordinated with eight $O^{2-}$, and the $O^{2-}$ is located in a tetrahedral void and coordinated with four RE$^{4+}$ (Fig. 1d). The RE in REO$_2$ also has a stable valence of +3, and it can transform between +3 and +4 through the generation and elimination of an oxygen vacancy.

As can be seen in the phase diagram in Fig. 2, RE$_2$O$_3$ (RE = La–Pr) has an A-type structure, RE$_2$O$_3$ (RE = Y, Dy–Lu) has a C-type structure, and the others are C-type at low temperature and become B-type at high temperature.

### 3. Synthesis of well-defined rare earth oxide nanostructures

Thus far, researchers have developed numerous methods for the synthesis of rare earth oxide nanomaterials with well-defined structures, including 0D nanocubes and nanoctahedra, 1D nanorods and nanowires, 2D nanosheets and nanobelts, and 3D dendritic and flower-like structures. Optimized strategies such as selective adsorption on specific facets, pH adjustment, templating and self-assembly are widely used in engineering well-defined rare earth oxide nanostructures. (Fig. 3). Rare earth oxide nanomaterials with different shapes usually have diverse physical and chemical properties due to their distinguishable surface structures and chemical states. Hence, controlling the shapes of rare earth oxide nanostructures will support the realization of different functions and applications. In this section, we mainly summarize the synthesis of well-defined rare earth nanostructures considering their morphologies, with the introduction of some typical synthetic examples. Furthermore, it should be noted that most of the rare earth oxides in the cases we discuss below are cubic structure according to their phase diagram. Actually, cubic fluorite CeO$_2$ is the most studied nanomaterial based on the current research status of rare earth oxides.

#### 3.1 0D rare earth oxide nanostructures

0D nanomaterials are defined as nanocrystals with a nanoscale size in three dimensions. They usually contain nanocubes, nanoctahedra, nanotetrahedra, nanopolyhedra, etc. In general, nanostructures with different morphologies will have diverse exposed crystal planes. For instance, nanocubes have exposed {100} facets, whereas nanoctahedra and nanotetrahedra have exposed {111} facets. The key factor for the preparation of rare earth oxide nanocrystals with specific shapes is controlling the relative crystal growth rate of specific facets during either the anisotropic growth mode or isotropic growth mode.8,33

![Fig. 1](Image1.png)

**Fig. 1** Schematic illustration of the crystal structure of rare earth oxides: (a) A-type RE$_2$O$_3$, (b) B-type RE$_2$O$_3$, (c) C-type RE$_2$O$_3$, and (d) fluorite REO$_2$.

![Fig. 2](Image2.png)

**Fig. 2** Phase diagram of RE$_2$O$_3$.

![Fig. 3](Image3.png)

**Fig. 3** Schematic illustration of the synthesis of rare earth oxide nanostructures with different morphologies.
Taking the synthesis of rare earth oxide nanocubes as an example, Zhang and Yan’s group prepared CeO<sub>2</sub> nanocubes through pH adjustment using a hydrothermal method. The precipitation reaction occurred between Ce(NO<sub>3</sub>)<sub>3</sub> and NaOH, and the secret of gaining CeO<sub>2</sub> nanocubes enclosed with \{100\} facets was applying a high pH and temperature to achieve a fast dissolution-recrystallization process for the transformation of Ce(OH)<sub>3</sub> into CeO<sub>2</sub> particles. In contrast, a slow dissolution-recrystallization process with a low pH and temperature resulted in the formation of CeO<sub>2</sub> nanopolyhedra with \{111\} and \{100\} planes. Besides, the same goal was completed by Dang et al.\textsuperscript{47} using a liquid–liquid interface with the assistance of oleic acid (OLA). As shown in Fig. 4a, \{111\}-dominated CeO<sub>2</sub> nanoctahedra or truncated nanooctahedra were obtained in the water phase initially owing to the lower surface energy of the \{111\} planes, then the OLA selectively adsorbed on the \{100\} planes, resulting in the transfer of the CeO<sub>2</sub> nanoparticles from the water phase to the toluene phase. Because of the coating of OLA on the \{100\} planes, the growth rate of the CeO<sub>2</sub> [100] direction was limited, and finally the CeO<sub>2</sub> nanoparticles turned into nanocubes (Fig. 4b). This was a typical case that using selective adsorption on a specific facet controlled the morphologies of the rare earth oxide nanostructures. Specially, Miao et al.\textsuperscript{48} prepared CeO<sub>2</sub> nanocubes through the doping of F. They concluded that the generation of CeO<sub>2</sub> nanocubes was a result of the etching effect by HF in the crystal growth process.

For the preparation of rare earth oxide nanooctahedra, they are easier to be obtained than nanocubes as a consequence of the lower surface energy of the \{111\} facets than that of the \{100\} facets. They can be facilely produced by tuning the precipitation step in the hydrothermal method.\textsuperscript{2,3} For example, Feng et al.\textsuperscript{33} synthesized CeO<sub>2</sub> nanoctahedra with a size of around 100 nm using the weak base Na<sub>3</sub>PO<sub>4</sub> in the hydrothermal process. The slow growth rate guaranteed the generation of the more stable morphology of nanooctahedra rather than nanocubes. The authors also demonstrated that replacing Na<sub>3</sub>PO<sub>4</sub> with the strong base NaOH would result in the formation of CeO<sub>2</sub> nanospheres and nanocubes. Similarly, CeO<sub>2</sub> nanooctahedra were successfully synthesized by Ren et al.\textsuperscript{49} through the hydrothermal route using Ce(NO<sub>3</sub>)<sub>3</sub> and a relatively small amount of NaOH. Also, they also showed that a high concentration of NaOH could yield nanocubes. Specially, single crystalline CeO<sub>2</sub> nanooctahedra were obtained through galvanostatic electrodeposition in a conventional three-electrode cell.\textsuperscript{50} It was also the first time that CeO<sub>2</sub> nanooctahedra were prepared via the electrochemical route.

In the case of other 0D rare earth oxide nanostructures, nanopolyhedra with no specific shape (called nanoparticles) are common nanomaterials. Their crystal facets usually consist of \{100\} and \{111\} planes, and they are easy to obtain because engineering of their morphology is not required. Furthermore, they can be used as reference samples in the study of the plane effect derived from diverse morphologies and are widely used in applications such as catalysis because of their easy accessibility. For their synthesis, Yang et al.\textsuperscript{51} used the sol–gel method combined with a solvothermal process to obtain CeO<sub>2</sub> nanoparticles with a high surface area. They carried out the solvothermal treatment after they obtained the gel powder, followed by calcination in air to obtain the final product. Additionally, Shiri et al.\textsuperscript{52} synthesized Sm<sub>2</sub>O<sub>3</sub> nanoparticles using a nitrate bath of Sm(NO<sub>3</sub>)<sub>3</sub> via pulse electrochemical deposition assisted by ultrasound. Different from the regular precipitation method, precipitation in reverse microemulsions based on different surfactants was applied to prepare CeO<sub>2</sub> nanoparticles by Shlapa et al.\textsuperscript{53} A schematic of the synthetic route is shown in Fig. 5. Compared with the traditional precipitation method, the precipitation reaction in reverse microemulsions is limited by the surfactant molecules, and the size can be easily controlled by tuning the length of the hydrophilic part of the surfactant. The as-prepared CeO<sub>2</sub> nanoparticles had a small and uniform size in the range of 6–10 nm and showed good catalase-like activity.

### 3.2 1D rare earth oxide nanostructures

Compared with 0D nanostructures, one non-nanoscale dimension is allowed to exist in 1D nanostructures, while the other two dimensions must be on the nanoscale. 1D rare earth oxide nanostructures including nanorods, nanowires and nanotubes are important nanomaterials for catalysis because of their unique exposed crystal planes, abundant defect sites, and good stability, and they can also provide good models for theoretical simulation.\textsuperscript{34,35} In the synthetic strategies for engineering 1D rare earth oxide nanostructures, pH adjustment in the hydrothermal procedure is the most common means because the acid–base balance can influence many key
factors in shape-control such as the crystal growth rate and stability of intermediates.\textsuperscript{34–37}

Furthermore, it should be noted that the hydrothermal method for the preparation of rare earth oxides can be divided into two types, alkali and acid methods. The alkali hydrothermal route is very common, for example, CeO\textsubscript{2} nanorods with a length in the range of 100–300 nm and width of 13–20 nm were firstly prepared by Zhou \textit{et al.}\textsuperscript{34} using Ce(NO\textsubscript{3})\textsubscript{3} and NaOH. The predominantly exposed facets were the unusually active \{001\} and \{110\} planes rather than the \{111\} plane. The authors provided inspiration for designing and controlling the synthesis of nanocrystals with different shapes. Our group\textsuperscript{35} synthesized CeO\textsubscript{2} nanowires \textit{via} the hydrothermal method at 180 °C using CeCl\textsubscript{3} and NaOH without the addition of any capping agent. In the synthetic process, NaCl was specially used to obtain uniform wire-like nanostructures dominantly enclosed by \{110\} facets. We also prepared Ln-doped (Ln = La–Lu) CeO\textsubscript{2} nanowires using the same method, and the distribution of dopant was very homogeneous. The key was the co-precipitation of Ce\textsuperscript{3+} and Ln\textsuperscript{3+} to form Ce(OH)\textsubscript{3}:Ln(OH)\textsubscript{3}, which transformed into CeO\textsubscript{2}:Ln through calcination. The dopant content was about 10%, and the aspect ratio of most of the CeO\textsubscript{2}:Ln nanowires were smaller than that of the pure CeO\textsubscript{2} nanowires due to the difference in the ionic radius between Ce and the dopant ion. As another example, Sohn\textsuperscript{36} successfully synthesized Yb\textsubscript{2}O\textsubscript{3} nanowires and nanorods \textit{via} the hydrothermal method at 210 °C using ammonia water as the precipitant, and YbCl\textsubscript{3} and Yb(NO\textsubscript{3})\textsubscript{3} as the precursor, respectively (Fig. 6). The abovementioned cases indicate that besides the vital role of pH adjustment, the formation of 1D rare earth oxide nanostructures also greatly relies on the transformation of the intermediates. It may be difficult to obtain rare earth oxide nanowires or nanorods directly, but it can be easy to obtain their corresponding hydroxides and transform them into oxides. Acid hydrothermal treatment is less used in the synthesis of 1D rare earth oxide nanostructures. As an example, Pr\textsubscript{2}O\textsubscript{3} nanowires were prepared by Sobahi\textsuperscript{37} using the hydrothermal method by tuning the pH value of the precursor solution of Pr(NO\textsubscript{3})\textsubscript{3} to 1.3 and adding glycine as the shaping reagent.

Rare earth oxide nanotubes are another type of important 1D nanomaterials on account of their high surface area and rich defects. Due to the hollow structure of the nanotubes, templating is a very suitable strategy for their preparation. As an example, Eu\textsubscript{2}O\textsubscript{3} nanotube arrays (Fig. 7a) could be obtained using the sol–gel method assisted by porous anode alumina templates.\textsuperscript{54} According to the synthetic mechanism shown in Fig. 7b, the alumina templates were impregnated in the mixture of Eu(NO\textsubscript{3})\textsubscript{3} solution and urea, and the solution filled the pores of the templates. After heating the solution, the pH value increased owing to the hydrolysis of urea, resulting in the formation of Eu(OH)\textsubscript{3} in both the template pores and solution. The sol particles of Eu(OH)\textsubscript{3} were negatively charged, while the templates were positively charged, and therefore the sol particles gathered at the walls of the templates and gradu-Publish Date: 02 September 2020. Downloaded on 2022-09-20 3:31:40 PM.

Fig. 5 Schematic illustration of the synthesis of CeO\textsubscript{2} nanoparticles \textit{via} precipitation in reverse microemulsions. Adapted with permission from ref. 53. Copyright 2019, Springer Nature.

Fig. 6 SEM images of as-synthesized Yb\textsubscript{2}O\textsubscript{3} (a) nanowires and (b) nanorods. Adapted with permission from ref. 36. Copyright 2018, Elsevier.

Fig. 7 (a) TEM image of Eu\textsubscript{2}O\textsubscript{3} nanotubes. (b) Schematic illustration of the formation mechanism of Eu\textsubscript{2}O\textsubscript{3} nanotubes. Adapted with permission from ref. 54. Copyright 2004, American Chemical Society.
ally extended to the center. Finally, the templates were removed from the sol solution and sintered in a furnace, generating Eu2O3 nanotubes. As another example, Tb2O3 nanotubes were synthesized by Tang et al.55 through the hydrothermal method using terbium chloride as the precipitant and sodium dodecyl benzenesulfonate as the template reagent. Tb(OH)3 nanotubes were initially obtained via the hydrothermal process after adjusting the solution pH to 12 with NaOH. Finally, they calcined the Tb(OH)3 nanotubes at 800 °C under a reducing atmosphere and obtained Tb2O3 nanotubes. Interestingly, Tb2O3 nanotubes could also be synthesized through a facile precipitation method using Tb(NO3)3 and ammonia.56 The precipitation process involved aging at room temperature for two days, which was necessary for the formation of the tube-like structure under a slow growth rate.

3.3 2D rare earth oxide nanostructures

Similar to the definition of 0D and 1D nanostructures, 2D nanostructures allow the existence of two non-nanoscale dimensions, and thus they usually contain nanosheets, nanoplates, nanobelts, etc. 2D rare earth oxide nanocrystals have many advantages for catalytic applications such as huge surface area, a variety of defects, and high atomic utilization owing to their thin structure.57–59 However, it is challenging to prepare 2D rare earth oxide nanomaterials due to the complex requirement of anisotropic growth. In general, a relatively slow growth rate of a specific crystal plane is preferred to realize anisotropic morphologies.

Nanoplates are well-known nanomaterials among the 2D rare earth oxide nanostructures, which have been successfully synthesized via several methods.57,59 The first reported synthetic work on 2D rare earth oxide nanocrystals was the Gd2O3 square nanoplates prepared by Cao7 using a solution-phase decomposition method. Soon afterwards, Zhang and Yan’s group9,10 prepared a series of cubic rare earth (RE = La–Lu,Y) oxide nanoplates or nanodisks via a non-hydrolytic route using various rare earth complexes as precursors with the assistance of oleylamine (OM), oleic acid (OA) and 1-oleadecene (ODE). Our group carried out control experiments to determine the specific effects of different experimental parameters. As shown in Fig. 8a, the whole shape evolution can be divided into two parts. Firstly, the rare earth oleates are formed through ion exchange with OA in solution. Secondly, decomposition of the rare earth oleates occurs via the catalysis of OM. Due to the selective adsorption of OA on the {100} planes, the RE2O3 crystals can realize anisotropic growth to generate 2D structures. Also, they would result in diverse morphologies because of the difference in growth rate, which is affected by the rare earth precursors. As another illustration, La2O3 nanoplates were obtained by Wu et al.60 via a combination of precipitation and calcination using La(NO3)3 and formamide. In the precipitation process, La(OH)3 nanoparticles were formed through nucleation and aggregated (Fig. 8b). Then they grew into 1D La(OH)3 nanorods because hexagonal La(OH)3 has an anisotropic crystal structure. During the calcination step, the –OH groups were removed and the nanocrystals underwent reconstruction to achieve the lowest surface energy. Consequently, the La(OH)3 nanorods transformed into hexagonal La2O3 nanoplates under the driving force of calcination. The high-resolution TEM (HRTEM) results showed the {002} exposed facet, suggesting that preferential growth occurred along the [002] direction.

In the case of engineering of rare earth oxide nanosheets, Hu et al.61 synthesized leaf-like CeO2 nanosheets mainly enclosed with {111} and {200} facets via the hydrothermal method using Ce(NO3)3 as the precursor, NH4HCO3 as the precipitant, and ethylenediamine as the complexant. As displayed in Fig. 8c, the product evolution could be divided into three stages. In the first stage, Ce3+ reacted with NH4HCO3 and generated a large amount of Ce(OH)2CO3 nanoparticles, which aggregated to form fluffy particles through self-assembly. Afterwards, nanorods and nanosheets emerged due to the dissolution-recrystallization and self-assembly of the fluffy particles. In the last stage, the nanorods continued to grow until the formation of leaf-like nanosheets. In the whole process, ethylenediamine was coordinated with Ce3+ and controlled the release of Ce3+, thus further controlling the crystal growth.

![Diagram of the formation mechanism of RE2O3 nanoplates and nanodisks](image-url)
direction to form nanosheets. Similarly, Dai et al.\textsuperscript{62} obtained CeO\textsubscript{2} nanobelts using Ce(NO\textsubscript{3})\textsubscript{3} and NH\textsubscript{4}HCO\textsubscript{3}, but they did not add ethylenediamine or any other reagents. As an alternative, they selected a low temperature of 30 °C to carry out the precipitation reaction in order to obtain an adequately slow growth rate for the formation of sheet-like nanostructures. As a supplement, the electrochemical method is also good for synthesizing 2D rare earth oxides. For example, Huang et al.\textsuperscript{18} obtained Eu-doped CeO\textsubscript{2} nanosheets through electrodeposition on a Ti substrate and subsequent calcination in N\textsubscript{2}. However, the formation mechanism was unclear and needs more exploration.

Rare earth oxide nanobelts is another type of 2D nanomaterials that are promising candidates for the fundamental study of physical and chemical properties in many fields.\textsuperscript{63,64} However, they are difficult to synthesize due to the preference to form 1D nanostructures or other nanocrystals with lower anisotropy. Some groups successfully achieved their synthesis through the solvothermal method, which is suitable for crystal shape control.\textsuperscript{63,64} For example, Eu-doped single-crystal Y\textsubscript{2}O\textsubscript{3} nanobelts with an average thickness of ca. 10 nm and width of 40–100 nm were obtained by Li et al.\textsuperscript{63} using a simple solvothermal method without the addition of any templates. The key factors for controlling the belt-like shape and size were the initial pH of the solution and reaction time of the solvothermal process. As another example, Rao et al.\textsuperscript{64} obtained mesoporous CeO\textsubscript{2} nanobelts via the hydrothermal method, and subsequent calcination without any template or surfactant. The authors researched the effect of the experimental conditions in the hydrothermal process on morphologies of the CeO\textsubscript{2} precursors, and they found that the temperature, ionic type of alkali and ratio of alkali/Ce contributed to the final shape of the products (Fig. 9a–e). Fig. 9f further illustrates the possible formation mechanism of the mesoporous CeO\textsubscript{2} nanobelts. Briefly, colloidal Ce(OH)\textsubscript{3} nuclei were initially formed, followed by dissolution-recrystallization in a mixture of OH\textsuperscript{−} and HCHO. Formates and carbonates were generated in the solution via the disproportionation reactions between OH\textsuperscript{−} and HCHO, and they could coexist due to the high concentration and small radius of Na\textsuperscript{+}, which was vital for the anisotropic growth to form belt-like nanostructures. During the calcination of the nanobelt precursors, they transformed into polycrystalline CeO\textsubscript{2} nanobelts and a mass of pores was generated via the decomposition of formates and carbonates, leaving sodium oxide on the surface. After washing with water, the final mesoporous CeO\textsubscript{2} nanobelts with a thickness of 10–30 nm and a width of 50–250 nm (Fig. 9g) were obtained. Since rare earth oxide nanobelts are similar to 1D nanostructures to a certain degree, the electrospinning method is also suitable for the preparation of rare earth oxide nanobelts. As an example, Eu\textsubscript{2}O\textsubscript{3} nanobelts with a uniform size were obtained via the electrospinning process.\textsuperscript{65}

### 3.4 3D rare earth oxide nanostructures

3D nanostructures can be regarded as composites of 0D, 1D, and 2D nanomaterials. 3D rare earth oxide nanostructures play a significant role in catalytic applications mainly because of three advantages.\textsuperscript{11,66–68} First, they usually have good robustness in catalytic processes due to their anti-sintering ability, which is attributed to their large size. Secondly, they possess a large surface area since they consist of small units such as nanoparticles and nanosheets. Thirdly, they are rich in defects and high-index facets due to the oriented attachment of the tiny building blocks. However, unlike 0D, 1D and 2D nanostructures, the 3D rare earth oxide nanostructures hardly have regular morphologies. They have well-known structures such as dendrites and flowers, but most of them are original nanomaterials.\textsuperscript{66–69}

As an instructive work, CeO\textsubscript{2} nanoflowers obtained via the rapid thermolysis of (NH\textsubscript{4})\textsubscript{2}Ce(NO\textsubscript{3})\textsubscript{6} in a mixture of OA/OM were reported by Zhang and Yan’s group.\textsuperscript{11} The ceria clusters
capped with OA and OM were generated as a result of the hydrolysis of (NH₄)₂Ce(NO₃)₆ at a low temperature (<220 °C). When the temperature increased to above 220 °C, the capping agents on the surface of the ceria particles disappeared quickly through the redox reaction. Consequently, the small particles spontaneously aggregated via 3D oriented attachment and generated CeO₂ nanoflowers. Self-assembly is often chosen for the construction of 3D rare earth oxide nanostructures, whose driving force is the hydrophobic effect of the surfactants adsorbed on the nanocrystals. For instance, ultra-thin nanodisks of Sm₂O₃ and hierarchical flower-like Gd₂O₃ surfactants adsorbed on the nanocrystals. For instance, ultra-thin nanodisks of Sm₂O₃ and hierarchical flower-like Gd₂O₃ surfactants adsorbed on the nanocrystals. For instance, ultra-thin nanodisks of Sm₂O₃ and hierarchical flower-like Gd₂O₃ surfactants adsorbed on the nanocrystals. 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The CO oxidation reaction (CO + O₂ → CO₂) is often used as a probe reaction to study the structure–activity relationship of catalysts owing to its simple reaction formula and mechanism. Besides, it also has applied value in practical applications such as automobile tail gas purification, CO sensors, and indoor air purification. For the mechanism of the CO oxidation reaction, the Mars-van Krevelen mechanism is accepted by most researchers, that is, a CO molecule reacts with the lattice oxygen of the oxide and in situ generates an oxygen vacancy, and then the oxygen molecule fills the vacancy and finishes the cycle. Consequently, oxygen vacancies play a vital role in the catalytic CO oxidation reaction, which are abundant in many rare earth oxide nanomaterials.

Obviously, rare earth oxide nanomaterials can independently catalyze the CO oxidation reaction without modulation with other non-rare earth metals, and their performance is closely correlated with their morphologies. As an example, the CeO₂ nanorods synthesized by Zhou et al. exhibited a T₅₀ (temperature of 50% CO conversion) of 186 °C towards CO oxidation, which is much lower than that of CeO₂ nanoparticles. The enhanced activity was ascribed to the well-defined reactive {001} and {110} planes. Our group implemented the dimension-manipulated synthesis of CeO₂ nanostructures and obtained 0D uniform crystals, 2D polycrystalline assembly, and 3D mesoporous framework. The 2D polycrystalline assembly sample showed the highest activity (T₅₀ = 310 °C) for CO oxidation, while the 3D mesoporous framework had the lowest activity (T₅₀ = 390 °C), and all three nanocatalysts were much more active than bulk CeO₂. In addition, Kang et al. prepared hexagonal Pr(OH)₃ and cubic Pr₆O₁₁ nanorods and tested their activity for CO oxidation. The Pr(OH)₃ nanorods had a T₁₀ (temperature of 10% CO conversion) of 525 °C in the first run and then transformed into Pr₆O₁₁ nanorods after the first run. Subsequently, in the second run, the T₁₀ was 465 °C due to the transformation from Pr(OH)₃ to Pr₆O₁₁. Although their activity was lower than that of commercial catalysts, they can be applied in catalysis and sensing. As another example, Zhang et al. synthesized 3D ordered porous Pr₆O₁₁ and Tb₂O₃ using a hard template method. The Pr₆O₁₁ and Tb₂O₃ nanostructures showed a T₅₀ of 305 °C and 360 °C, respectively, which were much more active than commercial Pr₆O₁₁ (550 °C). The enhanced activity may have originated from their large surface area, abundant oxygen vacancies, and higher low-temperature reducibility.

Doping is a common strategy for enhancing the catalytic activity of rare earth oxide nanomaterials. For instance, the CeO₂ nanowires prepared by our group could catalyze the CO oxidation reaction with a T₅₀ of 350 °C, which may be ascribed to the facile formation of oxygen vacancies in the CeO₂ {110} facet. We successfully doped lanthanide elements in the CeO₂ nanowires (Fig. 12a) to enhance the activity of CeO₂, and the most active sample of Nd-doped CeO₂ nanowires showed an order of magnitude higher activity (TOF at 200 °C = 5.4 × 10⁻⁴ s⁻¹) than that of the pure CeO₂ nanowires (TOF at 200 °C = 4.1 × 10⁻⁵ s⁻¹, Fig. 12b). We also found that the big difference in the activity of the doped catalysts was derived from two aspects. On the one hand, the oxygen vacancy formation energy of the light rare earth-doped samples was much lower than that of the heavy rare earth-doped samples (Fig. 12c), indicating that the former had more oxygen vacancies, which...
are beneficial for the catalytic activity. On the other hand, the concentration of the active intermediates of unidentate carbonates was also crucial for governing the activity, and Fig. 12d exhibits that CeO$_2$:Nd had the largest amount of these active species. These two factors together resulted in the volcano-like relationship between the catalytic activity and the ionic radius of the dopant elements. Similarly, Li et al.\textsuperscript{76} also demonstrated that doping with La remarkably enhanced the catalytic activity of CeO$_2$ for the CO oxidation reaction with a $T_{50}$ of 245 °C because the formation of non-stoichiometric Ce$_{1-x}$La$_{x}$O$_{2-δ}$ increased the formation of oxygen vacancies, and the optimal value of $x$ is 0.5. Besides doping to boost the concentration of oxygen vacancies in rare earth oxides, reduction treatment is also a suitable method for obtaining higher activity for the CO oxidation reaction. As an example, Gao et al.\textsuperscript{77} enhanced the activity of as-prepared CeO$_2$ nanorods via chemical redox etching with ascorbic acid.

According to the above examples, it can be concluded that single rare earth oxide nanocatalysts have limited activity for the CO oxidation reaction, and thus the introduction of other metals and engineering the local metal–support structure is a valid and common strategy for boosting their activity, in which rare earth oxide nanomaterials can act as a support.\textsuperscript{77–79} For example, our group\textsuperscript{77} systematically investigated the effect of the local coordination structure of Pt/CeO$_2$ nanocatalysts on their activity for CO oxidation. We prepared Pt/CeO$_2$ catalysts with different Pt–O coordination numbers by tuning the reduction temperature of the samples. A decrease in the activity of the catalysts was observed with an increase in the Pt–O coordination number, and the most active sample had a TOF at 50 °C of 2.0 × 10$^{-2}$ s$^{-1}$. The Pt atoms were over-stabilized at the catalyst surface, resulting in the inactivation of some of the Pt atoms when the Pt–O coordination number kept increasing, and thus the activity of the catalyst decreased. Specifically, it was the local structural effect that determined the catalytic performance. As another example, Huang et al.\textsuperscript{78} prepared Pr$_x$O$_{11}$ nanorods with a diameter of 20–40 nm and length of several microns using a hydrothermal method. They found that the pure Pr$_x$O$_{11}$ nanorods were not active for CO oxidation until 220 °C. However, when they loaded gold nanoparticles with a size of 8–12 nm on the surface of the Pr$_x$O$_{11}$ nanorods, the composites could achieve 100% CO conversion at 140 °C, and were also much more active than the Au/Pr$_x$O$_{11}$ bulk. Similarly, Zhang et al.\textsuperscript{79} synthesized and studied nanostructured Ag/Pr$_x$O$_{11}$ for CO oxidation. The authors prepared Pr$_x$O$_{11}$ nanorods and nanoparticles using different routes, and utilized them as supports to couple with Ag species via the conventional impregnation method (Fig. 13a). The XPS results indicated that the Ag/Pr$_x$O$_{11}$ nanorods possessed more oxygen vacancies than that of the Pr$_x$O$_{11}$ nanoparticles (Fig. 13b). Besides, the H$_2$-TPR profiles showed a stronger synergistic effect between Ag and Pr$_x$O$_{11}$ in the Ag/Pr$_x$O$_{11}$ nanorods (Fig. 13c), suggesting higher activity for this catalyst. As expected, the Ag/Pr$_x$O$_{11}$ nanorods showed a better performance than the Ag/Pr$_x$O$_{11}$ nanoparticles for CO oxidation, where the $T_{50}$ of the Ag/Pr$_x$O$_{11}$ nanorods was around 125 °C (Fig. 13d and e).

The well-known shape effect of rare earth oxide nanostructures also has a vital influence on the catalytic activity for
CO oxidation when they act as a support. Taking the work of Lykaki et al. as an example, they prepared CeO$_2$ nanorods (NR), nanopolyhedra (NP), and nanocubes (NC) via the hydrothermal method, and explored the shape effect of Cu/CeO$_2$ on their catalytic properties. The results of the catalytic test showed that the activity ($T_{50}$) of both the pure CeO$_2$ and Cu/CeO$_2$ followed the same order of NR (320/72 °C) > NP (350/83 °C) > NC (385/92 °C). The authors used multiple characterizations to investigate the structure–function correlation, and found that the activity had a direct correlation with the amount of Cu$^+$ and oxygen defects. They proposed the reaction mechanism based on the Mars-van Krevelen mechanism, which highlighted the significant roles of oxygen vacancies and Cu$^+$ in this benchmark reaction. Furthermore, it is known that the shape effect is equal to the plane effect. Also, NR have mainly exposed {110} and {100} facets, while NP are enclosed with {111} and {100} facets, and NC have exposed {100} facets. Therefore, the CeO$_2$ {110} planes were beneficial for CO oxidation due to their easy generation of oxygen defects.

In general, the nanostructural engineering of rare earth oxide-based catalysts for the CO oxidation reaction is mainly focused on the tuning of oxygen vacancies, the effect of which mainly embodied in stabilizing the metal loading on the surface of the rare earth oxides and providing sites for the adsorption and activation of O$_2$. Also, the strategies for modulating oxygen vacancies usually involve reduction treatment, doping, controlling the size and morphology, etc. Besides, other factors such as the surface area and metallic oxidation state of the rare earth oxide-based catalysts also have a significant effect on the catalytic performance. Thus, researchers should consider all these factors in the design of catalysts with excellent properties for CO oxidation.

4.2 WGSR

The WGSR (CO + H$_2$O → CO$_2$ + H$_2$) is mainly used for converting CO to CO$_2$ and H$_2$ in syngas, which has important application value in hydrogen production, fuel cells and ammonia synthesis. Most of the catalysts for the WGSR are supported nanomaterials since single materials hardly exhibit activity. Rare earth oxide nanomaterials are widely used as a support for the WGSR due to their good stability and abundant oxygen vacancies, which are significant for stabilizing the metal loading and activating H$_2$O molecules. Also, a good way for improving the catalytic performance is through tuning the morphologies of rare earth oxides since the shape effect is also important for the WGSR.

Among the various catalytic systems, noble metals such as Au and Pt supported by well-defined rare earth oxide nanomaterials have been extensively applied for the WGSR because of their high activity and good stability. For example, Si et al. investigated the catalytic performance of Au/CeO$_2$ with nanorod, nanoplane and nanopolyhedra structures. They found that the WGSR performance strongly depended on the exposed facets, and the sample of Au/CeO$_2$ nanorods showed the highest activity among the three samples. This could be explained by the lowest anion vacancy formation energy on the {110} planes, which meant more oxygen vacancies boosted the catalytic activity. As another example, Fu et al. prepared two types of Au/CeO$_2$ catalysts, including Au nanoclusters (<2 nm) and Au nanoparticles (3–4 nm), for the WGRS (Fig. 14a and b, respectively). Specially, the Au nanoclusters were in situ generated in the reaction process from Au single atoms. The Au nanoclusters showed higher activity (rate at 200 °C = 5.0 × 10$^7$ mol g$^{-1}$ s$^{-1}$) compared with that of the Au particles (rate at 200 °C = 1.0 × 10$^7$ mol g$^{-1}$ s$^{-1}$) because of their more abundant interfacial sites (Fig. 14c). The results of in situ Raman spectroscopy demonstrated that the oxygen vacancies were involved in the catalytic reaction, which were the most abundant in the Au cluster/CeO$_2$ sample (Fig. 14d). The authors also performed in situ infrared spectroscopy (IR) to investigate the adsorbed oxygen vacancies, and they found that the bridged –OH group was essential for the conversion of the CO adsorbed on the Au$^{6+}$ species to CO$_2$, which was verified by the isotopic labelling experiment, where one of the O atoms in CO$_2$ came from the bridged –OH group (Fig. 14e). Fig. 14f shows the whole cycle of the catalytic process, where H$_2$O was activated at the oxygen vacancy and generated a bridged –OH group in the first stage, then the bridged –OH group reacted with the CO adsorbed on the Au$^{6+}$ species to produce CO$_2$ in the second stage, and finally the CO$_2$ desorbed and left a new oxygen vacancy. The moderate Au$^{6+}$ species, bridged –OH group and oxygen vacancies were essential in the WGSR.

The use of non-Ce rare earth oxides for supporting noble metals has been less applied in the WGSR compared with CeO$_2$. For instance, novel Au/La$_2$O$_3$ and Au/La$_2$O$_3$SO$_4$ catalysts for the low-temperature WGSR were synthesized by Lessard et al. through an anion adsorption method. They found that both Au/La$_2$O$_3$ and Au/La$_2$O$_3$SO$_4$ had a good WGSR activity, and Au/La$_2$O$_3$SO$_4$ showed higher activity compared with that of Au/La$_2$O$_3$, which might be because of its higher content of Au$^{3+}$, as confirmed by the X-ray photoelectron spectroscopy (XPS) results. Besides, the authors carried out chemical leaching of the catalysts using NaCN, and the leached samples exhibited no difference in activity, indicating that the support of La$_2$O$_3$ and La$_2$O$_3$SO$_4$ could well stabilize the Au species. Besides, Pt supported by a composite oxide of Ce$_{0.6}$Y$_{0.4}$O$_2$ for the WGSR was obtained by Lee et al. via a sol–gel method. As can be seen in Fig. 15a, the activity of Pt/Ce$_{0.6}$Y$_{0.4}$O$_2$ (TOF at 250 °C = 5.5 × 10$^{-1}$ s$^{-1}$) was much higher than that of both Pt/CeO$_2$ (TOF at 250 °C = 1.6 × 10$^{-1}$ s$^{-1}$) and Pt/Y$_2$O$_3$ (TOF at 250 °C = 1.3 × 10$^{-2}$ s$^{-1}$), and also higher than that of many reported Pt-based WGSR catalysts. The H$_2$-TPR results (Fig. 15b) showed that the introduction of Y to CeO$_2$ obviously enhanced the reducibility and the oxygen mobility of the support. Furthermore, the CO-TPR profiles indicated that there were much more OH species in the Pt/Ce$_{0.6}$Y$_{0.4}$O$_2$ sample than the other two catalysts (Fig. 15c and d), which are beneficial for the WGSR. The authors also performed diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to explore the surface reactions on these catalysts (Fig. 15e). The results clearly showed that the CO adsorption on Pt/Ce$_{0.6}$Y$_{0.4}$O$_2$ was weaker than that on Pt/CeO$_2$ and Pt/Y$_2$O$_3$, indicating its more
efficient activation of CO. In general, the enhanced reducibility of the support and reduced CO adsorption contributed to the higher activity.

Although supported noble catalysts have superior catalytic properties for the WGSR, their high price limits their large-scale application. Accordingly, nowadays, many researchers aim to use a base metal in the nanostructural engineering of catalysts to obtain high performances for the WGSR. For instance, Ren et al. studied the plane effect on the activity of Cu/CeO₂ catalysts for the WGSR. The results showed that the Cu catalysts supported on CeO₂ nanooctahedra with {111} facets were more active than that of supported on nanorods and nanocubes, which could be attributed to the best dispersion of Cu, strongest Cu–CeO₂ interactions and the largest amount of Cu species with a moderate valence. She et al. studied the doping effect of RE₂O₃ (RE = Y, La, Sm, Nd) on the WGSR activity of CuO/CeO₂ catalysts. The evaluation of their catalytic performance showed that the introduction of La₂O₃ and Nd₂O₃ was beneficial for enhancing the activity and stability of CuO/CeO₂, but the doping of Y₂O₃ and Sm₂O₃ exhibited negative effects. The Raman spectra showed that the CuO/CeO₂–La₂O₃ and CuO/CeO₂–Nd₂O₃ samples had more oxygen vacancies than CuO/CeO₂, while that of the Y and Sm-doped samples were less. Besides, the authors measured the Cu dispersion using N₂O and found out that the order of Cu dispersion was consistent with the order of activity. The H₂-TPR results showed three peaks for non-crystalline copper oxide, moderate copper oxide (crystalline) and surface ceria. Interestingly, the order of the peak area for moderate copper oxide was also consistent with that of activity. In summary, the difference in activity mainly originated from the concentration of oxygen vacancies, Cu dispersion, and moderate Cu valence. Another Cu/CeO₂ catalyst for the WGSR was synthesized by Chen et al. using a co-precipitation method. In order to improve the activity, the authors attempted to calcine the catalyst at 300 °C in air, vacuum and H₂. They found that the catalyst annealed in H₂ had the highest performance due to the highest amount of oxygen vacancies and strongest synergistic interaction between CuO and CeO₂.

Based on the research thus far, it can be concluded that rare earth oxide nanomaterials are rarely used alone for the WGSR on account of their weak adsorption of CO. They are always used as a support and additive to improve the catalytic performance through the construction of well-defined structures and controlling the electronic and geometric structure of the catalysts. The effects of rare earth oxide nanomaterials are mainly reflected in dispersing metal catalysts, providing active sites such as oxygen vacancies and enhancing the metal support interaction and synergistic effect.

4.3 CO₂ hydrogenation reaction

The CO₂ hydrogenation reaction is not a specific reaction since it has several possible products, such as CO, methane and methanol. It is a significant reaction because it not only can weaken the greenhouse effect, but also ease the energy crisis. However, the high chemical stability of the CO₂ molecule and...
the complexity of its products are a big challenge for catalysts for this reaction. The abundant electronic structures and flexible oxidation states of rare earth oxide nanomaterials are beneficial for the CO2 hydrogenation reaction, which is ascribed to their facile activation of CO2 and selectivity control.92 Nevertheless, pure rare earth oxides are less used for catalyzing this reaction due to their poor activity. Here, we summarize the nanostructural engineering of rare earth oxide nanomaterials utilized in the CO2 hydrogenation reaction according to the different products.

The CO2 methanation reaction is also known as the reverse water gas shift (RWGS) reaction (CO2 + H2 → CH4 + H2O) when the product is methane. Although this reaction is thermodynamically preferred, the 8-electron reduction process is a big hindrance for obtaining high activity and selectivity. Thus, engineering the morphologies of rare earth oxides to obtain well-defined structures is beneficial to solve this problem. For example, our group96 synthesized three types of catalysts containing Ru single atoms, nanoclusters and nanoparticles supported by...
CeO2 nanowires for the CO2 methanation reaction. We found that the sample of Ru nanoclusters showed the highest activity (TOF at 190 °C = 7.4 × 10^{-3} s^{-1}), which was also much higher than that of other reported Ru/CeO2 catalysts. Unexpectedly, the order of activity was not consistent with that of the concentration of oxygen vacancies. According to our investigation, the strong metal support interaction (SMSI) decreased with an increase in the Ru size and facilitated the removal of H2O. Accordingly, the competition between the SMSI and H-spillover effect together determined the activity of the Ru/CoO2 catalysts (Fig. 16b). In the case of other rare earth oxides used in CO2 methanation, Ilsemann et al.97 obtained novel Sm3O5-Ni xerogel catalysts through the sol-gel method for the CO2 methanation reaction. The optimal loading of Ni was in situ active sites. The authors also performed sites of the Cu easy transformed into CO. In brief, it was the synergistic basic (Fig. 17e), which were stable on the catalyst surface and not seen in Fig. 17d, which suggested that Cu^6+ species were the active sites. The authors also performed in situ DRIFTS to reveal the reaction mechanism, and they found that the HCOCO and CHO species were the main active intermediates (Fig. 17e), which were stable on the catalyst surface and not easy transformed into CO. In brief, it was the synergetic basic sites of the Cu^6+ species tuned by the structure of the metal-support interface that contributed to the high activity. Some groups used rare earth oxide as promoters to adjust the catalyst structure for CO2 hydrogenation to methanol and obtained positive results.104,105 For instance, Ban et al.104 verified that the using of La and Ce as promoters boosted the methanol production of CuZnZr catalyst, especially Ce. However, the introduction of Pr and Nd as additives decreased the activity. The opposite effect of the different rare earth promoters on activity was mainly due to the enhanced synergistic effect and H2 adsorption caused by the addition of La and Ce, which were not found in the catalysts with Pr and Nd as additives. Similarly, Kourtelesis et al.105 found that La2O3 could promote 30% of the methanol yield for the CuO/ZnO/Al2O3 catalyst. La2O3 could be facilely introduced by a coprecipitation method, and the enhanced methanol yield could be attributed to enhanced adsorption of CO2 and active intermediates.

Considering the complexity of the product of the CO2 hydrogenation reaction, the choice and design of catalysts must be based on selectivity and avoiding side reactions. Thus, reasonably engineering catalysts with well-defined structures is vital. Based on the reported works, using rare earth oxide nanomaterials in the CO2 hydrogenation reaction as support or promoter can usually enhance the adsorption of CO2 and metal support interactions, which will result in improved activity and selectivity.
4.4 Methane oxidation reaction

Methane is an important resource due to its applications such as fuel and chemical synthesis. The methane oxidation reaction can be divided into two types, total oxidation and partial oxidation. The total oxidation of methane can be used for energy and heat production or solving the global warming caused by methane. The partial oxidation of methane can produce syngas for further utilization. Rare earth oxide nanomaterials are widely applied in both reactions as supports or promoters.

In the total oxidation of methane, CeO₂ is often used as a catalyst support on account of its high concentration of oxygen vacancies. Also, the well-defined structures of CeO₂-based catalysts are conducive for catalytic activity. For instance, Co₃O₄ nanoparticles supported by CeO₂ nanorods (Fig. 18a and b) for methane combustion were synthesized by Dou et al. using a deposition precipitation method. The catalyst of Co₃O₄/CeO₂ (T₅₀ = 475 °C) was found to be much more active than pure Co₃O₄ and CeO₂ due to the synergistic effect between Co₃O₄ and CeO₂, and also the activation energy, which was also much lower in the case of Co₃O₄/CeO₂ (Fig. 18c and d). Pd-based nanomaterials are some of the most effective catalysts for the total oxidation of methane, and using rare earth oxides as a support can be further beneficial due to their unique redox properties. As an example, Ozawa et al. tested the influence of the addition of La₂O₃ and Nd₂O₃ to PdO/Al₂O₃ for the combustion of methane. They found that adding La₂O₃ or Nd₂O₃ alone had an effect of stabilizing Al₂O₃ and enhancing the activity. However, when the authors introduced both La₂O₃ and Nd₂O₃ to PdO/Al₂O₃, they observed reduced activity and an extended lifetime. Besides, this group also investigated the stabilizing effect of La₂O₃, Nd₂O₃, and ZrO₂ on PtPdO/Al₂O₃ for methane combustion. Similarly, the introduction of both La₂O₃ and Nd₂O₃ prevented the deactivation of the catalyst, but the addition of ZrO₂ caused deactivation. Also, the addition of all three oxides resulted in the longest lifetime among the catalysts. As another example, Danielis et al. prepared Pd-embedded CeO₂ catalysts via a dry ball-milling method. The Pd–CeO₂ catalysts showed a core–shell structure, in which the shell consisted of Pd and CeO₂. The as-prepared catalyst could activate methane at a much lower temperature (T₁₀ = 291 °C) compared with that with the conventional Pd/CeO₂ catalyst (T₁₀ = 346 °C) synthesized by impregnation (Fig. 18e). The superior performance was ascribed to the creation of highly active and stable sites due to the robust contact between Pd and CeO₂.

In the partial oxidation of methane reaction, 1D rare earth oxide nanostructures are often used. For instance, Zhu et al. prepared a core–shell Ni/nanorod-CeO₂@SiO₂ catalyst using a microemulsion method. The as-prepared catalyst showed better activity and stability than that of Ni/nanorod-CeO₂ and Ni@SiO₂, benefitting from the greater amount of oxygen vacancies and stronger anti-sintering of Ni particles derived from the enhanced metal–support interactions. Even after testing at 750 °C for 140 h, the catalyst maintained a CH₄ conversion of 86% and CO selectivity of 94%. Besides, Ru nanoparticles supported over Ce₀.₅Zr₀.₅O₂ nanorods obtained by Das et al. were proven to be more active than Ru/CeO₂ and Ru/ZrO₂. Specifically, the stronger metal–support interactions and higher oxygen storage capacity of the CeO₂–ZrO₂ solid solution contributed to the increased catalytic performance. Innovatively, Singha et al. reported 3D Pt–CeO₂ nanoporouss spheres with a bimodal pore structure for the partial oxidation of methane. The unique bimodal pore structure was confirmed by an N₂-adsorption study, which resulted in a high surface area. The as-prepared Pt–CeO₂ catalysts were highly active and selective for the production of syngas (TOF at 400 °C = 1.3 × 10³ s⁻¹, CO selectivity = 50.0%). Briefly, the unique bimodal pore structure resulted in a high surface area and metal–support interactions as well as abundant oxygen vacancies, contributing to the superior catalytic performance for the partial oxidation of methane to produce syngas.

In the case of other rare earth oxides used in the partial oxidation of methane besides CeO₂, Ferreira et al. tested the catalytic performance of LnNi (Ln = Pr, Gd, Lu) binary oxides. They found that NiO–Gd₂O₃ and NiO–Lu₂O₃ exhibited much higher activity than that of NiO–Pr₂O₃, which was even comparable with that of the commercial 5% Pt/Al₂O₃ catalyst. The authors believed that there was an unusual synergistic effect between the two oxides, resulting in high activity and selectivity.
suitable rare earth oxides with designed well-defined structures as a support or promoter.

4.5 MOR

The MOR discussed below refers to the anode reaction of direct methanol fuel cells (DMFCs), which is very important for alleviating the energy crisis since it can directly transform chemical energy to electrical energy. Besides, methanol has a high energy density and is easier to store and transport compared with hydrogen. The catalytic application of rare earth oxide nanomaterials in the MOR is not as extensive as in other C1 chemical reactions such as the CO oxidation and CO2 hydrogenation reactions because of their weak conductivity. Although it is difficult for rare earth oxide nanomaterials to be used as a single catalyst in MOR, there are many cases that combine rare earth oxide nanomaterials with other well-conducting catalysts for the MOR. This not only can enhance the electronic metal support interactions, but also tune the chemical adsorption of the reactants and intermediates. As an example, Li et al.126 studied the introduction of Y2O3 on the MOR activity of the Pd/C catalyst. A 1.5 times higher specific activity (SA = 145 mA cm−2) was observed with the assistance of Y2O3 due to the relatively well-dispersed Pd nanoparticles, enhanced electrochemically active surface area and the synergistic interaction between Pd and Y2O3.

In the case that the role of rare earth oxides is a promotor in the MOR, a well-defined structure can also have a positive influence on the catalytic performance. As a good example, Feng et al.13 synthesized three types of well-defined CeO2 nanostructures containing nanoctahedra, nanospheres and nanocubes as promoters for Pt catalysts. Consequently, the Pt catalyst decorated with CeO2 nanospheres exhibited the best performance in both activity and stability. The explanation for the enhanced activity could be divided into two parts. One was that the loosened structure of nanospheres was beneficial for the dispersion of Pt particles, thus generating a strong physical interaction between Pt and CeO2. The other was the oxygen vacancies, which were the most abundant in the nanospheres. The rich oxygen vacancies led to the transfer of surplus electrons from CeO2 to Pt, and thereby increased the intrinsic activity of Pt. Besides, Wang et al.129 investigated the effect of the introduction of La2O3 in the Pd/C catalyst for the MOR. As can be seen in Fig. 20a, the Pd nanoparticles (ca. 2.6 nm) were uniform and well dispersed. Compared with the Pd/C catalyst, Pd–La2O3/C exhibited a lower onset potential and higher current density (Fig. 20b). The XPS results indicated that the introduction of La2O3 resulted in the formation of more metallic Pd species (Fig. 20c and d), resulting in enhanced activity. Furthermore, the authors loaded Pd–La2O3 on chitosan-functionalized carbon nanotubes and obtained a better performance than that with Pd–La2O3/C. In addition, a 3D core–shell nanocatalyst of Au@CeO2@Pt/C for the MOR was obtained by Dao et al.130 through a facile hydrothermal route. The as-prepared catalyst showed much higher activity (MA = 1360 mA mgPt−1) and durability than that of commercial Pt/C (MA = 670 mA mgPt−1) and CeO2@Pt/C (MA = 920 mA mgPt−1) owing to...
to the electronic and synergistic effects among Au, CeO₂ and Pt, which could easily remove the poisoner of CO intermediates (Fig. 20e).

When rare earth oxides are used as a support in the MOR, efforts must be made to improve their conductivity. For example, CeO₂ nanorod-supported Pt catalysts were prepared by Tao et al.¹³¹ and used for the MOR. They used plasma etching of the CeO₂ nanorods to modify the surface structure of the CeO₂ support (denoted as CeO₂-P), and used the untreated CeO₂ as a comparison sample (Fig. 21a). The authors found that the abundant oxygen vacancies in Pt/CeO₂-P played a significant role in the enhanced activity (MA = 714 mA mg⁻¹) and stability compared with the sample without plasma etching (MA = 164 mA mg⁻¹) (Fig. 21b and c), which influenced the interactions between Pt and CeO₂ and enriched the electronic density of Pt, resulting in the enhanced conductivity of CeO₂ and MOR activity. As another example, Tang et al.¹³³ combined the rare earth oxides of Pr and Ce with carbon black to support Pt species for the MOR. They found that the introduction of Pr₂O₃ and CeO₂ significantly improved the catalytic performance (Fig. 21d and e), and the ratio of Pr/ Ce had a crucial effect on the activity. According to their observations, Pt/Pr₃CeO₃-C exhibited the highest activity (SA = 118.3 mA cm⁻²) and best stability among the samples. The abundant surface oxygen-containing species as well as the high oxygen mobility derived from Pr₂O₃ and CeO₂ contributed to the enhanced CO-tolerance and catalytic performance.

In summary, although rare earth oxide nanomaterials have poor conductivity, which limits their activity for the MOR, they are widely used as a promotor or support for the rational engineering of their structures in the MOR since they can enrich the electronic density and improve the CO tolerance through electronic and synergistic effects.

5. Summary and perspective

In this review, we introduced the structural features of the rare earth oxides and summarized the engineering of rare earth oxide nanomaterials with well-defined structures mainly considering their morphology. Then we chose some representative C₁ chemical reactions including CO oxidation, water gas-shift reaction, CO₂ hydrogenation reaction, methane oxidation reaction and methanol oxidation reaction to summarize the struc-
Table 1  The synthesis and applications of rare earth oxide-based nanocatalysts for some C1 chemical reactions

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Synthetic route</th>
<th>Application</th>
<th>Conditions</th>
<th>Performance</th>
<th>Key factors in catalysts</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ln-Doped CeO2 nanowires (Ln = La-Lu) Pr2O3</td>
<td>Hydrothermal method</td>
<td>CO oxidation reaction</td>
<td>1% CO-20% O2–He Total speed: 40 mL min⁻¹</td>
<td>TOF at 200 °C = 5.4 × 10⁻³ s⁻¹</td>
<td>Doping effect</td>
<td>35</td>
</tr>
<tr>
<td>ThO2</td>
<td>Hard template method</td>
<td>CO oxidation reaction</td>
<td>1% CO-20% O2–N2 SV = 10.000 mL g⁻¹ h⁻¹</td>
<td>T₅₀ = 305 °C</td>
<td>Surface area</td>
<td>75</td>
</tr>
<tr>
<td>PtO2 nanoclusters/ CeO2</td>
<td>Hydrothermal method</td>
<td>CO oxidation reaction</td>
<td>13.3% CO–33.3% O2–53.3% He Total speed: 15 mL min⁻¹</td>
<td>TOF at 50 °C = 1.3 × 10⁻² s⁻¹</td>
<td>Oxygen vacancy Suitable Pt–O coordination number</td>
<td>77</td>
</tr>
<tr>
<td>Au/Pr₆O₁₁ nanorods</td>
<td>Hydrothermal method</td>
<td>CO oxidation reaction</td>
<td>1% CO–Air Total speed: 33.6 mL min⁻¹</td>
<td>T₁₀₀ = 140 °C</td>
<td>Synergistic effect</td>
<td>78</td>
</tr>
<tr>
<td>Ag/Pr₆O₁₁ nanorods</td>
<td>Hydrothermal method</td>
<td>CO oxidation reaction</td>
<td>1% CO–20% O₂–Ar Total speed: 50 mL min⁻¹</td>
<td>T₁₀₀ = 210 °C</td>
<td>Surface area</td>
<td>79</td>
</tr>
<tr>
<td>Au/CeO₂ nanorods</td>
<td>Hydrothermal method</td>
<td>WGSR</td>
<td>2% CO–10% H₂O–He Total speed: 70 mL min⁻¹</td>
<td>T₃₀ = 190 °C</td>
<td>Plane effect</td>
<td>87</td>
</tr>
<tr>
<td>Au nanoclusters/ CeO₂</td>
<td>Hydrothermal method</td>
<td>WGSR</td>
<td>2% CO–12% H₂O–N₂ Total speed: 30 mL min⁻¹</td>
<td>Rate at 200 °C ~ 5.0 × 10⁻³ mol g⁻¹ s⁻¹</td>
<td>Bridged –OH and Au⁺</td>
<td>15</td>
</tr>
<tr>
<td>Pt/Ce₀₅Y₁₀O₂</td>
<td>Sol–gel method</td>
<td>WGSR</td>
<td>5% CO–15% H₂O–N₂ WHSV = 30 000 mL g⁻¹ h⁻¹</td>
<td>TOF at 250 °C = 0.55 s⁻¹</td>
<td>Reducibility of the support</td>
<td>86</td>
</tr>
<tr>
<td>CuO/CoO–La₂O₃</td>
<td>Co-precipitation method</td>
<td>CO₂ methanation</td>
<td>10% CO–3% H₂O–He Total speed: 40 mL min⁻¹</td>
<td>T₉₀ = 375 °C</td>
<td>Oxidation state of Cu and oxygen vacancy</td>
<td>88</td>
</tr>
<tr>
<td>Cu/CeO₂ nanorods</td>
<td>Hydrothermal method</td>
<td>RWGS</td>
<td>10% CO₂–50% H₂–He Total speed: 20 mL min⁻¹</td>
<td>Rate at 250 °C = 1.8 μmol g⁻¹ s⁻¹</td>
<td>CeO₂ (110) facets</td>
<td>94</td>
</tr>
<tr>
<td>Ni/La₂O₃</td>
<td>Sol–gel method</td>
<td>RWGS</td>
<td>50% CO₂–50% H₂ Total speed: 20 mL min⁻¹</td>
<td>~100 °C: CO₂ conversion = 51.0%; CO yield = 39.1%</td>
<td>Ni dispersion and SMSI</td>
<td>95</td>
</tr>
<tr>
<td>Ru nanoclusters/ CeO₂</td>
<td>Hydrothermal method</td>
<td>CO₂ methanation</td>
<td>5% CO₂–20% H₂–He Total speed: 40 mL min⁻¹</td>
<td>TOF at 190 °C = 7.4 × 10⁻³ s⁻¹ Selectivity ~100%</td>
<td>SMSI and H-spillover</td>
<td>96</td>
</tr>
<tr>
<td>Ni–Sm₂O₃</td>
<td>Sol–gel method</td>
<td>CO₂ methanation</td>
<td>10% CO₂–40% H₂–Ar Total speed: 50 mL min⁻¹</td>
<td>T₁₀₀ = 100 °C Selectivity ~100%</td>
<td>Smaller size and more perimeter sites</td>
<td>97</td>
</tr>
<tr>
<td>Co/Gd₂O₃</td>
<td>Impregnation method</td>
<td>CO₂ methanation</td>
<td>10% CO₂–90% H₂ Total speed: 75 mL min⁻¹</td>
<td>TOF at 300 °C = 1.3 min⁻¹ Selectivity ~80%</td>
<td>Reducibility</td>
<td>98</td>
</tr>
<tr>
<td>Cu/La₂O₃CO₃ nanorods</td>
<td>Deposition–precipitation method</td>
<td>CO₂ hydrogenation to methanol</td>
<td>24% CO₂–72% H₂N₂ 3.0 MPa</td>
<td>TOF at 240 °C = 7.0 × 10⁻² s⁻¹ Selectivity = 92.5%</td>
<td>Cu⁺ and enhanced CO₂ adsorption</td>
<td>103</td>
</tr>
<tr>
<td>La₂O₃ doped CuO/ZnO/ZrO₂</td>
<td>Co-precipitation method</td>
<td>CO₂ hydrogenation to methanol</td>
<td>25% CO₂–75% H₂ 3.0 MPa</td>
<td>Selectivity = 92.5% CH₃OH productivity at 230 °C = 2.7 mol kg⁻¹ h⁻¹</td>
<td>Oxygen vacancy</td>
<td>104</td>
</tr>
<tr>
<td>La₂O₃–CuO/ZnO/Al₂O₃</td>
<td>Co-precipitation method</td>
<td>CO₂ hydrogenation to methanol</td>
<td>10% CO₂–90% H₂ Total speed: 50 mL min⁻¹</td>
<td>210 °C: CH₃OH yield = 0.9%; selectivity ~40%</td>
<td>Enhanced adsorption of CO₂</td>
<td>105</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Application</td>
<td>Conditions</td>
<td>Performance</td>
<td></td>
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<tr>
<td>LaNdPdAlO₄</td>
<td>Methane combustion</td>
<td>1% CH₄/Ar</td>
<td>Rate at 800 °C = 6.9 × 10⁸ mol g⁻¹ s⁻¹</td>
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<tr>
<td>LaNdPdAl₂O₅</td>
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<tr>
<td>NiO-Gd₂O₃</td>
<td>Controlled oxidation of the</td>
<td>28% CH₄/36% O₂</td>
<td>CO productivity at 700 °C = 8.0 mol g⁻¹ h⁻¹</td>
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<tr>
<td>NiO-Y₂O₃</td>
<td>Partial oxidation of methane</td>
<td>66% CH₄/33% O₂</td>
<td>H₂ selectivity at 700 °C = 6.3 mol g⁻¹ h⁻¹</td>
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<tr>
<td>PdCuO</td>
<td>Hydrothermal method</td>
<td>Microwave-assisted reduction</td>
<td>SA: 145 mA cm⁻²</td>
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<tr>
<td>PdCuO</td>
<td>Hydrothermal method</td>
<td>Reduction reaction</td>
<td>MA: 1360 mA mgPt⁻¹</td>
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<tr>
<td>PdCuO</td>
<td>Hydrothermal method</td>
<td>Hydrothermal method plasma etch</td>
<td>MA: 1360 mA mgPt⁻¹</td>
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<tr>
<td>LaNdPdAl₂O₅/Al₂O₃</td>
<td>Methane combustion</td>
<td>Impregnation method</td>
<td>Rate at 800 °C = 3.9 × 10⁷ mol g⁻¹ s⁻¹</td>
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<tr>
<td>LaNdPdAl₂O₅/ZrO₂·Al₂O₃</td>
<td>Methane combustion</td>
<td>Impregnation method</td>
<td>Rate at 800 °C = 3.9 × 10⁷ mol g⁻¹ s⁻¹</td>
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<tr>
<td>LaNdPdAl₂O₅/NiO·CeO₂·Al₂O₃</td>
<td>Methane combustion</td>
<td>Impregnation method</td>
<td>Rate at 800 °C = 3.9 × 10⁷ mol g⁻¹ s⁻¹</td>
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</table>

**Key factors in catalysis:**
- Stabilizing Pd species
- Structural effect
- Synergistic effect
- Oxygen defects
- Surface oxygen-containing species
- Oxygen mobility

- **Catalyst Synthetic route Application Conditions Performance Key factors in catalysis Ref.**

- **Inorg. Chem. Front.**

- **Ref.** 113

- **(Contd.)**

- **Inorganic Chemistry Frontiers**

- **View Article Online**

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In the table above, we present a comprehensive overview of catalysts used in C1 chemical reactions, highlighting their synthetic routes, application conditions, performances, and key factors in catalysis. This table is based on the reported works in Table 1, including their preparation methods and catalytic properties. The role of well-defined rare earth oxide-based catalysts in C1 chemical reactions mainly involves three aspects: (1) providing stable sites for the loading and dispersion of other metal catalysts, (2) providing strong metal support interaction and enhancing the electron density of the metal loading, and (3) providing sites for the adsorption and activation of small molecules such as H₂O, O₂, and CO₂. There is no doubt that rare earth oxide-based catalysts play a significant role in C1 chemical reactions, but there are also many problems that need to be solved.

Firstly, optimized synthesis strategies still need to be developed for the large-scale and low-cost production of rare earth oxide materials with high performances. Based on the current developed synthetic routes, on the one hand, methods such as thermal decomposition and precipitation are low-cost and efficient, but they are not suitable for designing and obtaining nanostructures with a specific morphology, which may result in desirable properties. On the other hand, routes such as the hydrothermal and sol–gel methods are suitable for the preparation of functional nanomaterials, but they cannot guarantee their large production and low cost. Besides, the role of rare earth oxides themselves in the catalytic reaction needs a deeper and clearer understanding. Many reported works have demonstrated that rare earth oxides exhibit catalytic activity for C1 chemical reactions. However, when the rare earth oxides are used as a support to form composite materials with other metal or metal oxides, it is not clear if they only work as support or they also provide active sites. In addition, the defects in rare-earth oxides also play a crucial role in C1 chemical reactions, such as stabilizing the active metal loading, providing sites for the adsorption of reactant molecules such as H₂O and CO₂, and promoting the electron transfer between the support and active metals, especially oxygen defects. However, other defects such as dislocation and grain boundaries in rare earth oxides are rarely discussed in C1 chemical reactions, and thus more research is needed to fill this blank. Furthermore, most of the characterizations of rare earth oxide-based catalysts are restricted to the ex situ level. Nevertheless, the surface structure of the catalyst always changes in the reaction process, and there are many intermediate species generated that disappear and cannot be observed by ex situ techniques. Consequently, in situ/operando characterizations combined with theoretical simulation need to be performed to uncover the real reaction mechanism behind the catalytic reaction. Finally, to date, most of the research on rare earth oxide-based catalysts for C1 chemical reactions has focused on CeO₂, but the catalytic properties of other rare earth oxides need to be explored to obtain more novel catalysts with high performances. Also, the powerful function of computational simulation in explaining and predicting the catalytic properties of rare earth oxides should be noted. There is also a problem that most computational works on rare earth oxides are based on CeO₂ nanomaterials. However, using theoretical computation...
to predict properties may result in the development of more non-ceria rare earth oxides nanostructures with high catalytic performances. We believe that all of these problems will be addressed in the future, and rare earth oxide-based nanomaterials will shine brightly at the stage of catalytic applications in C1 chemical reactions.

**Conflicts of interest**

There are no conflicts to declare.

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