

Effect of Exposed Facets and Oxidation State of CeO₂ Nanoparticles on CO₂ Adsorption and Desorption

Gimyeong Seong,* Akira Yoko, Takaaki Tomai, Takashi Naka, Haodong Wang, Anatoly I. Frenkel, and Tadafumi Adschiri*



Cite This: *ACS Sustainable Chem. Eng.* 2024, 12, 7532–7540



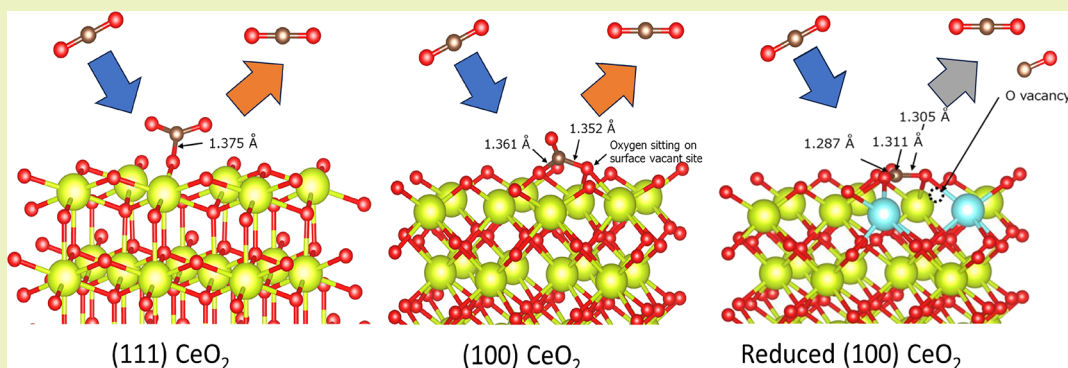
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ABSTRACT: CeO₂ nanoparticles exhibit potential as solid adsorbents for carbon dioxide (CO₂) capture and storage (CCS), offering precise control over various facets and enhancing their efficiency. This study investigated the adsorption and desorption behaviors of two types of CeO₂ nanoparticles: cubic CeO₂ with primarily {001} facets and polyhedral CeO₂ with mainly {111} facets. The results showed that despite polyhedral CeO₂'s lower quantity, it demonstrated successful adsorption–desorption cycles in both oxidized and reduced states. However, reduced CeO_{2-x} exhibited a higher adsorption capacity but displayed irreversible adsorption–desorption cycles. Reversible adsorption occurred through weak bond formation with CO₂, while cubic CeO₂ with a high oxygen vacancy concentration exhibited irreversible adsorption due to strong bond formation. These insights contribute significantly to understanding CeO₂ nanoparticle characteristics and their impact on the CO₂ adsorption and desorption processes, aiding in the development of advanced CCS techniques.

KEYWORDS: adsorbent, CeO₂, CCS, facet control, oxidation state

INTRODUCTION

Over the past 20 years, there has been an increasing focus on reducing greenhouse gases, such as CO₂, to mitigate global warming and air pollution.^{1–3} Significant research and development efforts have been made to selectively capture and store CO₂.^{4–6} Liquid sorbents such as amine and Selexol are commonly used in most industrial carbon dioxide capture and storage (CCS) processes, as evidenced by Yamada's research, which states that they account for 89% of existing large-scale CCS processes.⁷ Amino acid salts have recently gained attention as a promising class of adsorbents due to their lower evaporation and degradation rates.⁸ This makes them a potentially attractive option for the use in CO₂ capture applications. However, due to their high regeneration costs resulting from their decomposition during temperature cycling, solid sorbents are considered as a superior alternative to those liquid sorbents.⁹

In addition, metal–organic frameworks (MOFs), porous carbons, and zeolites have all been studied as potential

adsorbents due to their high specific surface area and porosity.¹⁰ MOFs have a low heat capacity, which is advantageous for regeneration since it reduces the energy required.¹¹ However, MOFs have been found to exhibit weak interactions with CO₂ in low-pressure processes, leading to poor performance. Moreover, their sensitivity to the temperature and humidity can result in poor stability.

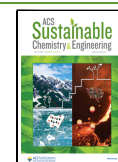
Metal oxides (e.g., Cs, Mg, and Si), which enable efficient CO₂ reversible capture, have been examined as alternative solid adsorbents.^{12–16} Especially, CeO₂ has a strong interaction with CO₂, and numerous mechanistic studies on CeO₂ over relatively low temperatures have been conducted.^{17–26}

Received: February 15, 2024

Revised: April 15, 2024

Accepted: April 15, 2024

Published: May 2, 2024



Baumann et al.²⁷ conducted density functional theory (DFT) calculations, which predicted that the presence of oxygen vacancies makes the adsorption energy of CO₂ more favorable. Additionally, Kumari et al.²⁸ reported that high concentration of oxygen vacancies promote the dissociation of CO₂. Recently, Slostowski et al.²⁹ conducted thermogravimetric analysis to evaluate the adsorption capacity and suitability of CeO₂ nanoparticles as a CO₂ adsorbent.

Recent studies have shown that the surface properties of CeO₂ have a greater impact on the catalytic performance than its specific surface area. For example, in a study by Zhou et al., CeO₂ nanoparticles with similar electrochemical specific areas but different morphologies in partnership with Pt or Pd showed varying performance in methanol and formic acid fuel cells.³⁰ Therefore, CeO₂, with specific exposed crystal facets and a large specific surface area, holds great potential as a solid adsorbent for CO₂. Specifically, cubic CeO₂ with relatively unstable {001} facets exposed can form oxygen vacancies through activation of oxygen at medium-low temperatures, which is advantageous for CO₂ adsorption.^{31,32}

The synthesis of cubic CeO₂, also known as CeO₂ nanocubes with {001} facets, can be achieved by using an environmentally friendly and sustainable method known as supercritical hydrothermal synthesis. This method utilizes water as a solvent and is highly advantageous for producing nanoparticles due to its reactivity and excellent solvent power.^{33–40} Recent research has demonstrated the scalability and potential for mass production of CeO₂ nanocubes through a continuous flow synthesizer, making them highly valuable for industrial applications.^{37,38} The authors' research group has confirmed high catalytic activity for the reforming of carbonaceous materials, such as heavy oil, lignin, and methane, at low temperatures (300–400 °C) using CeO₂ nanocubes with high oxygen vacancies. This suggests the tunable interaction of carbon atoms with CeO₂^{33–37} under oxidation or reduction conditions.

The above information suggests that CO₂ adsorption is affected by the morphology (exposed surface) of CeO₂ nanoparticles as well as the oxidation state. This information is critical for designing the CO₂ adsorption/desorption process and/or determining operational conditions. Therefore, in this study, the effects of (1) the exposed surface and (2) the oxidation state of CeO₂ on CO₂ adsorption were analyzed. Two facet-controlled CeO₂ systems, cubic CeO₂ with {001} facets vs polyhedral CeO₂ with {111} facets, were employed to elucidate the mechanism of CO₂ adsorption on CeO₂ and demonstrate different morphologies that require different treatment (oxidation/reduction).

EXPERIMENTS

Materials. Cubic CeO₂ exposing {001} crystal facets were synthesized through supercritical hydrothermal synthesis with *in situ* modification originally developed by this research group. For characterization and CO₂ adsorption–desorption, the organic modifier was removed via post-treatment (calcination). The synthesis and post-treatment methods were the same as previously reported methods.^{33,37} Polyhedral CeO₂ exposing multifacets (mainly {111} facets) was purchased from Sendai Wako Pure Chemicals Ltd. (544841, CeO₂ nanopowder, < 25 nm Sigma-Aldrich, Japan) and used without further treatment. Various high-purity gases (G1 grade, CO₂, Ar, O₂, He, 4% O₂ in Ar, and 4% H₂ in Ar) were purchased from Tanuma Sanso Shokai Co., Ltd. and used without further purification. Pure hydrogen gas was obtained using a hydrogen generator via water

electrolysis (Precision Hydrogen 300; Peak Scientific Instruments, UK).

Characterization. For morphological analysis, high-resolution transmission electron microscopy (HR-TEM, Topcon, Japan, EM-002B, 200 kV, LaB6) was used, and local crystal diffraction patterns were obtained using selected-area electron diffraction (SAED). The SAED patterns were analyzed using *SingleCrystal* (CrystalMaker Software Limited, UK, version 4.1.4). The crystallographic phases of the powder CeO₂ nanoparticles were analyzed using powder X-ray diffraction (XRD, RIGAKU, Japan, Smart Lab 9MTP/RASCO 3 M with Cu K α radiation, $\lambda = 0.154$ nm, $20 \leq 2\theta \leq 100^\circ$, operated at 45 kV and 200 mA, parallel beam, step = 0.02°). Standard Si (RSP43275 G, RIGAKU, Japan, $a = 5.4301$ Å) was used for calibration before the sample measurement. No internal standard was used for any of the measurements. Rietveld refinement was performed for all the XRD results using PDXL (RIGAKU, Integrated X-ray powder diffraction software, ver. 2.4.2.0). Raman spectroscopy (HORIBA, Japan, LabRAM HR-800, 532 nm laser excitation used) was used to analyze the internal and surface binding states of CeO₂. The temperature-programmed reduction using hydrogen, H₂-TPR (10% H₂ in He, 50 cm³/min, 10 °C/min, BELCAT-II, MicrotracBEL Corp. Japan), was used to obtain the oxygen storage capacity (OSC) of CeO₂ after 20% O₂ pretreatment at 400 °C for 30 min.

DRIFTS spectra were collected using a Thermo-Nicolet iSS0 FTIR spectrometer equipped with a rapid-scanning option, liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector, and a Praying Mantis high-temperature reaction chamber (Harrick Scientific Products). The experiments were performed at the Structure and Dynamics of Applied Nanomaterials (SDAN) laboratory at the Chemistry Division of Brookhaven National Laboratory. Prior to measurement, each sample was heated at 150 °C for 30 min under He with a flow rate of 20 mL/min to remove surface adsorbed species followed by collection of background spectra under He at room temperature and 400 °C. For the treatment at each temperature, 10% CO₂ (balanced with He, the flow rate is 20 mL/min) was flowed through the reaction chamber for 30 min to acquire CO adsorption spectra followed by flowing He with a flow rate of 20 mL/min for 30 min to acquire CO desorption spectra.

CO₂ Adsorption/Desorption. CO₂ adsorption/desorption was performed by using thermogravimetry differential thermal analysis (TG-DTA) with mass spectroscopy (MS). TG-DTA was performed using STA 2500 Regulus (NETZSCH, Japan), and mass spectrometry (MS) was connected to TG-DTA and performed in real time using JMS-Q1500GC (JEOL Ltd., Japan, see Figure S2 in the SI). Approximately 0.1 g of a sample was placed in the TG sample unit, and the gas type, flow rate, and temperature were controlled for each section of process. The gas concentrations were 10% CO₂, 4% O₂, and 4% H₂ in Ar. Part of the flowing gas was moved to the MS unit in real time using a gas transfer unit and analyzed. The pretreatment conditions and other information for the isothermal adsorption/desorption are described in the Results and Discussion section. For CO₂ temperature-programmed desorption, CO₂-TPD and a BELMASS connected to a BELCAT-II instrument (Quadrupole MS, MicrotracBEL Corp., Japan) were used. All samples were pretreated with oxygen (20% in Ar) for 30 min at 400 °C. For producing the reduction state of CeO₂, additional hydrogen pretreatment (10% in Ar) for 2 h at 400 °C was conducted. CO₂ adsorption (10% CO₂ in Ar for 3 h at room temperature) was performed before increasing the temperature. Total flow rate was 50 cm³/min, and the temperature increase rate was 10 °C/min.

Simulation. Plane-wave basis DFT calculations were conducted to understand the effects of CO₂ adsorption on the CeO₂ surface using the VASP code.^{41,42} The generalized gradient approximation proposed by Perdew et al.⁴³ was employed as the exchange correlation energy functional. The DFT+U method introduced by Dudarev et al.⁴⁴ was used to treat electron localization, and the parameter $U-J$ was set to 5.0 eV for Ce 4f.⁴⁵ The valence configurations of the pseudopotentials were 5s²5p⁶4f¹5d¹6s² for Ce, 2s²2p⁴ for O, and 2s²2p² for C. The energy cutoff for the plane-wave basis was set to 500 eV for all calculations. Slab model calculations were carried out

using 108 atoms for CeO₂ (111) and 216 atoms for the (100) facet with a Monkhorst–Pack k-point mesh of 2 × 2 × 1. The total energy differences were converged to less than 0.001 eV in all calculations. The calculated crystallographic structure models were visualized via VESTA code.⁴⁶

RESULTS AND DISCUSSION

Effect of Facet and Oxidation State on Surface Characteristics of CeO₂. Figure 1a shows polyhedral CeO₂

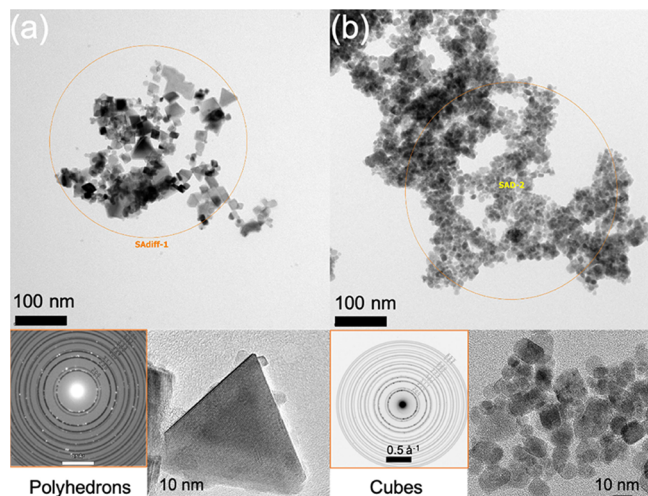


Figure 1. TEM images of different morphology of CeO₂ nanoparticles: (a) nano polyhedrons; (b) nanocubes. Bottom left is the SAED pattern, and bottom right is a high-resolution image, respectively.

nanoparticles. According to the specifications of this sample, the mean particle size was 25 nm, and the particles had a wide size distribution ranging from 5 to 60 nm. In the magnified image of a particle shown in the lower right of (a), well-ordered crystal fringes without defects were observed. The diffraction pattern of the selected area is shown in the lower-left panel of (a). The morphology was diverse and included octahedrons, truncated octahedrons, fragmented octahedrons, and triangles (termed polyhedral CeO₂ in this study). Octahedral CeO₂ mainly exposes the {111} facets, whereas the others have additional {100} and {110} facets. In other words, polyhedral CeO₂ has multiple exposed surfaces (multiple facets).

The exposed facets of CeO₂ can be controlled by adding capping agents that are preferentially adsorbed onto less stable facets (high surface energy). A supercritical hydrothermal synthesis method with in situ capping was used to control the facets of the CeO₂ nanoparticles.^{33,37} The cubic nanoparticles prepared in this study have an average size of approximately 10 nm, as shown in Figure 1b. The nanoparticles are well

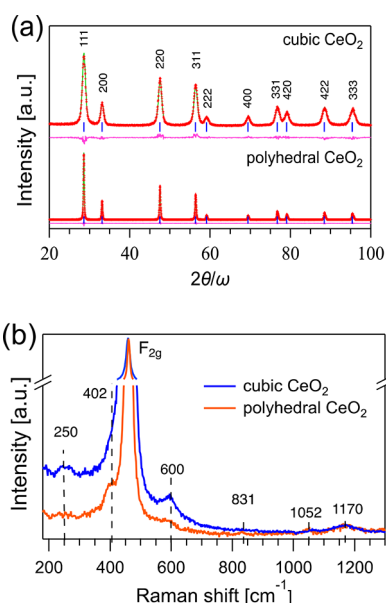


Figure 2. Physical and chemical properties of CeO₂ according to their morphologies: (a) powder XRD peak patterns; (b) Raman spectra (532 nm).

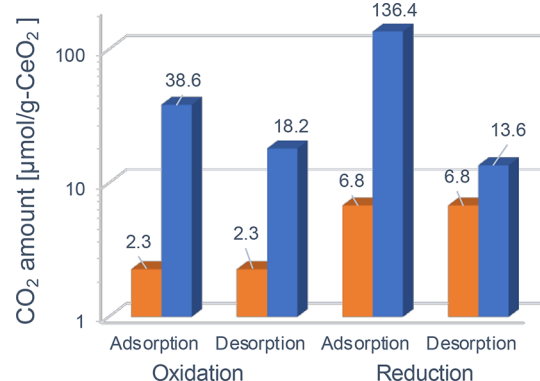


Figure 3. Isothermal adsorption and desorption of CO₂ at 400 °C according to oxidation state of CeO₂: (orange) multifacets exposed polyhedral CeO₂; (blue) {001} facets exposed cubic CeO₂.

dispersed even after calcination. An enlarged high-resolution photograph of the nanoparticles is provided in the bottom-right corner of Figure 1b. Most of the particles show specific crystal faces, mainly judged by the {001} facets, although some particles have rounded corners. The significantly greater OSC values compared to polyhedral CeO₂ support the notion that most particles expose the {001} facets (Table 1). The diffraction pattern of selected particles is shown in (b) (orange circle) on the lower left. This agrees well with the simulated

Table 1. Structural Analysis and Properties of Each CeO₂ Morphology Type

morphology type of CeO ₂	crystal size, XRD (TEM) [nm]	lattice constant [nm]	strain [%]	refinement parameters		BET [m ² /g]	OSC ^a [μmol-O/g] at 400 °C (β) ^b	Ce ³⁺ fraction ^c [%]
				R _{wp} [%]	S			
polyhedrons	28.8 (23.8)	5.4114	0.081	16.24	1.1258	6.57	49 (29)	0.01
cubes	7.2 (8.1)	5.4139	0.26	10.87	1.1432	94.04	198 (123)	0.63

^aEvaluated using the H₂-TPR method. ^bβ region OSC (250–400 °C) in H₂-TPR. ^cEvaluated by magnetic analysis (SI).

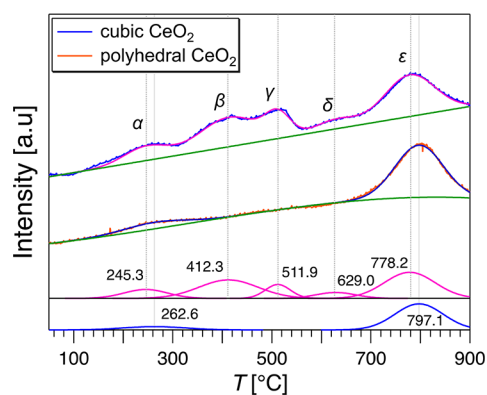


Figure 4. Temperature-dependent reduction behavior of cubic and polyhedral CeO₂ using H₂-TPR. The peaks were fitted using Multipole Fit of Igor Pro 8 (ver. 8.04).

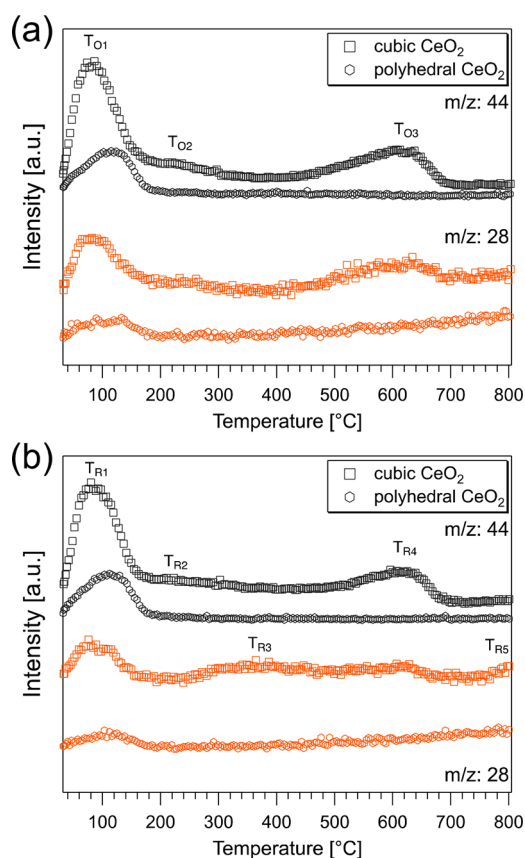


Figure 5. Temperature-programmed CO₂ desorption (CO₂-TPD) with mass spectrometry (MS) according to oxidation/reduction state and morphology (exposing facet) type of CeO₂ nanoparticles: (a) fully oxidized CeO₂; (b) reduced CeO₂. The *m/z* 44 represents for CO₂, and *m/z* 28 represents for CO₂ fragment or CO.

pattern of CeO₂ (SingleCrystal), which suggests good crystallinity without impurities.

Figure 2a shows the powder XRD peak patterns of the two different types of CeO₂, and the results of the Rietveld refinement are summarized in Table 1. Both samples exhibit a pure CeO₂ peak pattern. The crystallite size of the polyhedral sample, evaluated using the Halder–Wagner method,^{47,48} was 28.8 nm, which is similar to the average particle size of 25 nm specified for this sample (TEM, mean 23.8 nm, SD 10.6). For cubic CeO₂, the XRD patterns showed a relatively broad peak,

which implied the presence of small nanoparticles. The crystallite size evaluated was 7.2 nm, which is close to that confirmed by the TEM image (mean, 8.1 nm, SD 1.1). These results suggest that both types of CeO₂ particles are single crystals. The specific surface areas of the two CeO₂ samples were significantly different (14.3 times greater for cubic CeO₂ than for polyhedral CeO₂). Compared with polyhedral CeO₂, another characteristic of cubic CeO₂ observed in the XRD results is the lattice distortion and expansion of the lattice constant. This is attributed to the smaller crystal size and the formation of oxygen defects.^{31,32,38,49–52}

The surface nature of CeO₂ was analyzed by using Raman spectroscopy (Figure 2b), which revealed the Ce–O bonding state. For both CeO₂ nanoparticles, the peak (402 cm⁻¹) corresponding to the transverse Ce–O stretching vibration was observed. For cubic CeO₂, a red-shift in the F_{2g} mode and broadening occurred (465.2 cm⁻¹) from bulk CeO₂ (465 cm⁻¹), which was probably due to the nanosize effect. Additionally, clear peaks corresponding to the Ce–OH stretching vibration and oxygen vacancy at 250 and 600 cm⁻¹, respectively, were observed in the Raman spectra of cubic CeO₂. In contrast, polyhedral CeO₂ has weaker peaks at 600 and 831 cm⁻¹, suggesting fewer oxygen vacancies and peroxide vibrations (O₂²⁻).⁵³ All of these can act as CO₂ adsorption sites.

Effect of Facet and Oxidation State of CeO₂ on CO₂ Adsorption/Desorption. The above results suggest that the CO₂ adsorption/desorption behavior depends on the morphology (exposed facet) of CeO₂ due to the different surface characteristics such as oxygen vacancy that can be affected by the oxidation/reduction treatment of CeO₂.^{31–38,54–56} Figure 3 shows the CO₂ adsorption level measured by TG for both polyhedral CeO₂ (orange) and cubic CeO₂ (blue) at 400 °C. Here, a sufficiently high temperature was used to expect complete CO₂ desorption. The CO₂ adsorption/desorption amount was evaluated based on the weight change of CeO₂. The original TG data obtained using MS can be found in the SI (Figures S1 and S2, in the form of wt %). For polyhedral CeO₂, in both the oxidation and reduction states, the adsorption and desorption amounts were the same, indicating reversible CO₂ adsorption. The adsorbed amount was 3-fold higher after reduction treatment. This is likely due to the formation of oxygen vacancies on the CeO₂ particles, which could capture more CO₂ molecules. Thus, this finding led to an improvement in the CO₂ capture process using CeO₂ as an adsorbent by reducing the treatment beforehand.

Compared with polyhedral CeO₂, cubic CeO₂ has a greater amount of CO₂ adsorbed in both the oxidized and reduced states. Similarly to polyhedral CeO₂, the reduced cubic CeO_{2-x} exhibited a 3.53-fold increase in the adsorption capacity compared to its oxidized counterpart. The amount of CO₂ adsorbed on cubic CeO₂ was greater than that desorbed for both the oxidation and the reduction states. In other words, CO₂ desorption is relatively difficult because of the strong interactions between cubic CeO₂ and CO₂. Cubic CeO₂ strongly absorbs CO₂ owing to low CO₂ adsorption energy around oxygen vacancies.⁵⁷ Notably, the adsorption of CO₂ on CeO₂ through oxygen vacancies is not solely determined by oxygen vacancy concentration. In our previous study, it was found that small cubic CeO₂ of a few nanometers is easily reduced to the particle core as well as to the surface.^{31,32} This means that oxygen is easily released from the surface and can

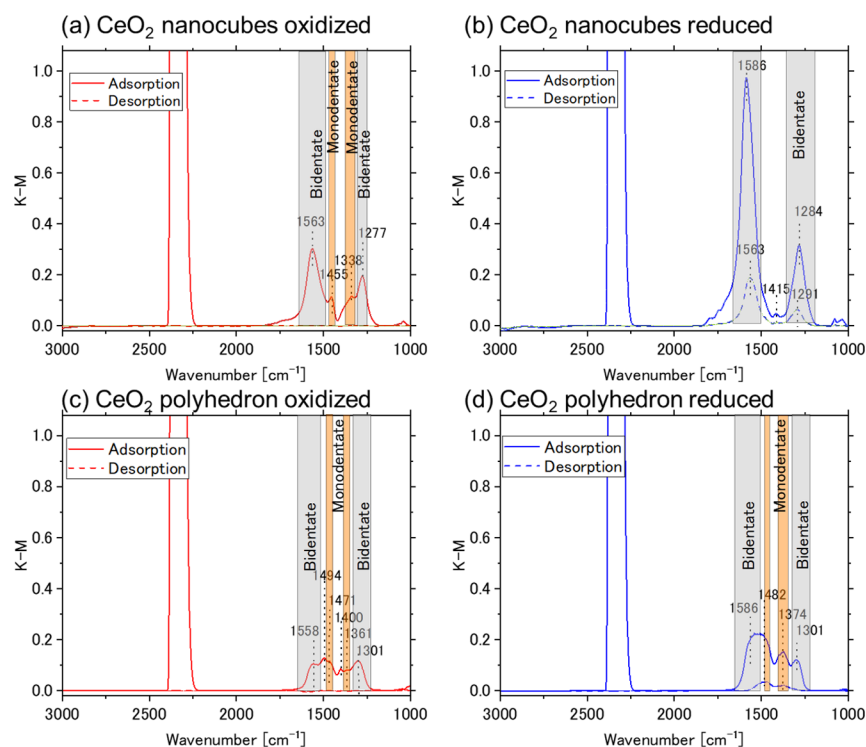


Figure 6. In situ DRIFTS data at 400 °C with CO₂ adsorption and following desorption with He flow. (a) Oxidized cubic CeO₂ (mainly bidentate-II); (b) reduced cubic CeO₂ (mostly bidentate-II); (c) oxidized polyhedron CeO₂ (monodentate and bidentate-II); (d) reduced polyhedron CeO₂ (monodentate and bidentate-II). Bidentate-II: 1575 and 1294 cm⁻¹, monodentate: 1442 and 1373 cm⁻¹.⁶⁵

diffuse through the particles. This property can provide favorable conditions for the formation of strong carbonate.¹⁹ The stable polydentate configuration requires temperatures of 500 °C or higher for the release of CO₂ to be released. The irreversible CO₂ adsorption observed in cubic CeO₂ at 400 °C, as shown in Figure 3, can be attributed to the strong CO₂ adsorption that mostly occurs in the first step and is irreversible. On the other hand, weaker CO₂ adsorption can be reversible, as confirmed through repeated CO₂ adsorption/desorption cycles (see Figure S3 in the SI).

The above results demonstrate that the number of oxygen vacancies present depends on the exposed facet species and redox treatment, which directly affects the CO₂ adsorption configuration. Freund's group⁵⁸ studied the dissociation of hydrogen on the surface of CeO₂ during hydrogen treatment and the change in Ce³⁺ ratio according to annealing temperature. Therefore, it is crucial to examine the CO₂ desorption process based on the number of oxygen vacancies in CeO₂. As shown in Figure 4, the H₂-TPR analysis revealed the reduction tendency of each CeO₂ sample, and the OSC of each CeO₂ sample was evaluated by the amount of hydrogen consumed (see Table 1). For cubic CeO₂, small peaks appeared at around 245 (α) and 629 °C (δ), and relatively large peaks are observed at around 412 (β) and 512 °C (γ). The largest peak was observed at 778.2 °C, (ε). The reducibility of cubic CeO₂ nanomaterials at low temperatures is high compared to other CeO₂-based composite nanomaterials, with a reduction rate of 54.2% up to 540 °C.^{31–38} On the other hand, for polyhedral CeO₂, a clear peak was not confirmed in the α, β, γ, δ regions, except the δ region of the high-temperature region. This suggests that cubic CeO₂ is easily reduced even at low temperatures, and the ratio of reduced CeO_{2-x} is high, while polyhedral CeO₂ is not

sufficiently reduced unless the temperature is approximately 800 °C.^{59,60}

The relationship between the adsorption strength and oxygen vacancies can be examined. In the case of polyhedral CeO₂, the peak in the β region is very weak, and there is no peak at all around 400 °C. Conversely, for cubic CeO₂, the peak in the β region is larger than that in the α region. This indicates that around 400 °C additional oxygen vacancies were formed, leading to strong CO₂ adsorption. Moreover, the formation of oxygen vacancies typically increases Lewis acidity, resulting in strong adsorption with Lewis bases such as CO₂.^{61,62} Although quantifying surface oxygen vacancy points is very difficult, the OSC in the β region is 123 μmol-O/g, which is very close to the irreversible CO₂ adsorption of cubic CeO₂, 122.8 μmol-CO₂/g, suggesting a one-to-one relationship between oxygen vacancy sites and strong carbonate bonding.

Because the reduced state of cubic CeO₂ is accompanied by strong CO₂ adsorption, various desorption patterns are expected depending on the temperature; therefore, the desorption process according to the temperature is examined as follows. Figure 5 shows the temperature-dependent desorption after CO₂ adsorption under an (a) oxygen or (b) hydrogen pretreatment for cubic CeO₂ and polyhedral CeO₂ (CO₂-TPD). For polyhedral CeO₂, CO₂ was desorbed below 180 °C, for both the oxidation state and reduction state. No clear desorption is observed at higher temperatures. Binet et al. reported that 300 °C or higher is required for the desorption of strongly adsorbed CO₂,¹⁹ and Slostowski reported a higher temperature of 500 °C.²⁹ This result indicated that only weak CO₂ adsorption occurred on the polyhedral CeO₂ surface. On the other hand, for cubic CeO₂, the TPD profiles were more complicated. First, a large amount of CO₂ is desorbed at low temperatures (T_{O1}, R₁). It is noteworthy that cubic CeO₂ has a

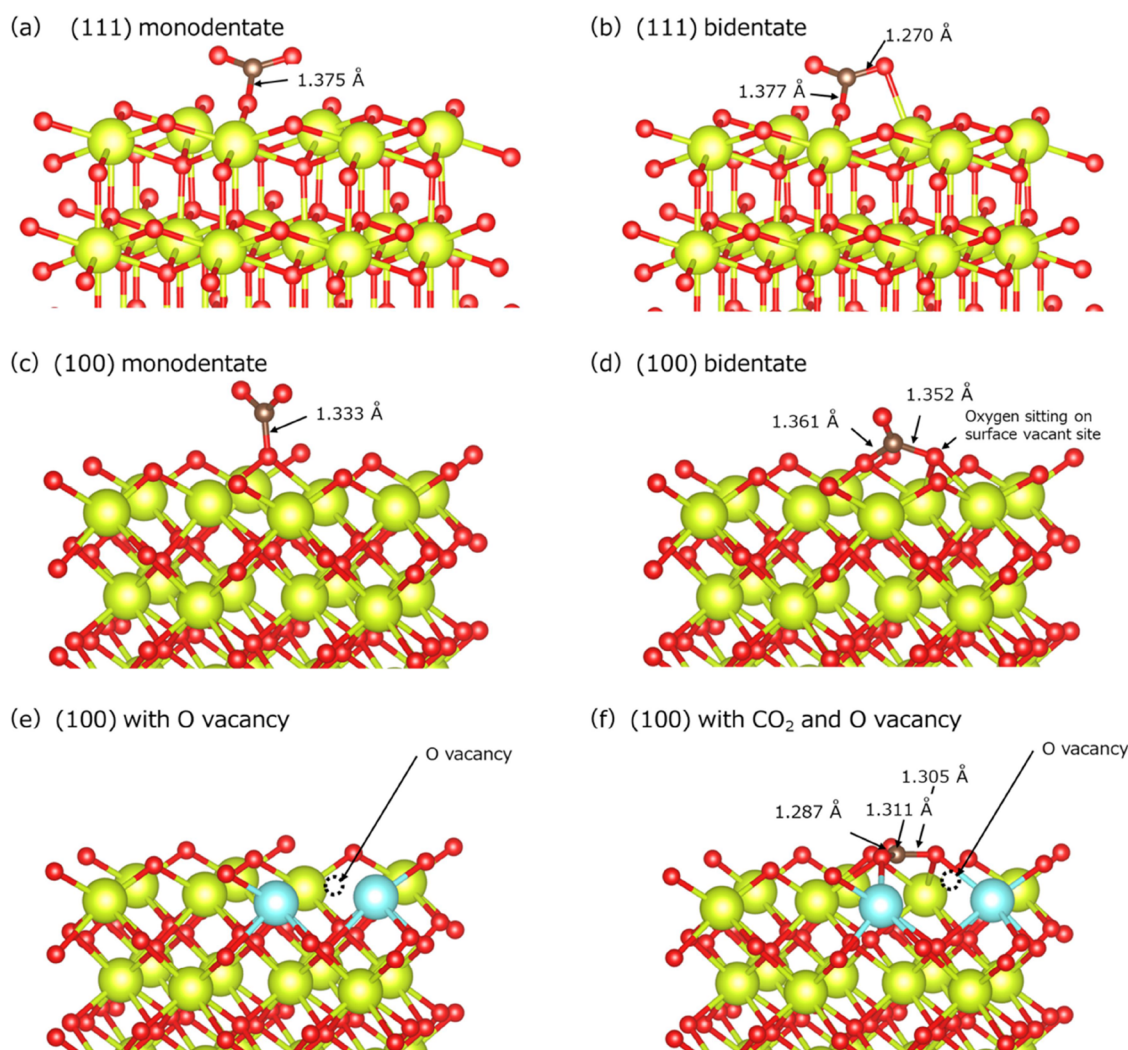


Figure 7. Adsorption state of CO₂ on CeO₂ (111) (a) monodentate, (b) bidentate, and CeO₂ (100) (c) monodentate, (d) bidentate. (e) CeO₂ (100) with an oxygen vacancy, light blue shows Ce³⁺, (f) strong CO₂ adsorption on CeO₂ (100) with an oxygen vacancy. The simulations were conducted for the slab models, and enlarged figures are shown.

peak position (81.7 °C) lower than that of polyhedral CeO₂ (119.3 °C) in the T_{O1} region. In addition, CO₂ was further desorbed near 200 °C (T_{O2, R2}). As demonstrated by the results of isothermal adsorption and desorption, weak CO₂ adsorption occurred even in cubic CeO₂, and it was confirmed that this ratio was also significant. As the temperature rises further, a large peak was detected in the range of temperature from 420 to 670 °C (T_{O3, R4}, 620 °C), which corresponds to the strongly bonded CO₂.

The differences between the oxidation and reduction treatments in cubic CeO₂ were clearly observed in the T_{R3} and T_{R5} regions. In the oxidation state, weakly adsorbed CO₂ were almost removed at around 300 °C, whereas a gentle peak continued up to approximately 450 °C for cubic CeO_{2-x}. In the reduced state, continuous desorption occurred from T_{R2} to T_{R4}. In the T_{R3} region, a gentle peak that appeared to be CO, that is, CO₂ dissociative desorption, was observed, rather than the CO₂ fragment peak. The reason for this is that CO₂ adsorption takes place at oxygen vacancy sites of CeO_{2-x} which can act as reducing sites.^{63,64} Typically, this reaction occurs at high temperatures of 800 °C or higher (T_{R5}).^{28,33} However, in the case of cubic CeO_{2-x} it occurred at much

lower temperatures between 250 and 450 °C, likely due to its high reduction potential.

Adsorption and Desorption Mechanism. The adsorption and desorption behaviors of CO₂ on different surface states of CeO₂ were studied using the DRIFTS technique. Figure 6 shows in situ DRIFTS data during the adsorption of CO₂ and the subsequent desorption under an inert atmosphere for both cubic and polyhedron particles with oxidized or reduced states at 400 °C. The adsorption state of CO₂ differed between cubic and polyhedron CeO₂. Specifically, CO₂ tends to be more strongly adsorbed on {001} facets (mainly bidentate-II) compared to {111} facets (mainly monodentate).⁶⁵ The reduction of these CeO₂ samples enhances the adsorption of CO₂ because of the formation of oxygen vacancies, which is particularly significant for cubic CeO₂ with a more reducible surface. During the inert gas flow after the introduction of CO₂ introduction, desorption of CO₂ was observed, although remaining adsorbed CO₂ was observed for reduced CeO₂, which is not observed in oxidized CeO₂. These results are consistent with the results of TG measurements for CO₂ adsorption and desorption (Figure 3). The difference in the CO₂ adsorption behavior depending on the morphology and reduction state of CeO₂ originates from the different

bonding states of CO₂. The {001} facets are inherently polar and include surface vacancy sites, whereas the oxidized {111} facets are nonpolar surfaces.

Figure 7 illustrates the adsorption states of CO₂ on CeO₂ (100) and (111) surfaces, which was calculated by first-principles simulations. On (111) surface, the CO₂ adsorption energy was −0.56 eV/molecule for both monodentate and bidentate states (Figure 7a,b). On the contrary, CO₂ adsorption energy for the (100) facet was −1.10 eV/molecule for bidentate state (Figure 7c) while monodentate state did not contribute surface stabilization (+0.26 eV/molecule, Figure 7d). The stoichiometric model of the (100) facet is terminated by an oxygen layer but with half of the vacancy sites because the (100) surface is polar and one of the oxygen atoms of adsorbed CO₂ located on the surface vacant site (Figure 7d), resulting in stronger adsorption. Because of these difference in the surface structure, stronger bidentate adsorption occurs on (100) surface, and the amount of adsorption increases by reducing the surface. Compared to (111) surface, more oxygen vacancies are easily formed on (100) surface and that causes a significant difference in the adsorption energies. When an oxygen vacancy is created on CeO₂ (100) facet, the adsorption energy of CO₂ was found to be −3.40 eV/molecule and the surface stabilization effects was more significant than the stoichiometric surface.

CONCLUSIONS

In this study, the CO₂ adsorption/desorption behaviors of cubic CeO₂ nanoparticles exposed to {001} facets and polyhedral CeO₂ with {111} facets were analyzed under oxidation and reduction conditions. Polyhedral CeO₂ exhibited reversible adsorption in both the oxidized and the reduced states, with a higher adsorption capacity observed in the reduced state. The formation of weaker bonds with adsorbed CO₂ contributed to the reversible adsorption at low temperatures (50–150 °C). In contrast, cubic CeO₂ displayed irreversible adsorption behavior due to the formation of a strong bidentate configuration with oxygen vacancies.

The distinctions in CO₂ adsorption and desorption behaviors, analyzed by TG-DTA with MS, were validated through in situ DRIFTS analysis and DFT calculations, providing insights into molecular behavior. High concentrations of oxygen vacancies induced dissociative desorption of CO₂ even at low temperatures (250–400 °C), significantly lower than that of polyhedral CeO₂ (>800 °C). Consequently, CO₂ adsorption and desorption exhibit dramatic differences depending on the facet species and redox treatment. Therefore, they are expected to contribute to more effective CCS through careful engineering of materials and control of process conditions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.4c01322>.

CO₂ adsorption and desorption TG-DTA original data, MS profiles, cyclic operation result, and Ce³⁺ fraction analysis (PDF)

AUTHOR INFORMATION

Corresponding Authors

Gimyeong Seong – *New Industry Creation Hatchery Center, Tohoku University, Sendai 980-8579, Japan; Department of Environmental and Energy Engineering, The University of Suwon, Hwaseong-si, Gyeonggi-do 18323, Republic of Korea;* orcid.org/0000-0003-4292-5936; Phone: +82-31-229-8829; Email: soppua4@suwon.ac.kr; Fax: +82-31-229-8829

Tadafumi Adschiri – *New Industry Creation Hatchery Center, Tohoku University, Sendai 980-8579, Japan; WPI-Advanced Institute for Materials Research (WPI-AIMR), Tohoku University, Sendai 980-8577, Japan; Phone: +81-22-217-6321; Email: tadafumi.ajiri.b1@tohoku.ac.jp; Fax: +81-22-217-6321*

Authors

Akira Yoko – *WPI-Advanced Institute for Materials Research (WPI-AIMR), Tohoku University, Sendai 980-8577, Japan; International Center for Synchrotron Radiation Innovation Smart, Tohoku University, Sendai 980-8579, Japan;* orcid.org/0000-0002-1278-272X

Takaaki Tomai – *Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan;* orcid.org/0000-0003-0296-6565

Takashi Naka – *National Institute of Materials Sciences (NIMS), Tsukuba, Ibaraki 305-0047, Japan*

Haodong Wang – *Department of Materials Science and Chemical Engineering, Stony Brook University, Stony Brook, New York 11794, United States*

Anatoly I. Frenkel – *Department of Materials Science and Chemical Engineering, Stony Brook University, Stony Brook, New York 11794, United States; Chemistry Division, Brookhaven National Laboratory, Upton, New York 11973, United States;* orcid.org/0000-0002-5451-1207

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acssuschemeng.4c01322>

Author Contributions

G.S.: conceptualization, methodology, investigation, and writing of the original draft. A.Y.: DFT calculation, review, and editing the manuscript. T.T.: review and editing the manuscript. T.N.: magnetic analysis. H.W. and A.I.F.: DRIFTS analysis. T.A.: conceptualization, supervision, funding acquisition, review, and editing the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by JSPS KAKENHI (Grant Number 20K20548, 20K21856, 21K04763, 21KK0085, and 21H05010), the JST CREST Grant Number JPMJCR16P3, JST-Mirai Program Grant Number JPMJMI17E4, the New Energy and Industrial Technology Development Organization (NEDO, Moonshot Research and Development Program, grant no. JPNP18016), the Materials Processing Science Project (Materialize; grant number JPMXP0219192801), the Core Research Cluster for Materials Science, and the World Premier International Research Center Initiative—Advanced Institute for Materials Research (WPI-AIMR), Tohoku University, established by the WPI, Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. This

work was also supported by the Japan-Korea Basic Scientific Cooperation Program between the JSPS and NRF (grant number JPJSBP120218803), the research grant of the University of Suwon in 2023 and supported by the collaboration programs of RIAM of Kyushu University. A.I.F. and H.W. acknowledge support of the U.S. DOE, Office of Science, Office of Basic Energy Sciences grant no. DE-SC0022199. Images and video generated using CrystalMaker®: a crystal and molecular structures program for Mac and Windows. CrystalMaker Software Ltd., Oxford, England (<http://www.crystallmaker.com>). Associate Professors Kumashiro and Mr. Saito (Technical Support Center, Tohoku University) supported the XRD and Raman measurements. The HR-TEM measurements were supported by Mr. Ito (Analytical Research Core for Advanced Materials, Institute for Materials Research, Tohoku University). We would like to thank Editage (<https://www.editage.jp>) for English language editing.

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