

CeO₂-based transition metal catalysts

Subjects: [Materials Science, Composites](#) | [Nanoscience & Nanotechnology](#) | [Energy & Fuels](#)

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The rational design and fabrication of highly-active and cost-efficient catalytic materials constitutes the main research pillar in catalysis field. In this context, the fine-tuning of size and shape at nanometer scale can exert an intense impact not only on the inherent reactivity of catalyst's counterparts but also on their interfacial interactions, opening up new horizons for the development of highly active and robust materials. The main implications of ceria nanoparticles' shape engineering (rods, cubes, polyhedra) in catalysis are revealed, on the ground of some of the most pertinent heterogeneous reactions, such as CO₂ hydrogenation, CO oxidation, and N₂O decomposition. It is clearly revealed that shape functionalization can remarkably affect the intrinsic features and in turn the reactivity of ceria nanoparticles. More importantly, by combining ceria nanoparticles (CeO₂ NPs) of specific architecture with various transition metals (e.g., Cu, Fe, Co, Ni) remarkably active multifunctional composites can be obtained due mainly to the synergistic metal-ceria interactions, providing the design principles of earth-abundant metal oxide catalysts for various real-life environmental and energy applications.

[CeO₂](#)[noble metal-free catalysts](#)[shape effects](#)[transition metal-based catalysis](#)[CO oxidation](#)[N₂O decomposition](#)[CO₂ hydrogenation](#)[ceO₂-based catalysts](#)

1. Background

Catalysis has gained ongoing attention from academic and industrial community, since it is massively involved in numerous energy and environmental processes, including, among others, the manufacture of value-added fuels and chemicals, hydrocarbons processing, fuel cell applications, photocatalytic degradation, abatement of hazardous substances, etc. To this end, the development of cost-efficient catalysts with improved activity and durability constitutes the main research pillar in the field of catalysis [\[1\]\[2\]\[3\]](#).

Although, noble metals (NMs) hold an integral role in catalysis for chemical bond activation and formation, their scarcity and high cost constitutes a major and inherent drawback. In this regard, the development of catalysts by combining the low cost with the high activity is a major driving force in contemporary research [\[1\]\[2\]\[3\]\[4\]](#). Metal oxides, composed of earth-abundant transition metals (TMs) have gained particular attention towards replacing the rare and costly NMs, owing to their unique characteristics, such as improved redox properties and thermal stability [\[1\]\[2\]\[5\]](#). More importantly, through admixing different metal oxides (MOs) in an exact proportion, mixed metal oxides (MMOs) can be obtained with unique physicochemical properties, which are mainly linked to interfacial phenomena. Moreover, several reducible oxides (e.g., CeO₂, ZnO, TiO₂), could serve as TMs supporting carriers, exerting a beneficial impact on the inherent activity through peculiar metal-support interactions [\[6\]\[7\]\[8\]\[9\]](#).

Among the different MOs, cerium oxide or ceria has gained tremendous interest in heterogeneous catalysis due to its exceptional redox properties driven by the high oxygen mobility and the rapid redox interplay between Ce³⁺ and Ce⁴⁺ [1][10][11]. In addition to these physicochemical advantages of cerium oxide, its average 2020 price stands at very low levels (ca. 1815 USD/metric ton), with a relative cost trend of ZrO₂ > ZnO > SiO₂ > TiO₂ > CeO₂, revealing the economic benefits of ceria-based catalytic materials [12]. Furthermore, the cost of base middle-late 3d metals, such as Cu, Ni, is about 3–4 orders of magnitude lower as compared to NMs, rendering extremely attractive, from a financial perspective, the development of ceria-based transition metal catalysts. More importantly, the combination of reducible oxides (e.g., CeO₂) with TMs (e.g., Fe, Co, Ni, Cu) could offer novel catalyst formulations with exceptional properties, arising mainly from the multifaceted electronic and geometric interactions amongst the different counterparts [6][7][8][13][14]. In this respect, it was recently appraised on account of both experimental and theoretical studies that various interconnected phenomena could be at work at metal-support interface, which in turn exert a profound influence on the catalytic activity, such as [6][7][8][13][14]:

1. electronic perturbations linked to bonding interactions between TMs and Ceria nanoparticles
2. facilitation of oxygen vacancies' formation resulting in enhanced reducibility and oxygen exchange kinetics
3. high intrinsic activity of interfacial sites

However, it is well known today—thanks to the huge progress in cutting-edge characterization techniques—that the individual characteristics of catalyst's counterparts can notably affect not only their own activity but also the interaction between them with great consequences in catalysis. In specific, by adjusting the geometrical and electronic features of the different counterparts through suitable synthetic and promotional routes highly active materials are obtained [7][10][15][16].

2. Synthesis and Characterization of CeO₂ NPs of Different Morphology

As shown in Figure 1, the hydrothermal method was successfully used in order to prepare three distinct ceria morphologies of well-defined shape, i.e., nanocubes (NC), nanorods (NR) and nanopolyhedra (NP), which are then employed as supporting carriers for various transition metal catalysts (Fe, Co, Ni, Cu) through the wet impregnation method (Figure 1).

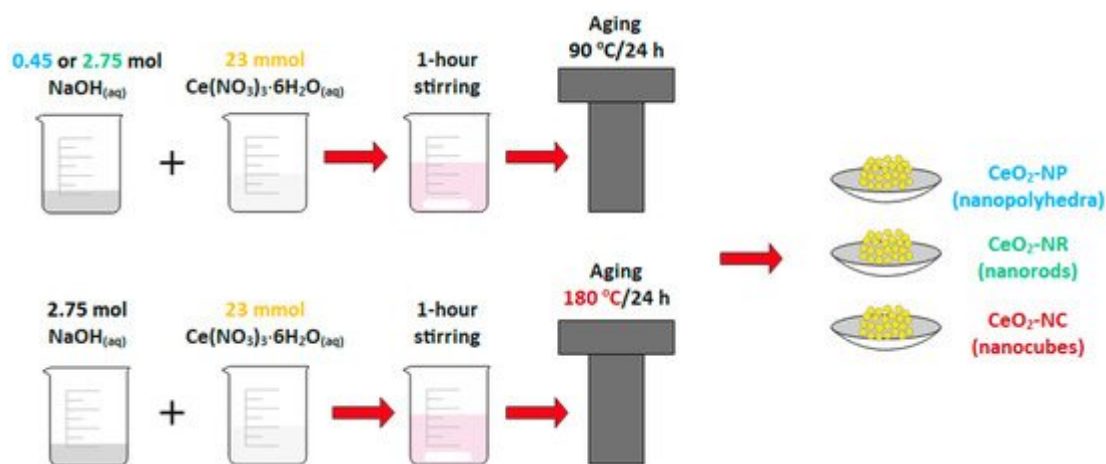


Figure 1. Schematic illustration of synthetic procedure of ceria nanoparticles of different shape (nanocubes = NC, nanorods = NR, and nanopolyhedra = NP).

3. Ceria Shape Effects on the Structural Defects and Redox Properties

Figure 2 shows indicative TEM images of ceria nanorods (NR), nanopolyhedra (NP), and nanocubes (NC). The CeO₂-NR sample (Figure 2a,d) shows a rod-like morphology with a length from 25 to 200 nm. In the case of CeO₂-NC (Figure 2c,f), a well-defined cube-like morphology is obtained (of about 20–30 nm), whereas nanopolyhedra of irregular size/shape are observed for CeO₂-NP (Figure 2b,e). Among the different ceria nanostructures, ceria nanocubes exhibit the lowest BET surface area, along with the highest mean particle size: NC (40 m²/g) < NR (92 m²/g) < NP (109 m²/g).

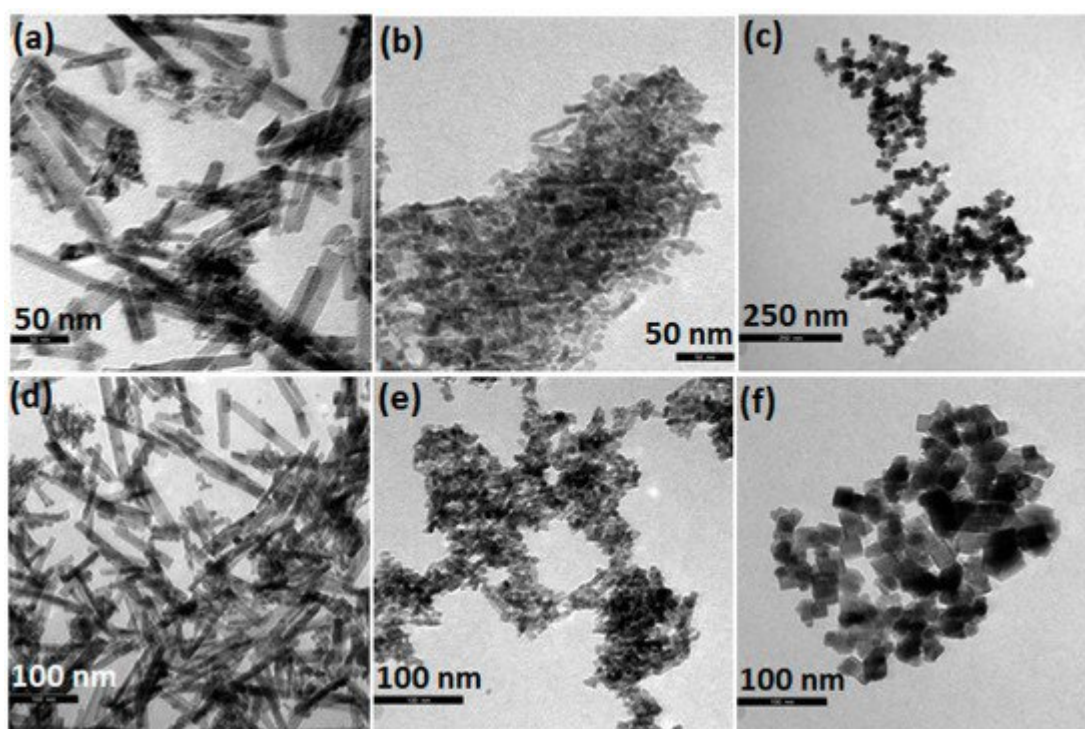


Figure 2. Indicative transmission electron microscopy (TEM) images of ceria (a,d) nanorods, (b,e) nanopolyhedra, and (c,f) nanocubes.

The research showed that the rod-shaped ceria nanoparticles possess the highest population of weakly bound labile oxygen species, which coincides with the oxygen storage capacity (OSC): NC (0.21 mmol/g) < NP (0.24 mmol/g) < NR (0.29 mmol/g). Hence, on the basis of the aforementioned results, it can be argued that, although ceria nanorods do not display the optimum textural properties (e.g., surface area), they possess the optimum redox characteristics in terms of population and facile reduction of loosely bound oxygen species, which is of paramount importance in several reaction processes obeying a redox mechanism.

4. Implication in Catalysis

The effect of ceria nanoparticles geometry on the catalytic behaviour of TMs/CeO₂ oxides is demonstrated on the grounds of indicative oxidation/reduction reactions, such as CO oxidation, nitrous oxide (N₂O) decomposition and CO₂ hydrogenation to value-added products [17][18][19][20][21].

Figure 3 depicts the CO oxidation performance of the different bare ceria nanoshapes (NR, NC, NP) in comparison to that of transition metal-based catalysts, i.e., Fe/CeO₂ and Cu/CeO₂ samples. Regarding, at first, the CO conversion of bare ceria, it is evident that significant differences are obtained between the samples, demonstrating the key role of morphology. On the basis of T₅₀, i.e., the required temperature for 50% conversion, the following order is observed for bare ceria: NR (320 °C) < NP (350 °C) < NC (385 °C). It is noteworthy that the conversion order of bare ceria samples totally coincides with their relative concentration in labile oxygen species (expressed by OSC) and oxygen vacancies (expressed by the ratio of I_D/I_{F2g}). The latter clearly reveals the major role of ceria shape towards determining the redox/structural properties and in consequence the catalytic behaviour [17][18]. Most significantly, the incorporation of transition metals (Fe, Cu) to ceria drastically improves the catalytic performance, without affecting, however, the activity order obtained for single CeO₂ samples. This clearly implies the guided role of support morphology on the catalytic performance of ceria-based transition metal catalysts. Apparently, the rod-shaped samples exhibit the optimum catalytic efficiency, demonstrating complete CO conversion at 250 °C and 100 °C for Fe/CeO₂ and Cu/CeO₂ samples, respectively.

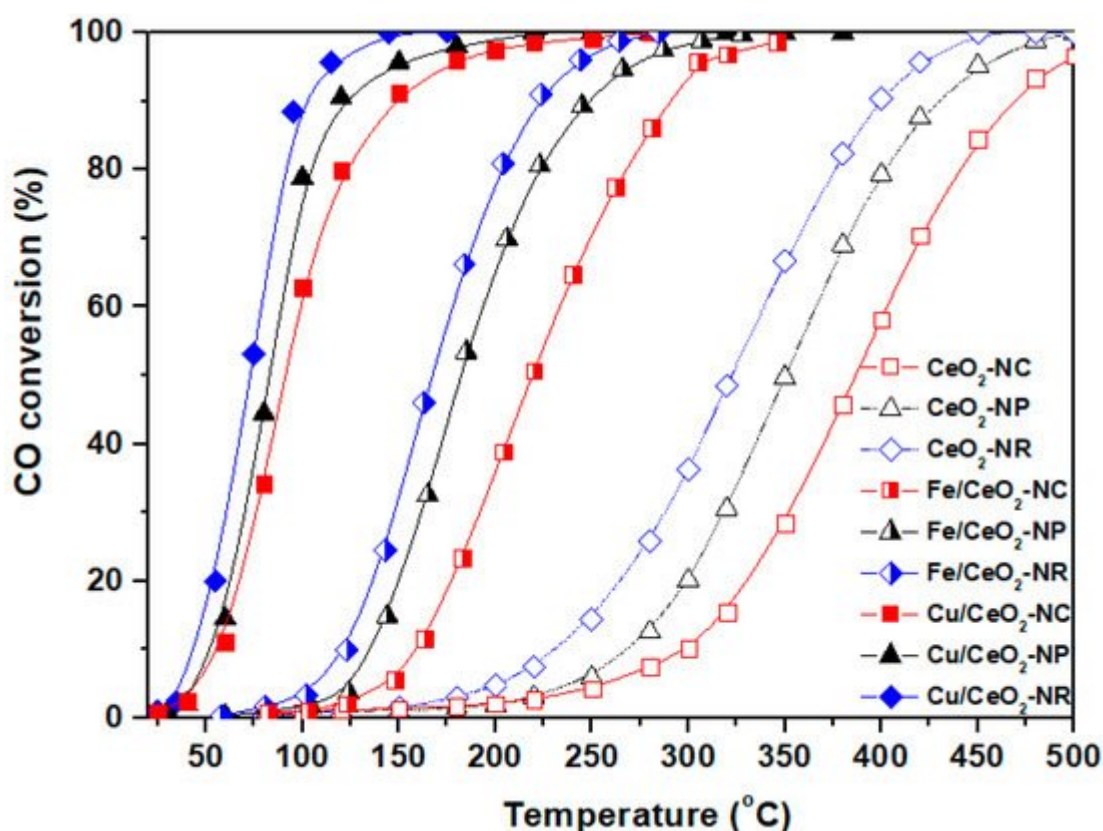


Figure 3. Ceria nanoparticles morphological effects (nanorods = NR, nanocubes = NC, nanopolyhedra = NP) on the CO oxidation performance of bare CeO₂, Cu/CeO₂, and Fe/CeO₂ samples.

The superior reactivity of samples with rod-like shape was further verified by a kinetic study under differential reaction conditions, which revealed the following order in relation to apparent activation energy (E_a): CeO₂-NR (44.2 kJ/mol) < CeO₂-NP (46.7 kJ/mol) < CeO₂-NC (49.8 kJ/mol) [18]. A similar trend was acquired for TMs/Ceria samples, indicating once again the pivotal role of ceria morphology towards determining the activity of ceria-based transition metal samples [18].

Perfect relationships between the reaction rate (r_{CO} , mmol s⁻¹ g⁻¹) and the following activity descriptors were disclosed: (i) population of oxygen vacancies expressed by $I_{\text{D}}/I_{\text{F2g}}$ ratio, (ii) oxygen storage capacity (OSC), as shown in Figure 4. Similar relationships have been obtained for Cu- and Fe-based samples, revealing the pivotal role of support morphology [17][18].

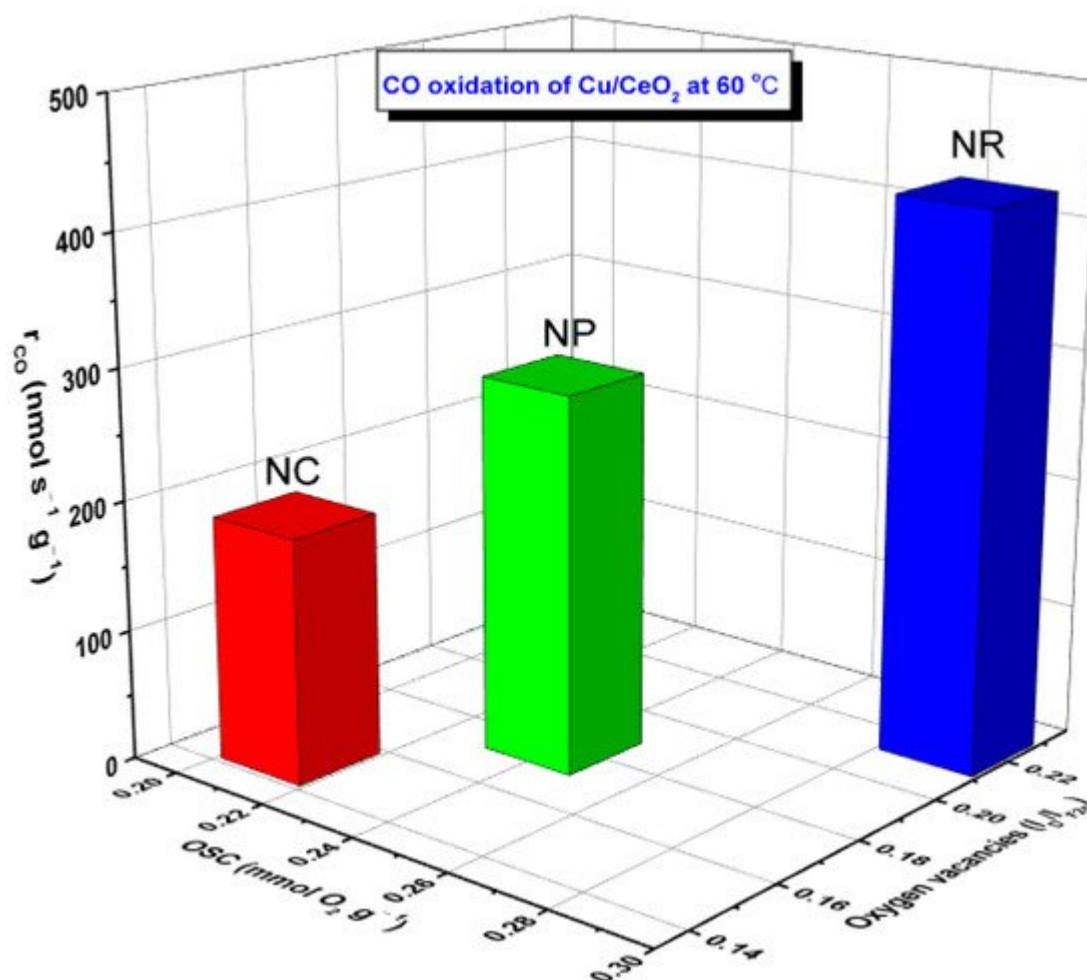


Figure 4. Relationship between the CO oxidation performance (r_{CO} , nmol s⁻¹ g⁻¹) of Cu/CeO₂ samples and the oxygen storage capacity (OSC, mmol O₂ g⁻¹) as well as the abundance of oxygen vacancies (in terms of $I_{\text{D}}/I_{\text{F2g}}$ ratio) of ceria nanorods (NR), nanopolyhedra (NP) and nanocubes (NC).

Figure 5a,b demonstrates the conversion of CO₂ as well as the selectivity to methane, respectively, for bare CeO₂-NR samples as well as for TMs (Fe, Co, Ni, Cu)/CeO₂-NR. It is obvious that there are significant differences between the samples, mostly depending on metal's nature. Regarding CO₂ conversion, the following order is

obtained: $\text{CeO}_2 < \text{Fe/CeO}_2 < \text{Cu/CeO}_2 < \text{Co/CeO}_2 < \text{Ni/CeO}_2$, signifying the pivotal role of metal-support combination. Ni/CeO₂-NR exhibits by far the optimum performance, offering ca. 92% conversion at 300 °C. In other words, by combining Ni with ceria nanorods extremely active CO₂ methanation catalysts can be obtained, which practically reach the equilibrium at very low temperatures of ca. 300 °C. More importantly, the high conversion performance of Ni catalysts is followed by 100% selectivity to CH₄ (Figure 5b) in the entire temperature range studied. Interestingly, Cu/CeO₂-NR catalyst is totally selective to CO (rWGS reaction), reaching the equilibrium at temperatures higher than 400 °C. Hence, the combination of Ni with CeO₂-NR favours the CO₂ methanation reaction, whereas the rWGS reaction is favoured over Cu/CeO₂-NR.

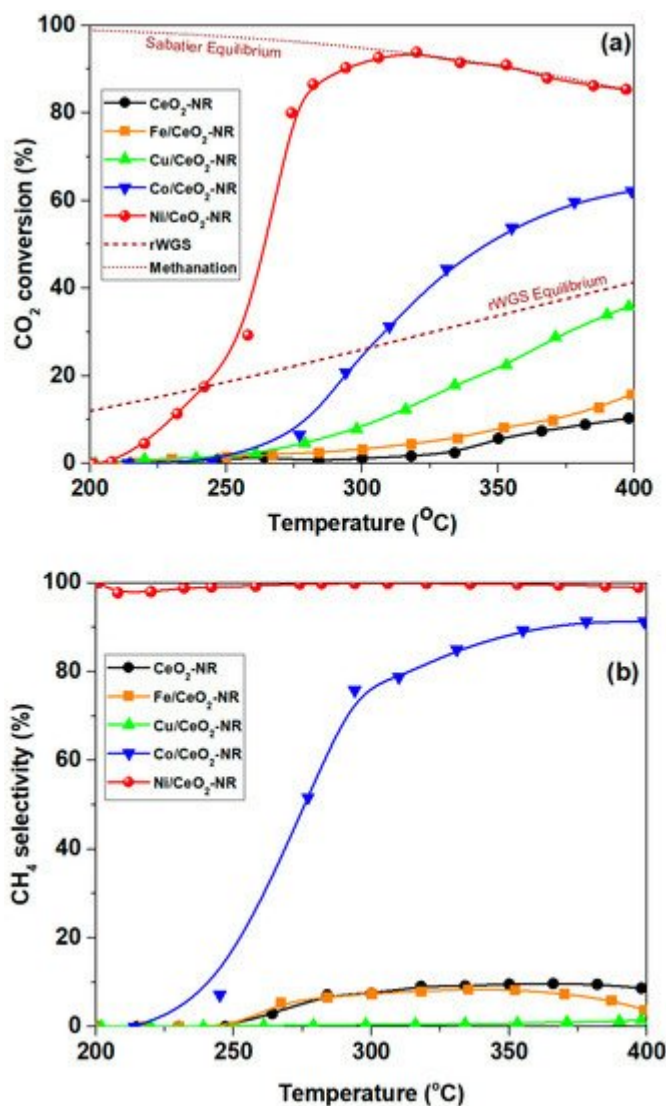


Figure 5. CO₂ conversion (a) and selectivity to CH₄ (b) for bare CeO₂-NR and various metal-based catalysts (Fe, Cu, Co, Ni). Reaction conditions: Weight Hourly Space Velocity (WHSV) = 30,000 mL g⁻¹ h⁻¹, H₂:CO₂ = 4:1, P = 1 atm [21]. Dotted lines represent the corresponding equilibrium for rWGS and Sabatier reactions.

From the practical point of view, novel catalyst formulations with similar or even superior reactivity to that of noble metals can be obtained by co-adjusting the shape and composition of mixed oxides, such as Cu/Ceria nanorods for CO oxidation and Ni/Ceria nanorods for CO₂ hydrogenation.

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