



Density functional theory study on the mechanism of calcium sulfate reductive decomposition by methane

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HIGHLIGHTS

- ▶ Our study investigates reaction mechanism by density functional theory (DFT).
- ▶ The reductive decomposition process of CaSO₄ in chemical looping combustion (CLC) system has been calculated.
- ▶ The DFT method, we used, can be a reliable method for predicting the reaction mechanism.
- ▶ A probably mechanism of CaSO₄ reacting with CH₄ is proposed.

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ABSTRACT

Fossil fuel combustion system is one of the major sources of carbon dioxide (CO₂) emissions, which is considered to be the main greenhouse gas contribution to the global warming. Chemical looping combustion (CLC) is a promising combustion technology with inherent separation of CO₂. Calcium sulfate (CaSO₄) can be used as a new oxygen carrier in this system. In CLC, CaSO₄ is reduced to calcium sulfide (CaS) in the fuel reactor firstly. Then CaS is oxygenated to CaSO₄ back in the air reactor. The decomposition of CaSO₄ is usually accompanied by some side reactions, and the products depended on the experimental conditions. In this paper, the decomposition mechanism of CaSO₄ reduced by methane (CH₄) was investigated in the frame of density functional theory (DFT). In the calculation, the exchange–correlation term was approximated by Perdew–Wang (PW91) equation, a function within the generalized gradient approximation (GGA) family. To understand the interaction between CH₄ and CaSO₄, the reaction pathways and TSs of CaSO₄ decomposition were investigated and identified. The calculated results showed that, in the interaction of CaSO₄ and CH₄, electrons were transferred from sp³ hybrid orbital to O p state and S s state when CH₄ was activated. C–H bond and S–O bond were activated and stretched with the electron transfer, which resulted in the dissociation of S–O bond finally. The objective product CaS could be obtained with the reductive decomposition of CaSO₄ by CH₄. A probably mechanism was proposed, that is, the reaction process of CaSO₄ and CH₄ is CH₄ + CaSO₄ → CH₃OH + CaSO₃ → CH₂OOH + CaSO₂H → HCHO + H₂O + CaSO₂ → HCOOH + H₂O + CaSO → 2H₂O + CO₂ + CaS.

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1. Introduction

Pronounced greenhouse effect has caused world-wide attention, and the control of greenhouse gas is the most challenging environmental issue. Carbon dioxide (CO₂) is considered to be the main greenhouse gas contribution to the global warming. Fossil fuel combustion system is one of the major sources of CO₂ emissions, which accounts for about 33–40% of the total anthropogenic carbon emissions worldwide [1]. In order to reduce CO₂ emissions into atmosphere, CO₂ capture provides a mid-term solution to mitigate environment impacts, and to allow human continue using the

fossil energy [2]. But the cost of CO₂ capture is high because of the low CO₂ content of traditional combustion.

Chemical looping combustion (CLC) is a promising combustion technology with inherent separation of CO₂ [3]. In CLC system, the combustion of fossil fuel is divided into two parts, fuel reactor and air reactor. Fuel is not mixed with oxygen. The transfer of oxygen is achieved by oxygen carrier, which is recycled in the system. Hence, the selection and development of oxygen carrier is a critical issue for the industrial application of CLC [4]. A good oxygen carrier for CLC should readily react with fuel gas and be reoxidized upon being contacted with oxygen.

The investigation of oxygen carrier focused on the metal oxides in the past decades, such as Ni [5], Cu [6], Fe, and Mn [7]. Nowadays, calcium sulfate (CaSO₄) is considered as a new oxygen carrier

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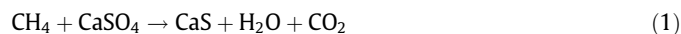
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Nomenclature

E_a	activation energy, kJ/mol	E_{slab}	total energy of slab, J/m ⁻²
E_{TS}	energy of transition state structure, kJ/mol	E_{surf}	energy of surface, J/m ⁻²
E_R	energy of reactant structure, kJ/mol	E_{bulk}	energy for bulk CaSO ₄ that has the same number of atoms with slab, J/m ⁻²
E	reaction energy, kJ/mol	A	surface area, m ⁻²
E_p	energy of product structure, kJ/mol		

which is the substitute of metal oxide because of its advantages of high oxygen capacity, mechanical strength and environmental friendly. Tests on the combined process of coal gasification and CaSO₄ reduction with coal syngas were conducted in a batch fluidized bed reactor at different reaction temperature and with different gasification intermediates by Zheng et al. [8], the results showed that high concentration of CO₂ product was thermodynamically feasible in the reduction of CaSO₄ oxygen carrier with carbon. Ding et al. [9] investigated CLC of methane (CH₄) with the compound CaSO₄ oxygen carrier (prepared by impregnation method) in a fixed bed reactor; the long time reduction–oxidation test demonstrated that compound CaSO₄ oxygen carrier has a higher conversion.

Taking methane (CH₄) as fuel, in the fuel reactor, CaSO₄ was reduced to calcium sulfide (CaS), and then CaS is reoxidized to CaSO₄ in the air reactor. The recycling of CaSO₄ is achieved through this process. This process is described by the following reactions.



The reducing of CaSO₄ by CH₄ is consisted of steps of redox reactions [10], because the structure of CaSO₄ is quite stable. The reductive decomposition of CaSO₄ to CaS is complicated and accompanied with many side reactions. The reaction of CH₄ with CaSO₄ oxygen carrier was investigated in a fixed bed reactor by Song et al. [11,12]. The results showed that the reduction reaction could be effected by reaction temperature, gas flow rate and sample mass, and particle size. CaS was the main reductive product, while a slight amount of calcium oxide (CaO) also formed in the cyclic test. But the insight into the elementary processes involved in the mechanism of CaSO₄ reductive decomposition is not clear, and few people have investigated the microscopic mechanism of CH₄ reacting with CaSO₄.

In the paper, theoretical calculation is undertaken to research the reductive mechanism of CaSO₄ reduced by CH₄ on molecular scale. All the calculations are done using density functional theory (DFT) to ensure the validity of the proposed mechanism. DFT calculation has been used to assess a correct estimation of the stability of surface and surface reaction [13]. The higher accuracy achievable and anticipated can be achieved by DFT with modern functional [14]. Activation energies and reaction energies in each step are calculated in this paper. According to our results, mechanism of CaSO₄ decomposition reduced by CH₄ is proposed.

2. Calculation

Unless otherwise stated, the DFT calculation is carried out with the nonlocal generalized gradient approximation (GGA) [15] functional by means of Perdew–Wang (PW91) [16] correlation functional in Dmol³ module of Materials Studio 5.0. Numeric atomic functions are used in Dmol³ and can support exactly solutions to the Kohn–Sham equations for the atoms. The calculation precision is set to ‘Fine’ to insure the accuracy of the calculation results. Double numerical plus polarization (DNP) function is utilized in

calculations, and the threshold values of convergence criteria for energy, gradient, displacement convergence, and self-consistent-field (SCF) density convergence are 1×10^{-6} Ha, 0.002 Ha/Å, 0.005 Å, and 1×10^{-6} Ha, respectively. A small electron thermal smearing value of 0.005 Ha is employed in calculations to speed up the SCF convergence efficiency during optimization.

CaSO₄ (010) surface, with the lowest energy, is adopted in the calculation. A vacuum region of 15 Å is added above the surface to ensure negligible interaction between periodic images normal to the surface. Other two directions still keep the space periodicity and the interaction among each molecule. In order to decrease the computational load, the bottom layer of surface is fixed at its equilibrium bulk phase position, while the top layer and CH₄ molecule are allowed to relax freely.

TS structures are searched by the linear/quadratic synchronous transit (LST/QST) algorithm. LST maximization is performed first, followed by an energy minimization in directions conjugate to the reaction pathway. Then, QST maximization is performed using the approximated TS conjugate to gradient minimization. The cycle is repeated until a stationary point is located. The nudged elastic band (NEB) method is used to map the reaction pathways and optimize the minimum energy path (MEP) between different minima. Then activation energies of CaSO₄ reductive decomposition can be calculated. All optimized structures are considered stabilized with the absence of imaginary frequencies but only one imaginary frequency for transition state (TS) structures.

The activation energy and reaction energy are defined as:

$$E_a = E_{TS} - E_R \quad (3)$$

$$E = E_p - E_R \quad (4)$$

where E_R , E_{TS} and E_p are the energies of reactants, TSs and products, respectively. E is the reaction energy.

3. Results and discussion

3.1. Selection of functional

Different functional is applicable in different system. To test the adequacy of the functional, the activation energy of sulfur trioxide (SO₃) reacting with carbon monoxide (CO) to form sulfur dioxide (SO₂) and CO₂ is calculated in this paper by PW91, BLYP, PBE, and RPBE functional. The reaction of SO₃ and CO can be described by the following equation,



The activation energies calculated by PW91, BLYP, PBE, and RPBE functionals are 114.52 kJ/mol, 127.30 kJ/mol, 115.61 kJ/mol, and 132.42 kJ/mol respectively. The experimental result [17] is 108.09 kJ/mol. It is obvious that the result calculated by PW91 functional is closer to the experimental value. The decomposition of CaSO₄ reduced by CO was calculated by PW91, and the calculated activation energy of the reactions had a good consistency with experimental values [18]. So, in this paper, all the calculations are completed by PW91 functional.

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