STRUCTURAL ANALYSIS OF $C_{an}O_{n-1}S$ CLUSTER OF DOLOMITE DESULFURIZATION

Using first-principles calculation method and comparing the difference between the free energy, the binding energy and electronic energy, the paper obtained $Ca_nO_{n-1}S$ clusters is possible by the presence of CaO to CaS desulfurization process. Compared with the $(CaO)_n$ clusters, $Ca_nO_{n-1}S$ clusters is in the lower energy side and the reaction has a tendency to lower energy spontaneously. As an excessive state, $Ca_nO_{n-1}S$ clusters forms before the nucleation CaS. According to analyze HOMO-LUMO energy difference, its chemical activity is higher than $(CaO)_n$.

Key words: dolomite , structure analyses , desulfurization , chemical activity , free energy

INTRODUCTION

Dolomite as a complex salt of $CaCO_3$ and $MgCO_3$ has long been used because it is an important raw material for the preparation of magnesium, but the nature of the $CaCO_3$ system has not been effectibely used, such as its pyrolysis products CaO has good desulfurization. From the microscopic point of view, the nucleation mechanism of oxide grains have the characteristics of growth element formation and intermolecular bridging [1]. Broadly speaking, the growth element can be an atom, a molecule, or an aggregate of atoms or molecules with a certain geometric configuration. Clusters have been seen as a new structure between atoms, molecules and crystals. Therefore, it is meaningful to discuss the interaction between CaO and sulfur atoms from the microscopic cluster level, which is a new possibility for the study of its desulfurization properties.

CALCULATION METHOD AND PARAMETER SETTING MANUSCRIPT

Based on the DMol[3] module developed by density functional in Materials Studio software [2] , the BLYP mixed exchange function in generalized gradient approximation is used to study the structure and stability of $Ca_nO_{n-1}S$ [3]. And the BFGS mechanism is used to optimize the precision. The precision is set as follows: energy $\leq 1,0 \times 10^{-5}$Ha, maximum stress is 0,002Ha / Å, maximum displacement is 0,005Å, maximum number of iterations is 500, the maximum step is 0,3Å. In the case of self-negotiation, the convergence rate of the total energy and charge density of the system is set to $1 \times$

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10^{-6}Ha, and "Use smearing" is checked. This is set to 0,005Ha, that is, the truncation effect is used here. Since the Ca atom contains the d-polarization function, the DNP basis set with d orbit is used, and the Basis set is 3,5Å. After the geometric optimization of the above set of convergence, the atomic charge [4] , of the cluster was obtained by Mülliken analysis.

The average binding energy formula is [5]

$$E_b(n) = [nE(Ca) + (n-1)E(O) + E(S) - E(Ca_nO_{n-1}S)] / 2n \quad (1)$$

Where E (Ca) is the energy of a single Ca atom, E (O) and E (S) are the energy of a single O atom and S atom, respectively. Is the total energy at the lowest energy of the cluster.

Sum and can calculate the formula for [6]

$$\Delta E_{b,n} = E_{b,n} - E_{b,n-1} \quad (2)$$

Where: represents the junction energy of $Ca_nO_{n-1}S$, represents the junction energy of $Ca_{n-1}O_{n-2}S$.

Calculating the second order difference energy can better analyze the relative stability of the cluster [7].The formula is

$$\Delta^2 E_n = E_{n+1} + E_{n-1} - 2E_n \quad (3)$$

Where E_{n+1}, E_{n-1} and En represent the binding energies of $Ca_{n+1}O_nS$, $Ca_{n-1}O_{n-2}S$ and $Ca_nO_{n-1}S$, respectively.

$Ca_nO_{n-1}S$ CLUSTER FREE ENERGY AND FREE ENERGY DIFFERENCE

Because of the similarity of previous studies [8], clusters and CaO-related properties, this paper proposes a cluster of $Ca_nO_{n-1}S$, suggesting that it may be a certain form of CaO desulfurization process. At this stage, Experimental equipment and research on the basis of observation of a process of micro-process is difficult to achieve, so the theoretical guess and experimental proof of the combination of ideas is not applicable with this

hypothesis, so try to Gibbs free energy from the point of formula (1) If the Gibbs free energy difference is less than zero, the correctness and rationality of the hypothesis proposed in this chapter are open to question.This section must be in one column.

Figure 1 (a) - (c) is the change of the Gibbs free energy G of the $Ca_nO_{n-1}S$ cluster with the increase of the number of atoms n and the increase of the temperature. The change in the free energy of the $Ca_nO_{n-1}S$ cluster is discussed in this temperature range, limited by the calculation interval of the Materials Studio software 0 - 1 000 K. As can be seen from Figure 1, the free energy of the $Ca_nO_{n-1}S$ cluster decreases with increasing tempera-
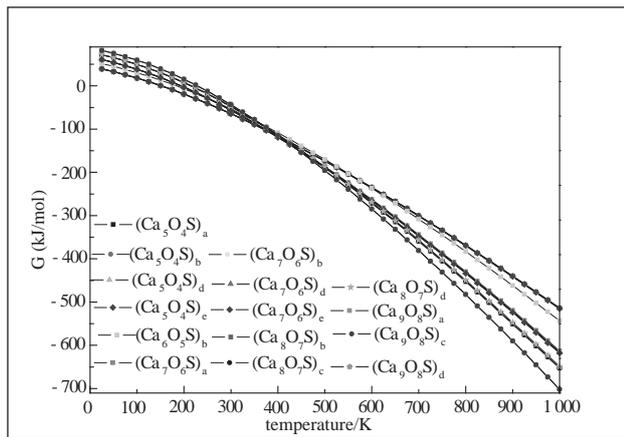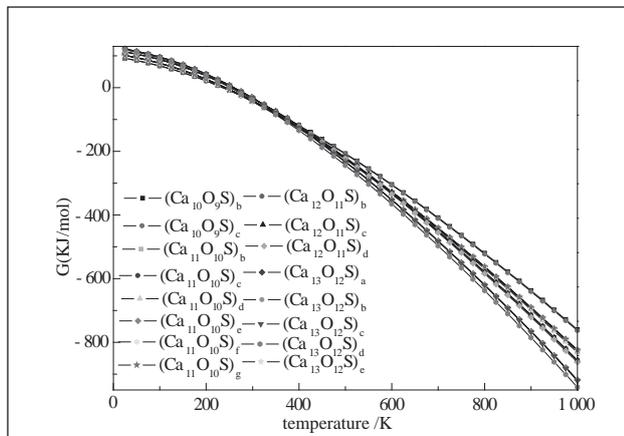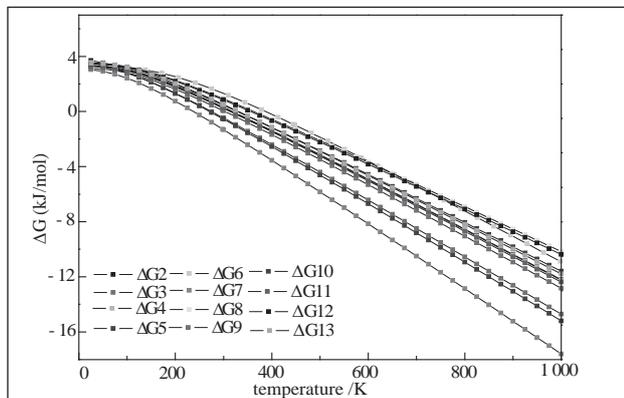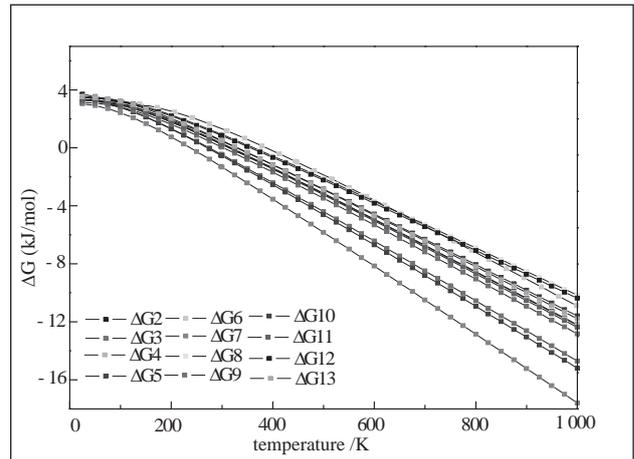
Figure 2 The ΔG between Ca_nO_{n-1}, atom S and $Ca_nO_{n-1}S$ chang with temperature.

ture. Figure 1 (a) shows the free energy change of the lowest energy structure of $Ca_nO_{n-1}S$ clusters in isomers of different atomic numbers. (b) and (c) record n = 5 - 9 and n = 10 - 13 non-minimum energy state of the free energy changes. Compared with Figure 1 (a) - (c), each cluster curve intersects at one point, and G in (a) changes obviously with the increase of n, and tends to decrease gradually. (b) In the same case, the free energy is different, but when the number of atoms is the same, the difference of free energy of different isomers is not large, most of the curve appears similar phenomenon, the naked eye can not distinguish.

From the macroscopic point of view, the thermodynamic properties of the materials are dimensionally independent, but the thermodynamic properties of the $Ca_nO_{n-1}S$ clusters show varying degrees of change with the change of n due to the dimensional dependence of the thermodynamic properties of the nanoscale materials.

Figure 2 shows the variation of the free energy difference ΔG of the Ca_nO_{n-1} cluster, S atom and $Ca_nO_{n-1}S$ cluster with temperature (1), and ΔG decreases gradually with the increase of temperature. However, unlike the law obtained in Figure 1, ΔG does not decrease with the increase of n Trend, where the value of ΔG is the smallest when n = 7. It can be clearly seen from Figure 1 that the Gibbs free energy difference ΔG of the equation (1) is less than zero at a certain temperature, and the $Ca_nO_{n-1}S$ cluster is proved from the thermodynamic properties as a microcosm in the CaO desulfurization process State of the feasibility of the state.

DISCUSSION ON THE STABILITY OF $Ca_nO_{n-1}S$ CLUSTERS

Figure 3 shows the change of the average bond length (Rmean / Å) of $Ca_nO_{n-1}S$ (n = 13) with the change of n; Figure 4 shows the corresponding variation between ΔE_b, n and $\Delta 2E_n$ and atomic number n.

It can be seen from Figure 3 that the average bond length of $Ca_nO_{n-1}S$ (n = 13) increases with the increase of n, and the average bond length of Ca_5O_4S, Ca_9O_8S

(a)

(b)

(c)

Figure 1 The free energy of $Ca_nO_{n-1}S$(n=13) changes with the temperature
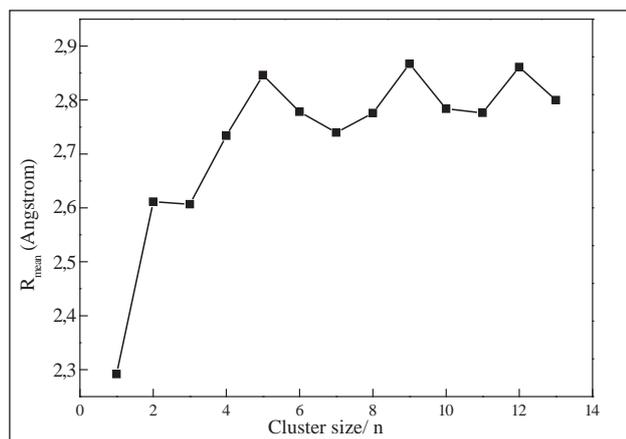
Figure 3 Size dependence of the average bond lengths (R_{mean}/Å) for the $Ca_nO_{n-1}S$(n= 1 - 13)
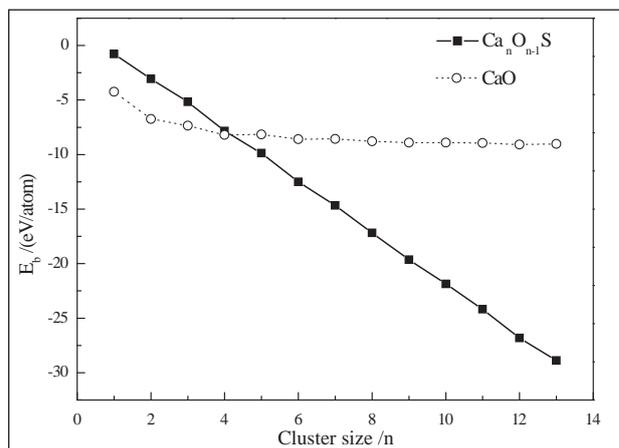
Figure 5 Size dependence of the bonding energies per atom
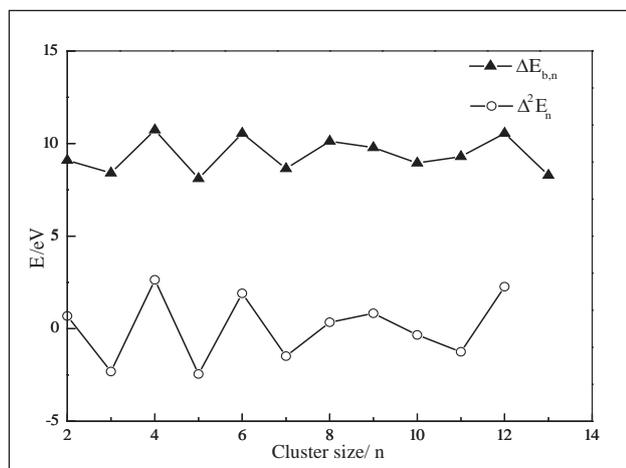
Figure 4 Size dependence of the $\Delta E_{b,n}$ and Δ^2E_n for the $Ca_nO_{n-1}S$(n= 1 - 13)
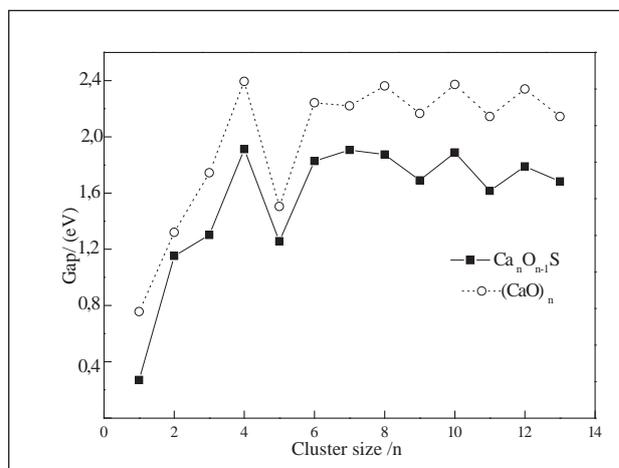
Figure 6 Size dependence of the HOMO-LUMO gaps for the $Ca_nO_{n-1}S$ and $(CaO)_n$(n = 13)

and $Ca_{12}O_{11}S$ is larger, and the average bond The longest is Ca_9O_8S. It can be seen from Figure 4 that the three maxima of ΔE_b and n appear in the sum and show that the stability of the three twisted cube structures is higher than that of other configurations. The second order energy difference Δ^2E_n of $Ca_nO_{n-1}S$ (n = 13) also shows that the twisted cubic structure, the twisted cubic structure and the stacked twisted cube structure are more stable at the peak point.

In order to further study the effect of S-doping with the original $(CaO)n$ cluster system, Figure 5 and Figure 6 will compare the binding energy and energy difference between $(CaO)n$ cluster and $Ca_nO_{n-1}S$. As shown in Figure 5, the average binding energy of $Ca_nO_{n-1}S$ and $(CaO)_n$ (n = 13) varies with n. As can be seen from Figure 6, the binding energy decreases with the increase of cluster The binding energy of the $Ca_nO_{n-1}S$ cluster is lower than that of the $(CaO)n$ cluster at n > 3, and the reaction is more likely to have a lower energy get on.

Figure 6 shows the comparison of $Ca_nO_{n-1}S$ and $(CaO)_n$ (n = 13) from the HOMO-LUMO energy difference, and its typical electronic properties play an important role in the stability of the cluster . The HOMO-LUMO energy difference of the $Ca_nO_{n-1}S$ cluster is negative, which means that the cluster is not easy to lose electrons,

and the larger the energy gap, the more stable, the lower the chemical activity , when n = 4,7,10, 12, the energy gap is at the peak, indicating that the four kinds of cluster structure has low chemical activity and high stability, the reason is that HOMO in the electrons have been a strong effective nuclear potential, so that the orbit of the electrons The shielding of electrons on the same orbit. The energy difference between $Ca_nO_{n-1}S$ and $(CaO)_n$ (n = 13), the energy difference of $Ca_nO_{n-1}S$ clusters is less than that of $(CaO)_n$ clusters, indicating that the addition of S The chemical activity of the group is higher than that of the $Ca_nO_{n-1}S$ cluster, and the chemical activity of the $Ca_nO_{n-1}S$ cluster is high, and the result is realistic. As a feasibility of CaO desulfurization in a microscopic state.

CONCLUSIONS

1) For $Ca_nO_{n-1}S$ clusters, the free energy decreases with the increase of temperature. There is a negative correlation between G and n of the lowest structure of the cluster, that is, with the increase of n, G And the Gibbs free energy difference ΔG is obtained by solving the fundamental condition when the value of the Gibbs free energy difference ΔG is less than zero when the temperature reaches a certain temperature range.

2) The Ca-S bond length increases with the increase of the number of atoms n, because the increase of n makes the average number of electrons participating in a given chemical bond decrease. The second order energy difference Δ^2E_n of $Ca_nO_{n-1}S$ (n = 13) also shows that the twisted cubic structure, the twisted cubic structure and the stacked twisted cube structure are more stable at the peak point.

3) In order to further study the effect of S-doped and CaO n-cluster system, the $Ca_nO_{n-1}S$ cluster was found on the lower energy side from the binding energy, and the reaction had a low energy side And the $Ca_nO_{n-1}S$ cluster was obtained from the HOMO-LUMO energy difference as a transition state before CaS nucleation, and the chemical activity was higher than that of $(CaO)_n$.

Acknowledgments

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Note: Wei Ye is responsible for English language, Anshan, China. Kun Liu is the corresponding author.