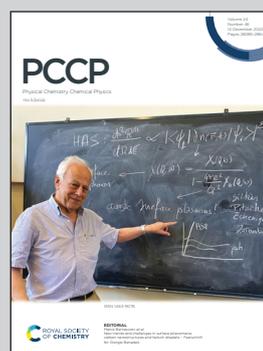


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Theoretical investigation of selective CO₂ capture and
desorption controlled by an electric field

CO₂ adsorption/desorption on CeO₂ partially substituted
with hetero-cations was investigated using theoretical
calculations for establishing low-cost CO₂ capture.
The amount of change in CO₂ adsorption energy by
the application of an electric field depended on the
electronegativity of the doped cations. These results
suggest a tuning strategy for the material properties
necessary for CO₂ separation and capture using an
electric field.

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Theoretical investigation of selective CO₂ capture and desorption controlled by an electric field†

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Low-cost carbon dioxide (CO₂) capture technologies have been studied widely. Among such technologies, the control of CO₂ adsorption by the application of an electric field to solid materials has been shown to be a promising technology that can combine high CO₂ adsorption with low energy consumption. Suitable materials must be found for electric field-assisted CO₂ adsorption. For this study, the CO₂ adsorption energies of CeO₂ partially substituted with hetero-cations were investigated using theoretical calculations. The differences in adsorption performance attributable to the application of an electric field were clarified for different doped cations. The results show that the amount of change in the CO₂ adsorption energy by the application of an electric field depended on the different doped cations. Furthermore, it is found that this difference in cations is related to the electronegativity of the doped cations. These results suggest a tuning strategy for the material properties necessary for CO₂ capture and separation using an electric field.

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1. Introduction

Intensive and extensive consumption of fossil fuels has increased the atmospheric concentrations of carbon dioxide (CO₂), thereby causing global warming and climate change.¹ Suitable technologies must be found to reduce CO₂ emissions while maintaining the industry and providing power generation: CO₂ capture and separation is one promising technology to reduce CO₂ emissions to a net-zero amount.^{2,3}

Various materials have been developed for CO₂ capture, including liquid absorbents^{4,5} and solid adsorbents.^{6,7} Among them, amine-based absorbents are widely used in the industry, but they have shortcomings such as high energy consumption during regeneration and poor handling because of toxicity.^{8,9} Pressurised conditions are beneficial, to a certain degree, for physical absorption into Selexol and other materials. For these reasons, solid adsorbents are attracting attention because they are expected to consume less energy during regeneration. Solid adsorbents including carbon-based materials,¹⁰ metal-organic frameworks,¹¹ and metal oxides^{12,13} have been examined widely. Although many studies have been undertaken to improve their selective CO₂ adsorption capacity, these improvements simultaneously

entail difficulties in regeneration. A trade-off exists between high CO₂ separation capacity and low energy consumption in the control of adsorption and desorption by temperature and pressure swings.

Here, CO₂ capture controlled by an electric field has been proposed as a process that combines high CO₂ selectivity with low energy consumption. This electric-field-assisted CO₂ capture has been investigated in supercapacitive swing adsorption using liquid electrolytes^{14,15} and electric field-assisted adsorption using solid 2D materials.^{16,17} Sun *et al.*¹⁸ reported, using density functional theory (DFT) calculations, that applying an external electric field to a boron nitride sheet can create a charge distribution in the sheet and can promote electron transfer selectively to the adsorbed CO₂. This facilitation stabilises CO₂ adsorption. Switching the electric field can weaken CO₂ adsorption without significant barriers. Therefore, applying an external electric field to the supports of CO₂-activation catalysts, containing inorganic solid materials, is expected to be able to control the CO₂ adsorption selectively with low consumption energy and successive conversion of CO₂ into a useful product. However, the design strategy for materials of CO₂ capture controlled by a DC electric field remains unclear.

In this study, we focus on CO₂ adsorption with an electric field over cerium oxide (CeO₂). Although MgO has been reported to exhibit high performance in previous CO₂ adsorption studies without an electric field,¹⁹ it is difficult to control the nature by a DC electric field because of its dielectric nature, and also it is difficult to tune the structure by hetero-cation doping. On the other hand, CeO₂ has *f* electrons and is known

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as a semi-conductor, so CeO₂ adsorption can be greatly controlled by applying an electric field, and its performance can be easily tuned by hetero-cation doping; since the valence of Ce can be changed, there is a high level of structural freedom through doping with cations of different valence states. Therefore, DFT calculations were performed using CeO₂ doped with various hetero-cations,²⁰ which have been studied as CO₂ adsorbents^{21,22} and as supports for CO₂-activation catalysts.^{23,24} Then, differences between the doped cations were investigated with regard to the changes in the CO₂ adsorption performance by application of the electric field. This study identified the material properties required for CCS with an electric field.

2. Computational method

2.1. Computational details

All DFT calculations for this work were conducted using the Vienna *Ab initio* Simulation Package (VASP) 5.4.4.^{25,26} Core-valence interactions were represented using a projector augmented wave (PAW) method.^{27,28} The generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) was applied to describe the exchange correlation.²⁹ The plane-wave cutoff was 400 eV. We used the DFT-D3 method proposed by Grimme to assess van der Waals interactions between the surface and adsorbates.³⁰ The DFT+*U* method^{31,32} was used to introduce an on-site correction for the localised electrons. The value of *U* was set to 5.0 eV for the Ce 4*f* orbital.^{33–37} Optimisation of bulk and slab models was carried out respectively with a Γ -centred *k*-point grid of (5 × 5 × 5) and that of (1 × 1 × 1) using Gaussian smearing. Furthermore, the electric field direction was vertical to the CeO₂ surface. Applied electric field amounts of −0.50, −0.10, 0.10, and 0.50 eV Å^{−1} along the *z*-direction were considered. In addition, the Bader charge analysis was performed to evaluate the electron transfer from the surface to adsorbates.^{38–41}

The CO₂ adsorption energy when applied to an electric field of *x* eV Å^{−1} (which is represented as *E*_{ad}(*x*)) was calculated using the following equation:

$$E_{\text{ad}}(x) = E_{\text{surface adsorbed CO}_2}(x) - (E_{\text{surface}}(x) + E_{\text{CO}_2}(x)) \quad (1)$$

Herein, *E*_{surface adsorbed CO₂}(*x*) and *E*_{surface}(*x*) respectively denote the total energy of the surface model with adsorbed CO₂ and without adsorbed CO₂. Also, *E*_{CO₂}(*x*) denotes the total energy of a CO₂ molecule, as obtained by the calculation of an isolated CO₂ molecule in a 10 × 10 × 10 Å vacuum cubic box.

2.2. Calculation models

In this study, CeO₂ has been selected as a material for investigation. Herein, we investigated a (4 × 4) expansion of the CeO₂(111) surface with three O–Ce–O tri-layers, which is the most stable surface on CeO₂.⁴² In this slab model, the bottom tri-layer was fixed during geometry optimisation. The vacuum layer was set to 20 Å along the *z* direction (shown in Fig. 1(a) and (b)). The optimised lattice parameter of CeO₂ bulk was

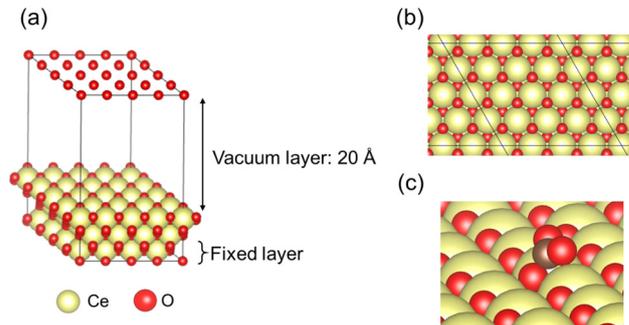


Fig. 1 Calculation models of pure CeO₂: (a) perspective view, (b) top view, and (c) CO₂ adsorption form on a pure CeO₂(111) surface: yellow, Ce; red, O.

5.43 Å, which shows good agreement with the results reported from an earlier investigation (5.47 Å)⁴³ and an experimentally obtained result (5.41 Å).⁴⁴ The doped models were prepared by replacing two Ce atoms at the uppermost surface of the CeO₂ slab model with various cations: Ba, Ca, Ga, La, Sc, Sr, Y, and Zr. Additionally, doping hetero-cations with different valences (divalent or trivalent) to the valence of the Ce atom (tetravalent) is known to require charge compensation by creating oxygen vacancies. Therefore, we prepared models with oxygen vacancies as presented in Fig. 2 and investigated the CO₂ adsorption behaviour when applying an electric field using these models with oxygen vacancies. Regarding the arrangements of the doped cations and the positions of oxygen vacancies, the most stable arrangements and positions were found from an earlier study.⁴⁵ Moreover, the drawing of all calculation models was performed using Visualization for Electronic and STructural Analysis (VESTA).⁴⁶

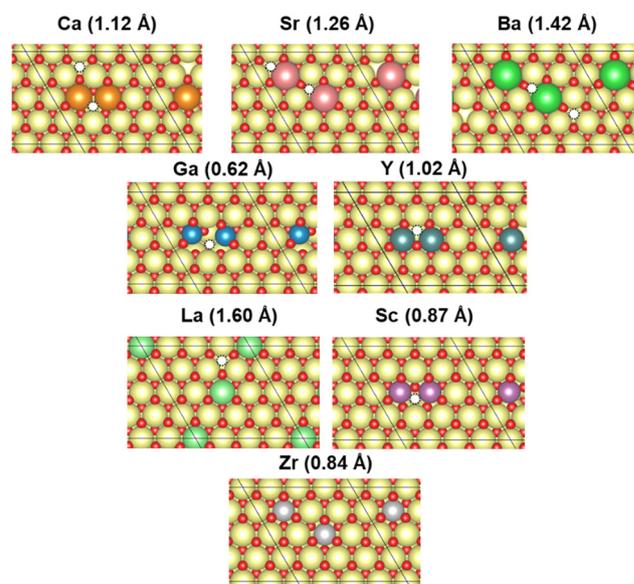


Fig. 2 The most stable surface model with oxygen vacancy: white, oxygen vacancy; yellow, Ce; red, O; orange, Ca; pink, Sr; green, Ba; blue, Ga; purple, Sc; moss green, Y; light green, La; and gray, Zr.



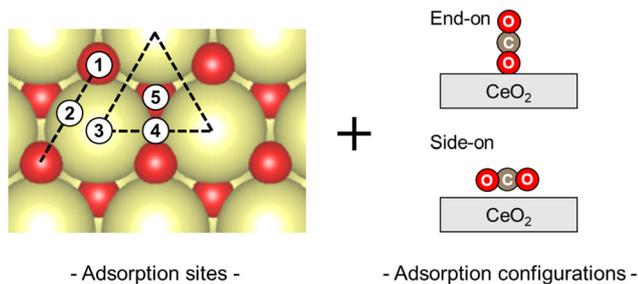


Fig. 3 Considering CO₂ adsorption sites and configurations.

3. Results and discussion

3.1. Optimisation of the CO₂ adsorption model on non-doped CeO₂

First, the CO₂ adsorption models were investigated along with their various adsorption sites and various configurations over non-doped CeO₂. The adsorption models and the relevant results are presented in Fig. 3 and Table 1. The CO₂ adsorption model with a side-on arrangement on the surface oxygen (O_{lat}) was found to be the most stable adsorption arrangement. Geometry optimisation of this adsorption model led to an adsorption energy of -0.46 eV, a C–O_{lat} bond length of 1.38 Å, and an O–C–O angle of 129.5° . These results are consistent with those of earlier theoretical studies: 1.38 Å and 129.7° , respectively.³⁶ This optimised model includes

Table 1 CO₂ adsorption energy in different configurations on the CeO₂(111) surface

Adsorption No.	site	End-on/eV		Side-on/eV	
		Without EF	With EF (0.50 eV Å ⁻¹)	Without EF	With EF (0.50 eV Å ⁻¹)
1	O _{lat} atom (on top)	-0.04	-0.04	-0.46	-0.69
2	O _{lat} atom (bridge)	-0.09	-0.07	-0.06	-0.04
3	Ce atom (on top)	-0.08	-0.06	-0.07	-0.05
4	Ce atom (bridge)	-0.05	-0.05	-0.06	-0.06
5	Ce atom (hollow)	-0.04	-0.04	-0.06	-0.05

interactions between the carbon molecule of CO₂ and the surface oxygen, and between the oxygen of CO₂ and the surface cerium. Among the various adsorption sites and configurations, these interactions involve the smallest adsorption energy. However, all other models show weak interaction or no interaction, causing the adsorption to be unstable at less than -0.10 eV. Therefore, the model presented in Fig. 1(c) was regarded as a suitable computational model to study the adsorption of CO₂ on each surface oxygen of the CeO₂ surface.

3.2. Influence of doping hetero-cation on CO₂ adsorption without an electric field

The DFT calculations were then performed to assess the behaviour of CO₂ adsorption without an electric field on CeO₂ with various dopants after optimising the structure of the doped-oxide. Fig. 4(a) shows the relationship between the ionic radius of the dopants and the adsorption energies, as classified by the average adsorption energy of the surface oxygens next to the dopant and that of the surface oxygen next to the cerium atom. The results show that, as the ionic radius of the dopant decreases, CO₂ adsorption stabilises irrespective of the adsorption site. Among them, the adsorption sites adjacent to the dopant were found to bring about this tendency to a greater degree than the adsorption sites adjacent to the cerium atom. The results show that CO₂ adsorption on the doped CeO₂ surface is influenced strongly by the ionic radius of the dopant. The influence of a dopant on adsorption over the doped CeO₂ surface was also examined in an earlier study,²⁰ which showed the same trend for the adsorption of hydrogen atoms. This report revealed that the difference in the ionic radius from the Ce atom has a greater effect on the adsorption energy than the electron transfer from the dopant to the lattice oxygen. A smaller ionic radius of the dopant can reflect a more stable adsorption structure because the surface around the smaller dopant has more spatial freedom and room for lattice distortion during adsorption. This trend is more pronounced for CO₂ adsorption in the vicinity of the dopant, indicating that

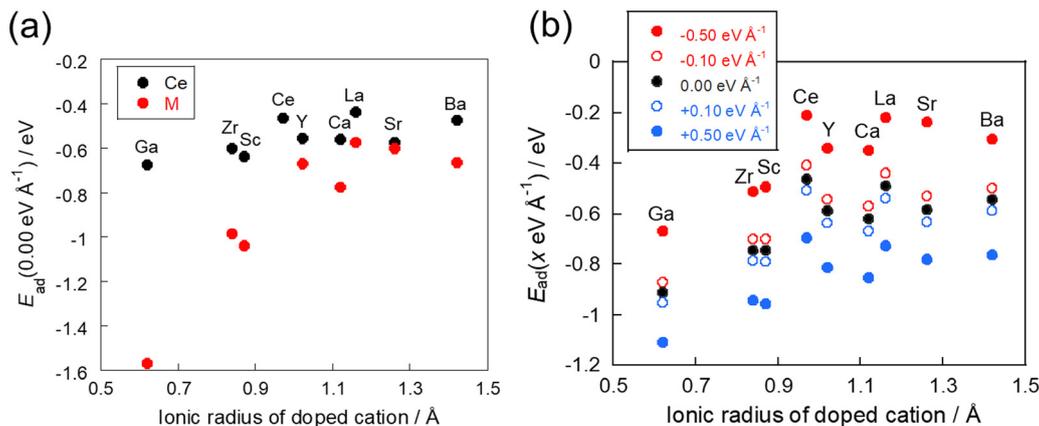


Fig. 4 Relationship between the ionic radius and the adsorption energy: (a) without application of an electric field and (b) with application of an electric field.



structural factors such as the ionic radius are the main factors controlling CO₂ adsorption.

3.3. CO₂ adsorption with an electric field

Next, we investigated CO₂ adsorption when electric fields of -0.50 , -0.10 , 0.10 , and 0.50 eV Å⁻¹ were applied to CeO₂ with various dopants. Fig. 4(b) depicts the relationship between the ionic radius of the dopant and the CO₂ adsorption energies when the electric fields were applied. The results show that the doped CeO₂ surface is positively charged when negative electric fields of -0.50 and -0.10 eV Å⁻¹ are applied. The adsorption becomes unstable. However, application of positive electric fields of 0.50 eV Å⁻¹ and 0.10 eV Å⁻¹ caused the doped CeO₂ surface to become negatively charged and adsorption-stabilised. Therefore, the results confirmed that the adsorption and desorption of CO₂ can be controlled by switching the direction of application of the electric field, as reported in earlier studies.^{17,47} Furthermore, the amounts of change in the adsorption energies have been found to be strongly related to the amount of CO₂ adsorption that can be controlled. Therefore, the amount of change in adsorption energy has been calculated for application of electric fields of -0.50 and 0.50 eV Å⁻¹. The results are shown in Fig. 5. In this figure, a greater change in adsorption energy means that a greater amount of CO₂ adsorption can be controlled. This figure clarifies that the amount of change in the adsorption energy by application of an electric field differs among dopants, even if the same amount of electric field is applied. In particular, gallium (Ga) and zirconium (Zr) doping have a smaller change in adsorption energy than that of undoped CeO₂, whereas lanthanum (La) doping has a greater change in adsorption energy than undoped CeO₂.

3.4. Analytical method for dominant factors on CO₂ adsorption with an electric field

To clarify the material properties necessary to control CO₂ adsorption and desorption by the application of an electric field, the change in adsorption energy was analysed: it occurs because of the application of the varied electric field on dopants. Three factors influence the amount of change in

Table 2 Geometric property change and charge transfer by application of an electric field on the CeO₂(111) surface

The amount of EF [eV Å ⁻¹]	E_{ad} [eV]	d_{O-Ce} [Å]	$d_{C-O_{lat}}$ [Å]	d_{C-O} [Å]	a_{OCO} [deg]	Charge/e
-0.50	-0.21	2.464	1.382	1.266	129.7	0.18
0.00	-0.46	2.511	1.379	1.269	129.5	0.22
+0.50	-0.69	2.566	1.375	1.270	129.2	0.28

adsorption: charge transfer factor, CO₂ molecular structural relaxation factor, and surface structural relaxation factor. The charge transfer factor represents the electron transfer effects between the doped CeO₂ surface and the CO₂ molecules because of the application of the electric field on the adsorption energy. The CO₂ molecular structural relaxation factor indicates the effect of changes in the C-O_{lat} length and O-C-O angle because of the application of the electric field to the adsorption energy. Indeed, it has been observed that the bond length between the CO₂ molecule and the surface oxygen changes with the application of the electric field, as Table 2 shows. Finally, the surface structural relaxation factor reflects the effects of changes in the surface structure because of the application of the electric field on the adsorption energy. The results of the present study demonstrated that the surface structure relaxation during adsorption dominates the adsorption behaviour in the adsorption without applying an electric field of CO₂ molecules as well as a recent study about H atom adsorption.²⁰ This finding suggests that the relaxation of the surface structure also affects the adsorption energy. Based on the points above, three factors are inferred as involved in the change in adsorption energy. Partial optimisation of the adsorption model is used to separate and study the effects of these factors and to elucidate the controlling factors.

A schematic diagram showing the prepared adsorption models of four types used to separate these three factors is presented in Fig. 6. First, the adsorption model optimised without an electric field is called the 'initial model', which is the same as the model calculated as described in Section 3.2. Next, a model in which the electric field is applied to this 'initial model' and in which the positions of all atoms are fixed is called the 'all-fixed model'. In this 'all-fixed model', only electron transfer attributable to the application of the electric field occurs from the 'initial model'. Therefore, only the effect of the charge transfer factor is included. Furthermore, a model in which the atomic positions on the doped CeO₂ surface are fixed and only the atomic positions of the CO₂ molecule are optimised for the 'initial model' is called the 'surface-fixed model'. This model includes the effects of the charge transfer factor and the CO₂ molecular structural relaxation factor as the application of an electric field causes the electron transfer and structural relaxation of the CO₂ molecule. Finally, a model in which an electric field is applied to the 'initial model' and the atomic positions of the CO₂ molecule and the surface atoms of the doped CeO₂ are optimised is called the 'total relaxation model', which is the same as the model investigated in Section 3.3. In this model, the electron transfer, the structural relaxation of the CO₂ molecule, and the structural relaxation of

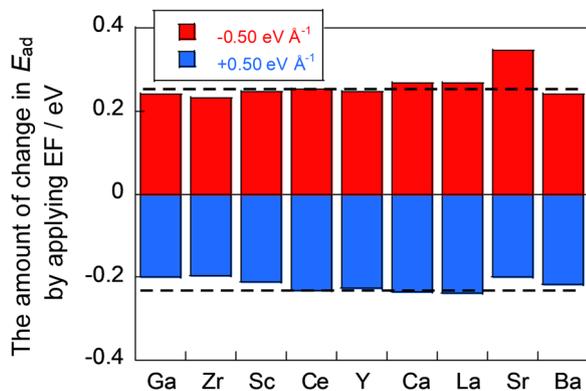


Fig. 5 Adsorption energy differences upon electric field application.



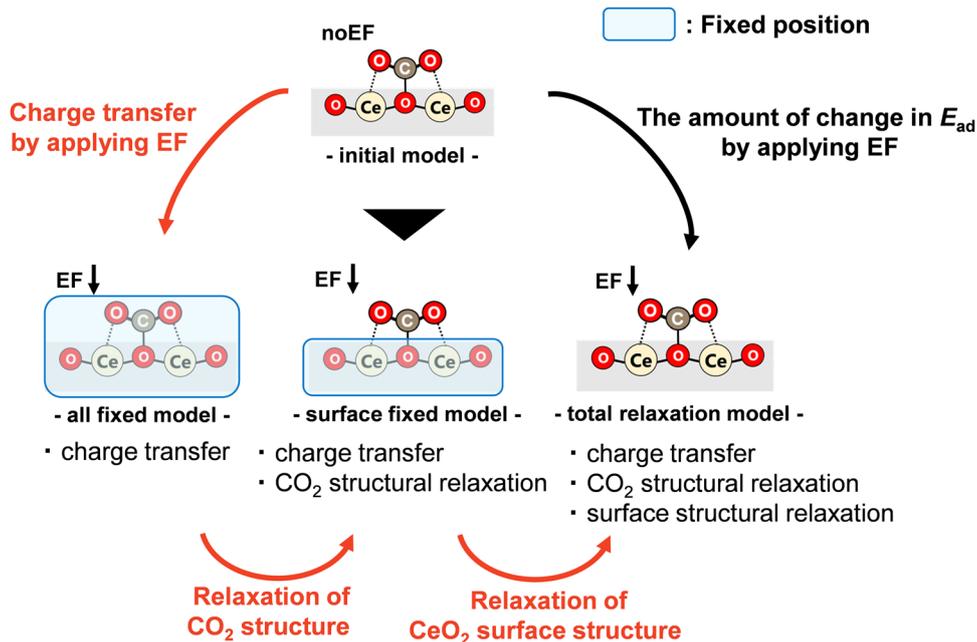


Fig. 6 Schematic image of DFT calculation flows.

the doped CeO₂ surface created by the application of the electric field occur. This model includes all three factors.

Therefore, the influence of charge transfer factors, CO₂ molecular structural relaxation factors, and surface structural relaxation factors can be considered respectively from a comparison between the 'initial model' and the 'all-fixed model', between the 'all-fixed model' and the 'surface-fixed model', and between the 'surface-fixed model' and the 'total relaxation model'. Here, a comparison between the 'initial model' and the 'total relaxation model' can elucidate the amount of change in adsorption energy attributable to the application of the electric field, as obtained in Fig. 5. Herein, dopants are classified into the following three types from Fig. 5: dopants (Ga, Zr, Sc, Y, and Ba) with small changes by applying the electric field, dopants (Ca and La) with large changes, and dopants (Sr) with different changes in the direction of the electric field, compared to undoped CeO₂. Therefore, in this investigation of the dominant factor, we focused on Ba, Ga, Ca, and Sr doping in consideration of the difference in the valence states. For each dopant, only three adsorption sites were selected for the study. The maximum, minimum, and average changes in the adsorption energy by the application of the electric field were observed. The calculated models are shown in Fig. S1 (ESI[†]).

3.5. Influence of doping hetero-cations on CO₂ adsorption with an electric field

The effects of each factor were assessed by calculating the difference in adsorption energies between the models prepared in the preceding section. The effects of all factors on the adsorption energy are depicted in Fig. 7(a), whereas the effects on adsorption energy of the charge transfer factor, CO₂ molecular structural relaxation factor, and surface structural

relaxation factor are presented respectively in Fig. 7(b), (c) and (d). Here, it was observed that the inhibition of adsorption because of the electron transfer from the CO₂ molecule was greater than the promotion of adsorption because of the electron transfer to the CO₂ molecule in light of the change in adsorption energy because some electrons had already transferred to the CO₂ molecule during the adsorption. Therefore, some attention was devoted to the relationship between the ionic radius of the dopant and the amount of change in adsorption energy because of the influences of the respective factors by application of a $-0.50 \text{ eV \AA}^{-1}$ electric field, which suppresses CO₂ molecule adsorption.

By comparison of Fig. 7(a) and (b), we investigated the influence of the charge transfer factor. The results show that the same trend was obtained among all factors and the charge transfer factor with regard to the ionic radius of the dopant. A comparison between the effects on the energy of all factors and the effects on the energy of the charge transfer factor confirmed a strong correlation, as shown in Fig. S2 (ESI[†]). Next, similar to the investigation of the effect of the charge transfer factor, a comparison was conducted between Fig. 7(a) and (c) and between Fig. 7(a) and (d). As a result, the effects of the CO₂ molecular structural relaxation factor and the surface structural relaxation factor showed different trends from the effects of all factors. These results indicate that the dominant factor influencing the amount of change in adsorption energy because of the application of the electric field is the charge transfer factor.

To confirm the electron transfer further, the amounts of charge transfer to CO₂ molecules and to the adsorption site when the electric field is applied were calculated using the Bader charge analysis. The relationship between the amount of charge transfer obtained from the Bader charge analysis and



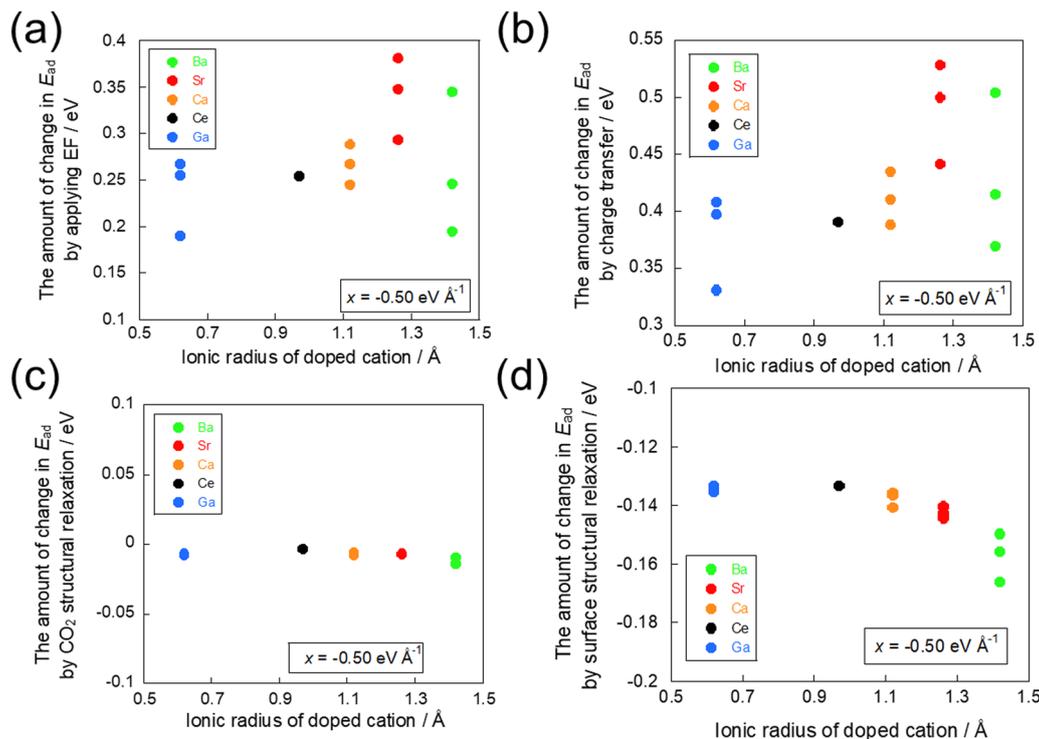


Fig. 7 Effects of factors on the change in the CO₂ adsorption energy in $-0.50 \text{ eV } \text{Å}^{-1}$. The amount of change in the CO₂ adsorption energy (a) by application of EF, (b) by charge transfer, (c) by CO₂ molecule structural relaxation, and (d) by surface structural relaxation.

the amount of change in adsorption energy by the application of the electric field is presented in Fig. 8. This diagram shows that electron donation to the CO₂ molecule decreases and the CO₂ adsorption becomes more unstable as the amount of charge held at the adsorption site increases. These results are also confirmed by the amount of charge transfer on the CO₂ molecule itself, which indicates that a lower amount of charge transfer to the CO₂ molecule leads to greater instability of adsorption. The relationship between the amount of charge transfer and the change in adsorption energy is not very linear:

interaction exists not only with the surface oxygen, which is the adsorption site, but also simultaneously with the cation. This interaction between the CO₂ molecule and the cation engenders the opposite direction of charge transfer to that of the interaction between the CO₂ molecule and the surface oxygen because the cation acts as a Lewis acid for CO₂ adsorption. Therefore, the presence of interaction with the cation shows an almost linear relationship.

The results of the Bader charge analysis confirm that the charge transfer from the adsorption site to the CO₂ molecule is

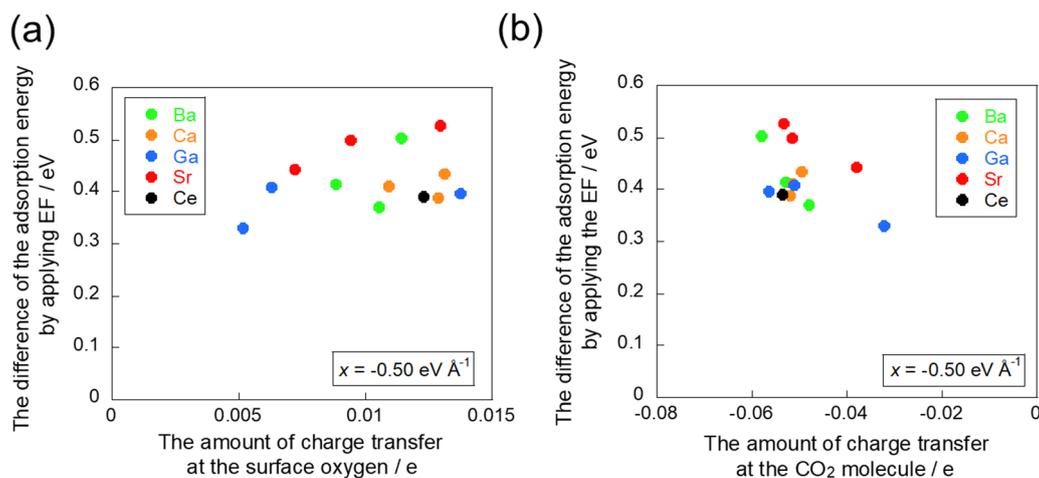


Fig. 8 Relationship between the difference of adsorption energy and the amount of charge transfer: (a) at the surface oxygen and (b) at the CO₂ molecule in $-0.50 \text{ eV } \text{Å}^{-1}$.



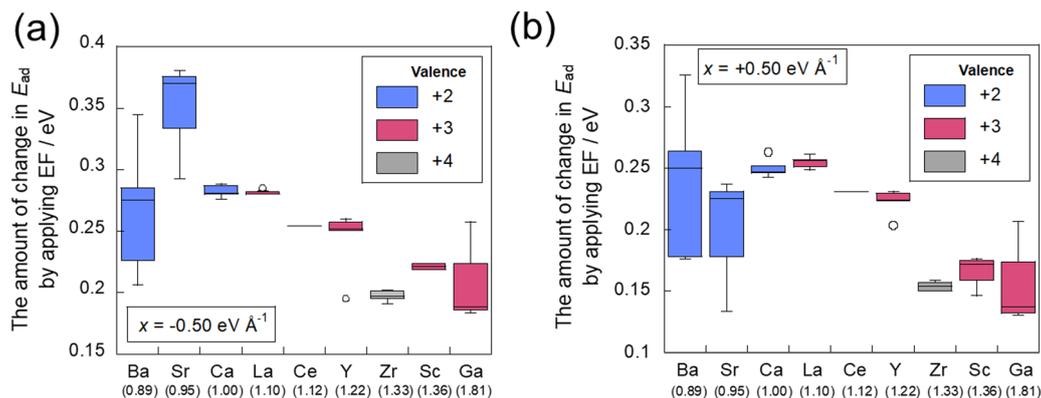


Fig. 9 Relationship between the difference of adsorption energy and the electronegativity of the dopant (a) in $-0.50 \text{ eV \AA}^{-1}$ and (b) in $+0.50 \text{ eV \AA}^{-1}$.

dominant in the amount of change in the CO_2 adsorption energy because of the application of the electric field. This study was also conducted with an electric field of 0.50 eV \AA^{-1} . The results revealed a similar trend to that found in the previous section as shown in Fig. S3 (ESI[†]).

3.6. Correlation between dopants and the CO_2 adsorption behaviour with an electric field

The results obtained from the studies described above indicate that the charge transfer factor has important effects on the amount of change in adsorption energy by applying the electric field. Nevertheless, the relationship between the doped cation species and the charge transfer factor remains unclear. Therefore, the relationship between the CO_2 adsorption-desorption behaviour and the doped species by the application of the electric field was clarified. Because the charge transfer from the adsorption site to the CO_2 molecule is a key factor for CO_2

adsorption behaviour with the electric field, the Lewis basicity of the surface oxygen on the metal oxide was found to be important. In other words, the Lewis basicity of the surface oxygen that can be changed more easily by application of an electric field is associated with more controllable adsorption and desorption of CO_2 molecules. Here, the charge on the oxygen atoms of metal oxides is known to be more negative and more Lewis basic for a lower electronegativity of the cation.^{48,49}

The correlation between the amount of change in adsorption energy attributable to the application of the electric field and the dopant electronegativity is presented in Fig. 9. In these figures, the numbers in brackets below the horizontal axis represent the electronegativity of each dopant. Variation of these data is influenced by the position of the doped cation species, with a symmetrical arrangement leading to a smaller variation. The results show that the amount of change in the adsorption energy caused by the application of an electric field

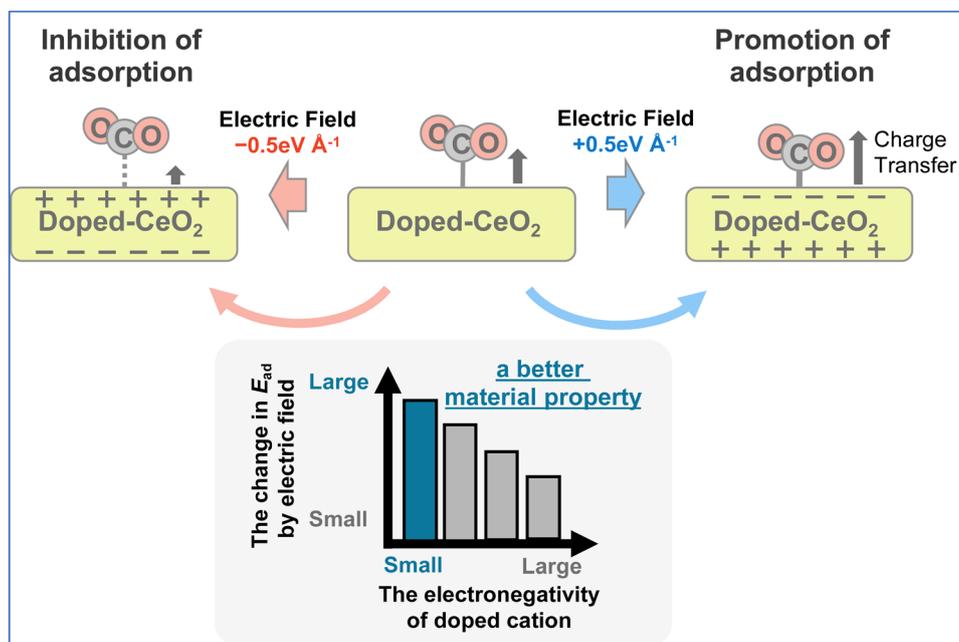


Fig. 10 The schematic image of this work.



can be varied easily by doping cations with small electronegativity. The results for Ba, Sr, and Zr are slightly off from this trend. These three cations are uniformly doped (see Fig. 2), so that the doped cations are not adjacent to each other. Therefore, it is considered that the amount of electron transfer to the CO₂ molecule changes depending on the absence of the adjacent element. In conclusion, this indicates that doping with cations of small electronegativity can readily perform control of adsorption and desorption by application of an electric field, which is predicted theoretically to lead to a higher CO₂ separation capacity (see Fig. 10).

4. Conclusion

The material properties necessary for CO₂ capture control by application of an electric field were elucidated using doped CeO₂ models and DFT calculations. The calculations showed that the application of an electric field for any doped cation can control the CO₂ adsorption energy. Selective CO₂ capture and desorption can be performed by switching the direction of the electric field. However, the amounts of change in adsorption energy were observed to be different for each doped cation because of the application of the electric field. This amount of change corresponds to the degree to which the adsorption or desorption can be controlled by the application of the electric field. To clarify the reason why these values differ for doped cations, we prepared computational models in which the atomic positions were partially fixed. Then we calculated the energy of the prepared models. This investigation revealed that the difference in charge transfer from the adsorption site to the CO₂ molecule has a strong correlation with the difference in the amount of change in the adsorption energy caused by the application of the electric field. This result was also confirmed using the Bader charge analysis. Moreover, the results showed a relationship between the electronegativity of the doped cation, which affects the Lewis basicity of metal oxides, and the controllable amount of CO₂ adsorption. In summary, the low electronegativity of the doped cation is associated with a greater amount of electron transfer and a greater amount of change in CO₂ adsorption by application of the electric field. These results can lead to better material prediction for CO₂ capture controlled using an electric field, which can be expected to contribute to methods for low-cost CO₂ capture.

Conflicts of interest

The authors have no conflicts to declare.

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