

Effect of Dopants on the Adsorption of Carbon Dioxide on Ceria Surfaces

Meijun Li,^[b] Uma Tumuluri,^[a] Zili Wu,^{*[a]} and Sheng Dai^{*[a, b]}

High-surface-area nanosized CeO₂ and M-doped CeO₂ (M = Cu, La, Zr, and Mg) prepared by a surfactant-templated method were tested for CO₂ adsorption. Cu, La, and Zr are doped into the lattice of CeO₂, whereas Mg is dispersed on the CeO₂ surface. The doping of Cu and La into CeO₂ leads to an increase of the CO₂ adsorption capacity, whereas the doping of Zr has little or no effect. The addition of Mg causes a decrease of the CO₂ adsorption capacity at a low Mg content and a gradual increase at a higher content. The CO₂ adsorption capacity fol-

lows the sequence Cu-CeO₂ > La-CeO₂ > Zr-CeO₂ ≈ CeO₂ > Mg-CeO₂ at low dopant contents, in line with the relative amount of defect sites in the samples. It is the defect sites on the surface, not in the bulk of CeO₂, modified by the dopants that play the vital role in CO₂ chemisorption. The role of surface oxygen vacancies is further supported by an in situ IR spectroscopic study of the surface chemistry during CO₂ adsorption on the doped CeO₂.

Introduction

Acid gases are ubiquitous in multiple large-scale energy applications. CO₂ is the most important greenhouse gas that affects climate change and also represents an important future carbon feedstock.^[1–3] In addition, SO_x, NO_x, and H₂S are critical components of energy-related gas mixtures. The control of CO₂ in the atmosphere is a challenging research topic; therefore, there is growing interest in the development of technologies for the efficient adsorption or storage of large quantities of CO₂.^[4,5] There are many techniques available to remove CO₂ with different advantages and limitations. One of the most advanced methods for the removal of CO₂ is either physical or chemical sorption of CO₂ on solid surfaces. To achieve a sustainable energy future there is a great need to find inexpensive, effective, and suitable sorbents for CO₂ capture.

Recently, various porous materials with good structural and chemical properties for CO₂ sorption have been investigated widely, which include zeolites,^[6–8] carbon,^[9–11] silica-based materials,^[12–14] and metal–organic frameworks.^[15,16] With high stability, abundant availability and low cost, sorbents based on metal oxides have shown great potential for the effective sorption of CO₂ from synthesis gas and flue gas. A few studies have re-

ported that various metal oxides are able to adsorb CO₂ molecules on their surface, which include iron oxide, lithium oxide, magnesium oxide, aluminum oxide, titanium oxide, and zirconium oxide.^[17–21] CeO₂ and CeO₂-based oxides have been investigated intensively as catalysts, metal supports, and promoters.^[22–24] Particularly, doped CeO₂ materials have been investigated extensively because of their improved physiochemical properties and decreased oxidation enthalpies compared to pure CeO₂. CeO₂ has an ability to endure both acid and base properties on the surface that depends on the nature and temperature of the pretreatment. Vivier and Duprez have indicated that CeO₂ exhibited the highest number of surface basic sites among a number of selected metal oxides, which is advantageous in terms of CO₂ capture.^[25] Another favorable feature is that the thermal stability, oxygen vacancies, redox properties, and base–acid properties can be tuned by doping M (M = Zr, La, Mn, etc.) into CeO₂.^[26–29] Yang and co-workers reported that a Sm-doped CeO₂ nanomaterial showed an excellent CO₂ capture ability. They attributed the CO₂ adsorption ability to the abundant oxygen vacancies of Sm-doped CeO₂.^[30] However, Lykhach et al. reported that CO₂ activation on CeO₂ led to the rapid formation of a carbonate and surface carboxylates.^[31] So far, the practical application of CeO₂ for CO₂ capture has not been investigated fully, and the mechanism of CO₂ interaction with CeO₂ and doped CeO₂ at room temperature is poorly understood. Thus, an understanding of the chemistry that occurs at the CeO₂ surface in the presence of CO₂ is of significance in the development of more effective oxide-based CO₂ sorbents.

In this paper, a series of high-surface-area CeO₂ and M-doped (M = Cu, La, Zr, and Mg) CeO₂ nanomaterials was prepared by a surfactant-templated method, and the CO₂ capture behavior of these materials was tested at 303 K. Mesoporous CeO₂ exhibits a significant CO₂ adsorption capacity. Furthermore, it has been shown that the presence of dopants can fur-

[a] Dr. U. Tumuluri, Dr. Z. Wu, Dr. S. Dai
Chemical Sciences Division
Oak Ridge National Laboratory
1 Bethel Valley Road
Oak Ridge, TN 37831 (USA)
E-mail: wuz1@ornl.gov
dais@ornl.gov

[b] Dr. M. Li, Dr. S. Dai
Department of Chemistry
University of Tennessee
1420 Circle Drive
Knoxville, TN 38996 (USA)

Supporting Information for this article is available on the WWW under <http://dx.doi.org/10.1002/cssc.201500899>.

ther tune the surface functionalities, such as the surface acid–base properties and defect sites, which impact the adsorption behavior of CO₂ on the CeO₂ surface.

Results

Physical properties and structural characterization

Representative SEM images of CeO₂ and 4 mol% Cu–CeO₂ are shown in Figure 1. Pure CeO₂ shows a wormlike pore structure, which results from the closely aggregated metal oxide nanoparticles. A comparison of the microscopy images shows that the addition of the dopants does not alter the primary structure of the CeO₂. The overall structure of the doped CeO₂ is similar to the wormlike structure of the pure CeO₂, and the nanoparticle size appears to be in the range of 5–8 nm for all samples.

The textural properties of the CeO₂ and doped CeO₂ materials were examined by measuring their N₂ adsorption isotherms. Representative N₂ adsorption isotherms and the corresponding pore size distribution for pure CeO₂ and 4 mol% M–CeO₂ are shown in Figure 2. All the samples exhibit Type IV isotherms, which indicates the mesoporous nature of the materials. The BET surface area, pore volume, and actual dopant content

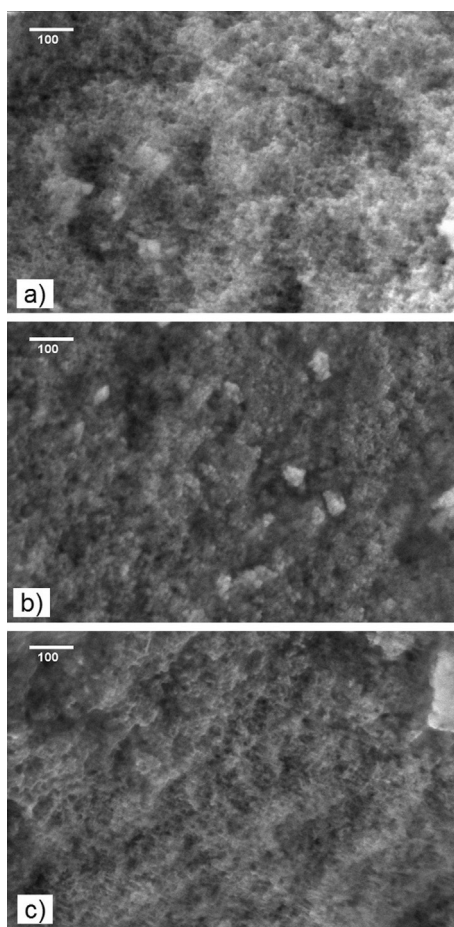


Figure 1. Representative SEM images of a) CeO₂, b) 4 mol% Cu–CeO₂, and c) 4 mol% La–CeO₂.

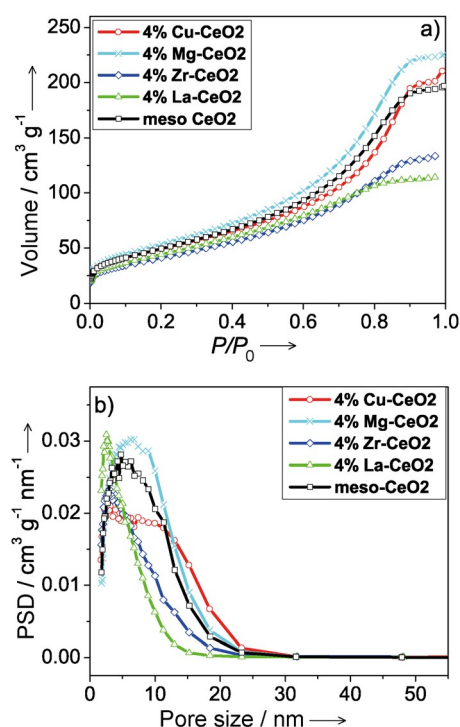


Figure 2. a) N₂ adsorption isotherms and b) corresponding pore size distributions of pure CeO₂ and 4 mol% M–CeO₂.

Table 1. The BET surface area, pore volume and actual dopants content (measured from ICP) of all samples.

Samples		Surface area [m ² g ^{−1}]	Pore volume [cm ³ g ^{−1}]	ICP concentration [mol %]
CeO ₂		181	0.300	
CuCeOx	5 %	179	0.311	4.2
	15 %	171	0.341	13.1
	34 %	138	0.189	29.2
LaCeOx	5 %	162	0.177	4.0
	15 %	159	0.266	11.6
	34 %	146	0.175	22.4
ZrCeOx	5 %	150	0.207	3.8
	15 %	172	0.194	11.6
	34 %	160	0.178	21.8
MgCeOx	5 %	195	0.346	3.8
	15 %	173	0.359	13.2
	34 %	160	0.434	27.0

(measured by inductively coupled plasma; ICP) of all samples are listed in Table 1. The BET surface area of the mesoporous CeO₂ is 181 m² g^{−1}. Compared with pure CeO₂, the surface areas were decreased for all 4 mol% M–CeO₂ samples except 4 mol% Mg–CeO₂. The decrease was more severe if the dopant content was further increased to 15 and 34 mol% for the Cu-, La-, and Mg-doped CeO₂ samples. The surface area was slightly enhanced with the increased Zr content for the Zr–CeO₂ samples. In addition, ICP results suggested that the actual dopant concentration is lower than the dopant concentration in the starting solution for all samples (Table 1).

The XRD profiles of CeO₂ and doped CeO₂ investigated in the present study are shown in Figure 3. The distinct fluorite

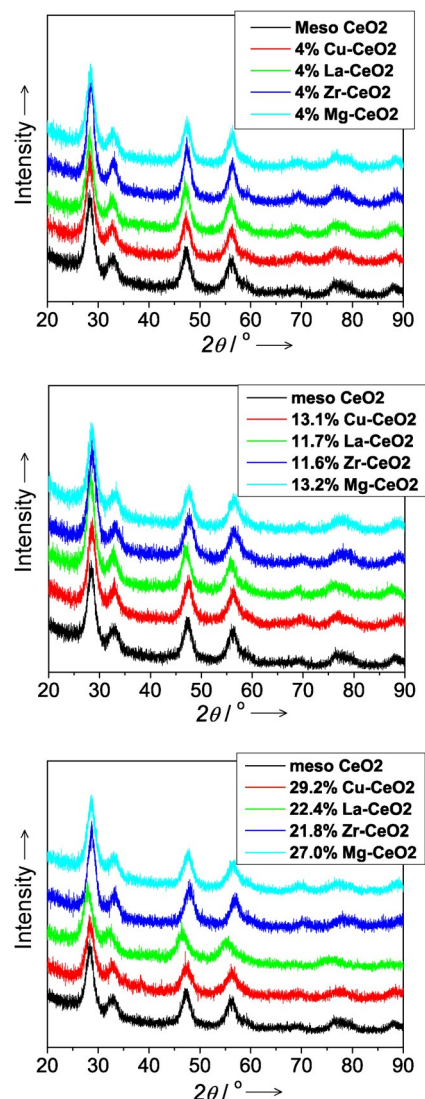


Figure 3. XRD patterns of CeO₂ and doped CeO₂ with different dopant concentrations.

oxide diffraction pattern of CeO₂ is seen in all of the samples. XRD measurements did not show any evidence of dopant metal oxide formation for La₂O₃, ZrO₂, and MgO at all concentrations. There were no CuO diffraction peaks observed at a low Cu content (4 and 13.1 mol%), however, weak diffraction peaks of CuO appeared if the Cu content was increased to 29.2 mol%, which indicates that bulk CuO was formed at this content. Interestingly, the diffraction peaks of the La- and Zr-doped CeO₂ samples are slightly shifted to various extents with respect to that of pure CeO₂ with increased dopant concentrations. These observations demonstrate that the dopants have been incorporated successfully into the lattice of CeO₂, and either lattice contraction or expansion is exhibited for La-CeO₂ and Zr-CeO₂ samples.^[32–34] The diffraction peaks of the Zr-CeO₂ samples are shifted to a higher angle relative to pure CeO₂, whereas the La-CeO₂ patterns are shifted to a lower angle. A shift in the peak positions could be elucidated by comparing the ionic radii of the dopants (~0.084 nm for Zr⁴⁺

and ~0.11 nm for La³⁺) and host ions (~0.097 nm for Ce⁴⁺). The ionic radius of La³⁺ is larger than that of Ce⁴⁺, hence lattice expansion is noticed for La-CeO₂ because of the incorporation of La³⁺ into the CeO₂ lattice. Conversely, lattice contraction is found for Zr-CeO₂ because of the substitution of Ce⁴⁺ by smaller Zr⁴⁺ cations. The observed key features for La-CeO₂ and Zr-CeO₂, peak shift and the absence of dopant oxide XRD peaks, confirm the formation of CeO₂-based solid solutions. In addition, the nonshifted XRD peaks together with the absence of diffraction peaks of MgO suggest that MgO may be well dispersed on the surface of CeO₂. The XRD pattern of Cu-CeO₂ (Figure 3) showed neither CuO diffraction peaks at a low Cu content (4 and 13.1 mol%) or a peak shift. This may be attributed to either the good dispersion of CuO on the surface of CeO₂, the formation of a solid solution, or a combination of both phenomena. The crystallite size of all samples calculated from XRD patterns is listed in Table 1. For all samples, the crystallite size is < 7 nm, which is in good agreement with the SEM results.

Raman spectroscopy is an excellent technique to investigate the structural properties of CeO₂-based materials because of its sensitivity to both M–O bond arrangement and lattice defects.^[35] Raman spectra of CeO₂ and 4 mol% M-CeO₂ are presented in Figure 4. All spectra exhibit the main peak at $\tilde{\nu}$ = 464 cm^{−1}, which could be assigned to the F_{2g} Raman-active

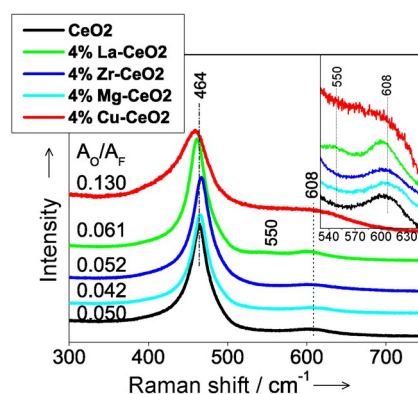


Figure 4. Raman spectra of CeO₂ and 4 mol% M-CeO₂.

mode of the fluorite-structured CeO₂. An additional small band at around $\tilde{\nu}$ = 608 cm^{−1} is caused by the defects related to oxygen vacancies (Ov).^[32–34] No Raman bands that correspond to dopant oxides are detected, which is in agreement with the XRD results. Notably, the F_{2g} band of 4 mol% Zr-CeO₂ is shifted to a higher wavenumber ($\tilde{\nu}$ = 468 cm^{−1}), whereas the F_{2g} bands of 4 mol% Cu-CeO₂ and 4 mol% La-CeO₂ are shifted to a lower wavenumber ($\tilde{\nu}$ = 460 cm^{−1} for La-CeO₂ and $\tilde{\nu}$ = 458 cm^{−1} for Cu-CeO₂) relative to pure CeO₂. There is no shift observed for 4 mol% Mg-CeO₂. The shift in the F_{2g} mode reveals the variation of the M–O vibration frequency, which is attributed to the difference in the radii of Ce⁴⁺ and the dopants.^[32–34] The difference in the ionic radius of the dopants enables changes in the lattice parameter caused by cell contraction or expansion. Hence vibrations are stiffer in a contracted lattice and more re-

laxed in an expanded lattice so that the bands shift to higher and lower wavenumbers, respectively. The shift in the F_{2g} band for 4 mol% Zr-CeO₂ and La-CeO₂ is consistent with the conclusions drawn from the results of XRD, which confirms the formation of CeO₂-based solid solutions for Zr-CeO₂ and La-CeO₂. Analogous to that of La-CeO₂, the shift of the F_{2g} mode in the Raman spectrum of Cu-CeO₂ indicates that a solid solution may have formed at a low Cu content.

Further, the incorporation of dopant ions into the CeO₂ changes the relative amount of oxygen vacancies (Figure 4, inset). The Cu-, Zr-, and Mg-doped CeO₂ and pure CeO₂ samples exhibited only one type of Ov band at around $\tilde{\nu}=608\text{ cm}^{-1}$, however, the La-CeO₂ samples displayed two bands at $\tilde{\nu}=550$ and 608 cm^{-1} . The lower-wavenumber band is caused by the extrinsic oxygen vacancies, and the higher-wavenumber band is induced by the intrinsic oxygen vacancies.^[34,36] Generally, the extrinsic vacancies could be formed because of the oxygen vacancies introduced into the CeO₂ to maintain the charge neutrality if Ce⁴⁺ ions are replaced with trivalent cations, whereas the intrinsic vacancies are generated by the presence of Ce³⁺ ions. Therefore, the Cu-, Zr-, and Mg-doped CeO₂ and pure CeO₂ promote only intrinsic vacancies attributed to the presence of Ce³⁺ ions in the samples. For La-doped CeO₂, both extrinsic and intrinsic vacancies were found, which can be ascribed to the doping of lower-valence La³⁺ as well as the presence of Ce³⁺ ions, respectively.

As the bands at $\tilde{\nu}=550$ and 608 cm^{-1} are related to oxygen vacancies and the band at $\tilde{\nu}=464\text{ cm}^{-1}$ is the main band of the CeO₂-based samples, the area ratio of these bands $A_{Ov}/A_{F_{2g}}$ (Figure 4, inset) can reflect the relative concentration of oxygen vacancies. As a result, $A_{Ov}/A_{F_{2g}}$ follows the sequence Cu-CeO₂ > La-CeO₂ > Zr-CeO₂ ≈ pure CeO₂ > Mg-CeO₂, which indicates that the Cu-doped sample had the most defect sites and the Mg-doped sample had the least. Notably, Raman spectroscopy is essentially a bulk technique. Therefore, the detected oxygen vacancies in the ceria and doped ceria samples are a sum of both the surface and bulk defects. As the particle size of all the samples here is small (~8 nm) and similar, it is reasonable to compare the relative amount of defect sites by Raman spectroscopy.

The F_{2g} bands further shifted to higher (for Zr) or lower (for Cu and La) wavenumbers with increasing dopant concentrations (Figure 5). Moreover, the amount of oxygen defects sites

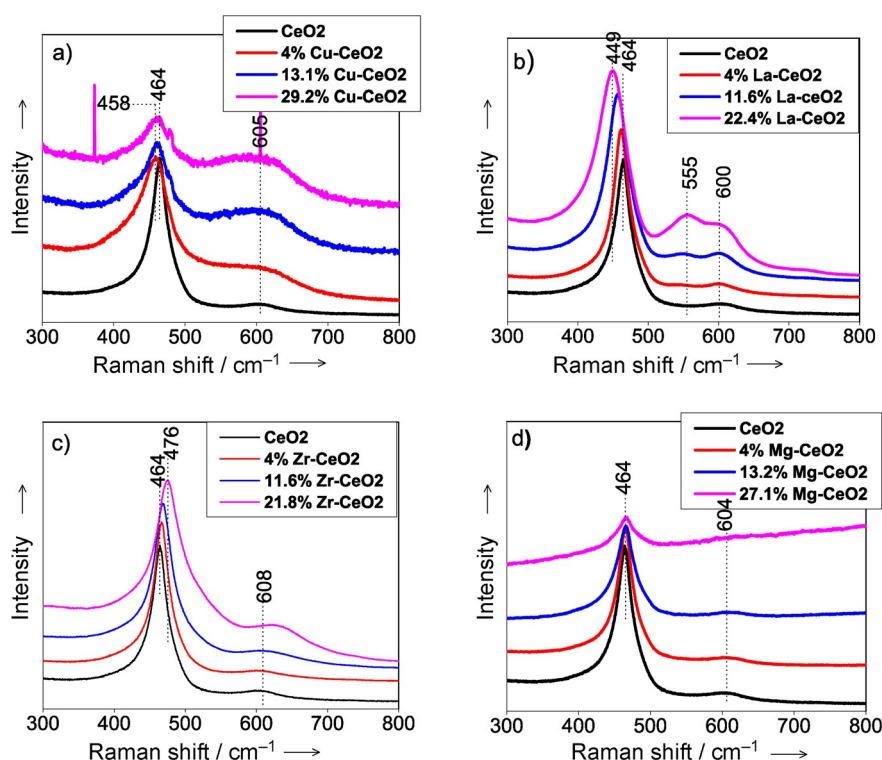


Figure 5. Raman spectra of a) Cu-CeO₂, b) La-CeO₂, c) Zr-CeO₂, and d) Mg-CeO₂ with different dopant concentrations.

increased with the increasing contents for Cu- and La-doped CeO₂, and there is no clear change observed with the enhanced Zr contents for Zr-CeO₂ (the corresponding $A_{Ov}/A_{F_{2g}}$ data are presented in Table 2). In addition, the presence of Mg leads to the disappearance of the oxygen vacancy band as shown in Figure 5 for Mg-CeO₂. Furthermore, there is no shift observed for Mg-doped CeO₂ at all concentrations. Samples with a higher Mg concentration caused a strong fluorescence background in the Raman spectra. This suggests that most of the MgO is distributed on the surface of the CeO₂, which is in good agreement with the XRD results. At a high Cu content, there is no CuO Raman band observed, probably because of the weak signal of CuO in Raman spectroscopy. Raman spectra combined with XRD results suggest the possible coexistence of the bulk CuO and CuCeO_x solid solution at a high Cu loading for Cu-CeO₂ samples.

To further investigate the distribution of dopants in ceria, low-energy ion scattering (LEIS) was used to analyze all the doped ceria samples. LEIS is particularly suited to determine the composition of the top atomic monolayer of a material (~0.3 nm) with a sensitivity on the order of 0.1 at%.^[37,38] The

Table 2. The Relative area ratio of $A_{Ov}/A_{F_{2g}}$ calculated from Raman spectra.

Samples	CeO ₂	Cu-CeO ₂	La-CeO ₂	Zr-CeO ₂	Mg-CeO ₂
4 mol %	0.050	0.13	0.061	0.052	0.042
~12 mol %		0.52	0.066	0.050	0.058
> 22 mol %		0.98	0.12	0.083	–

La-CeO₂ samples could not be profitably analyzed as there would not be sufficient mass resolution between peaks attributable to Ce and La even with the use of a Ne⁺ probe beam in LEIS. So only the results for Mg-, Zr-, and Cu-doped ceria samples are shown. To compare the trends of the Ce signal relative to the dopant signal with depth, the relative Ce signals to Mg, Cu, and Zr are each normalized by the value of this ratio after a sputter dose of $1 \times 10^{15} \text{ cm}^{-2}$ (Figure 6). The corresponding sputter depth was chosen instead of the native surface peak as the latter would have values that would be sensitive to original surface contaminants. The relative composition of Ce/dopants does not show a clear change with depth at low concentration (4 mol%; Figure 6A), which suggests that the dopants are well distributed in the ceria. At higher dopant concentrations (Figure 6B and C), the relative depth-dependent Ce signal appears to be affected sensitively by the presence of Mg, especially for the 27.0 mol% Mg-CeO₂ sample. Clearly, Mg tends to stay on the surface of ceria, which confirms the XRD and Raman spectroscopy results that suggest the dispersion of

Mg in the form of MgO on the ceria surface regardless of the dopant concentration. The effects of Zr and Cu seem similar to each other, and the relative ratio of Ce to Zr or Cu remains relatively unchanging for Zr at all doped concentrations and Cu at low concentration (4 and 13.1 mol%) or increases slightly for Cu at high concentration (29.2 mol%). This also agrees well with the results from XRD and Raman spectroscopy, that is, for Zr-CeO₂ samples, there is evident formation of a CeO₂-based solid solution, and for Cu-CeO₂, at a low loading Cu is inserted into the lattice of ceria, whereas CuO is formed on the ceria surface at the highest doping concentration.

In summary, La and Zr are well doped into the lattice of ceria without clear surface segregation. Cu incorporates into ceria at a low doping concentration and segregation occurs at the highest Cu concentration. Mg appears only disperses on the ceria surface at all doping levels. The incorporation of dopants (Cu, La, and Zr) into the ceria lattice results in larger amounts of oxygen vacancies relative to the pure ceria. The dispersion of MgO on the ceria surface does not change the vacancy density clearly.

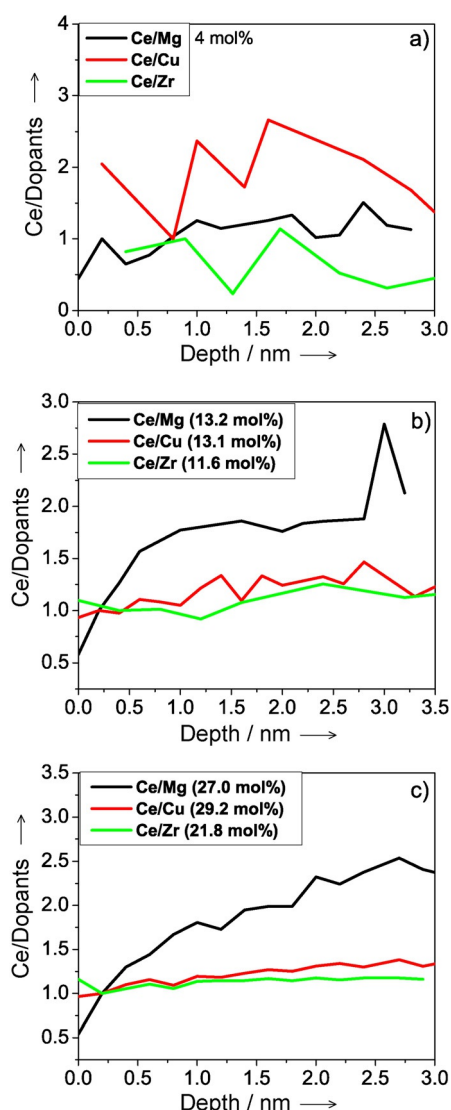


Figure 6. Normalized ratio of Ce to dopant LEIS signal with depth.

CO₂ sorption

The CO₂ adsorption isotherms shown in Figure 7 were measured for 4 mol% M-CeO₂ and CeO₂ samples up to a maximum pressure of 1 bar at 303 K. For the pure CeO₂, the CO₂ adsorption capacity was 0.77 mmol g^{-1} at 1 bar. If we take into account the textural parameters, the CO₂ capacities for 4 mol% Cu-CeO₂ and La-CeO₂ increased to 1.08 and 0.88 mmol g^{-1} , respectively, ≈ 40 and 14% higher than that for pure CeO₂. However, the total capacity decreased to 0.67 mmol g^{-1} for 4 mol% Zr-CeO₂ and 0.62 mmol g^{-1} for 4 mol% Mg-CeO₂. Clearly, Cu- and La-doped CeO₂ are much better adsorbents, whereas the presence of Zr and Mg decreases the CO₂ capacity compared with pure CeO₂, despite the differences in the surface area and pore volume for all materials (Table 1). This indicates that the adsorption capacity does not correlate exclusively with the textural parameters. Instead, the surface properties tuned by the presence of dopants may play an important role. Notably, the CO₂ adsorption capacity of the ceria and doped ceria samples is below the monolayer CO₂ coverage. The adsorption capacity

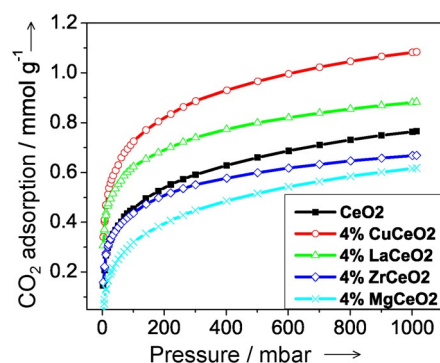


Figure 7. CO₂ adsorption isotherms for CeO₂ and 4 mol% M-CeO₂ samples up to a maximum pressure of 1 bar at 303 K.

of CO₂ on an oxidized ceria (100) thin film was measured to be 8.3 $\mu\text{mol m}^{-2}$ and that for a reduced ceria (100) surface increased to 12.9 $\mu\text{mol m}^{-2}$.^[39] Therefore, the measured CO₂ sorption in our case should be exclusively from chemisorbed CO₂ on the ceria and doped ceria surfaces.

To see the effect of dopants on the CO₂ adsorption behavior clearly, the CO₂ capacities were normalized to the total surface area (Figure 8). Notably, if the CO₂ capacities are normalized to

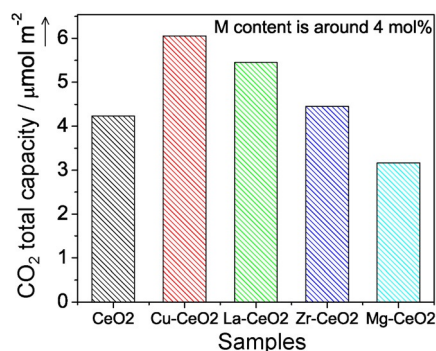


Figure 8. Total CO₂ capacity of CeO₂ and 4 mol% M-CeO₂ normalized to surface area.

the surface area, the 4 mol% Cu- and La-doped CeO₂ samples showed a higher capacity than pure CeO₂, which suggests enhanced CO₂ interaction with the incorporation of dopants into the pure CeO₂. However, the presence of Mg decreased the CO₂ adsorption capacity at 4 mol% concentration. The addition of Zr had little or no effect on the normalized CO₂ adsorption capacity. Notably, the sequence of the CO₂ adsorption capacities are 4 mol% Cu-CeO₂ > 4 mol% La-CeO₂ > 4 mol% Zr-CeO₂ ≈ pure CeO₂ > 4 mol% Mg-CeO₂, which is in line with the sequence of oxygen defect sites of the samples (Table 2). This suggests that the high density of oxygen vacancies in CeO₂ modified by dopants can play a vital role in CO₂ adsorption at a low-dopant concentration (4 mol%).

To explore the effect of the dopant concentration on CO₂ adsorption capacity, we measured the CO₂ adsorption capacity of the Cu-, La-, Zr-, and Mg-doped CeO₂ with different dopant concentrations (Figure 9; data are normalized to the surface area). Compared with the pure CeO₂, the presence of Cu and La increases the CO₂ capacity at ambient pressure for all the contents, but the capacity shows no further increase at higher concentrations. The Zr concentration has little effect on the CO₂ adsorption capacity. The CO₂ adsorption capacity increases with the elevated dopant contents for Mg-CeO₂. Interestingly, the number of oxygen defect sites as calculated from Raman spectra increased with enhanced concentration from 4 to ~25 mol% for Cu and La, whereas the number of oxygen defects sites increased slightly only for 21.8 mol% Zr-CeO₂. This again suggests that the surface oxygen defect sites play an important role in CO₂-adsorption behavior, but the total amount of defect sites (both surface and bulk) is not related to the CO₂ adsorption capacity linearly. However, for Mg-CeO₂ samples, the relative amount of defect sites is barely dependent on the Mg content (Table 2). Therefore, the increased CO₂ adsorption

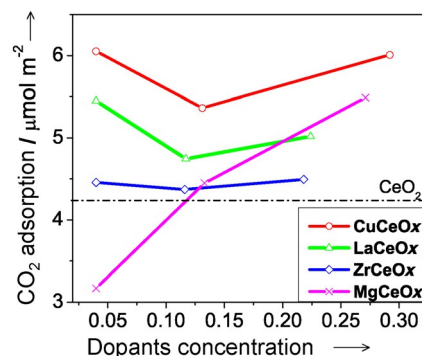


Figure 9. Normalized CO₂ adsorption capacity of M-CeO₂ with different concentrations.

capacity with Mg content cannot be explained based solely on defect sites in the samples. It is possible that the increased CO₂ capacity is correlated to the amount of MgO dispersed on the CeO₂ surface as indicated by the XRD, Raman spectroscopy, and LEIS results. As a result of the strongly basic character of MgO, the Mg-CeO₂ surface possibly represents more basic properties with the higher concentration of MgO so that interaction with the acidic CO₂ is enhanced.

In situ IR spectroscopy of the surface chemistry

We can learn how the dopants affect the surface species generated from CO₂ chemisorption from in situ IR spectroscopy. Generally, there are two types of basic sites on metal oxides, basic hydroxyl groups and basic surface oxygen (normally designated as Lewis base), that can interact with the acidic CO₂. CO₂ adsorption on these two types of basic sites can result in bicarbonate (with OH groups) and various carbonate species (with surface O). These species can be discriminated by their characteristic IR vibrational modes. We selected the 4 mol% M-CeO₂ and CeO₂ samples and employed IR spectroscopy to understand the surface chemistry upon CO₂ adsorption. The IR spectra from CO₂ adsorption on 4 mol% M-CeO₂ for 1 h at room temperature are compared in Figure 10. Upon initial CO₂ adsorption, various surface species are formed readily with IR features in the range of $\tilde{\nu}$ = 1800–800 cm⁻¹ (Figure S1 in the Supporting Information). These IR features evolve as a function of CO₂ adsorption time, that is, surface coverage. The IR bands at after 1 h CO₂ adsorption on 4 mol% Cu-, La-, and Zr-doped CeO₂ are similar in frequency and intensity, whereas the IR bands of Mg-CeO₂ are similar to those of pure CeO₂. The IR bands in the region of $\tilde{\nu}$ = 1800–800 cm⁻¹ are caused by various carbonate species and their assignments are summarized in Table 3 based on previous IR studies of CO₂ adsorption on CeO₂-based materials.^[40–42] For all the samples, the reactive adsorption of CO₂ with OH groups leads to bicarbonate ($\tilde{\nu}$ = 3617, 1610, 1414, 1216, and 1025 cm⁻¹). The interaction of the basic OH groups with CO₂ is also evidenced by the consumption of the OH groups (Figure 10B) as shown by four negative bands at $\tilde{\nu}$ = 3712, 3687, 3666, and 3649 cm⁻¹ for 4 mol% Cu-, La-, and Zr-doped CeO₂ and five negative bands at $\tilde{\nu}$ = 3738,

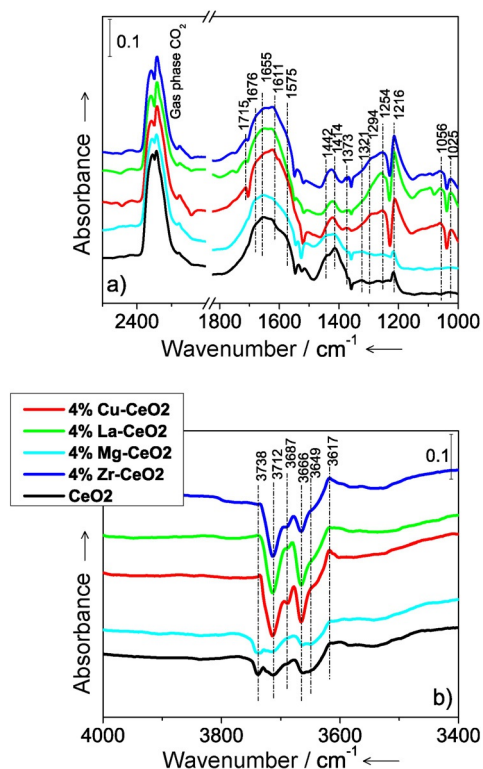


Figure 10. IR spectra from CO₂ adsorption at room temperature for 4 mol% M-CeO₂ for 1 h: a) in the carbonate spectral range and b) in the hydroxyl group region.

Table 3. The Assignment of IR bands observed upon room temperature CO₂ adsorption on CeO₂ and M-CeO₂.

Sorbents	Species	$\nu_{as}(\text{CO}_3)$ [cm ⁻¹]	$\nu_s(\text{CO}_3)$ [cm ⁻¹]	$\nu(\text{C=O})$ [cm ⁻¹]	$\delta(\text{OH})$ [cm ⁻¹]	$\nu(\text{OH})$ [cm ⁻¹]	Desorption temperature [°C]
CeO ₂	bicarbonate	1610	1414	1025	1216	3617	> 150
4% Mg-CeO ₂	monodentate	1442	–	1025			> 200
	polydentate	1575	1414	1025			> 250
	bidentate-I	1575	–	1025			
	bidentate-II	1655	–				> 150
	bridged	1715, 1683		1025			> 100
4% Cu-CeO ₂	bicarbonate	1610	1414	1025	1216	3617	> 300
4% La-CeO ₂	monodentate	1442	1373	1025			> 300
4% Zr-CeO ₂	polydentate	1575	1414	1025			> 300
	bidentate-I	1575	1294	1025			> 200
	bidentate-II	1655	1254				
	bridged	1683		1025			> 200

3712, 3687, 3666, and 3649 cm⁻¹ for 4 mol% Mg-CeO₂ and pure CeO₂. These negative bands are caused by the consumption of surface OH groups by interaction with CO₂. The bands at $\tilde{\nu}$ =3738 and 3712 cm⁻¹ are caused by on-top OH groups, whereas the bands at $\tilde{\nu}$ =3687, 3666, and 3649 cm⁻¹ can be ascribed to bridging OH groups on the CeO₂ surface. Apparently there are two types of on-top OH groups on 4 mol% Mg-CeO₂ and pure CeO₂.

The reactive adsorption of CO₂ with surface basic oxygen results in bidentate I ($\tilde{\nu}$ =1655, 1254, and 1025 cm⁻¹), bidentate II ($\tilde{\nu}$ =1575, 1294, and 1025 cm⁻¹), monodentate ($\tilde{\nu}$ =1442, 1373, and 1025 cm⁻¹), polydentate ($\tilde{\nu}$ =1575, 1474, and 1025 cm⁻¹),

and bridged ($\tilde{\nu}$ =1683 and 1025 cm⁻¹) carbonates. The type of surface carbonate species does not vary with the presence of different dopants (Figure 10), however, the same type of surface carbonate species shows some slight differences in both the vibrational frequency and relative intensity (amount), which depends on the type of dopant in the sample. For example, two types of bidentate carbonates (type I: $\tilde{\nu}$ =1655, 1254, and 1025 cm⁻¹; type II: $\tilde{\nu}$ =1575, 1294, and 1025 cm⁻¹) and monodentate carbonates ($\tilde{\nu}$ =1442, 1373, and 1025 cm⁻¹) are much stronger on 4 mol% Cu-, La-, and Zr-CeO₂ than those on 4% Mg-CeO₂ and pure CeO₂ samples as the $\nu(\text{CO}_3)$ modes at $\tilde{\nu}$ =1254, 1294, and 1373 cm⁻¹ are barely observed on the surfaces of 4 mol% Mg-CeO₂ and pure CeO₂.

To investigate the stability of the various carbonate species formed on the samples, IR spectroscopy combined with online mass spectrometry (QMS) was used to perform the temperature-programmed desorption (TPD) of the surface species formed from CO₂ adsorption on the pure CeO₂ and 4 mol% M-CeO₂. The IR spectra recorded during TPD on 4 mol% Cu-, La-, Zr-, and Mg-doped CeO₂ and pure CeO₂ are shown in Figure 11 A–E, respectively. The corresponding TPD–MS profiles of CO₂ on all samples are presented in Figure 11 F. Prolonged purging (30 min in flowing He) at room temperature did not change the IR features of the carbonates noticeably on all of the samples. The IR bands that correspond to all types of carbonates on pure CeO₂ and 4 mol% Mg-CeO₂ almost vanished upon heating to 423 K, whereas those bands of 4 mol% Cu-, La-, and Zr-CeO₂ only show a slight decline in intensity. At

473 K, the carbonate features disappeared on the pure CeO₂ and 4 mol% Mg-CeO₂ samples but were still present with a decreased intensity on 4 mol% Cu-, La-, and Zr-CeO₂ samples. On pure CeO₂ and 4 mol% Mg-CeO₂, the intensity decrease of IR bands measured below 373 K is mostly caused by the loss of bridged carbonates. Further heating gradually removed the IR features of bicarbonate, bidentate carbonate, and eventually monodentate carbonate, together with polydentate carbonates species. For 4 mol% Cu-, La-, and Zr-CeO₂, the initial loss up to 473 K is caused by the bridged and bidentate carbonates. Heating to 573 K still leaves some IR features of bicarbonate ($\tilde{\nu}$ =1615 cm⁻¹), monodentate carbonate ($\tilde{\nu}$ =1440 and 1373 cm⁻¹), and polydentate carbonate ($\tilde{\nu}$ =1575 cm⁻¹) on the surfaces, which implies the decomposition of these carbonate species at high temperatures. The contrast suggests that the bonding of the carbonate species is much weaker on the pure CeO₂ and 4 mol% Mg-CeO₂ surfaces than that on 4 mol% Cu-, La-, and Zr-CeO₂ surfaces. The different stability of bicarbonates versus other carbonate species for pure CeO₂ and 4 mol% Mg-CeO₂ indicates that the basicity of the hydroxyl groups is weaker than that of the surface oxygen

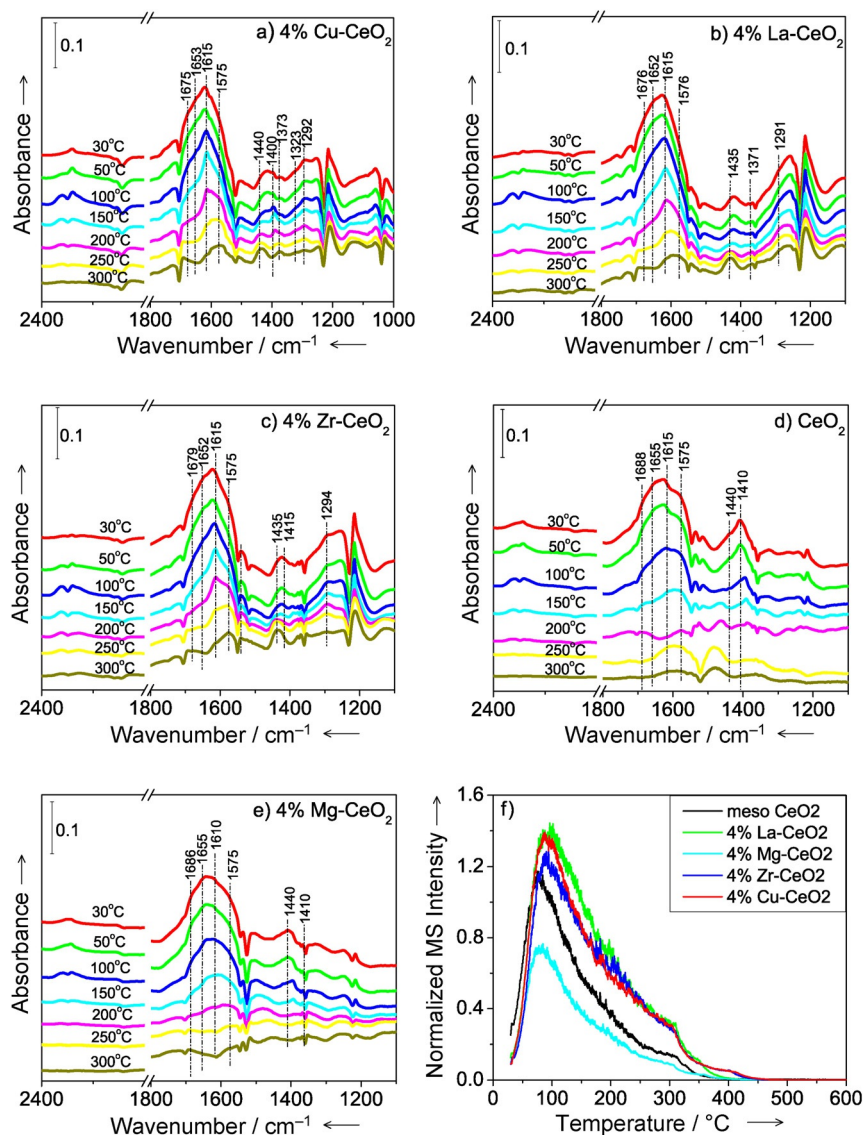


Figure 11. IR spectra collected during TPD after CO₂ adsorption for a) 4 mol% Cu-CeO₂, b) 4 mol% La-CeO₂, c) 4 mol% Zr-CeO₂, d) CeO₂, and e) 4 mol% Mg-CeO₂. f) The corresponding QMS profiles of desorbed CO₂ (mass 44 signal; signal multiplied by 10⁻¹⁰).

on the sample surfaces, whereas the basicity of the hydroxyl groups is similar to that of the surface oxygen on 4 mol% Cu-, La-, and Zr-CeO₂ samples as there is no apparent difference in the thermal stability of the various carbonate species.

The TPD-MS profiles shown in Figure 11F show CO₂ desorption for all samples as soon as the temperature is elevated above room temperature with a desorption maximum at temperature below 373 K. CO₂ desorption extends up to the final desorption temperature of 573 K. The lowest desorption temperature occurs on 4 mol% Mg-CeO₂ at 348 K. Pure CeO₂ shows a maximum desorption at 353 K. The 4 mol% Cu-CeO₂, La-CeO₂, and Zr-CeO₂ samples all give a maximum desorption at 363 K. The higher the desorption temperature, the stronger the interaction is for CO₂ with the sorbents. So the observations from both the IR and MS data during CO₂-TPD suggest that the basic sites on 4 mol% Cu-, La-, and Zr-CeO₂ are stronger than that on pure CeO₂ and 4 mol% Mg-CeO₂. The pres-

ence of oxygen vacancies on the CeO₂ surface was able to improve the surface basicity^[40,43] and thus enhance the interaction between CeO₂ and CO₂. So the stronger basicity of Cu-, La-, and Zr-doped ceria may be partly because of the presence of more oxygen vacancies than the other samples as shown in the Raman spectra (Figures 4 and 5). The very similar IR observations among the 4 mol% Cu-CeO₂, La-CeO₂, and Zr-CeO₂ samples during CO₂ adsorption and desorption suggest that the nature of the surface adsorbents is similar on the three samples, although the amount of these species differs.

Discussion

As the measured CO₂ sorption on the doped ceria samples is exclusively from chemisorbed CO₂ in the form of surface carbonate species, it is reasonable to postulate that the surface properties of the samples play a key role in the capture of CO₂. The surface properties of the doped ceria are determined by three factors: the surface basicity, surface oxygen vacancies (redox properties), and the surface segregation of the dopants. It was shown that the surface basicity of ceria can be enhanced by the presence of

oxygen vacancies.^[40,43] So on a doped ceria sample with more defect sites, stronger basic sites are present and can thus bind CO₂ more strongly; meanwhile, the surface oxygen vacancies can participate directly in the binding of CO₂ to form carbonate species.^[39] Therefore, more and strongly bonded CO₂ is expected for M-CeO₂ with more defect sites than that on pure ceria. This explains the CO₂ sorption capacity for the M-CeO₂ with 4 mol% dopant concentration, that is, the most defective 4 mol% Cu-CeO₂ shows the highest CO₂ capacity, whereas the least defective 4 mol% Mg-CeO₂ gives the lowest CO₂ capacity among the lowest-dopant-concentration samples. This result is also consistent with recent studies of CO₂ adsorption on CeO₂,^[30,44] in which CeO₂ with more vacancies on the surface had a higher CO₂ adsorption capacity.

At higher dopant concentrations (> 4 mol%), although Raman spectroscopy (Table 2) shows a continuous increase in defects density for La-, Cu-, and Zr-doped ceria, there is no in-

crease in CO₂ sorption. This is probably because Raman spectroscopy is a bulk technique so that the amount of surface oxygen vacancies may be relatively constant, whereas the amount of bulk vacancies continues to increase with the increase of the amount of dopant incorporated into the ceria lattice. The segregation of CuO on the ceria surface at 29.2% concentration also contributes to the similar CO₂ sorption capacity to that of the 4 mol% Cu-CeO₂. The segregation of dopant on the ceria surface is the most important factor in the CO₂ sorption behavior on Mg-CeO₂ samples. The initial decrease of the CO₂ sorption capacity at 4 mol% Mg doping is probably because of the blocking of surface oxygen vacancies present on the parent ceria surface. As a result of the strongly basic character of MgO, the Mg-CeO₂ surface possibly presents more basic properties with a higher concentration of MgO than pure ceria so that the CO₂ sorption capacity increases at higher Mg concentrations.

Conclusions

CO₂ sorption has been studied over mesostructured ceria and Mg-, Zr-, La-, and Cu-doped ceria in this work. The 4 mol% Cu-CeO₂ sample gives the highest CO₂ adsorption, whereas the 4 mol% Mg-CeO₂ exhibits the lowest CO₂ adsorption capacity. The addition of Zr had little or no effect on the normalized CO₂ adsorption capacity. The sequence of CO₂ adsorption capacities at a low dopant concentration (4 mol%) is Cu-CeO₂ > La-CeO₂ > Zr-CeO₂ ≈ pure CeO₂ > Mg-CeO₂, which is in line with the sequence of the amount of oxygen vacancies in the samples. Compared with that of pure CeO₂, the presence of Cu and La increases the CO₂ capacity at ambient pressure for all the contents, but the capacity shows no further increase at higher concentrations although the defect sites increase in content with increased concentration from 4 to ~25 mol% for Cu and La. The contrast suggests that the oxygen vacancies (oxygen mobility) present on the surface of CeO₂ modified by dopants play the vital role in CO₂ adsorption, whereas those in the bulk ceria are insignificant for CO₂ capture. For the Mg-CeO₂ samples, the surface defect sites are barely dependent on the Mg content. The increased CO₂ adsorption capacity observed with the Mg content might be correlated to the increasing amount of MgO dispersed on the CeO₂ surface as indicated by the XRD, Raman spectroscopy, and low-energy ion scattering results. Compared with pure ceria and Mg-CeO₂, the stronger basicity of Cu-, La-, and Zr-doped ceria was probed by CO₂ adsorption using in situ IR spectroscopy. The very similar IR features from CO₂ adsorption on the Cu-CeO₂, La-CeO₂, and Zr-CeO₂ samples indicate that the nature of the surface carbonates is similar on the three samples, but the amounts of these species differ.

This work shows the potential advantage of using doped ceria for application in CO₂ capture. The results suggest that the adsorption properties of the materials are not only influenced by their textural characteristics but also related to the surface properties such as acid-base sites and oxygen vacancies, which are affected by the type and concentration of the dopants in the ceria.

Experimental Section

Materials

The following raw materials were used as provided: Ce(NO₃)₃·6H₂O (Alfa Aesar); Cu(NO₃)₂·3H₂O (Acros Organics); La(NO₃)₃·6H₂O (Strem Chemicals); ZrOCl (Acros organics); Mn(NO₃)₂·4H₂O (Sigma-Aldrich); Mg(NO₃)₂·6H₂O; cetyltrimethyl ammonium bromide (CTAB, Chem-Impex, Int'l Inc.); NaOH (Fisher Scientific).

Sample preparation

The CeO₂ and M-doped (M = Cu, La, Zr and Mg) CeO₂ (M-CeO₂) with different M contents (5, 15, 34 mol%) were prepared using a surfactant-templated method as reported in Ref. [22]. Typically, CTAB (6 mmol) was dissolved in distilled water (200 mL) followed by the addition of Ce(NO₃)₃·6H₂O (10 or 9.5 mmol) and Cu(NO₃)₂·H₂O (0 or 5 mmol). The mixture was stirred for 0.5 h, after which a solution of NaOH (50 mmol) in distilled water (300 mL) was added, and the mixture was stirred for 12 h. The final precipitate was aged at 363 K for 3 h, washed with hot water, dried at 383 K for 6 h, and finally calcined at 673 K for 4 h. Other doped samples with different M contents were prepared in a similar manner. The actual M content in the material was analyzed by ICP. It was found the actual M content (4 mol%) was lower than that in the starting solution (5 mol%).

Characterization

SEM imaging was performed by using a Zeiss Auriga microscope with an electron beam operation of 5 keV, which is a dual beam FIB (Focused Ion Beam) with a field-emission electron column for high-resolution electron imaging and a Canion Ga+ column for precision ion beam milling.

N₂ adsorption isotherms were measured at 77 K by using a Gemini VII 2390 Surface Area Analyzer (Micrometrics Instrument Corp.). Before the adsorption measurements, the CeO₂ powders were degassed under flowing N₂ for 2 h at 473 K to remove any residual water and surface species. The surface area was calculated using the BET method in the relative pressure range of 0.05–0.25. The total pore volume was estimated from the N₂ adsorption isotherm at a relative pressure of $P/P_0 = 0.97$. The pore size distributions (PSD) were calculated using the Barrett-Joyner-Halenda (BJH) algorithm for cylindrical pores according to the improved Kruk-Jaroniec-Sayari (KJS) method.

XRD patterns were collected by using a PANalytical powder diffractometer using CuK_α radiation. The working voltage was 40 KV, and the current was 40 mA. The intensity data were collected at RT at $2\theta = 20\text{--}90^\circ$.

Raman spectra of the doped samples under ambient conditions were measured with $\lambda = 532$ nm laser excitation (Princeton Scientific, MSL 532-50). The Raman signal was collected by a fiber-optics bundle (Princeton Instruments) to the spectrograph stage of a triple Raman spectrometer (Princeton Instruments Acton Trivista 555). Edge filters (Semrock) were used in front of the UV/Vis fiber-optic bundle to block the laser irradiation.

LEIS was used to analyze the distribution of dopants in the doped ceria samples. LEIS spectra were collected by using an IONTOF Qtac100 spectrometer (ION-TOF GmbH, Münster, Germany) at Lehigh University. The specimen, placed within an ultra-high vacuum system, was subjected to a beam of ions with well-charac-

terized initial kinetic energy. Typically He^+ or Ne^+ ions were used in an energy range of 1–8 keV. (A fraction of these ions elastically scatter from surface atoms of the specimen. The technique then measures the number distribution of recoiling rare gas ions versus kinetic energy, and this system particularly collected backscattered ions at a scattering angle of 145° .) The mass of the atom from which an ion scattered was determined from the final kinetic energy of the scattered ion. Rare gas atoms that have scattered from specimen atoms beneath the surface layer typically become neutralized and are not detected by the LEIS analyzer, which makes this method particularly sensitive to the immediate surface of the specimen.

CO_2 adsorption measurements were performed at 303 K by using a Gemini VII 2390 Surface Area Analyzer (Micrometrics Instrument Corp.). Before the CO_2 adsorption measurements, all CeO_2 and doped CeO_2 samples were treated under flowing N_2 for 12 h at 573 K.

In situ IR spectra of CO_2 adsorption on the doped ceria samples were collected using a Thermo Nicolet Nexus 670 spectrometer in diffuse reflectance mode (DRIFTS), and the exiting stream was analyzed by using an OmniStar GSD-301 (Pfeiffer-Balzer) QMS. The samples were pretreated in a DRIFTS cell (HC-900, Pike Technologies, nominal cell volume of 6 cm^3) at 573 K in a He flow (25 mL min^{-1}) for 1 h before cooling to 298 K for CO_2 adsorption. A gas mixture of 5% CO_2/He (25 mL min^{-1}) was flowed over the samples at RT for 1 h before switching to He purging for another 30 min. The samples were then heated for TPD study. Time-resolved IR spectra were collected during the adsorption process and the subsequent thermal desorption process.

Additional IR spectra are available in the Supporting Information for the comparison of CO_2 adsorption on pure CeO_2 and 4 mol% Cu- CeO_2 as a function of time.

Acknowledgements

This work is supported by the Center for Understanding and Control of Acid Gas-Induced Evolution of Materials for Energy (UNCAGE-ME), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences. Part of the work including the IR and Raman was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

Keywords: cerium • copper • doping • raman spectroscopy • surface chemistry

- [1] J. Goldemberg, *Science* **2007**, *315*, 808–810.
- [2] N. B. Grimm, S. H. Faeth, N. E. Golubewski, C. L. Redman, J. Wu, X. Bai, J. M. Briggs, *Science* **2008**, *319*, 756–760.
- [3] M. M. Maroto-Valer, C. Song, Y. Soong, *Environmental challenges and greenhouse gas Control for Fossil Fuel Utilization in the 21st Century*, Springer, New York, **2002**, P.1.
- [4] J. D. Figueroa, T. Fout, S. Plasynski, H. Mclvried, R. D. Srivastava, *Int. J. Greenhouse Gas Control* **2008**, *2*, 9–20.
- [5] J. Wang, L. Huang, R. Yang, Zh. Zhang, J. Wu, Y. Gao, Q. Wang, D. O'Hare, Z. Zhong, *Energy Environ. Sci.* **2014**, *7*, 3478–3518.
- [6] J. Shang, G. Li, R. Singh, Q. Gu, K. M. Nairn, T. J. Bastow, N. Medhekar, C. M. Doherty, A. J. Hill, J. Z. Liu, P. A. Webley, *J. Am. Chem. Soc.* **2012**, *134*, 19246–19253.
- [7] T. D. Pham, Q. Liu, R. F. Lobo, *Langmuir* **2013**, *29*, 832–839.

- [8] R. V. Siriwardane, M. S. Shen, E. P. Fisher, J. A. Poston, *Energy Fuels* **2001**, *15*, 279–284.
- [9] S. Mahurin, J. Gorka, K. Nelson, R. Mayes, S. Dai, *Carbon* **2014**, *67*, 457–464.
- [10] J. Wang, A. Heerwing, M. R. Lohe, M. Oschatz, L. Borchardt, S. Kaskel, *J. Mater. Chem.* **2012**, *22*, 13911–13913.
- [11] J. Yu, M. Guo, F. Muhammad, A. Wang, F. Zhang, Q. Li, G. Zhu, *Carbon* **2014**, *69*, 502–514.
- [12] O. Leal, C. Bolivar, C. Ovalles, J. J. Garcia, Y. Espidel, *Inorg. Chim. Acta* **1995**, *240*, 183–189.
- [13] J. Yu, Y. Le, B. Cheng, *RSC Adv.* **2012**, *2*, 6784–6791.
- [14] G. Goeppert, H. Zhang, M. Czaun, R. B. May, G. K. S. Prakash, G. A. Olah, S. R. Narayanan, *ChemSusChem* **2014**, *7*, 1386–1397.
- [15] Y. Liu, Z. U. Wang, H. C. Zhou, *Greenhouse Gases: Sci. Technol.* **2012**, *2*, 239–259.
- [16] Z. Zhang, Y. Zhao, Q. Gong, Z. Li, J. Li, *Chem. Commun.* **2013**, *49*, 653–661.
- [17] J. Baltrusaitis, V. H. Grassian, *J. Phys. Chem. B* **2005**, *109*, 12227–12230.
- [18] J. Baltrusaitis, J. Schuttelfield, E. Zeitler, V. H. Grassian, *Chem. Eng. J.* **2011**, *170*, 471–481.
- [19] H. A. Mosqueda, C. Vazquez, P. Bosch, H. Pfeiffer, *Chem. Mater.* **2006**, *18*, 2307–2310.
- [20] J. Kapica-Kozar, E. Kusiak-Nejman, A. Wanag, L. Kowalczyk, R. J. Wrobel, S. Mozia, M. A. Morawski, *Microporous Mesoporous Mater.* **2015**, *202*, 241–249.
- [21] V. Hornebecq, C. Knofel, P. Boulet, B. Kuchta, P. L. Llewellyn, *J. Phys. Chem. C* **2011**, *115*, 10097–10103.
- [22] N. Izu, W. Shin, N. Murayama, S. Kanzaki, *Sens. Actuators B* **2002**, *87*, 95–98.
- [23] Z. L. Wu, M. J. Li, S. H. Overbury, *J. Catal.* **2012**, *285*, 61–73.
- [24] M. J. Li, Z. L. Wu, S. H. Overbury, *J. Catal.* **2013**, *306*, 164–176.
- [25] L. Vivier, D. Dupree, *ChemSusChem* **2010**, *3*, 654–678.
- [26] J. S. Elias, M. Risch, L. Giordano, A. N. Mansour, Y. Shao-Horn, *J. Am. Chem. Soc.* **2014**, *136*, 17193–17200.
- [27] T. Yuzhakova, V. Rakic, C. Guimon, A. Auroux, *Chem. Mater.* **2007**, *19*, 2970–2981.
- [28] S. Collins, G. Finos, R. Alcantara, E. Rio, S. Bernal, A. Bonivardi, *Appl. Catal. A* **2010**, *388*, 202–210.
- [29] M. Yashima, T. Takizawa, *J. Phys. Chem. C* **2010**, *114*, 2385–2392.
- [30] S. Yang, W. Su, J. Rick, S. D. Lin, J. Y. Liu, C. J. Pan, J. F. Lee, B. J. Hwang, *ChemSusChem* **2013**, *6*, 1326–1329.
- [31] T. Staudt, Y. Lykhach, N. Tsud, T. Skala, K. C. Prince, V. Matolin, J. Libuda, *J. Catal.* **2010**, *275*, 181–185.
- [32] X. J. Yao, Q. Yu, Z. Y. Ji, Y. Y. Lv, Y. Cao, C. J. Tang, F. Gao, L. Dong, Y. Chen, *Appl. Catal. B* **2013**, *130*, 293–304.
- [33] D. H. Prasad, S. Y. Park, H. I. Ji, H. P. Kim, J. W. Son, B. K. Kim, H. W. Lee, J. H. Lee, *J. Phys. Chem. C* **2012**, *116*, 3467–3476.
- [34] P. Sudarsanam, B. Mallesham, P. S. Reddy, D. Großmann, W. Grünert, B. M. Reddy, *Appl. Catal. B* **2014**, *144*, 900–908.
- [35] Z. L. Wu, M. J. Li, J. Howe, H. M. Meyer III, S. H. Overbury, *Langmuir* **2010**, *26*, 16595–16606.
- [36] M. Guo, J. Lu, Y. Wu, Y. Wang, M. Luo, *Langmuir* **2011**, *27*, 3872–3877.
- [37] H. R. J. ter Veen, T. Kim, I. E. Wachs, H. H. Brongersma, *Catal. Today* **2009**, *140*, 197–201.
- [38] S. P. Phivilay, A. A. Puzetzy, K. Domen, I. E. Wachs, *ACS Catal.* **2013**, *3*, 2920–2929.
- [39] P. M. Albrecht, D. E. Jiang, D. R. Mullins, *J. Phys. Chem. C* **2014**, *118*, 9042–9050.
- [40] Z. L. Wu, A. K. P. Mann, M. J. Li, S. H. Overbury, *J. Phys. Chem. C* **2015**, *119*, 7340–7350.
- [41] G. Finos, S. Collins, G. Blanco, E. del Rio, J. M. Cies, S. Bernal, A. Bonivardi, *Catal. Today* **2012**, *180*, 9–18.
- [42] C. Li, Y. Sakata, T. Arai, K. Domen, K. I. Maruya, T. Onishi, *J. Chem. Soc. Faraday Trans. 1* **1989**, *85*, 1451–1461.
- [43] H. Metiu, S. Chretien, Z. Hu, B. Li, X. Sun, *J. Phys. Chem. C* **2012**, *116*, 10439–10450.
- [44] C. Li, X. Liu, G. Lu, Y. Wang, *Chin. J. Catal.* **2014**, *35*, 1364–1375.

Received: July 2, 2015

Published online on September 25, 2015