Proceedings of CONF-MSS 2026 Symposium: Advanced Composite Materials and Polymer Chemistry
DOI: 10.54254/2755-2721/2026.AD32079

Mechanisms and Strategies of Oxygen Vacancy Regulation for High-Performance CaO-Based Thermochemical Energy Storage

Yuchen Xiao[1], Nana Wang[12*]

[1]*College of Electrical and Power Engineering, Taiyuan University of Technology, Taiyuan, China*
[2]*Key Laboratory of Cleaner Intelligent Control on Coal & Electricity, Ministry of Education, Taiyuan University of Technology, Taiyuan, China*
**Corresponding Author. Email: 1170134241@qq.com*

Abstract. Calcium looping (CaL) is a great way to store thermal energy because it holds a lot of energy. But there is a big problem: CaO adsorbents quickly lose their activity. When they get hot, they sinter. Also, the product layer blocks diffusion. Because of these issues, we cannot easily use CaL on a large scale right now. To fix this, researchers are adding oxygen vacancies at the atomic level. This paper reviews how oxygen vacancies change CaO-based materials for the better. First, we look at how people make these vacancies in the lab. For example, they use aliovalent doping or change the material's shape. We also list the main tools used to check them. Next, the paper explains the science behind this using Density Functional Theory (DFT) calculations. These calculations show us exactly how the vacancies work. They give ions an easier path to travel, which speeds up the physical movement (better kinetics). At the same time, the vacancies act as Lewis basic sites. They grab CO_2 molecules tighter, which helps the reaction happen (better thermodynamics). Finally, we talk about the remaining hurdles, especially keeping the materials stable at very high heat. We suggest that future work should combine live testing (in-situ) with data-driven computer models to build much stronger energy storage materials.

Keywords: thermochemical energy storage, calcium looping, oxygen vacancy, defect engineering, density functional theory (DFT)

1. Introduction

Sun and wind are our main renewable energy sources today. But they do not produce power all the time, and their output changes a lot. This makes it really hard for power grids to handle peak times. We urgently need cheap and large-scale ways to store thermal energy to solve this. Among all the choices, calcium looping (CaL) thermochemical energy storage looks very promising. It works by switching back and forth between CaO and $CaCO_3$ ($CaO + CO_2 \leftrightarrow CaCO_3$). People like CaL because it does not cost much, it can store heat for a long time, and it has a huge theoretical energy density of 3.2 GJ/m³ [1-4].

DOI: 10.54254/2755-2721/2026.AD32079

Even so, CaO materials have two big issues when they cycle at high temperatures. First, they suffer from severe sintering. This shrinks the active surface area a lot. Second, when $CaCO_3$ forms, it creates a thick layer that stops CO_2 from getting inside. Both problems make the reaction go very slowly. After a few cycles, the materials just stop working well [5,6]. This is the main reason why we do not see CaL used everywhere yet.

To get around these bottlenecks, scientists started using a new trick: regulating oxygen vacancies. This means changing the material at the atomic level. An oxygen vacancy is basically a missing oxygen atom. It turns out that this tiny defect can fix the big performance problems. For one, the empty spaces give ions (like O^{2-} and CO_3^{2-}) a shortcut to move through the thick product layer. This lowers the resistance and speeds up the process [7,8]. Also, the empty spots hold extra electrons, making them act as strong Lewis basic sites. They pull in CO_2 molecules very well, which boosts the surface reaction [9,10].

So, managing these oxygen vacancies is currently one of the best ways to make CaO materials last longer and react faster. We should note that playing with defects is already common in other energy fields. For instance, lots of studies show that oxygen vacancies help battery cathodes conduct electricity better [11-13]. They also make different kinds of catalysts work faster [14-20] and change the traits of many oxide materials [21,22]. Seeing these successes, researchers are now trying the exact same ideas on CaO thermal storage.

In this review, we summarize the newest studies on using oxygen vacancies to improve CaO energy storage. First, we cover how labs actually put these vacancies into the materials, mostly through doping. We also list the machines used to detect them, like XPS and EPR. Then, we explain the science behind why the reaction and thermodynamics get better. We do this by comparing computer models (DFT) with real lab tests. At the end, we talk about what scientists still disagree on and where the field should go next.

2. Fundamental theories of calcium looping thermochemical energy storage and oxygen vacancy regulation

2.1. Reaction kinetics and diffusion limitation mechanisms of calcium looping

CaL thermochemical energy storage runs on the simple $CaO/CaCO_3$ cycle. The equation for this is: $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$. This reaction releases or takes in 178 kJ/mol of heat. The numbers look great on paper, but the actual reaction kinetics are tricky. That makes it tough to use in real life [23].

Experiments show that the carbonation of CaO follows a typical two-stage mechanism. It goes from chemical reaction control to product layer diffusion control. In the first step, CO_2 hits the fresh CaO surface and reacts almost instantly. The chemical kinetics are very fast here. But there is a catch. The $CaCO_3$ that forms takes up a lot more space than the original CaO. In fact, its volume is about 2.2 times larger (36.9 cm^3/mol vs 16.9 cm^3/mol). So, the new $CaCO_3$ expands, covers the surface, and blocks all the tiny pores.

Once the product layer gets to a certain thickness (usually around 30 to 50 nm), the reaction changes gears [7]. It enters the diffusion-controlled stage. Now, the CO_2 gas and the ions have a really hard time pushing through that solid $CaCO_3$ wall. The resistance goes way up, and the reaction basically hits the brakes. Computer simulations at the micro-level explain this perfectly. A perfect crystal lattice does not leave any room for ions to squeeze through. The energy needed to move them is just too high. That is why the CaO becomes useless after many cycles [24]. If we want to fix these materials, we have to find a way to punch holes through that dense barrier.

DOI: 10.54254/2755-2721/2026.AD32079

2.2. Multi-scale regulation mechanism of oxygen vacancies on energy storage performance

Oxygen vacancy (Ov) is an intrinsic anion defect. It solves the kinetic problems mentioned above at the atomic scale by changing the material's electronic structure and how ions move through it.

First, looking at the electronic structure, oxygen vacancies clearly lower the surface reaction activation energy. When lattice oxygen escapes, the local charge density changes. The Ca^{2+} ions nearby become coordinatively unsaturated, creating an electron-rich center right at the vacancy site. DFT calculations show that this does two things. First, oxygen vacancies add defect energy levels into the wide band gap of CaO. This narrows the surface band gap and makes charge transfer easier. Second, these electron-rich Ov sites act as strong Lewis bases. They easily grab onto Lewis acidic CO_2 molecules through orbital hybridization. Calculations show this strong interaction increases the adsorption energy by over 80%. It also bends the C=O bonds, making it easier for carbonate to form [10].

Second, regarding ion transport, oxygen vacancies create fast ion channels with low energy barriers. During the difficult diffusion-controlled stage, these vacancies act like stepping stones. Ions can hop from one vacancy to another inside the dense $CaCO_3$ product layer. This drastically cuts down the migration resistance for O^{2-} or CO_3^{2-}. DFT data prove that compared to a perfect crystal, having oxygen vacancies can lower the ion diffusion energy barrier by 0.5 to 1.0 eV. This means the ion diffusion rate speeds up by an order of magnitude [25]. Because of these fast channels, the unreacted CaO inside can still exchange materials even when it is wrapped in a thick product layer. This prevents the reaction from stopping early and increases the final conversion rate.

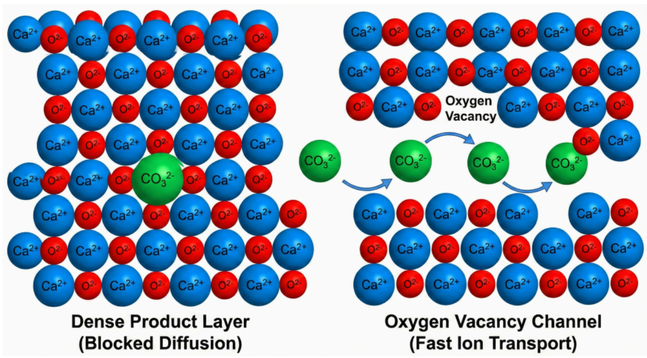

Figure 1. Schematic diagram of the mechanism by which oxygen vacancies promote ion diffusion in CaO-based materials

3. Experimental research progress on oxygen vacancy CaO-based materials

The introduction and regulation of oxygen vacancies (Ov) through experimental means has become a core strategy to improve the reaction kinetics and cyclic stability of CaO-based materials. This chapter summarizes existing research progress from three dimensions: defect introduction methods, key characterization techniques, and structure-performance relationships.

3.1. Strategies for introducing oxygen vacancies

To create stable oxygen vacancies, researchers usually disrupt the regular lattice (by doping) or change the chemical environment on the surface (by controlling the morphology).

(1) Element doping. Right now, this is the most popular method. The basic idea is to add foreign ions, which forces the material to generate vacancies to balance the charge. Rare earth and transition

DOI: 10.54254/2755-2721/2026.AD32079

metal doping: By using dopants that can change their valence states, we can create a lot of vacancies. For example, Li et al. proved that adding Ce greatly improved the material's ability to resist sintering [6]. Guo et al. did several studies on dual-doping, like Zr-Mn [26] and Zr-Ce [27,28]. They found that these combinations can effectively control how electrons transfer and improve the coordination environment on the surface. Also, Zhang et al. tested different bimetallic combinations, such as Co-Ni, to find which one lowers the vacancy formation energy the most [24]. Recently, Fang et al. showed that modifying the material with both Al and Zr not only increased the vacancy concentration but also created a better pore structure [29]. Other multi-doped Ca-based composites have shown similar good results [30]. Alkali and alkaline earth metal doping: Adding low-valence ions creates vacancies due to charge balance. Ren et al. used Na^+ doping to build channels for ion transport [7]. Moreover, doping with alkaline earth metals like Mg helps to stabilize the crystal. Guo et al. reported that adding Mg stopped the grains from growing too big at high temperatures [31]. This matches what other studies found in Mg-doped oxide systems [12]. Sorption-enhanced reforming applications: It is also worth mentioning that in the field of sorption-enhanced steam reforming, researchers heavily use doping strategies (like Ni/CaO) to capture more CO_2 and improve the catalytic efficiency [32,33].

(2) Special morphology and process control. The heating process during preparation directly decides how defects are frozen in place. Yao et al. made CaO modules with hierarchical pore structures, which made mass transfer much easier [34]. Chen et al. used a template method to build hollow-shell structures. This design exposed more unsaturated sites on the surface [5]. In a similar way, Yuyuan et al. used hydrocalumite to make CaO-$Ca_{12}Al_{14}O_{33}$ materials. The structural memory effect helped to improve the cyclic performance [35].

3.2. Key characterization techniques

Before we can link structure to performance, we need to prove the vacancies are there and count them. The main tools researchers use are: X-ray Photoelectron Spectroscopy (XPS): This is the best method for getting numbers. By looking at the O 1s spectrum, researchers calculate the area ratio of defect oxygen ($O\beta$, ~531.5 eV) to lattice oxygen ($O\alpha$, ~529.5 eV). This gives a direct reading of the surface vacancy concentration [26,36]. Electron Paramagnetic Resonance (EPR/ESR): This is a very sensitive tool to find single-electron-trapped oxygen vacancies. If there is a signal around $g \approx 2.003$, it acts like a fingerprint proving the vacancies exist. Raman Spectroscopy: Researchers use this to see if the lattice symmetry is broken. This usually shows up as wider characteristic peaks or new peaks caused by defects.

3.3. Regulation mechanisms of oxygen vacancies on energy storage performance

Lab tests clearly show that more oxygen vacancies lead to better energy storage performance in CaO-based materials. This improvement mostly comes down to two things: better kinetics and higher stability.

(1) Constructing High-Speed Ion Channels (Kinetic Enhancement) During the diffusion stage, oxygen vacancies build pathways inside the dense $CaCO_3$ layer that have low resistance. Ren et al. did an experiment showing that their Na-doped sorbent kept a conversion rate of 49.5% even after 30 cycles. That is a 147.5% increase compared to normal pure CaO. This proves that oxygen vacancies really stop the reaction from slowing down, keeping the efficiency high even with a thick product layer [7].

DOI: 10.54254/2755-2721/2026.AD32079

(2) Grain Boundary Pinning Effect (Stability Enhancement) When you introduce oxygen vacancies, the lattice usually distorts a bit. This change in the microstructure creates a "pinning effect." It stops the grains from growing larger when the temperature gets very high. For instance, Zhang et al. made a Mg/Zn co-doped honeycomb ceramic. After 25 cycles, it still kept over 90% of its capacity [8]. Combining better activity from oxygen vacancies with a stronger physical skeleton is the secret to making long-lasting energy storage materials.

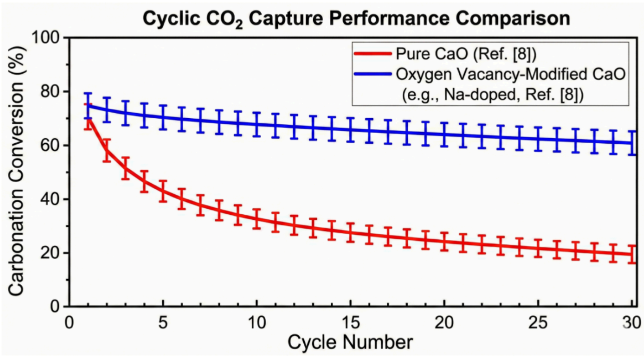

Figure 2. Comparison of cyclic carbonation conversion between pure CaO and oxygen vacancy-modified CaO materials

3.4. Key influencing factors

How well oxygen vacancies work depends on several things acting together: Doping Threshold: There is always a "sweet spot" for how much to dope. If you add too much, the impurities will clump together. This wastes active sites and can even break the crystal lattice [6]. Heat Treatment Temperature: You have to find a balance between the grain size and how many defects you have. If the calcination temperature is too high (above 900°C), the high-energy oxygen vacancies on the surface will just anneal and disappear, which lowers the activity [37]. Atmosphere Environment: A reducing atmosphere helps to create more vacancies. On the flip side, heating the material in a purely oxidizing atmosphere might fill up the vacancies and make the material inactive [14].

4. Progress in theoretical computational research on the regulation mechanism of oxygen vacancies

As computer science gets better, using Density Functional Theory (DFT) to run first-principles calculations has become a normal way to figure out how materials work at the microscopic level. This section explains how oxygen vacancies change the electronic structure, improve adsorption, and speed up ion transport from an atomic point of view.

4.1. Calculation models and parameter settings

Most studies use software like VASP or CASTEP to do the math. When dealing with transition or rare earth metals (like Ce, Mn, and Co), the electrons are strongly correlated. So, researchers usually apply the DFT+U (Hubbard U correction) method. This fixes the errors that the normal GGA-PBE method makes when predicting band gaps and locating electrons [24,25]. When building models, people usually start with the stable CaO crystal face. They use 2×2 or 3×3 supercells and add a vacuum layer larger than 15 Å to stop the boundaries from affecting the results [38]. To create

DOI: 10.54254/2755-2721/2026.AD32079

oxygen vacancies in the model, they just delete oxygen atoms from the surface or just below it. Then, they check if the system is stable by looking at the vacancy formation energy.

4.2. Localized reconstruction of electronic structure

Computer models prove that changing the electronic structure by adding oxygen vacancies is the real reason why the chemical activity goes up. Band Reconstruction: Yan et al. looked at the Density of States (DOS). They found that oxygen vacancies create new defect states near the Fermi level inside the wide CaO band gap. This narrows the surface band gap a lot. It means electrons need less energy to get excited, so they can move around the surface much more easily. Charge Density Redistribution: When we look at electron density difference plots, we can see that oxygen vacancies act like traps for electrons. Because the O^{2-} is missing, the electron clouds from the Ca ions nearby gather around the empty spot, creating a local electric field. Shi Wei et al. studied the Cr/Co system and found that this area packed with electrons makes the surface much more nucleophilic. This makes it very easy for Lewis acidic CO_2 molecules to interact and hybridize their orbitals [25].

4.3. Thermodynamic adsorption and kinetic diffusion mechanisms

DFT calculations quantitatively evaluate the regulation mechanism of oxygen vacancies throughout the reaction process:

Thermodynamic Adsorption Transition: On a perfect CaO surface, CO_2 exhibits only weak physical adsorption. Calculations by Zhang Youhao et al. show that at oxygen vacancy sites, the absolute value of the adsorption energy (E_{ads}) of CO_2 molecules increases significantly (e.g., from -0.5 eV to over -1.5 eV), accompanied by C-O bond elongation and bond angle bending from linear to 120°~130° [24]. This indicates that oxygen vacancies induce a transition from physical adsorption to strong chemical adsorption, forming stable carbonate precursors.

Kinetic Energy Barrier Reduction: Simulations using the Climbing Image Nudged Elastic Band (CI-NEB) method confirm that oxygen vacancies construct low-resistance channels within the dense product layer. Calculations show that vacancies induced by dual variable-valence metals (e.g., Co-Ni) can reduce the migration energy barrier of carbonate ions by 0.5~1.0 eV [24,25]. This explains, at the atomic scale, why modified materials can maintain high reaction rates during the diffusion-controlled stage.

4.4. Structure-activity correlation between theory and experiment

Existing literature shows a high degree of self-consistency between theoretical predictions and experimental results:

(1) Correspondence between Formation Energy and Concentration: Doping systems with lower vacancy formation energies in DFT calculations (e.g., Ce doping) typically exhibit higher ratios of defect oxygen (O_β/O_α) in experimental XPS characterization [6];

(2) Correspondence between Energy Barrier and Rate: The trend of reduced diffusion energy barriers derived from calculations aligns perfectly with the increased reaction rate observed in the diffusion stage of thermogravimetric analysis (TGA). This closed-loop verification of "microscopic mechanism-macroscopic performance" establishes the scientific rationality of the oxygen vacancy regulation strategy.

DOI: 10.54254/2755-2721/2026.AD32079

5. Challenges and future perspectives

Although a consensus has been reached that oxygen vacancy engineering improves the performance of CaO-based materials—specifically, that doping with rare earths (Ce, La) or transition metals (Mn, Co) significantly enhances cyclic stability [6,24]—challenges remain regarding mechanism elucidation and engineering application. Future research must address these controversies while moving toward low-cost and large-scale applications.

5.1. Key scientific controversies and challenges

The Adsorption vs. Diffusion Debate: Scientists still argue about exactly what the oxygen vacancies do best. For example, Yan's team did computer models and believes the "surface effect" is the main hero. They say the vacancies mostly help by grabbing CO_2 better. On the other hand, Ren's team used kinetic models and thinks the "bulk effect" is the real answer. They argue the most important thing is how vacancies help ions travel through the thick product layer [7]. Going forward, researchers need to run different kinds of tests to see which effect matters more during each step of the reaction.

Are They Stable at High Heat?: Typical CaL systems run really hot (over 900°C) with lots of oxygen around. People worry that the oxygen vacancies on the surface might just get filled in and disappear (thermal annealing). Right now, most DFT computer models just look at the materials at 0 K. They do not show what happens in a hot, moving environment. If a material stops working in a lab test, we still aren't 100% sure if it is because the vacancies vanished. We need to test this more.

Testing Limitations: Sometimes, different research papers give conflicting results. This usually happens because they made the materials differently. For instance, fast spray pyrolysis creates weird, unstable defects, while slow baking creates normal defects. Also, looking at the material in a cold vacuum (like in a standard XPS machine) does not tell us what it looks like in a super-hot, atmospheric reactor.

5.2. Future research directions

Make it Cheap and Big: We need to find ways to make these materials without spending too much. One idea is to use industrial trash. Solid wastes like red mud or steel slag are full of Ti, Fe, and Al. We could use them instead of buying expensive pure chemicals [1]. We should also try 3D printing or extrusion molding to make strong, self-supporting pellets or honeycombs. That is how we move from making tiny amounts in a lab to making tons of it for real engineering projects.

Live Testing (In-situ/Operando): We need to stop guessing what happens inside the reactor. By using live tools like in-situ XRD, Raman, and Environmental TEM, we can watch the oxygen vacancies change in real-time. If we record them while the material is baking in CO_2 and N_2 at 900°C, we will finally understand exactly how they form and why they die.

Data-Driven Models: We should build computer models that connect the tiny atomic level all the way to the giant reactor level. We can use Ab Initio Molecular Dynamics (AIMD) to see how molecules stick to the surface when it is 900°C. Also, Machine Learning (ML) can do a lot of the heavy lifting. A good AI model could quickly check thousands of doping recipes and predict which one will give the best vacancy formation energy [24].

DOI: 10.54254/2755-2721/2026.AD32079

6. Conclusions

This paper systematically reviewed the latest progress in utilizing oxygen vacancy engineering to enhance the performance of CaO-based thermochemical energy storage materials, drawing the following main conclusions:

Effectiveness of Modification: Through aliovalent element doping (especially variable-valence rare earth/transition metals) or special morphology design, thermodynamically stable oxygen vacancies can be effectively introduced into the CaO lattice, significantly improving CO_2 capture capacity and sintering resistance over long-term cycling.

Dual Enhancement Mechanism: Oxygen vacancies play a dual role as "electron pumps" and "ion channels." On one hand, acting as strong Lewis basic sites, they regulate the surface electronic structure, increasing CO_2 adsorption energy by over 80% and activating C=O bonds (thermodynamic enhancement); on the other hand, they construct low-energy-barrier ion transport channels within the dense product layer, drastically reducing solid-phase diffusion resistance (kinetic acceleration).

Application Prospects: Oxygen vacancy regulation is a key technology to break the "activity-stability" trade-off in CaO-based materials. With the development of in-situ characterization techniques and multi-scale calculations, this strategy is expected to play a decisive role in the development of low-cost, long-life thermal storage materials, providing a solid material foundation for the efficient consumption of renewable energy and the "Dual Carbon" goals.

References

[1] Geng, B., & Xiong, Y. (2025). Research progress on modification methods for calcium looping thermochemical heat storage. Integrated Intelligent Energy.

[2] Jiang, Y., et al. (2025). Synergistic enhancement of Ca-based materials via CeO2 and Al2O3 co-doping for enhanced CO2 capture and thermochemical energy storage in calcium looping technology. Separation and Purification Technology, 358. https: //doi.org/10.1016/j.seppur.2024.130264.

[3] Zhang, Y., Li, L., et al. (2025). Research progress of calcium-based thermochemical energy storage technology. Chemical Industry and Engineering Progress. https: //doi.org/10.16085/j.issn.1000-6613.2025-0915.

[4] Dai, J., & Luo, C. (2024). Research progress on calcium looping thermochemical energy storage and coupled CO2 capture technology. Clean Coal Technology, 30(10). https: //doi.org/10.13226/j.issn.1006-6772.CN23011602.

[5] Chen, J., et al. (2025). Constructing hollow CaO particles with abundant oxygen vacancies via co-adding Ce and Al to achieve superior CO2 capture performance in the calcium looping technique. Chemical Engineering Journal, 523. https: //doi.org/10.1016/j.cej.2025.168565.

[6] Li, Y., et al. (2025). Promotion mechanism of rare-earth elements doping on performance of CaO/CeO2 sorbent for high temperature CO2 capture. Chemical Engineering Journal, 507. https: //doi.org/10.1016/j.cej.2025.160675.

[7] Ren, L., Li, M., Wang, S., Li, L., & Wu, Y. (2022). Effects of oxygen-vacancy-promoted ion diffusion on CO2 capture behavior of CaO-based sorbents. Industrial & Engineering Chemistry Research, 61(16), 5527-5535. https: //doi.org/10.1021/acs.iecr.2c00190.

[8] Zhang, Y., et al. (2023). CaO/CaCO3 thermochemical energy storage performance of MgO/ZnO co-doped CaO honeycomb in cycles. Journal of Energy Storage, 66. https: //doi.org/10.1016/j.est.2023.107447.

[9] Zhang, Z. (2024). Research progress on oxygen vacancies in metal oxide catalysts. Shandong Chemical Industry, 53.

[10] Shi, W., Li, R., Bao, X., Yang, H., & Kong, D. (2025). DFT investigation into adsorption–desorption properties of Mg/Ni-doped calcium-based materials. Crystals, 15(8). https: //doi.org/10.3390/cryst15080711.

[11] Zhang, Y.-H., et al. (2024). Oxygen vacancy chemistry in oxide cathodes. Chemical Society Reviews, 53(7), 3302-3326. https: //doi.org/10.1039/d3cs00872j.

[12] Li, G., et al. (2025). Mg-doped MnO2 cathode with tailored oxygen vacancies for high-rate high-capacity calcium storage. Batteries & Supercaps, 8(12). https: //doi.org/10.1002/batt.202500331.

[13] Chen, K., et al. (2025). Preparation and electrochemical performance of AlPO4 coated oxygen-deficient LiNi0.5Co0.2Mn0.3O2 cathode material. Materials Reports. https: //doi.org/10.19799/j.cnki.2095-4239.2025.0932.

[14] Wang, K., He, S., Lin, Y., Chen, X., Dai, W., & Fu, X. (2022). Photo-enhanced thermal catalytic CO2 methanation activity and stability over oxygen-deficient Ru/TiO2 with exposed TiO2 {001} facets: Adjusting photogenerated electron behaviors by metal-support interactions. Chinese Journal of Catalysis, 43(2), 391-402. https: //doi.org/10.1016/s1872-2067(21)63825-1.
[15] Wang, Y., Liu, Y., et al. (2024). Preparation of oxygen-vacancy-rich TiO2 for efficient photothermal catalytic CO2 reduction. Journal of Functional Materials, 55(4), 4122-4129.
[16] Zhao, W., et al. (2025). Preparation and photothermal properties of oxygen vacancy ceria. Guangdong Chemical Industry. https: //doi.org/10.3969/j.issn.1007-1865.2025.006.055.
[17] Zhang, X., et al. (2024). Review on oxygen vacancy regulation of photoelectrodes for photoelectrochemical water splitting. Journal of Functional Materials.
[18] Wang, F., Li, J.-q., Murali, A., Chen, C.-y., Zhang, W., & Lan, Y.-p. (2025). Co-enhancement of doped N and oxygen vacancies on the photocatalytic performance of ceria: Mechanism and influence of crystal faces. Journal of Central South University, 32(6), 2129-2147. https: //doi.org/10.1007/s11771-025-5990-7.
[19] Yan, J., et al. (2024). Research progress on application of bismuth-based oxygen vacancy photocatalysts. Materials Reports.
[20] Liu, S., et al. (2024). Research progress of anion vacancies in electrocatalysts for oxygen evolution reaction. Chemical Industry and Engineering Progress.
[21] Wang, H., Wang, G., Wei, X., & Cui, J. (2012). First-principles study of CaTiO3 oxygen-vacancies (001) surface. Physica B: Condensed Matter, 407(19), 3970-3974. https: //doi.org/10.1016/j.physb.2012.06.022.
[22] Liang, E., et al. (2024). Study on the effect of oxygen vacancies on thermal expansion properties of molybdenum-containing oxides and ruthenates. Acta Physica Sinica.
[23] Kong, D., et al. (2024). Enhancement of thermochemical energy storage by alkali metal chloride salts-doped Ca-based sorbents: A combined DFT and experimental study. Molecules, 29(24). https: //doi.org/10.3390/molecules29246058.
[24] Zhang, Y., et al. (2025). Screening dual variable-valence metal oxides doped calcium-based material for calcium looping thermochemical energy storage and CO2 capture with DFT calculation. Journal of Energy Chemistry, 107, 170-182. https: //doi.org/10.1016/j.jechem.2025.03.052.
[25] Shi, W., Li, R., Yang, H., Kong, D., & Chen, Q. (2025). Influence of Cr- and Co-doped CaO on adsorption properties: DFT study. Molecules, 30(13). https: //doi.org/10.3390/molecules30132820.
[26] Guo, H., Kou, X., Zhao, Y., Wang, S., & Ma, X. (2018). Role of microstructure, electron transfer, and coordination state in the CO2 capture of calcium-based sorbent by doping (Zr-Mn). Chemical Engineering Journal, 336, 376-385. https: //doi.org/10.1016/j.cej.2017.11.186.
[27] Guo, H., Feng, J., Zhao, Y., Wang, S., & Ma, X. (2017). Effect of micro-structure and oxygen vacancy on the stability of (Zr-Ce)-additive CaO-based sorbent in CO2 adsorption. Journal of CO2 Utilization, 19, 165-176. https: //doi.org/10.1016/j.jcou.2017.03.015.
[28] Guo, H., Kou, X., Zhao, Y., Wang, S., Sun, Q., & Ma, X. (2018). Effect of synergistic interaction between Ce and Mn on the CO2 capture of calcium-based sorbent: Textural properties, electron donation, and oxygen vacancy. Chemical Engineering Journal, 334, 237-246. https: //doi.org/10.1016/j.cej.2017.09.198.
[29] Fang, Z., et al. (2025). Elucidating the enhanced CO2 capture in core-shell Al-Zr modified CaO adsorbent: origins in microstructure and oxygen vacancy. Separation and Purification Technology, 378. https: //doi.org/10.1016/j.seppur.2025.134676.
[30] Da, Y., & Zhou, J. (2022). Multi-doping strategy modified calcium-based materials for improving the performance of direct solar-driven calcium looping thermochemical energy storage. Solar Energy Materials and Solar Cells, 238. https: //doi.org/10.1016/j.solmat.2022.111613.
[31] Guo, H., Xu, Z., Jiang, T., Zhao, Y., Ma, X., & Wang, S. (2020). The effect of incorporation Mg ions into the crystal lattice of CaO on the high temperature CO2 capture. Journal of CO2 Utilization, 37, 335-345. https: //doi.org/10.1016/j.jcou.2020.01.012.
[32] Zhang, C. (n.d.). Research on sorption-enhanced steam reforming for hydrogen production and in-situ CO2 conversion over calcium-based composites. CNKI.
[33] Wang, F. (n.d.). DFT simulation study on sorption-enhanced steam methane reforming and in-situ CO2 conversion over Ni/CaO. CNKI.
[34] Yao, L. (2024). Preparation and thermal storage performance of CaO-based thermal storage modules with hierarchical pore structure. Materials Reports. https: //doi.org/10.19799/j.cnki.2095-4239.2024.0863.
[35] Yuyuan, Z., et al. (2024). The role of oxygen vacancy in CaO-Ca12Al14O33 materials derived from hydrocalumite for enhanced CO2 capture cyclic performance. Chemical Engineering Journal, 481. https: //doi.org/10.1016/j.cej.2023.147955.

DOI: 10.54254/2755-2721/2026.AD32079

[36] Sun, J., Ge, C., An, D., et al. (2020). Review on characterization methods of oxygen vacancies in ceria-based catalytic materials. CIESC Journal, 71(8), 3403-3415. https: //doi.org/10.11949/0438-1157.20200131.
[37] Luo, T., Luo, C., Tan, Z., et al. (2025). Atomization characteristics of Ca-based solution by two-fluid nozzle and thermal storage performance of CaO microspheres prepared by spray pyrolysis. Clean Coal Technology, 31(6). https: //doi.org/10.13226/j.issn.1006-6772.GPF25042901 [38]. Yamamoto, T., & Mizoguchi, T. (2013). First principles study on oxygen vacancy formation in rock salt-type oxides MO (M: Mg, Ca, Sr and Ba). Ceramics International, 39, S287-S292. https: //doi.org/10.1016/j.ceramint.2012.10.079.
[38] Yamamoto, T., & Mizoguchi, T. (2013). First principles study on oxygen vacancy formation in rock salt-type oxides MO (M: Mg, Ca, Sr and Ba). Ceramics International, 39, S287-S292. https: //doi.org/10.1016/j.ceramint.2012.10.079.