Ionic Transfer Mechanism of COS Reaction with CaO: Inert Marker Experiment and Density Functional Theory (DFT) Calculation

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Introduction

High-temperature (<1000°C) dry removal of carbonyl sulfide (COS) from coal-derived synthesis gas (syngas) using CaO sorbent is a promising technique due to the sorbent's high-sulfur capture capacity, favorable reaction kinetics, versatility in capturing multiple acidic gases from syngas, and potentially high process efficiency.[1] The direct reaction of CaO and COS is given in Eq. 1

$$\mathrm{CaO\ (s) + COS\ (g) \leftrightarrow CaS\ (s) + CO_2\ (g)} \\ \Delta H^\circ(298\,\mathrm{K}) = -93.2\,\mathrm{kJ\,mol^{-1}} \tag{1}$$

Due to the larger molar volume of CaS compared with CaO, the formed CaS product layer tends to cover the fresh CaO surface area and plug the internal pores. Hence, direct COS-CaO contact is subsequently hindered. Further CaO conversion is most likely caused by the ionic diffusion through the CaS product layer. Thus, clear understanding of the ionic transfer mechanism in this reaction process is of interest as it helps illustrate ways to improve the sorbent performance.

In most solid-phase ionic transfer processes, ions diffuse via crystal defects which are imperfections of crystal structure.[2] Generally, such ionic diffusion process needs to maintain local and global electroneutrality. For this specific reaction scheme, the overall ionic transfer in the CaS layer can be dominated by (1) counter-current diffusion of inward S^{2-} anions and outward O^{2-} anions, (2) outward co-current diffusion of Ca^{2+} cations and O^{2-} anions, or (3) a combination of both processes (see Figure 1). In this study, the inert marker experiment and DFT calculation are used to identify and explain the dominating solid-phase ionic transfer mechanism in the reaction of COS and CaO.

Experimental and Calculation Studies

Inert marker experiment

99.95% pure CaO powder (Aldrich Chem) was pelletized into tablets of 6 mm dia. and 3 mm thickness. The tablets were sintered at 1200°C under N_2 for 48 h in a horizontal tubular furnace. The purpose of sintering these tablets at such conditions is to eliminate the internal pore structure in order to avoid gas diffusion into the center of the tablet during sulfidation reaction. After the CaO tablets were well sintered and cooled down to room temperature, a strip of Pt paint (SPI supplies) was applied to one side of each tablet. CaO tablets were then put into a thermogravimetric analyzer (TGA) (PerkinElmer Pyris 1), and heated to 400°C for 15 days under a reactant gas mixture consisting of 5000 ppm COS, and balance N_2 at a total flow rate of 120 mL min^{-1}. After that, the tablets were cooled down to room temperature and prepared for the followed analyses. A sample was examined by X-ray diffraction (XRD). A tablet was mounted in epoxy resin, diagonally cut, and polished on its cross section. This polished cross section was then analyzed by a scanning electron microscope (SEM), and an energy dispersive spectrometer (EDS).

Density Functional Theory (DFT) Calculation. Density functional theory (DFT) calculations were employed to estimate the diffusion energy barriers for Ca^{2+}, O^{2-}, and S^{2-} ions in CaS crystal structure. These calculations were carried out using Vienna *ab initio* simulation package (VASP).[3,4] Projector augmented wave (PAW) approach of generalized gradient approximation in the Perdew-Burke-Ernzerhof (GGA-PBE) form was applied to the calculations.[5]

The CaS is of NaCl-type structure, in which calcium cations occupy all the octahedral interstices within the closed-packed cubic sulfur lattice as shown in Figure 2. The crystal structure ($a = b = c = 5.6903$ Å, $\alpha = \beta = \gamma = 90°$) used in this study was taken from the American mineralogist crystal structure database (AMCSD). A 2 × 2 × 1 super-cell was constructed to represent the CaS bulk phase. For the ionic diffusion, the transition states between the initial and final configurations were determined by the climbing image

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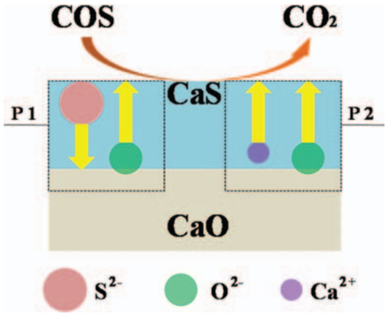

Figure 1. Illustration of the ionic transfer processes in the reaction of COS and CaO.

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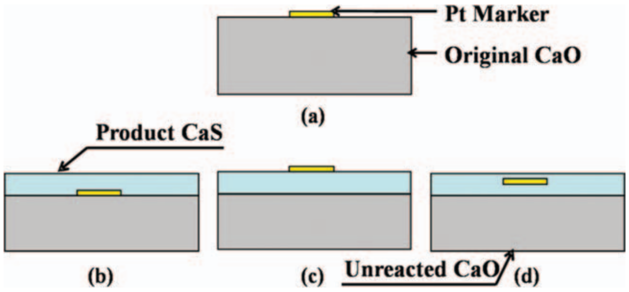

Figure 3. Principle of inert marker experiment: (a) original CaO pellet with Pt marker, (b) outward growth mode, (c) inward growth mode, and (d) mixed growth mode.

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nudged elastic band (CI-NEB) method.[6] The initial state of the diffusion process was obtained by removing one ion from the bulk phase, followed by structure relaxation. The final configuration on the diffusion pathway was the relaxed bulk phase structure after a closest corresponding ion (e.g., cation to cation vacancy) moves to the initially generated vacancy. Four configurations in-between were generated. The spring force constant was set to be -5.0 eV Å^{-2}. A kinetic energy cut-off of 350 eV was used, and 2 × 2 × 3 Monkhorst-pack scheme was used for bulk CaS structure. Ions were relaxed by a conjugate-gradient algorithm until the forces on unconstrained ions decreased to below 0.01 eV Å^{-1}. The energy barrier for ionic diffusion is defined as the difference between the system energy at the transition state and that of the initial configuration prior to diffusion. As illustrated in Figure 2, three diffusion processes, i.e., Ca^{2+} cation, S^{2-} anion, and O^{2-} anion diffusions in CaS, were investigated in this study.

Results and Discussion

Inert marker experiment

As an effective method of identifying dominating ionic transfer mechanism of solid-state reactions,[2,7,8] inert marker experiment is performed. This experiment involves attachment of small inert particles to the original COS-CaO interface as a marker (see Figure 3a). When the COS-CaO reaction takes place, there forms a CaS layer on the solid CaO surface. The CaS layer thickens as the reaction and ionic transfer proceed. When the reaction proceeds to a certain extent, the relative location of the inert marker depends on the overall diffusion direction of ionic species through the product layer. If the outward co-current diffusion of Ca^{2+} cations and O^{2-} anions dominates the ionic transfer process, the inert marker's relative location would change from the original COS-CaO interface to the CaS-CaO interface (see Figure 3b). If the ionic diffusion through the product layer is dominated by the counter-current diffusion of inward S^{2-} anions and outward O^{2-} anions, the CaS product layer would grow at CaS-CaO interface. The resulting inert marker is still at gas–solid interface (see Figure 3c). If the "co-current diffusion" and "counter-current diffusion" are comparable, the CaS layer would grow both at the COS-CaS interface and CaS-CaO interface, leaving the marker buried in the CaS layer (see Figure 3d).

The X-ray pattern of the partially reacted powder is shown in Figure 4, which indicates that the partially reacted sample is composed of CaO and CaS. Thus, the reaction represented by Eq. 1 is valid in this study, and no unexpected solid product was produced.

Figure 5a shows the scanning electron micrograph of the cross-section of a partially reacted tablet. As shown in this figure, the final location of the Pt marker is at the gas–solid interface, which indicates that the CaS product layer grows inward into CaO bulk phase. To identify the solid phases, energy dispersive spectroscopy (EDS) was performed to obtain elemental mappings of the sample. The mappings of platinum, sulfur, and calcium are presented in Figure 5(b–d).

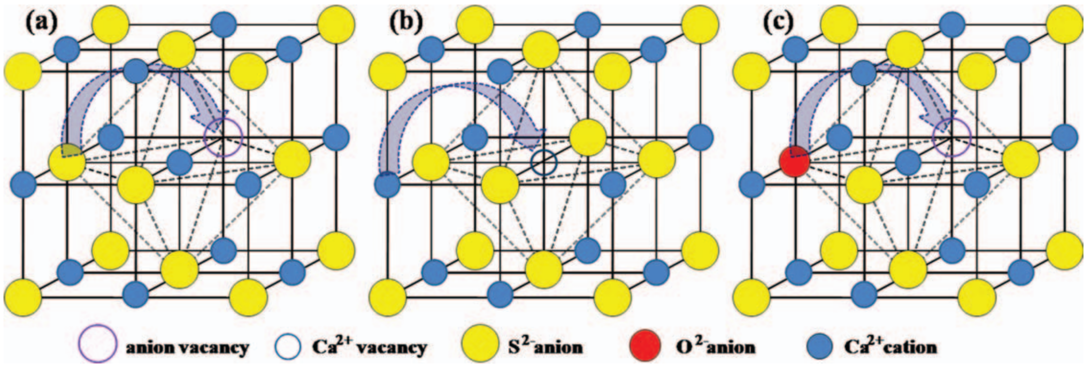

Figure 2. Illustration of CaS crystal structure and the three key ionic migration processes in the DFT calculations: (a) S^{2-} anion diffusion, (b) Ca^{2+} cation diffusion, and (c) O^{2-} anion diffusion.

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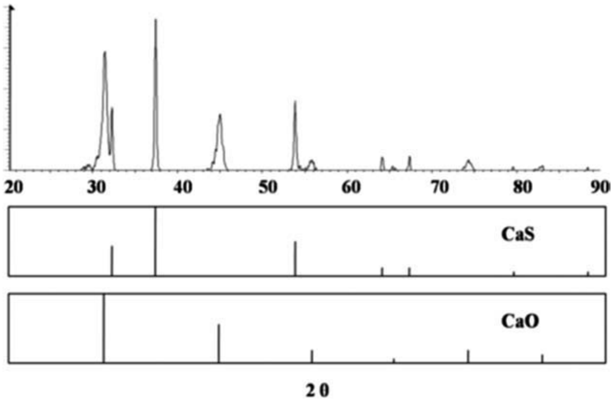
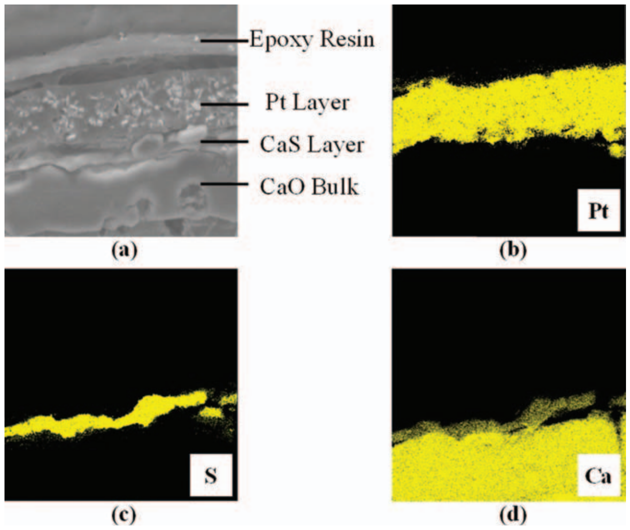


Figure 4. **X-ray diffraction pattern of the partially reacted CaO sample.**

From these three mappings, relative locations of Pt marker, CaS layer, and CaO bulk phase can be clearly identified: the CaS layer is "sandwiched" between the Pt layer and CaO bulk phase with the Pt layer located at the gas–solid interface. This layout corresponds to the case of "inward growth mode". That is, the dominating ionic transfer mechanism is that the S^{2-} anions derived from COS diffuse inward through the CaS layer to react with CaO at CaS-CaO interface, counter-currently with the outward diffusion of O^{2-} anions from CaO to COS-CaS interface to form CO_2.

DFT calculation

It was suggested in the literature that Schottky disorder and related vacancy (ionic) migration predominate in CaS and other alkaline earth sulfides.[9] Therefore, the concentrations of cation vacancies and anion vacancies in CaS are assumed to be comparable, and the competition in ionic transfer is determined by the energy barrier of ionic diffusion via vacancies. Figure 6 illustrates the diffusion energy barriers of Ca^{2+} cation, O^{2-} anion, and S^{2-} anion during their migration from one site to an adjacent corresponding vacant site in the CaS crystal structure, respectively. As illustrated in the same figure, the transition state appears around the middle point on the diffusion pathway, where the diffusing ion "pushes away" the counterions to the greatest extent. From these calculations, the Ca^{2+} cation diffusion is the most difficult, and the diffusion energy barrier of O^{2-} anion is lower than that of S^{2-} anion. The highest energy barrier for Ca^{2+} cation migration can be interpreted based on the CaS crystal structure. Since the CaS is of rock-salt structure, all the S^{2-} anions form close-packed structure with Ca^{2+} cations being loosely located in the octahedral interstices. In order to penetrate a S^{2-} anion layer and migrate to a neighboring Ca^{2+} vacancy, a Ca^{2+} cation has to "push away" close-packed S^{2-} anions. This distortion of the S^{2-} lattice increased the overall energy. The greater the extent is, the more energy it takes to overcome this distortion. Therefore, even though the Ca^{2+} cation has an advantage in terms of smaller size, diffusing through a close-packed anion layer is relatively difficult. In contrast, since the S^{2-} anion or the O^{2-} anion only needs to diffuse through a loosely "packed" Ca^{2+} cation layer, the corresponding diffusion energy barrier can be significantly lower than that of the close-packed case. Due to the smaller size, the diffusion of an O^{2-} anion is easier than that of a S^{2-} anion. Given the highest diffusion energy barrier for Ca^{2+} cations, the outward co-current diffusion of Ca^{2+} cations and O^{2-} anions is a less favorable transfer pattern, which is consistent with the result from the inert marker experiment. The diffusion energy barriers for the three ions are mainly determined by the intrinsic structural constraints of the CaS crystal system. Hence, the change in temperature can only quantitatively change the three energy values, but cannot qualitatively alter their order. So the results from this work can be qualitatively representative, unless the rigid solid crystal structure is altered by an extremely high temperature (e.g., > 1500°C).



(a) (b) (c) (d)

Figure 5. **(a) SEM micrograph of the cross-sectional area, (b) platinum mapping, (c) sulfur mapping, and (d) calcium mapping.**

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

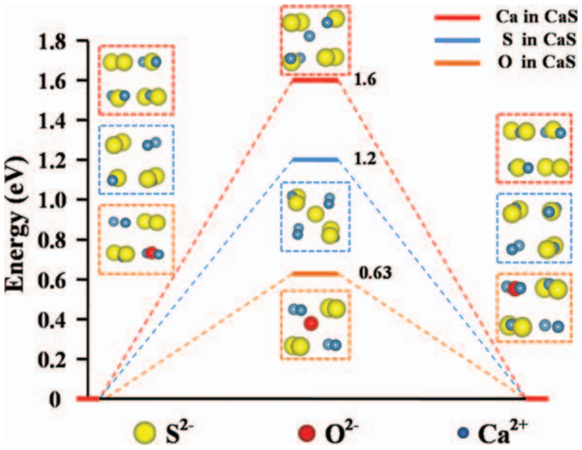


Figure 6. **The DFT-calculated energy barriers of three key ionic migration processes.**

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Concluding Remarks

Through inert marker experiment, the ionic transfer process in the reaction of COS and CaO is found to be dominated by the counter-current diffusion of inward S^{2-} anions and outward O^{2-} anions through CaS product layer. This result is further confirmed by the DFT calculation result, which shows that this counter-current diffusion is a more favorable pattern in terms of ionic diffusion energy barrier.

Acknowledgments

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