

Reaction Mechanism and Kinetics of the Sulphation of Li_4SiO_4 for High-Temperature CO_2 Adsorption

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Abstract

CO₂ adsorption is an important approach to control the excessive CO₂ emission from energy and industrial plants and mitigating the greenhouse effect. As an acknowledged high-temperature adsorbent, Li₄SiO₄ shows advantages in capturing a large amount of CO₂ with a fast reaction rate and excellent cyclic stability. However, its CO₂ adsorption capacity would be significantly affected by the flue gas impurities, such as SO₂ and O₂. The underlying reaction mechanism of such impurities and Li₄SiO₄ is still unclear. For this reason, the work studied the reaction path and kinetics between Li₄SiO₄ and SO₂ through experiments, thermodynamic calculations and characterizations. The results showed that Li₄SiO₄ reacts with SO₂ to produce Li₂SiO₃ and Li₂SO₄ in the presence of O₂ at 500-700 °C, and to form Li₂SiO₃ and Li₂SO₃ in the absence of O₂ at 500-682 °C. Furthermore, this study revealed a very low activation energy of 7.47 kJ/mol for Li₄SiO₄ sulphation with O₂ presented in the kinetic-controlled stage, and the value goes up to 249.7 kJ/mol in the diffusion-controlled stage. These results will provide valuable references for the industrial applications of CO₂ adsorption by Li₄SiO₄.

Keywords: CO₂ capture, CO₂ adsorption, Li₄SiO₄ adsorbent, sulphation, kinetics.

Introduction

Global warming caused by greenhouse gas emissions has now caused many adverse effects on the society and environment ^[1]. According to the special report "Global Warming 1.5 °C" of the Intergovernmental Panel on Climate Change (IPCC) in 2018, the global mean temperature will increase by 1.5 °C in the next 10-30 years compared with the temperature before the industrial revolution ^[2]. Hence, it is imminent to reduce the massive anthropogenic emissions of CO₂, which is the most important contributor to global warming.

Carbon Capture, Utilization and Storage (CCUS) is an effective approach to reducing excessive CO₂ emissions into the atmosphere ^[3]. CO₂ capture is the basis of CCUS and, therefore, the development of CO₂ capture technologies is of great significance. High-temperature adsorption is a promising CO₂ capture technology. For a typical CO₂ adsorption process, adsorbent capture CO₂ in an adsorption reactor from the flue gas, and then it enters a desorption reactor to release CO₂, thereby obtaining high-purity CO₂. The regenerated adsorbent is sent back to the adsorption reactor for the next adsorption-desorption cycle. The adsorbents used in the high-temperature CO₂ adsorption are mainly CaO-based adsorbents ^[4-8] and Li₄SiO₄-based adsorbents, besides, Li₂ZrO₃ ^[9], Li₅AlO₄ ^[10], K₂Ti₂O₅ ^[11] etc. are reported to have a certain CO₂ adsorption capacity under high temperatures. Li₄SiO₄-based adsorbents have recently attracted great interest worldwide ^[12-15], because of their high and stable CO₂ adsorption capacity (theoretical 0.367 g-CO₂/g-adsorbent) over long-term cycles, high compressive strength and resistance to attrition.

The current research on CO₂ adsorption by Li₄SiO₄ mainly focuses on three aspects: synthesis methods, kinetic modeling and performance enhancement. The commonly reported synthesis methods of Li₄SiO₄ include solid-state reaction method ^[16-18], sol-gel method ^[19-21], precipitation method ^[22-24], and combustion method ^[25]. The kinetic models used for CO₂ adsorption by Li₄SiO₄ are shrinking core model (SCM) ^[26-27], Jander model ^[28-29], double exponential model ^[30], and Avrami-Erofeev model ^[31].

The performance enhancement of Li_4SiO_4 is mainly achieved by doping a second phase (i.e. K_2CO_3 , Na_2CO_3) or changing the microstructure of Li_4SiO_4 [32-33].

However, there are relatively few studies on challenges that possibly met in the potential industrial applications of Li_4SiO_4 [34-40]. Besides CO_2 , there are complex gas components in the flue gas. For example, the flue gas from coal-fired power plant usually contains 200-2000 ppm SO_2 , and 6-12% steam [34]. Therefore, it is necessary to understand the influence of these impurities on the CO_2 adsorption of Li_4SiO_4 and the underlying reaction mechanisms. Essaki and Ochoa-Fernández, et al [35-37] reported that steam can promote CO_2 capture of Li_4SiO_4 , possibly due to the physical and chemical adsorption of H_2O on Li_4SiO_4 surface. Furthermore, Wang et al [38] conducted ab initio-based energetic calculations on the adsorption of H_2O on Li_4SiO_4 , and revealed that CO_2 capture was promoted by the H_2O pre-adsorbed surface characterized by chemical sorption. Kong et al [39] found that the adsorbed H_2O mainly interacts with O and Li atoms of the Li_4SiO_4 surface by using first principles.

Besides steam, SO_2 can influence the CO_2 adsorption capacity of Li_4SiO_4 . Pacciani et al. [34] and Puccini et al. [40] reported that the presence of SO_2 largely reduced the CO_2 capture capacity of Li_4SiO_4 , but the underlying mechanism was not clear and needs to be investigated. Therefore, in this work, experiments, thermodynamic calculations, and characterizations were conducted comprehensively to explore the reaction mechanism of Li_4SiO_4 sulphation and to understand the kinetics of sulphation in the presence of O_2 . These results could provide a valuable reference for the industrial applications of Li_4SiO_4 adsorbents in the CO_2 capture field.

Experiments and Thermodynamic Analysis

Materials Preparation

In this work, Li_2CO_3 powder (AR, >99%, Aladdin), and fumed SiO_2 (AR, >99%, Aladdin) were adopted to synthesize Li_4SiO_4 via a solid-state reaction method. Specifically, Li_2CO_3 and SiO_2 were mixed with a molar ratio of $\text{Li}:\text{Si}=4.1:1$ and ball milled for 1 h. After ball milling, the mixed powder

was calcined in a muffle furnace at 750 °C for 6 h and then ground to a particle size of around 100 µm before testing.

Tube Reactor Tests

To study the reaction mechanism of Li_4SiO_4 sulphation with/without the presence of O_2 , sulphation reaction under different temperatures was conducted in a quartz tube reactor with a length of 1200 mm and an inner diameter of 40 mm. The tube reactor was electrically heated by a 2-stage horizontal furnace, and the temperature of each stage was separately controlled. The inlet gases from gas cylinders were controlled by mass flow controllers and mixed in a gas collection chamber before entering the furnace.

To obtain sulphation-treated samples in the absence of O_2 , about 0.5 g Li_4SiO_4 was loaded on a quartz boat, and it was heated to target temperature (500-700 °C) at a rate of 10 °C/min in N_2 with a flow rate of 400 ml/min. When the target temperature was reached, a new gas containing 1 % SO_2 and 99 % N_2 was supplied at a rate of 100 ml/min to obtain an atmosphere of 2000 ppm SO_2 with N_2 balanced, and the reaction was kept for 4 h. In contrast, for the sulphation process with the presence with O_2 , the atmosphere was 2000 ppm SO_2 and 5 % O_2 balanced by N_2 , while all the other parameters were kept the same.

Thermogravimetric Analysis

Sulphation kinetics of Li_4SiO_4 were tested in a NETZSCH thermogravimetric analyzer (TGA, model 209). Each time, around 15 mg Li_4SiO_4 was placed on a quartz pan, which was held by a holder in the TGA, and heated to a set temperature at a rate of 20 °C/min in N_2 . Once the set temperature was reached, the reaction was kept at constant temperature for 60 min under different gas atmospheres. During the TGA test, sample mass was monitored and sulphation conversion of Li_4SiO_4 was calculated on the basis of mass change.

Specifically, temperature dependence of Li_4SiO_4 sulphation was studied in the range of 500-700 °C under the gas atmosphere of 1500 ppm SO_2 balanced by N_2 with/without 5 % O_2 . The gas atmosphere was varied in 200-1500 ppm SO_2 , 5 % O_2 balanced by N_2 at 600 °C to obtain the concentration

dependence of Li_4SiO_4 sulphation in the presence of O_2 . In addition, a test at a constant heating rate of 5°C was conducted to study the mass change of Li_4SiO_4 under 1500 ppm SO_2 balanced by N_2 in the absence of O_2 .

Thermodynamic Calculation

To understand the reaction direction and potential of Li_4SiO_4 sulphation, the change of enthalpy, entropy and Gibbs free energy were obtained through thermodynamic calculations following the procedure presented below ^[41-42].

(1) Enthalpy change

For a chemical reaction, the change in enthalpy of reaction (ΔH_r) at temperature T can be calculated as formula (1):

$$\Delta H_r(T) = \sum_i \nu_i \Delta H_{f,i}^0(298) + \int_{298}^T (\sum_i \nu_i C_{p,i}) dT \quad (1)$$

where, i is the reactant or product in the reaction, $\Delta H_{f,i}^0(298)$ is the standard enthalpy of formation of i at 298 K, ν_i is the stoichiometric coefficient of i , $C_{p,i}$ is the heat capacity at a constant pressure of i in the reaction.

(2) Entropy change

The change in entropy of reaction (ΔS_r) at temperature T can be calculated as formula (2):

$$\Delta S_r(T) = \sum_i \nu_i S_i^0(298) + \int_{298}^T \left(\frac{\sum_i \nu_i C_{p,i}}{T} \right) dT \quad (2)$$

where $S_i^0(298)$ is the standard molar entropy of i at 298 K. $\Delta H_{f,i}^0(298)$, $C_{p,i}$ and $S_i^0(298)$ can be found in thermodynamics manuals ^[42].

(3) Gibbs free energy change

The change in Gibbs free energy of reaction (ΔG_r) at temperature T can be calculated as formula (3):

$$\Delta G_r(T) = \Delta H_r(T) - T \Delta S_r(T) \quad (3)$$

Material Characterization

Phase compositions of the fresh and sulphated Li_4SiO_4 were tested by using a Spectris X-ray diffractometer (model PANalytical) with diffraction angle (2θ) varying from 10° to 80° at a scanning speed of $3.5^\circ/\text{min}$.

Surface morphology and sulphur distribution of the fresh and sulphated Li_4SiO_4 were investigated using a Thermo Scientific Scanning Electron Microscope and Energy Dispersive Spectrometer (SEM-EDS, model Quattro S). Before image capturing, the sample powers were dispersed on a conductive adhesive which was pasted on a holder and coated with aurum for 30 s to obtain a better electronic signal. All SEM images were obtained from secondary electrons with 20 kV of accelerating voltage.

X-ray photoelectron spectroscopy (XPS) characterizations were conducted to understand the element composition and chemical state of sulphur in sulphated Li_4SiO_4 by using a Thermo Fisher Scientific X-ray photoelectron spectrometer (model ESCALAB250Xi).

Results and Discussion

Reaction Mechanism of Li_4SiO_4 Sulphation

To explore the sulphation process of Li_4SiO_4 , its products are necessary to be known. Therefore, in this work, sulphation experiment of Li_4SiO_4 was first carried out under different temperatures ($500\text{--}700^\circ\text{C}$) and gas atmospheres (2000 ppm SO_2 with/without the presence of 5% O_2) in a tube reactor, and the reaction products of all seven groups of experiments were characterized by XRD, as shown in Figure 1. It is seen that there is only Li_4SiO_4 phase in the fresh Li_4SiO_4 . For the sorbent with sulphation treatment, besides the unreacted Li_4SiO_4 phase, Li_2SiO_3 and $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$ are detected in the whole temperature range of $500\text{--}700^\circ\text{C}$ when O_2 is presented during sulphation. The presence of H_2O in $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$ results from the adsorption of moisture from the air during the storage of these materials before the XRD characterization. These results mean that with the presence of O_2 , Li_4SiO_4 reacts with SO_2 and O_2 to produce Li_2SiO_3 and Li_2SO_4 . In Figure 1(b), it is very interesting to observe the presence of some

Li_2SiO_3 phase in the 500 °C-sulphated sample in the absence of O_2 . However, no any sulphur-containing materials can be found at all temperatures. It is possible that the reaction between SO_2 and Li_4SiO_4 is too weak in the absence of O_2 , and the amount of sulphur-containing products is too low and below the detection limit of XRD.

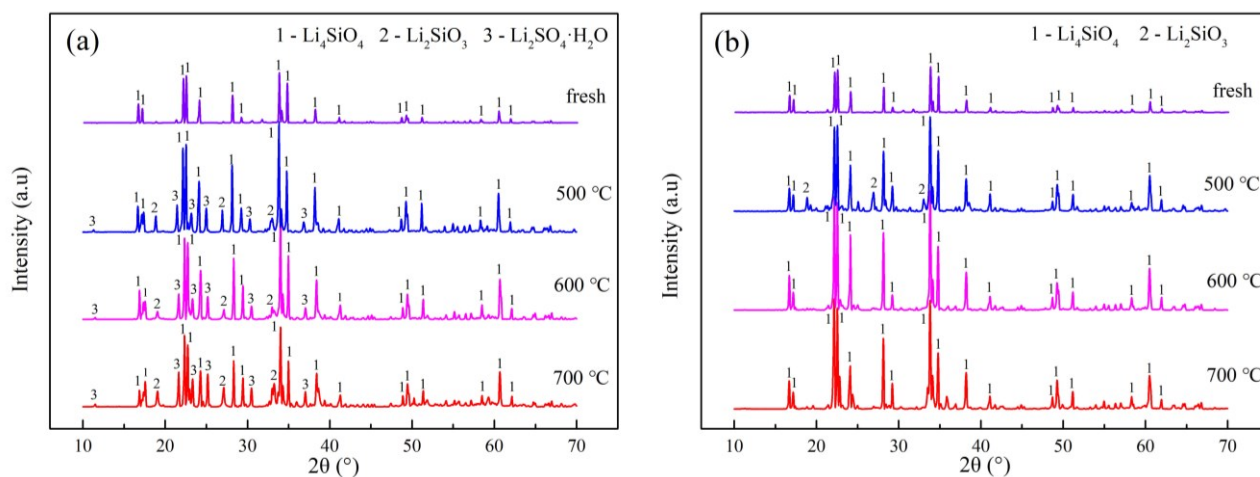


Figure 1. XRD patterns of fresh Li_4SiO_4 and products after the sulphation of Li_4SiO_4 under 2000 ppm SO_2 for 4 h. (a) with the presence of O_2 , and (b) without O_2 .

SEM-EDS characterizations were also conducted for fresh Li_4SiO_4 , sulphated Li_4SiO_4 under 600 °C with/without the presence of O_2 . The results are presented in Figure 2. It can be seen that the shape and size of Li_4SiO_4 are kept almost the same, though the surface becomes a little rougher after sulphation. In Figure 2(c, f, and i), no S element is detected on the surface of fresh Li_4SiO_4 , while there is a clear observation of a large amount of sulfur distributed on the surface of Li_4SiO_4 after its sulphation with/without O_2 . Additionally, it is also found that the content of S element formed with O_2 is significantly higher than that without O_2 by EDS analysis. These results clearly show that the sulphation of Li_4SiO_4 would occur regardless of the presence of O_2 , but the sulphation reaction is much stronger with O_2 at 600 °C.

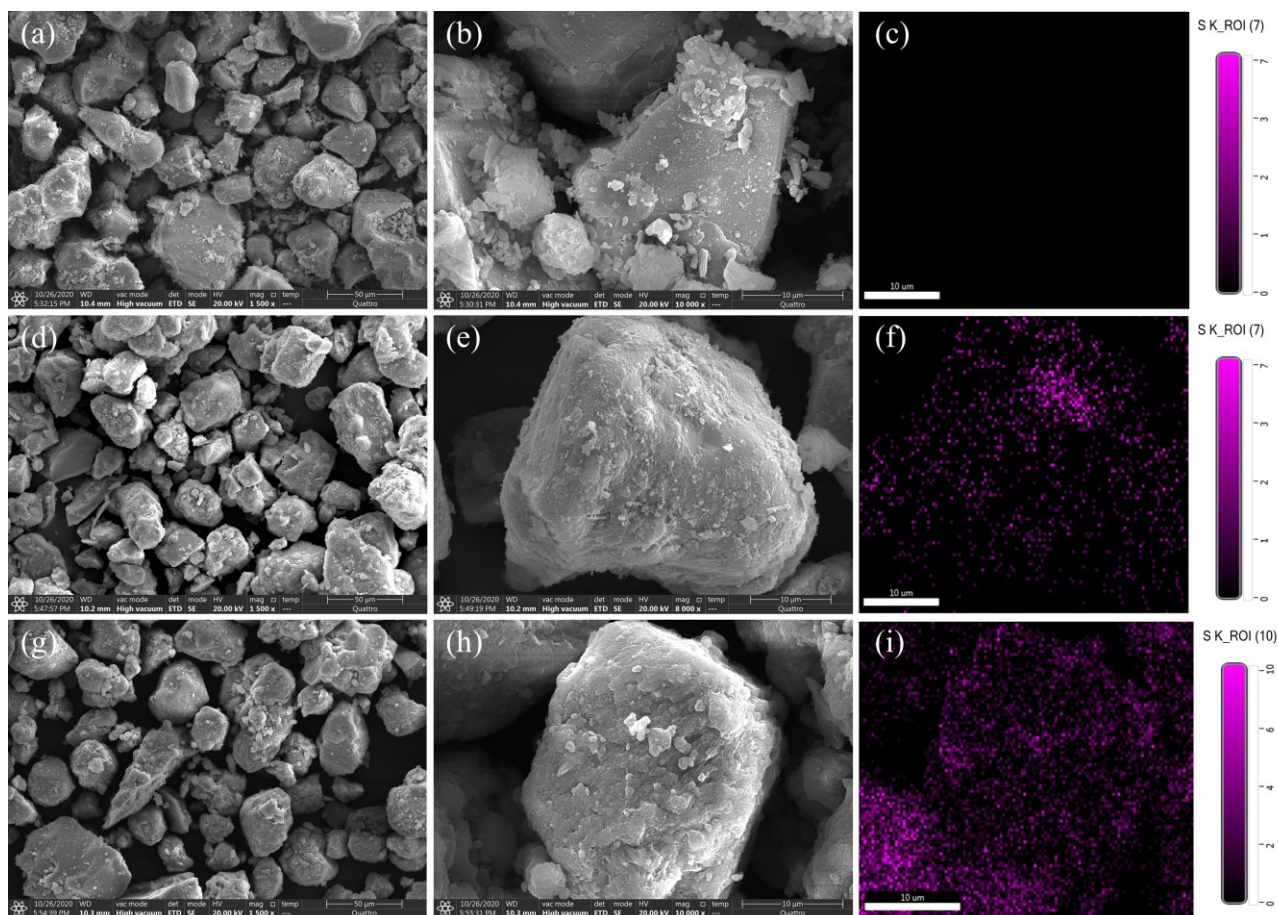
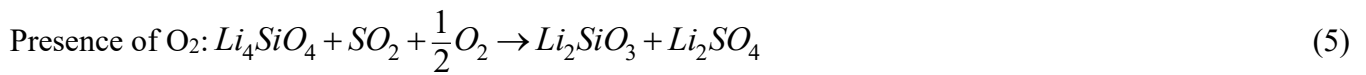


Figure 2. SEM-EDS images of (a-c) fresh Li_4SiO_4 , sulphated Li_4SiO_4 (d-f) without O_2 , and (g-i) with O_2 under 2000 ppm SO_2 at 600 °C.

To understand the sulphation path of Li_4SiO_4 under different conditions, XPS technique was used to test the chemical state of main elements in the sulphated products of Li_4SiO_4 under 600 °C with/without O_2 , and the results are shown in Figure 3. The survey spectrum in Figure 3(a) indicates that the main elements in the fresh Li_4SiO_4 sample are Li, Si, O, and C, and the presence of C should be a result of CO_2 adsorption from air, while there is S element in both the sulphated Li_4SiO_4 . At the same time, the peak of S element obtained from the sulphation with O_2 presented is higher than that without O_2 . It means that the sulphation reaction in the absence of O_2 at 600 °C is indeed relatively weak, which is in line with the results from the SEM-EDS tests presented above. Furthermore, narrow sweeps of S element segment and peak fitting were completed to confirm the chemical state of S in the sulphated

Li_4SiO_4 samples, and the results are shown in Figure 3(b). For the sulphated sample without O_2 , the peak of SO_3^{2-} is dominant and it is a little higher than that of SO_4^{2-} . The presence of SO_4^{2-} is very likely to be a result of oxidation in the air. In contrast, in the sulphated Li_4SiO_4 with the presence of O_2 , there is a very strong peak of SO_4^{2-} . In addition, a small peak of SO_3^{2-} is also observed, which is possibly a result of the incomplete oxidation of S. Moreover, narrow sweeps of Si element were also conducted to verify the possible reaction of produced Li_2SiO_3 with SO_2 in Figure 3(c)^[40]. The peak of silicate could be found in all three samples, but no SiO or its oxidized SiO_2 was observed in the absence of O_2 . Besides, narrow sweeps of O element were completed in Figure 3(d), and it further confirm that no SiO_2 is formed. These results show that Li_2SiO_3 will not further react with SO_2 .

Through the characterizations of XRD, SEM-EDS and XPS on the sulphation of Li_4SiO_4 , two sulphation paths of Li_4SiO_4 can be proposed as shown in expression (4) and (5) for conditions with O_2 absent or present, respectively.



It is well known that there is a significant dependence of the non-catalytic gas-solid reactions on the temperature. To explore the potential effect of temperature on the occurrence of Li_4SiO_4 sulphations, TGA tests and thermodynamic calculations were conducted. Figure 4(a) demonstrates the conversion of Li_4SiO_4 as a function of time under 1500 ppm SO_2 with/without the presence of 5% O_2 . It demonstrates that sulphation conversion of Li_4SiO_4 with the presence of O_2 reaches 0.048, 0.104, 0.177 in 60 min at 500, 600, 700 °C, respectively. Conversely, in the absence of O_2 , a reduction of the sulphation conversion of Li_4SiO_4 on an increase of temperature was observed. After 60 min, a conversion of 0.109 was observed at 500 °C, decreasing to 0.056 and 0.038 at 600 and 700 °C, respectively. To verify the unusual changes observed during sulphation of Li_4SiO_4 without the presence of O_2 , a TGA test under a constant heating rate was carried out, as shown in Figure 4(b). It can be seen that there is a steep

increase in the mass of the sorbent from 500 °C to around 650 °C, and a further rise of the temperature leads to a loss of the mass. It implies that the sulphation of Li_4SiO_4 in the absence of O_2 occurs at temperatures lower than approximately 650 °C under the gas atmosphere tested. Consequently, the increase in the temperature results in a reverse reaction.

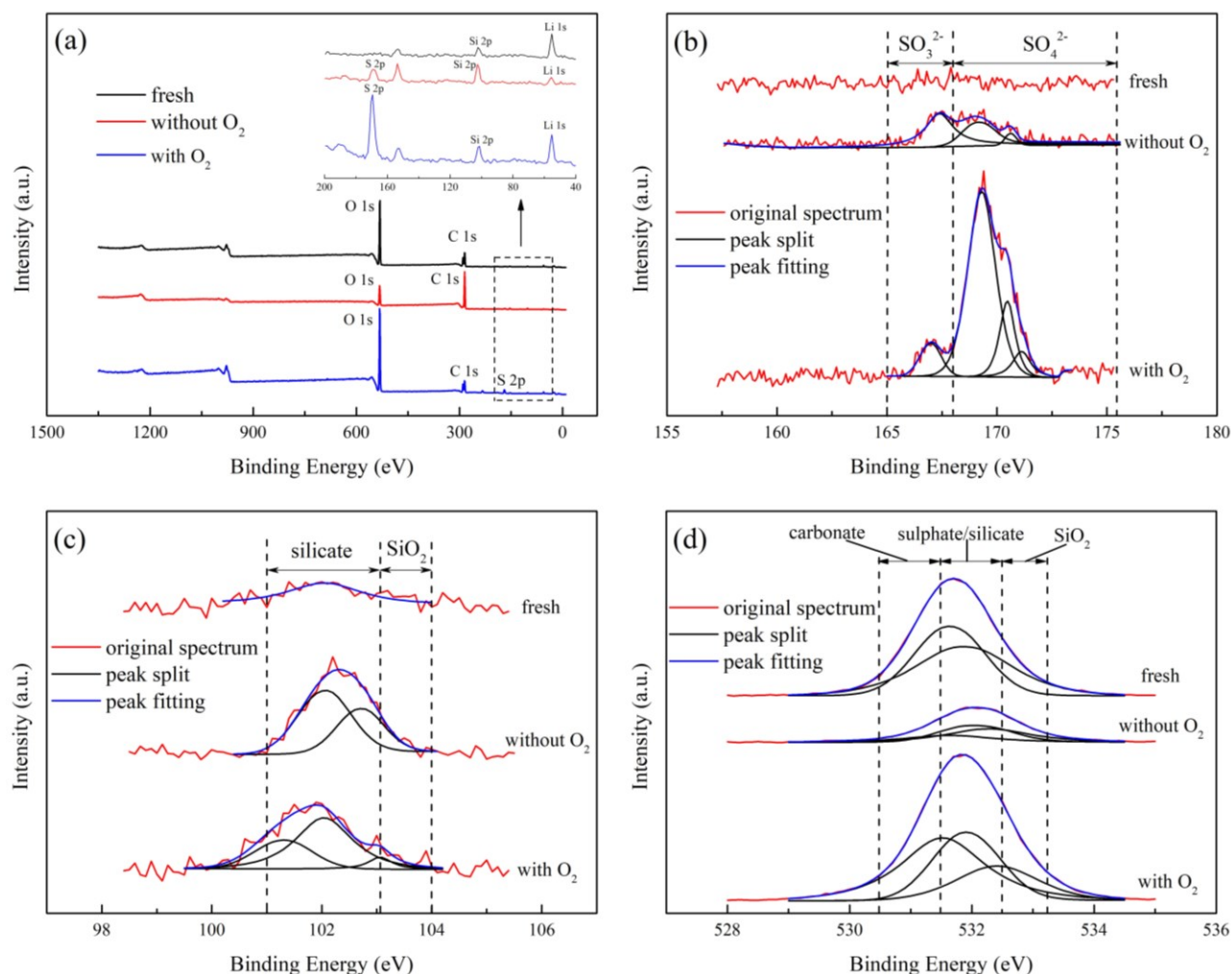


Figure 3. XPS spectrums of fresh Li_4SiO_4 , sulphated Li_4SiO_4 with/without O_2 under 2000 ppm SO_2 at 600 °C. (a) Original spectrum, (b) Spectrum of S 2p region and peak fitting, (c) Spectrum of Si 2p region and peak fitting, and (d) Spectrum of O 1s region and peak fitting.

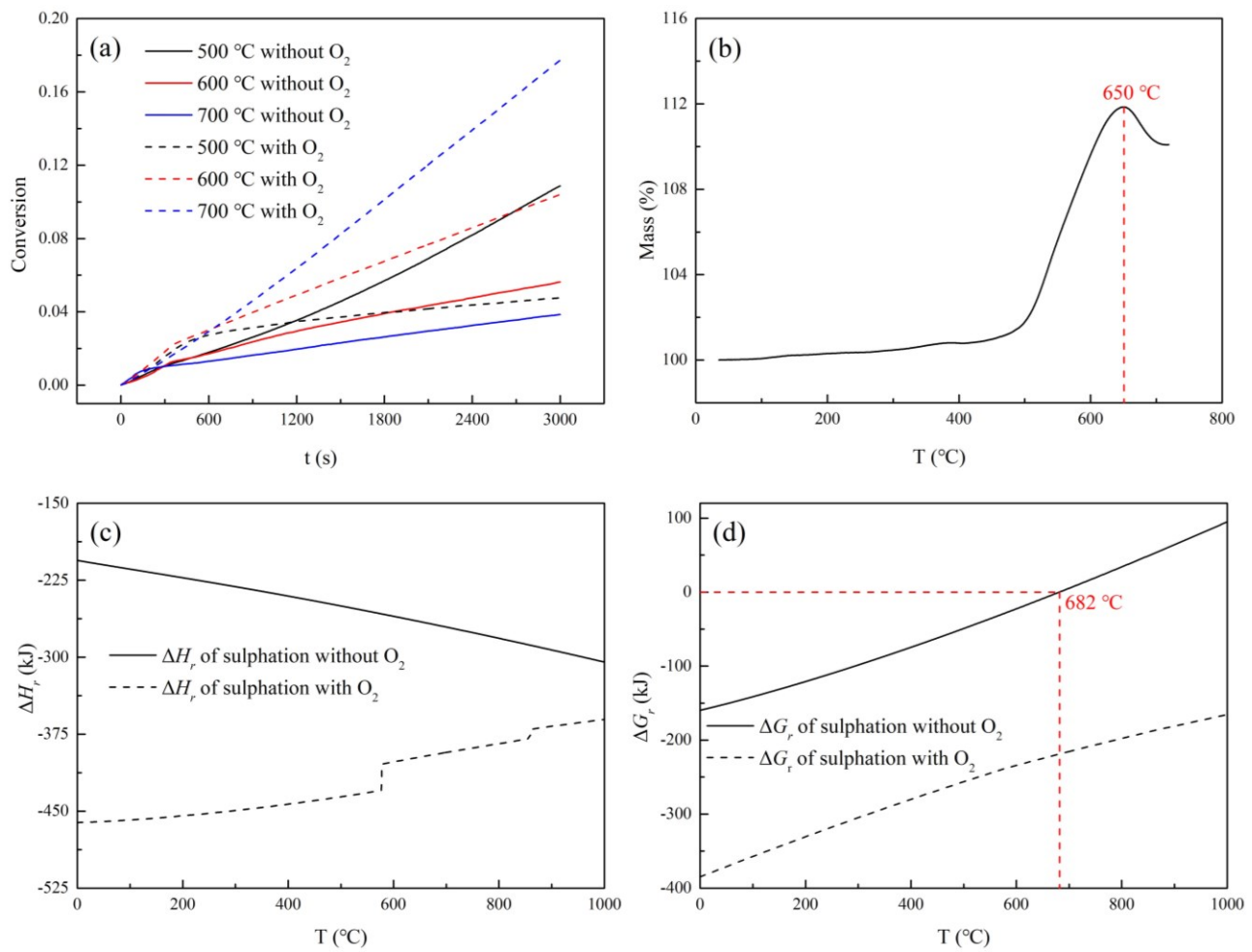


Figure 4. TGA tests and thermodynamic calculations of the sulphation of Li_4SiO_4 . (a) Temperature dependence of Li_4SiO_4 sulphation under 1500 ppm SO_2 with/without 5% O_2 , (b) TGA test of Li_4SiO_4 sulphation in 1500 ppm SO_2 without O_2 under a constant heating rate, (c) Thermodynamic calculations of ΔH_r , and (d) Thermodynamic calculations of ΔG_r .

Moreover, thermodynamic calculations were completed to reveal the theoretical conditions for the occurrence of Li_4SiO_4 sulphation with/without O_2 . Figure 4(c) depicts that ΔH_r values of two reactions are always negative in the temperature range of 0-1000 °C, indicating that the sulphation of Li_4SiO_4 with/without O_2 are exothermic. According to Figure 4(d), ΔG_r of sulphation with O_2 is a negative number from 0 to 1000 °C, in other words, the sulphation of Li_4SiO_4 with O_2 presented is a spontaneous reaction under the condition studied. In contrast, ΔG_r of sulphation without O_2 increases from a negative

value to a positive one and the turning point of $\Delta G_r = 0$ is 682 °C. It indicates that the sulphation of Li_4SiO_4 in the absence of O_2 is spontaneous below 682 °C, and the reverse reaction will occur above the temperature.

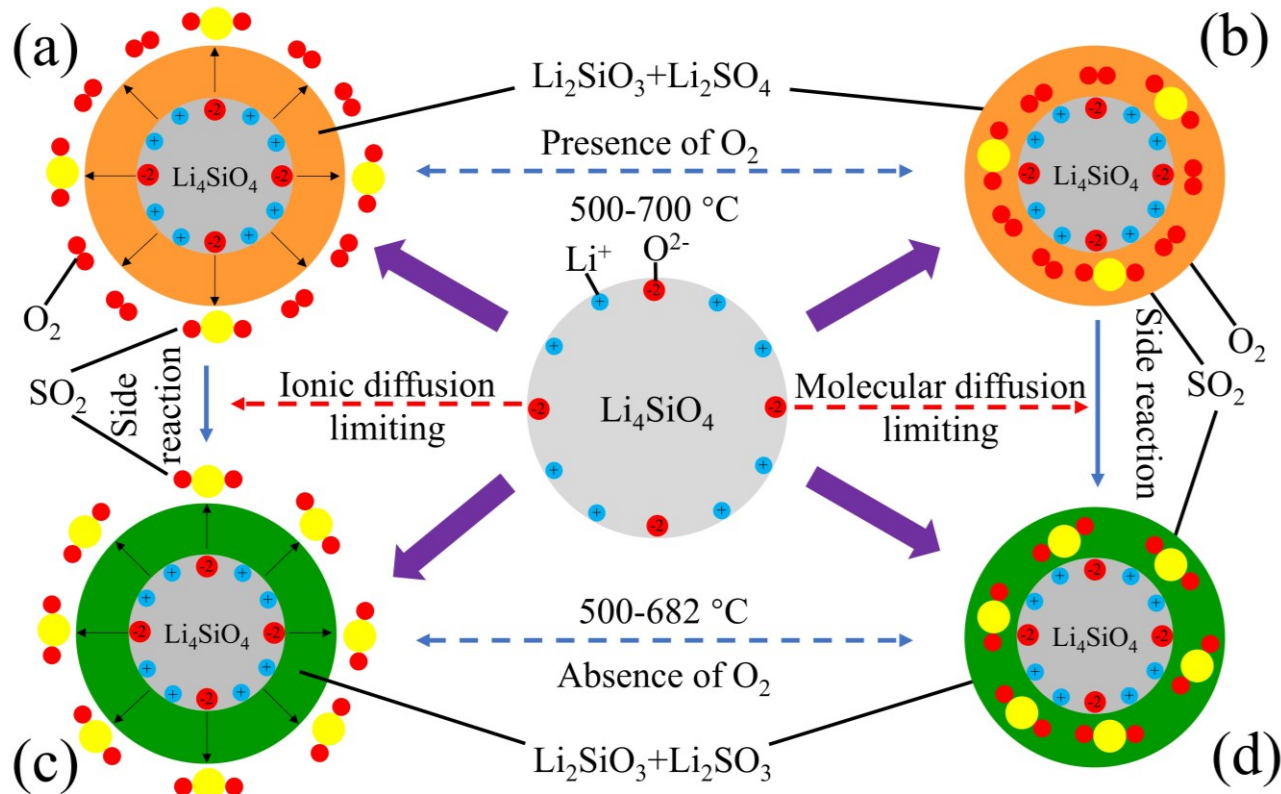


Figure 5. Illustration of the proposed reaction mechanism between Li_4SiO_4 and SO_2 . (a, b) With the presence of O_2 , and (c, d) In the absence of O_2 .

In summary, reaction mechanisms of Li_4SiO_4 sulphation are presented in Figure 5. Li_4SiO_4 reacts with SO_2 to produce Li_2SiO_3 and Li_2SO_4 in the presence of O_2 at 500-700 °C, as shown in Figure 5(a, b), and to form Li_2SiO_3 and Li_2SO_3 in the absence of O_2 at 500-682 °C, as shown in Figure 5(c, d). Once the product shell is formed, the bulk diffusion process will occur for the further sulphation of Li_4SiO_4 . In the diffusion-controlled reaction stage, we supposed two possible diffusion ways according to CO_2 adsorption of Li_4SiO_4 [43-44]. One is ionic diffusion limiting, where Li^+ and O^{2-} transfer from Li_4SiO_4 to product surface to react with SO_2 (and O_2), as shown in Figure 5(a, c). The other is molecular diffusion

limiting, where SO₂ (and O₂) molecule diffuse through the product shell into the Li₄SiO₄ surface to take part in the further sulphation, as depicted in Figure 5(b, d).

Sulphation Kinetics of Li₄SiO₄ with the Presence of O₂

Considering the weak sulphation of Li₄SiO₄ without O₂ above 600 °C and the common presence of O₂ in the flue gas of industrial processes, the following work would only focus on studying the kinetics of Li₄SiO₄ sulphation with O₂ present in the flue gas. First, we obtained the basic CO₂ adsorption/desorption characteristics of fresh Li₄SiO₄ as Figure S1 (see Supporting Information). Then, the variation of sulphation conversion as a function of time under various temperatures and SO₂ concentrations were tested by TGA. Figure 6(a) demonstrates that the conversion of Li₄SiO₄ increases as the rise of temperature under the 1500 ppm SO₂, 5% O₂, balanced by N₂. Inflexion points are observed in the curves obtained below 650 °C at a conversion of approximately 0.02 and at the time of around 400 s. It means the reaction initially takes place in a kinetic-controlled stage and then enters a diffusion-controlled stage ranging in 500-600 °C under the gas atmosphere. In contrast, for the reaction at 650 °C, the diffusion-controlled stage maintains in the whole 60 min tested because of the high reactivity of sulphation. Figure 6(b) depicts that the sulphation of Li₄SiO₄ is enhanced at a higher concentration of SO₂. There are also distinct kinetic and diffusion-controlled stages as the concentration of SO₂ varying in 500-1500 ppm. However, when SO₂ concentration is as low as 200 ppm, only the diffusion-controlled stage is observed due to the weak reactivity of sulphation under low SO₂ concentrations.

To obtain kinetic parameters of Li₄SiO₄ sulphation with the presence of O₂, a shrinking core model was used to analyze the kinetic-controlled stage, and the conversion-time expression can be written as expression (6) ^[26]. Avrami–Erofeev model was used to analyze the diffusion-controlled reaction and the conversion-time relationship follows expression (7) ^[31] :

$$1 - (1 - x)^{\frac{1}{3}} = \frac{t}{t^*}, \quad t^* = \frac{\rho R}{C_{SO_2} k_1} \quad (6)$$

$$\ln(-\ln(1 - x)) = n \ln k_2 + n \ln t \quad (7)$$

where x is the conversion of Li_4SiO_4 , t is time, ρ represents the molar density of Li_4SiO_4 , R is the initial radius of Li_4SiO_4 , C_{SO_2} is the concentration of SO_2 , n represents the kinetic parameter, k_1 and k_2 is the reaction rate constant in the kinetic- and the diffusion-controlled stage, respectively.

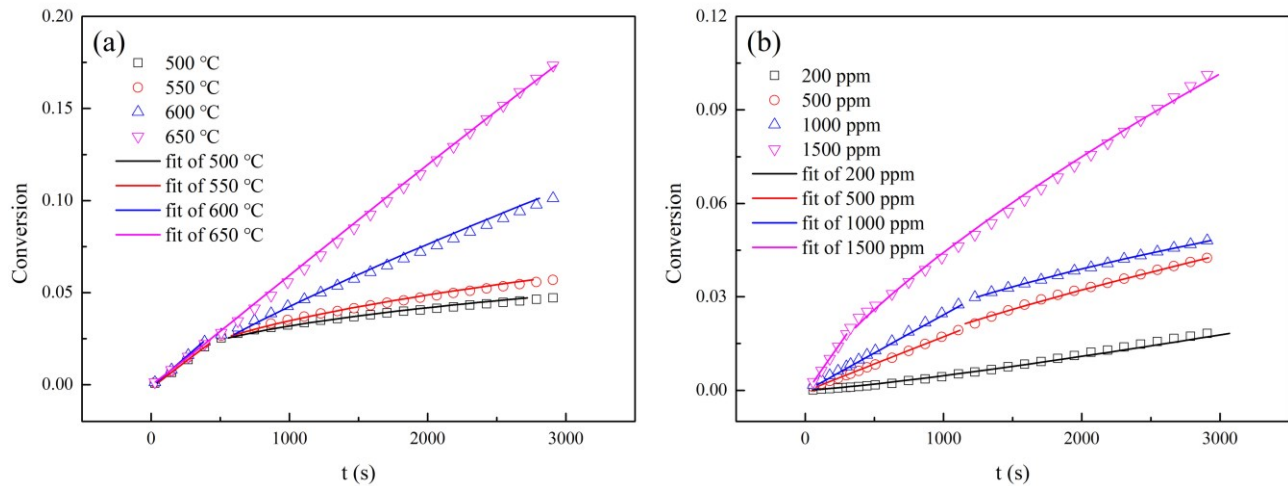


Figure 6. TGA tests of the sulphation process of Li_4SiO_4 with the presence of O_2 . (a) Temperature dependence of Li_4SiO_4 sulphation, and (b) Concentration dependence of Li_4SiO_4 sulphation.

The results of curves fitting and Arrhenius plots are shown in Figure 7. Figure 7(a, c) demonstrates very good linearity of $1 - (1 - x)^{\frac{1}{3}} - t$ plots in the kinetic-controlled stage for reactions under 500-600 °C or 500-1500 ppm of SO_2 . It is the same for $\ln(-\ln(1 - x)) - \ln t$ plots in the diffusion-controlled stage, as shown in Figure 7(b, d). By curve fitting, k_1 is obtained as 5.00×10^{-4} , 5.43×10^{-4} , 5.70×10^{-4} m/s at 500, 550, 600 °C in Figure 7(a), and k_2 is 1.84×10^{-7} , 1.22×10^{-6} , 2.75×10^{-5} , 7.11×10^{-5} s $^{-1}$ at 500, 550, 600, 650 °C respectively in Figure 7(b). All these results indicate that a higher temperature leads to a faster sulphation rate. Furthermore, through Arrhenius plots shown in Figure 7(e, f), the activation energy and pre-exponential factor for the sulphation of Li_4SiO_4 with O_2 presented were determined to be 7.47 kJ/mol, 1.6×10^{-3} in the kinetic-controlled stage, and 249.7 kJ/mol, 1.28×10^{10} in the diffusion-controlled stage, respectively. The lower activation energy reveals that it is much easier for the occurrence of the reaction in the kinetic-controlled stage.

Discussion

The presence of SO₂ in industrial flue gas will have an adverse effect on the CO₂ capture capacity of Li₄SiO₄. Here, we comprehensively explored the reaction path of Li₄SiO₄ sulphation with/without the presence of O₂ through experiments, calculations and characterizations, as well as deriving the kinetics of Li₄SiO₄ sulphation with O₂ presented. It was found that Li₄SiO₄ reacts with SO₂ to produce Li₂SiO₃ and Li₂SO₄ in the presence of O₂ at 500-700 °C, and to form Li₂SiO₃ and Li₂SO₃ in the absence of O₂ at around 500-682 °C. In addition, calculation results showed that the activation energy of Li₄SiO₄ sulphation with O₂ presented is relatively small, just 7.47 kJ/mol in the kinetic-controlled stage, but it goes up to 249.7 kJ/mol in the following diffusion-controlled step.

It was reported by Pacciani et al. ^[34] that Li₄SiO₄ reacts with SO₂ to form Li₂SiO₃ and Li₂SO₃ in the absence of O₂, and consequently reduces the CO₂ adsorption performance of Li₄SiO₄, which is well proved in this work. Additionally, Puccini et al. ^[40] stated that Li₂SiO₃ could further react with SO₂ to produce Li₂SO₄ and SiO. However, in this work, no SiO or its oxidized SiO₂ was detected by the XRD and XPS techniques in the absence of O₂. Moreover, activation energy is a well-acknowledged index in evaluating whether a reaction is easy to occur. According to the literature ^[26-31], the activation energy for CO₂ adsorption by Li₄SiO₄ varies in 13.9-27.1 kJ/mol in the kinetic-controlled stage, and it is calculated to be 180-301 kJ/mol by Avrami-Erofeev and Jander models in the diffusion-controlled stage. The much lower activation energy of sulphation in the kinetic-controlled stage means that Li₄SiO₄ is easier to be sulphated than carbonated, though the values for sulphation and carbonation are comparable in the diffusion-controlled stage. Therefore, it is necessary to remove SO₂ impurity before the CO₂ capture using Li₄SiO₄. Otherwise, the reaction between Li₄SiO₄ and SO₂ will inevitably reduce the CO₂ adsorption capacity of Li₄SiO₄, reducing the viability of the entire CO₂ capture process.

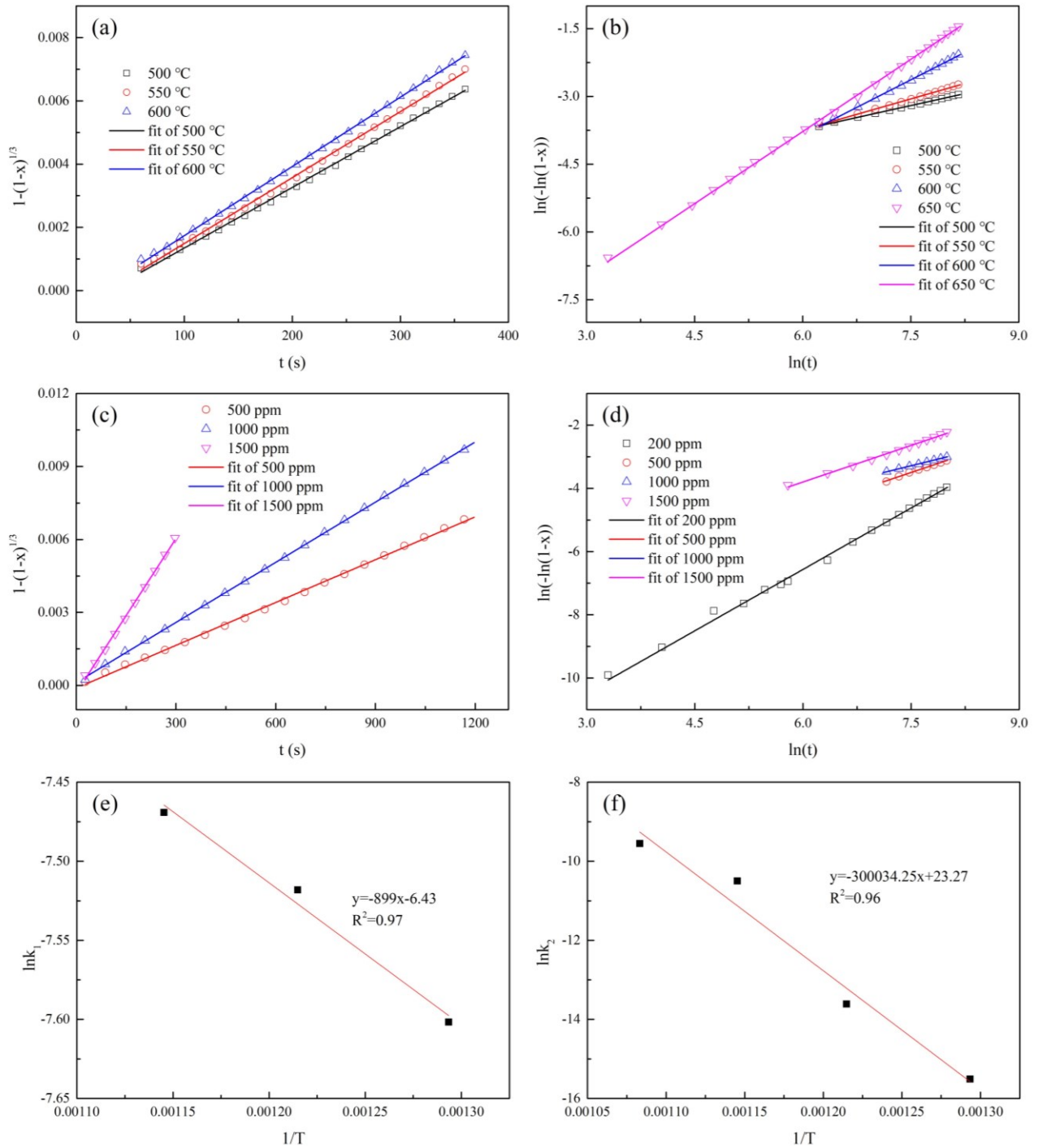


Figure 7. Fitting of Li_4SiO_4 sulphation with the presence of O_2 using (a) SCM and (b) Avrami–Erofeev model under different temperatures, (c) SCM and (d) Avrami–Erofeev model under various SO_2 concentrations, and Arrhenius plot of the (e) kinetic-controlled stage and (f) diffusion-controlled stage.

Conclusions

Through characterizations of the sulphated Li_4SiO_4 with/without O_2 , we found that the sulphation of Li_4SiO_4 occurs in both aerobic and anaerobic atmospheres, but the reaction mechanisms and conditions are very different. After studying the kinetics of the sulphation reaction in the presence of O_2 , it was found that the activation energy of Li_4SiO_4 sulphation in the kinetic-controlled stage is very low. This implies that Li_4SiO_4 can be easily sulphated. As sulphation will reduce the CO_2 capture capacity of this sorbent, it is necessary to remove SO_2 impurity before CO_2 can be removed from the flue gas. These results will serve as a valuable reference for the potential industrial CO_2 capture by Li_4SiO_4 .

Supporting Information

Basic CO_2 adsorption/desorption characteristics of fresh Li_4SiO_4 .

Acknowledgement

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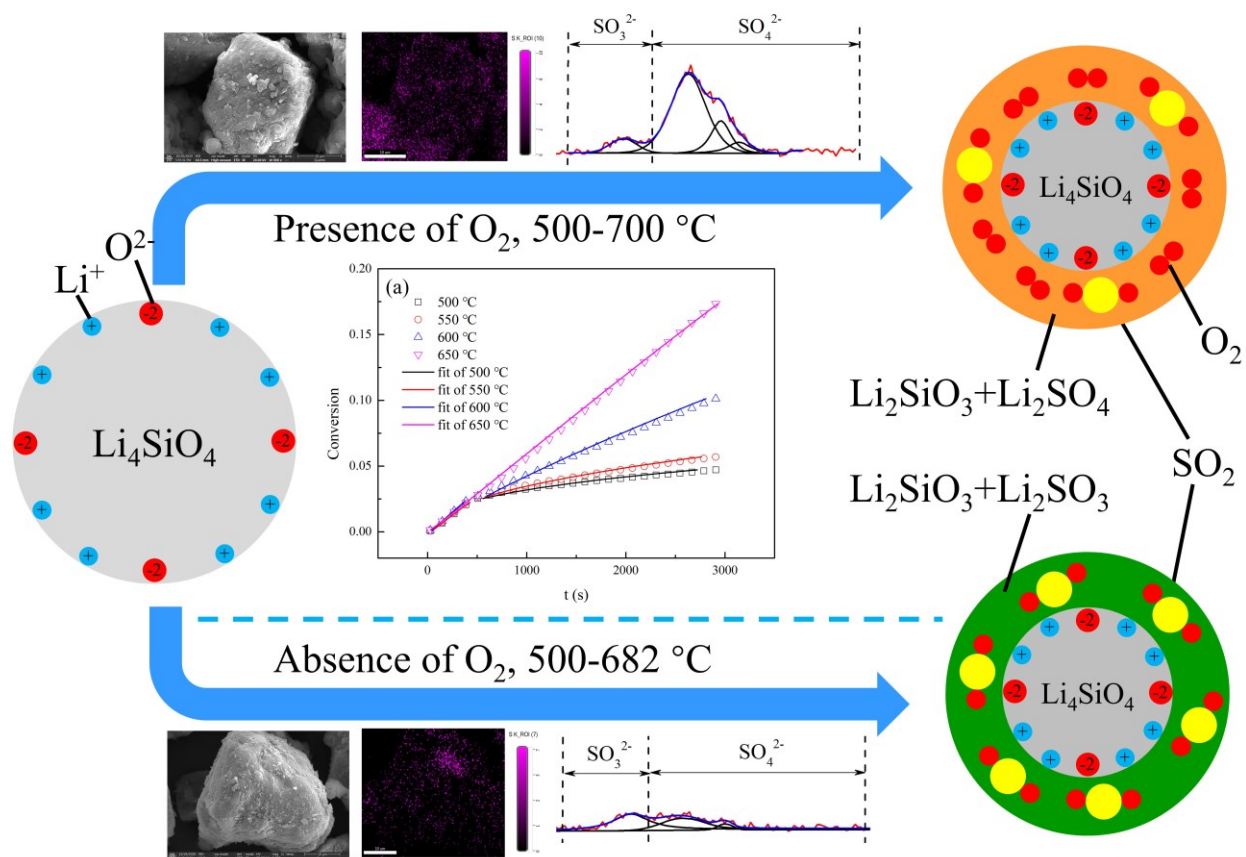


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Understanding reaction mechanisms between Li_4SiO_4 adsorbents and SO_2 impurity with/without the presence of O_2 and kinetic modeling for aerobic sulphation during CO_2 capture from flue gas.



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Reaction mechanism and kinetics of the sulfation of Li₄SiO₄ for high-temperature CO₂ adsorption

Yuan, Weiyang; Chen, huzhen; Qin, Changlei; Hanak, Dawid P.; Zhou, Xu

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