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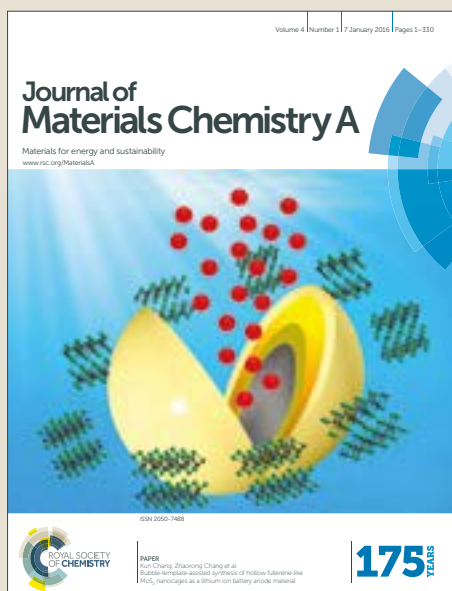
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Large CO₂ uptake on a monolayer of CaO[†]

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Density functional theory calculations are used to study gas adsorption properties of recently synthesized CaO monolayer, which is found to be thermodynamically stable in its buckled form. Due to its topology and strong interaction with the CO₂ molecules, this material possesses a remarkably high CO₂ uptake capacity (~0.4 g CO₂/g adsorbent). The CaO+CO₂ system shows excellent thermal stability (up to 1000 K). Moreover, the material is highly selective towards CO₂ against other major greenhouse gases such as CH₄ and N₂O. These advantages make this material a very promising candidate for CO₂ capture and storage applications.

1 Introduction

Capturing, storing and converting greenhouse gasses, especially CO₂, has become a major problem due to recent climate changes^{1–5}. Together with metal-organic framework based adsorbents^{6–9}, low dimensional materials, such as graphene, carbon nanotubes and boron nitride nanomaterials have attracted a lot of interest in recent years as promising materials for the capture of greenhouse gases (see Refs.^{10–14} for reviews). Surface functionalization has already been shown to be an effective tool to enhance the carbon-uptake capacities of such low dimensional materials^{15–19}. For example, decoration with Calcium (Ca) atoms can triple the CO₂ uptake capacity of graphene due to the stronger interaction between the molecule and the Ca dopants¹⁷. This effect becomes even more pronounced in carbon nanotubes due to topological changes in the system¹⁷.

In this work we conduct density functional theory (DFT) calculations to investigate CO₂ adsorption on the surface of a free standing CaO monolayer. Such two-dimensional (2D) crystals were recently synthesized between two graphene layers due to the large vdW pressure inside the nano-enclosures^{20,21}. Phonon spectrum calculations show that the CaO monolayer is stable only in its buckled form (see Fig. 1(b)). We show that this material possesses a large CO₂ uptake capacity (~0.4 g CO₂/g adsorbent)

due to strong interactions between the gas molecules and the adsorbent. Desorption of the CO₂ molecules are predicted by our DFT molecular dynamics (MD) simulations only above 1000 K. We also study the selectivity of the CaO monolayer to other gas molecules including greenhouse gases such as CH₄ and N₂O. Our findings show the large potential of CaO for CO₂ capture and storage applications.

2 Computational details

Calculations are performed using the generalized gradient approximation of Perdew-Burke-Ernzerhof for the exchange-correlation energy²². For the unit cell of CaO (containing 2 Ca atoms and 2 O atoms) the Brillouin zone integration was performed using 12×12×1 Monkhorst-Pack *k*-point sampling. 6×6×1 *k*-point mesh is employed for the 4×4×1 supercell. Double-zeta-polarized basis sets of local numerical orbitals were used for all atoms and the electrostatic potentials were determined on a real-space grid with mesh cutoff energy of 150 Ry. The vdW interaction is introduced using Grimme's empirical dispersion correction²³. The convergence criteria for total energy and Hellman-Feynman forces were 0.001 eV and 0.01 eV/Å, respectively. A vacuum spacing of more than 15 Å is used in the perpendicular direction to the CaO layer. The adsorption energy is defined as

$$E_{\text{ads}} = (E_{\text{CaO}+\text{g}} - E_{\text{CaO}} - NE_{\text{g}}) / N, \quad (1)$$

where $E_{\text{CaO}+\text{g}}$ is the total energy of monolayer CaO adsorbed with gas molecules, E_{CaO} is the total energy of monolayer CaO, E_{g} is the total energy of isolated gas molecule, and N is the number of adsorbed gas molecules. Spin-polarized calculations are conducted to calculate the adsorption energies. DFT molecular dynamics (MD) simulations were conducted using the canonical (NVT) ensemble with a time step of 1 fs. Nose-Hoover thermo-

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[†] Electronic Supplementary Information (ESI) available: the dynamics of the system at T=300 K and T=1000 K when the CO₂ molecule is attached to the T-site and the bridge site of CaO monolayer, respectively. See DOI: 10.1039/b000000x/

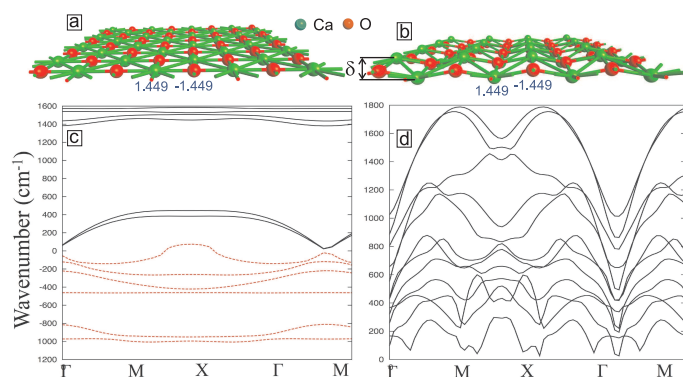


Fig. 1 (color online) (a,b) Optimized structures of planar (a) and buckled (b) monolayer CaO. Numbers show the partial charges of the corresponding atoms. (c,d) Phonon dispersion spectra of the planar (c) and the buckled (d) structures. The red-dashed lines indicate imaginary phonon frequencies for planar CaO.

stat was used with a damping constant of 100 fs. The computational package Atomistix toolkit²⁴ was used. Phonon spectrum calculations are conducted using the SIESTA software package²⁵ within the localized spin density approximation and the LDA+U (Hubbard-corrected DFT energy functionals). The vibrational frequencies of CaO monolayers are determined within the linear response framework. Dynamical matrices are computed at eight wave (\vec{q}) vectors in the irreducible wedge of BZ, i.e., on a $8 \times 8 \times 8$ grid²⁶. The density derived electrostatic and chemical (DDEC) charges method^{27,28} was used to calculate partial atomic charges, which is known to be the most suitable method for systems consisting of both organic and inorganic components²⁹.

3 Structural properties

Geometry optimizations resulted in two different structures for the CaO monolayer: planar (Fig. 1(a)) and buckled (Fig. 1(b)). The planar structure has a lattice parameter of 4.56 Å with a Ca-O distance of 2.28 Å. The buckled system has a smaller lattice parameter (4.459 Å) and buckling of $\delta = 0.797$ Å, resulting in an interatomic distance that is reduced to 2.26 Å. To assess the stability of the considered systems, we calculated their cohesive energies as

$$E_{\text{coh}} = (E_{\text{CaO}} - m * E_{\text{Ca}}/2 - m * E_{\text{O}}/2) / m, \quad (2)$$

where m is the number of atoms in the simulation cell, E_{CaO} is the total energy of the CaO monolayer and $E_{\text{Ca}}/E_{\text{O}}$ is the total energy of isolated Ca/O atom. Note that we have conducted spin-polarized calculations to obtain cohesive energies of both systems. The obtained cohesive energies are $E_{\text{coh}} = -5.69$ eV/atom and $E_{\text{coh}} = -5.71$ eV/atom, respectively for planar and buckled structures.

In order to study the stability of 2D-CaO we performed phonon structure calculations. Figures 1(c,d) show the phonon band structure at high symmetry points for both planar (a) and buckled (b) systems. For the buckled CaO monolayer (Fig. 1(d)), we obtained twelve phonon branches including three acoustic branches with zero frequency at the zone center and nine optical branches. All phonon modes have positive frequencies indicating the stabil-

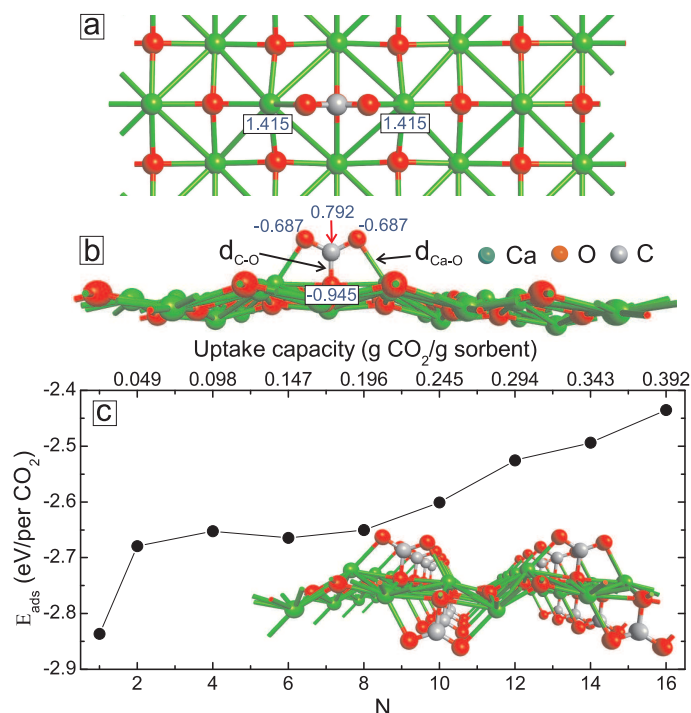


Fig. 2 (color online) (a,b) Top (a) and side (b) views of CaO monolayer with a single CO₂ molecule. Numbers show the partial charges of the corresponding atoms. (c) The adsorption energy as a function of the number of CO₂ molecules, N . Inset shows the optimized structure for $N=16$.

ity of the bucked structure. On the contrary, we found imaginary frequencies for some of the acoustic and optical phonon bands of the planar CaO (see Fig. 1(c)), which make the system thermally unstable. We have also conducted additional frequency calculations using hybrid B3LYP/6-31G(d) functional and did not find any negative frequencies for the buckled system.

4 CO₂ uptake capacity

A computational cell consisting of 4×4 unit cell is used in the gas adsorption calculations. Contrary to other 2D materials, such as graphene or boron nitride, where CO₂ molecules undergo weak physisorption (see, e.g., Ref.¹⁷), a strong chemisorption of the CO₂ molecule is obtained on the surface of CaO (see Fig. 2(b)). In the minimum energy configuration, the CO₂ molecule is adsorbed on the “bridge” site with C-O distance of $d_{\text{C-O}} = 1.41$ Å and Ca-O distance of $d_{\text{Ca-O}} = 2.31$ Å. Molecular attachment results in a local deformation of the CaO monolayer. Note that we have considered all the possible adsorption sites and orientations of the gas CO₂ molecule when finding the minimum energy configuration. To calculate the uptake capacity of the CaO monolayer, which is determined as the mass ratio of the adsorbed CO₂ molecules and the CaO monolayer, we started by gradually increasing the number of adsorbed gas molecules and calculated the adsorption energies E_{ads} . The results are shown in Fig. 2(c), where we plot the adsorption energy per CO₂ molecule as a function of the number of adsorbed CO₂ molecules in the computational unit cell. Although, E_{ads} increases with N , the molecules are strongly adsorbed even for full coverage of the material ($N=16$). In the latter case every

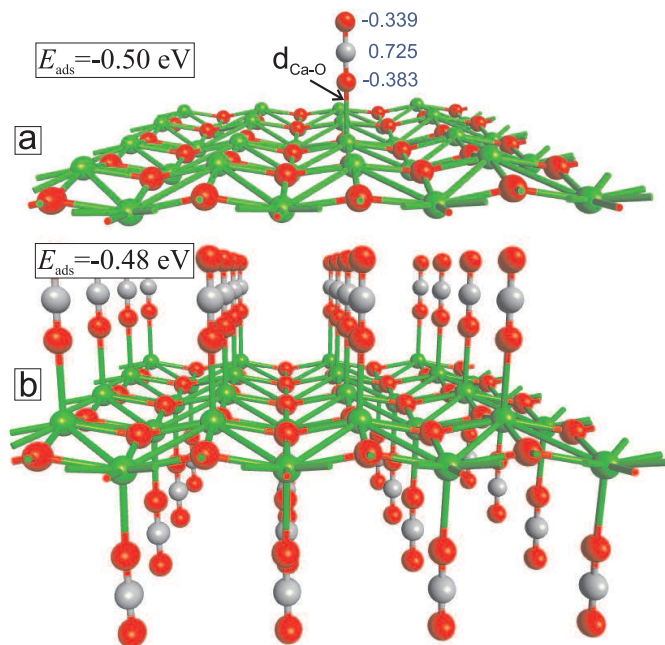


Fig. 3 (color online) “T”-site adsorption of CO₂ molecules on CaO monolayer for N=1 (a) and N=32 (b). The adsorption energies are given in each panel (eV per CO₂ molecule). The partial charges of the CO₂ molecule are also shown in (a).

Ca atom is connected to one O atom of the CO₂ molecules (see inset of Fig. 2(c)). This configuration gives an estimate of 0.392 g CO₂/g adsorbent for the uptake capacity of the material (see top axis of Fig. 2(c)).

The uptake capacity of the CaO monolayer can be greatly increased if the CO₂ molecules are adsorbed on the “T”-site, as shown in Fig. 3(a). The Ca-O distance in this case becomes $d_{Ca-O} = 2.51$ Å. A full coverage with such T-site adsorbed molecules gives an uptake capacity of 0.784 g CO₂/g adsorbent, which is significantly larger than the EU required minimum value of 0.132 g CO₂/g adsorbent under a pressure within the range of 0.1–1 bar³⁰. However, the adsorption energy of such T-site molecules are more than 5 times smaller than the adsorption energy of the bridge-site molecules (see the numbers in Fig. 3).

To understand such strong chemisorption of CO₂ molecules on the surface of CaO, we have calculated DDEC charges of the considered systems. In the absence of the molecules, the partial charges of Ca and O atoms are 1.449|e| and -1.449|e|, respectively, for both planar and buckled geometries (see Figs. 1(a,b)). Molecular adsorption significantly changes the partial charges in the material. For example, single CO₂ molecule reduces the charges of Ca atoms connected to the molecule to 1.415|e| (Fig. 2(a)). The partial charge of the O atom of the monolayer connected to the C atom of the molecule becomes -0.945|e| (Fig. 2(b)). Interestingly, we observed a transfer of -0.582|e| charge from the 2D material to the molecule. This explains the large adsorption energy of the CO₂ molecules on the CaO monolayer. However, a negligible charge transfer is observed when the molecule is adsorbed on the T-site (see Fig. 3(a)). Consequently, the adsorption energy of the molecule is small. Note that the charges of the

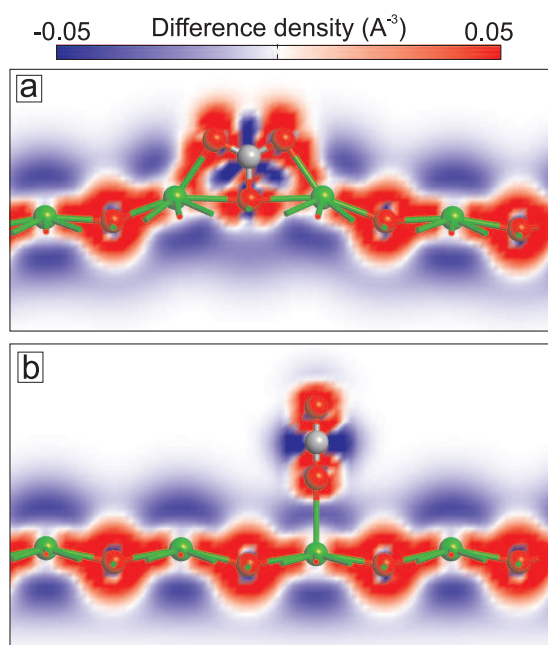


Fig. 4 (color online) Density plots of the electron density difference for carbon dioxide chemisorption on bridge-site (a) and T-site of CaO monolayer. The results are shown in the plane crossing the molecules.

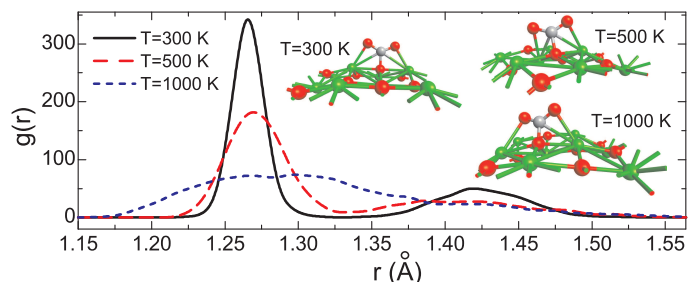


Fig. 5 (color online) Radial distribution function between C and O atoms for the bridge-site adsorbed CO₂ molecule at T=300 K (solid-black curve), T=500 K (dashed-red curve) and T=1000 K (dotted-blue curve). Insets show snapshots of the structures at different temperatures.

O atoms of the molecule are not equal. We have also calculated the electron density difference (EDD), which shows the difference between the self-consistent valence charge density and the superposition of atomic valence densities. Figure 4 shows the EDD of the system when the CO₂ molecule is adsorbed on the bridge-site (Fig. 4(a)) and T-site (Fig. 4(b)). In the former case, there is a strong charge exchange between the molecule and the adsorbent. However, much smaller charge transfer is obtained when the molecule is attached to the T-site (see Fig. 4(b)). This explains the weaker adsorption energy of T-site CO₂ molecules. Note the EDD is always positive on O atoms because of more electrons on these atoms.

5 Thermal stability

In order to check the thermal stability of CO₂ molecules adsorbed on monolayer CaO, we have conducted finite temperature MD simulations. As a typical example we have considered a supercell consisting of 2×2 unit cell with a single CO₂ molecule attached.

We found that T-site adsorption is less stable as compared to bridge-site adsorption: the desorption of the CO₂ molecule occurs already at room temperature (see supplemental online video³¹ for the dynamics of the system at T=300 K). On the contrary, the CO₂ molecule adsorbed on the bridge site is found to be stable up to T=1000 K (see supplemental online video³²). To characterize the behavior of the bridge-site adsorbed CO₂ molecule at finite temperature, we calculated the radial distribution functions $g(r)$. Trajectories are collected during 8 ps after equilibrating the system at a given temperature for about 2 ps. Fig. 5 shows $g(r)$ between C and O atoms for three different temperatures. At room temperature (see solid-black curve in Fig. 5), two pronounced peaks are clearly seen on the $g(r)$ curves corresponding to the distance between the C atom and the O atoms of the substrate (~ 1.41 Å) and the distance between C and O atoms of the molecule (~ 1.26 Å). With increasing temperature, the peaks in the $g(r)$ curve becomes less pronounced (dashed-red and dotted-blue curves). However, the CO₂ remains attached to the substrate at all considered temperatures (see the insets in Fig. 5).

6 Selectivity

Next, we investigate the selectivity of the CaO monolayer to different gas molecules. We consider 8 common molecules, including major greenhouse gases (such as water vapor, methane, and nitrous oxide) and common resources in chemical industry (such as NH₃), which are very harmful to the human body. Figure 6(b-i) show the most stable structures of these gas molecules adsorbed on the surface of the CaO monolayer. H₂ and CH₄ molecules are weakly physisorbed due to van der Waals interactions (Figs. 6(b,c)). Consequently, they have smaller adsorption energies (see Fig. 6(a)). CO, N₂, NH₃ and N₂O molecules form covalent bonding with the Ca atoms of the substrate (Figs. 6(d-h)), resulting in an increase of the adsorption energy. Among the considered molecules, the largest adsorption energy is found for the water molecule ($E_{ads} = -1.95$ eV). Splitting of the water molecule is also obtained during the optimization process (see Fig. 6(i)). Still, CO₂ molecule shows the strongest adsorption strength on this material ($E_{ads} = -2.84$ eV), which indicates the selectivity of the CaO monolayer for carbon dioxide molecules. This selectivity can be used for separating CO₂ from a natural gas mixture using CaO layers.

7 CO₂ adsorption on (100) surface of bulk CaO

As a reference to our predictions to CaO monolayer, we have also studied the CO₂ adsorption on the (100) surface of bulk CaO material. The latter has a face centered cubic lattice with lattice parameter 4.782 Å. The simulations are conducted for 4×4 unit cell (Fig. 7(a)). The slab has 4 layers and the last layer was fixed during the simulations (highlighted in Fig. 7(b)). In the minimum energy configuration, the CO₂ molecule is adsorbed on the bridge site with $d_{C-O} = 1.42$ Å and $d_{Ca-O} = 2.34$ Å. The DDEC charge calculations show that there is a charge transfer of $-0.562|e|$ from the substrate to the molecule, which is smaller than the one in the

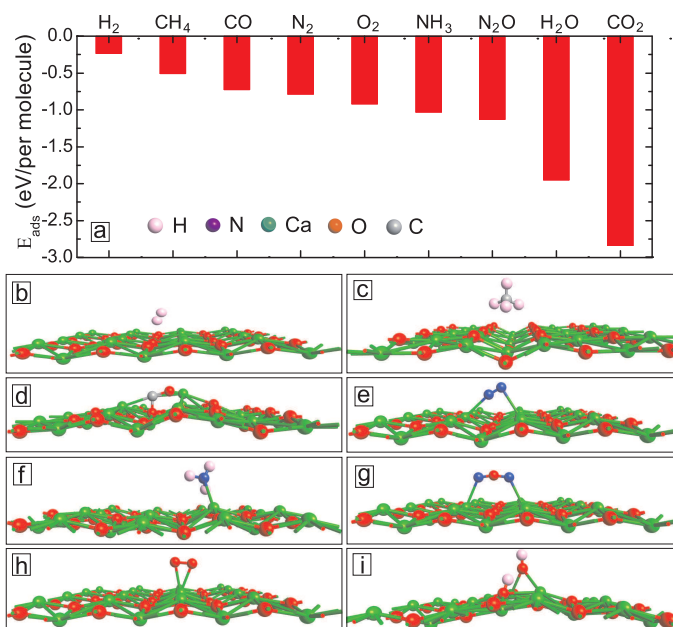


Fig. 6 (color online) (a) Adsorption energies of different gas molecules on the surface of CaO monolayer. (b-g) Optimized structures of different gas molecules adsorbed on CaO.

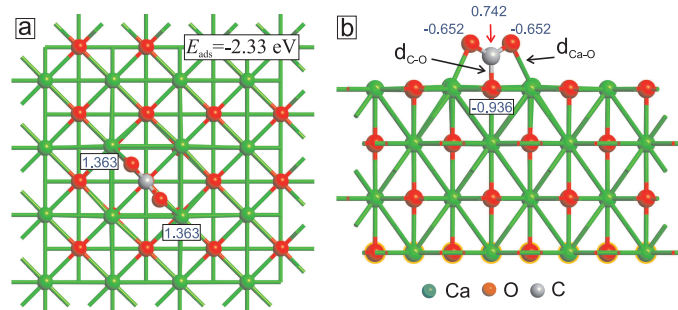


Fig. 7 (color online) Top (a) and side (b) views of CO₂ adsorption on (100) surface of CaO crystal. The adsorption energy of the molecule is given in panel (a). Numbers show the partial charges of the corresponding atoms.

case of CO₂ adsorption on CaO monolayer (see Fig. 2). This explains the smaller adsorption energy of the CO₂ molecule on the surface of bulk CaO ($E_{ads} = 2.33$ eV) as compared to the adsorption energy of the molecule on CaO monolayer ($E_{ads} = 2.84$ eV). In addition, the latter sample has a very large surface-to-volume ratio, which indicates the promising potential of the material for CO₂ storage.

8 Conclusions

DFT calculations were performed to study CO₂ adsorption on the surface of free standing CaO monolayer. This material is thermally stable in its buckled form and has relatively large cohesive energy. However, the planar structure of CaO is thermodynamically unstable due to the negative frequencies in the phonon spectra, which requires other methods for its stabilization. We predict that the buckled CaO monolayer possesses a very large CO₂ uptake capacity due to its 2D topology and strong interaction with

the CO₂ molecules. In addition, the system is remarkably selective towards CO₂ as compared to other common gas molecules, including the major greenhouse gases (such as methane and nitrous oxide) and hazardous gas molecules of the chemical industry (such as NH₃). 10 ps long DFT MD simulations show the stability of the CaO+CO₂ system up to 1000 K. These findings indicate a great potential of this novel material for CO₂ capture and storage applications.

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References

- R. A. Betts, O. Boucher, M. Collins, P. M. Cox, P. D. Falloon, N. Gedney, D. L. Hemming, C. Huntingford, C. D. Jones, and D. M. H. Sexton, M. J. Webb, *Nature (London)*, 2007, **448**, 1037-1041.
- J. Meyer, *Nature (London)*, 2008, **455**, 733.
- R. S. Haszeldine, *Science*, 2009, **325**, 1647-1652.
- D. W. Keith, *Science*, 2009, **325**, 1654-1655.
- S. Chu and A. Majumdar, *Nature (London)*, 2012, **488**, 294-303.
- Q.-L. Zhu and Q. Xu, *Chem. Soc. Rev.*, 2014, **43**, 5468-5512.
- B. Sreenivasulu, I. Sreedhar, P. Suresh, and K. V. Raghavan, *Environ. Sci. Technol.*, 2015, **49**, 12641-12661.
- S. Y. Lee and S. J. Park, *J. Ind. Eng. Chem.*, 2015, **23**, 1-11.
- S. Li and F. Huo, *Nanoscale*, 2015, **7**, 7482-7501.
- S. Gadipelli and Z. X. Guo, *Progress in Materials Science*, 2015, **69**, 1-60.
- R. Balasubramanian and S. Chowdhury, *J. Mater. Chem. A*, 2015, **3**, 21968-21989.
- A. T. Najafabadi, *Renewable & Sustainable Energy Reviews*, 2015, **41**, 1515-1545.
- S. Bontemps, *Coord. Chem. Rev.*, 2016, **308**, 117-130.
- A. E. Creamer and B. Gao, *Environ. Sci. Technol.*, 2016, **50**, 7276-7289.
- M. G. Plaza, C. Pevida, A. Arenillas, F. Rubiera, and J. J. Pis, *Fuel*, 2007, **86**, 2204-2212.
- C. Pevida, M. G. Plaza, B. Arias, J. Feroso, F. Rubiera, and J. J. Pis, *Appl. Surf. Sci.*, 2008, **254**, 7165-7172.
- C. Cazorla, S. A. Shevlin, and Z. X. Guo, *J. Phys. Chem. C*, 2011, **115**, 10990-10995.
- M. S. Shafeeyan, W. M. A. Wan Daud, A. Houshmand, and A. Arami-Niya, *Fuel*, 2012, **94**, 465-472.
- S. Chowdhury, G. K. Parshetti, R. Balasubramanian, *Chem. Eng. J.*, 2015, **263**, 374-384.
- K. S. Vasu, E. Prestat, J. Abraham, J. Dix, R. J. Kashtiban, J. Beheshtian, J. Sloan, P. Carbone, M. Neek-Amal, S. J. Haigh, A. K. Geim, and R. R. Nair, *Nat. Commun.*, 2016, **7**, 12168.
- G. R. Berdiyrov, M. Neek-Amal, F. M. Peeters, and Adri C. T. van Duin, *Phys. Rev. B*, 2014, **89**, 024107.
- J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
- S. Grimme, *J. Comp. Chem.*, 2006, **27**, 1787-1799.
- Distributed by QuantumWise company, Copenhagen, Denmark. <http://www.quantumwise.com>.
- J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón and D. J. Sánchez-Portal, *J. Phys.: Condens. Mater.*, 2002, **14**, 2745.
- B. B. Karki and R. M. Wentzcovitz, *Phys. Rev. B*, 2000, **61**, 13.
- T. A. Manz and N. G. Limas, *RSC Adv.*, 2016, **6**, 47771-47801.
- N. G. Limas and T. A. Manz, *RSC Adv.*, 2016, **6**, 45727-45747.
- M. E. Madjet, F. El-Mellouhi, M. A. Carignano, and G. R. Berdiyrov, *J. Appl. Phys.*, 2016, **119**, 165501.
- R. Irons, B. Goh, C. E. Snape, A. Arenillas, T. Drage, K. Smith, J. Maier, B. Dhungel, P. Jackson, G. Sakellariopoulos, V. Stathopoulos, and G. Skodras, Assessment of options for CO₂ capture and geological sequestration. Comparison of CO₂ capture technologies and enhancing CMM production with CO₂, European Commission, ISBN-9789279115905 (2007).
- See supplemental material for the dynamics of the system at T=300 K when the CO₂ molecule is attached to the T-site of CaO monolayer.
- See supplemental material for the dynamics of the system at T=1000 K when the CO₂ molecule is attached to the bridge-site of CaO monolayer.