CHEMICAL ENGINEERING TRANSACTIONS

VOL. 71, 2018

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Xiantang Zhang, Songrong Qian, Jianmin Xu

ISBN 978-88-95608-68-6; **ISSN** 2283-9216

DOI: 10.3303/CET1871201

Microcosmic Process Analysis of Chemical Elemental Crystallization Based on Computer Simulation Technology

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Computer simulation technology is frequently applied to the analysis of the microscopic processes of chemical reaction with its powerful functionality and wide applicability. The paper takes aluminum phosphate as the research object and uses the quantum chemistry, reaction kinetics and computer simulation to study the microscopic crystallization mechanism of chemical elements. Based on the replica exchange dynamics method, the simulation parameters of the reaction force field are optimized and this method is used to verify the zeolite system. The results show that the polymerization reaction occurs in the early stage of the crystallization of chemical elements. A preliminary simulation is conducted based on the parameters of reaction force field, obtaining the parameters of reaction force field of various elements. The temperature used in the simulation is set slightly higher than the ultimate temperature, ensuring the simulation efficiency and simulation accuracy; the optimized simulation temperature can be reduced to the experimental temperature, which can also guarantee the simulation accuracy and simulation speed; in the crystallization process of the structure-directing agent, the concentration of the chemical crystal in the reaction can be reduced, which can accelerate the polymerization rate, hinders the formation of other gel clusters and has a structural guiding effect on hydrogen bond interaction. The research results can provide a scientific reference for understanding the mechanism of crystallization process.

1. Introduction

Chemical elements have important application prospects in catalysis and ion exchange and the research on the synthesis of specific structural materials by chemical elements has attracted more and more attention. The crystallization process of chemical elements involves microscopic and mesoscopic and requires accurate characterization methods for the detail description of crystallization. In recent years, there have been some advancements in the characterization method and simulation analysis method of the crystallization of chemical elements, but people still know little about the microscopic crystallization process. With the rapid advancement of computer technology, the theoretical analysis methods based on computer technology can provide new ideas for the crystallization mechanism of chemical elements. The detail description method of crystallization guided by computer simulation technology has become a research hotspot. Choi et al., (2013) developed the reaction force field based on bond energy (ReaxFF) to describe the basic process of chemical reaction. Peyronel et al., (2015) optimized the ReaxFF reaction field based on a low-gradient model to predict the crystal structure state of high-energy materials. Huang et al., (2003) adopted a key sampling method to make a more accurate description of the chemical reaction process.

It can be seen from the above researches that the combination of computer technology and quantum chemistry can not only clearly describe the chemical reaction process, but also increase the simulation speed and the two-dimensional and three-dimensional scale of the reaction, which is of important research value for seeking the microscopic reaction mechanism of chemical materials and the synthesis and development of chemical substances. However, in existing researches, there is little description of microporous crystal materials, and theoretical simulation methods and analytical synthesis mechanisms need to be explored.

Based on this, the paper takes aluminum phosphate as the research object and uses the combination of quantum chemistry and computer technology to study the microscopic crystallization mechanism of aluminum

Please cite this article as: Li H., 2018, Microcosmic process analysis of chemical elemental crystallization based on computer simulation technology, Chemical Engineering Transactions, 71, 1201-1206 DOI:10.3303/CET1871201

phosphate materials, which can express the crystallization process more intuitively and further promotes researchers' understanding of crystallization mechanism.

2. Overview of Computer Simulation Technology

At present, there are three common computer simulation techniques (Matino et al., 2017), namely quantum chemical method (density functional method, solvent model method), molecular simulation method and reaction kinetic simulation method; among them, the quantum chemistry analytical method is of high precision, but the analysis time is too long and it is too complex, so it is difficult to adapt to the analysis of complex reaction process. The molecular simulation analysis method is based on the resolvable molecular force field to obtain the force condition and performance characteristics of each particle, but the calculation process is a little clumsy.

The computer parallel technology can achieve freer and simpler simulation of the atomic reaction force field and the computational cost is also reduced. The crystallization process analysis based on computer simulation technology has been more and more valued by researchers. A representative computer simulation analysis method is ReaxFF reaction force field analysis method. The translational and rotational partition function of this reaction model is constant before and after the reaction, but only the change of vibration distribution function. The equilibrium constant expression is as follows:

$$\mathrm{K}_i = e^{-\Delta EIK} e^{(\theta_{v,AB}-\theta_{V,BC})/2T} \frac{1-e^{-\theta_{v,AB}/T}}{1-e^{-\theta_{v,BC}/T}} \tag{1}$$

In this formula: $\theta_{v,AB}$—AB molecular vibration characteristic temperature; $\theta_{V,BC}$—AC molecular vibration characteristic temperature;

The average exchange probability estimation method is as follows:

$$P_{acc}(N) = erfc\left[\sqrt{C}\frac{\alpha(N)-1}{\alpha(N)+1}\right] \tag{2}$$

$$\alpha(N) = (\frac{T_H}{T_L})^{1/(N-1)} \tag{3}$$

In this formula: $erfc$—error function; C —heat capacity; The reaction model AB+C=A+BC, where A, B and C represent different elements in the model and the corresponding potential-energy functions are as follows:

$$E_{system} = E_{bond} + E_{val} + E_{pen} + E_{vdw}$$

In this formula: E_{bond}—bond energy; E_{val}—bond angle energy; E_{pen}—error of the coordination energy; E_{vdw}—Van der Waals force;

The corresponding flat constants of the reaction model are as follows:

$$\mathrm{K} = \frac{[A][BC]}{[AB][C]} \tag{4}$$

3. Analysis of the Crystallization Microscopic Process of Chemical Elements

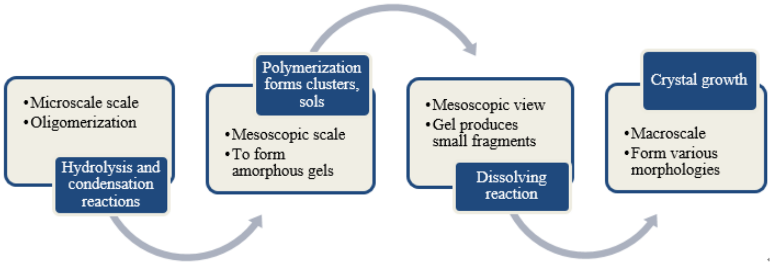


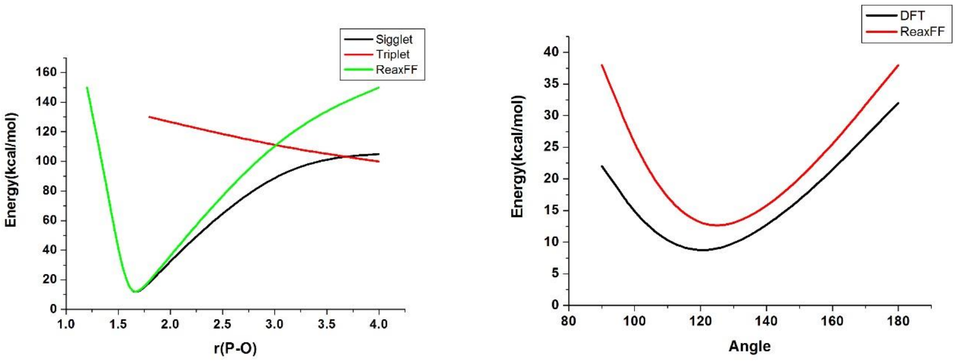
Figure 1: Schematic diagram of chemical single crystallization process

The crystallization process of chemical elements is shown in Figure 1. The crystallization process is mainly divided into four periods, which are the initial stage of crystallization, gel formation, gel digestion and crystal formation. The polymerization reaction in the initial stage of crystallization and the role of structure-directing agent during the crystal formation period are the focus of the crystallization process.

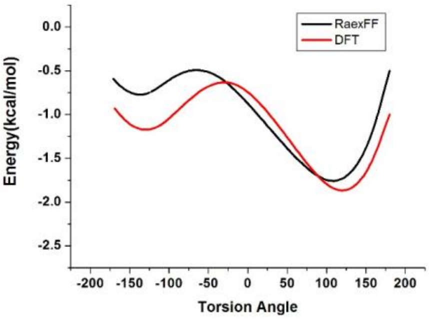
The open framework aluminum phosphate has good thermal stability and unique pore structure. It is widely used in adsorption, multiphase catalysis and other fields. There are more than 200 kinds of molecular sieves available (Sajjadi, 2015). Many scholars have studied the crystallization mechanism and found that for different synthesis conditions, the corresponding mechanisms were also different. The mechanism can be roughly divided into three types. The first is the solid-phase transformation process from gel directly into crystal. The second is the liquid-phase transformation process of the gel relying on the ionic concentration in the solution. The third is the co-existence of the solid-phase transformation and liquid-phase transformation. This paper takes the aluminum phosphate as the research object and analyzes its chemical crystallization microscopic process.

3.1 Reaction Force Field Model and Parameter Setting

Based on quantum chemical data, the ReaxFF reaction force field parameters are developed using the density functional method to determine the charge parameters. Referring to the research results of Park et al., (2007), the paper selects the chemical bond of inorganic phosphorus compounds as the research object and obtains the effect of structural parameters such as chemical bond length, bond angle and the dihedral angle between the bonds, as is shown in Figure 2.



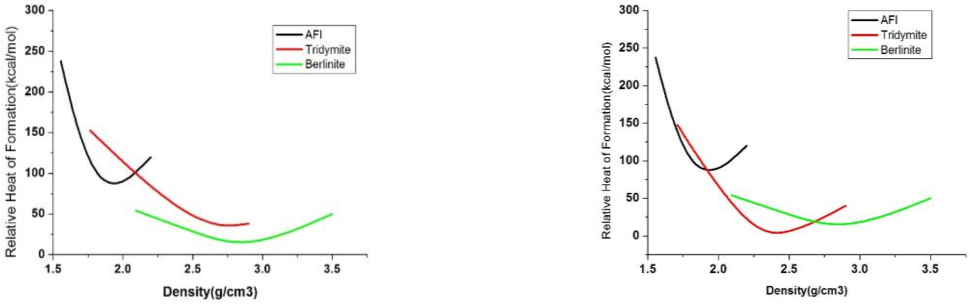
(a) Bond length *(b) Angle*



(c) Torsion Angle

Figure 2: Structural parameters affect renderings

It can be seen from the analysis of the above Figure that the chemical bond cleavage is a process from singlet state to triplet state. The ReaxFF force field function describes the accuracy of a slightly smaller atom. In order to consider the impact of crystal at the same time, the paper abandons the corresponding train set of some small molecules but selects two representative dense aluminum phosphate structure and the microporous structure with good stability AFI for the quantum chemical calculation. Then, the ReaxFF force field parameters are fitted and the fitting results are shown in Figure 3. It can be seen from the Figure that the heat formation relationship and quantum chemical correspondence of the microporous structural material and dense structural material are good, which can be used for the fitting of the ReaxFF force field parameters.



(a) ReaxFF *(b) QM*

Figure 3: Quantum chemistry and ReaxFF calculate the equation of state for several aluminum phosphate crystals

Based on the above analysis and research, this paper obtains the train set corresponding to about 500 energy and structures, involving chemical crystal information, reaction clusters and reaction type information, which lays the foundation for the simulation of chemical reaction process. Considering that the reaction dynamics simulation time reaches the nanosecond level the time extension scale is extremely short (Hanpattanakit et al., 2018). Therefore, this paper uses the replica exchange dynamics method to study the crystallization process of chemical elements based on the ReaxFF force field. Therefore, based on the ReaxFF method system of replica exchange dynamics, the paper first studies the temperature and other parameters. In order to set a reasonable temperature sequence, the paper studies the change of heat capacity under multiple temperature states, as shown in Figure 4. It can be seen from the Figure that there is always a peak for the temperature corresponding to the heat capacity in different models, which means that when the temperature is beyond the peak, the rise of temperature will no longer bring about an increase in the simulation efficiency. However, if the temperature is too low, it is difficult to sample the free radical state. Based on this, the temperature set in this paper is slightly higher than the ultimate temperature.

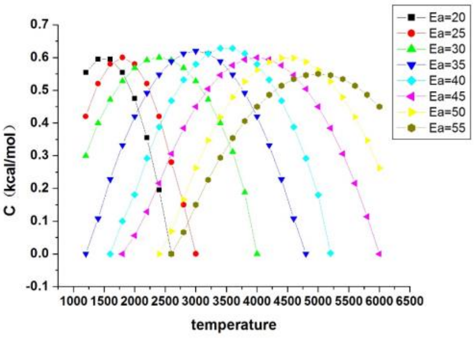


Figure 4: Heat capacity curve under multiple temperature conditions

Referring to Formula 2 and Formula 3, the temperature value can be analyzed through the known exchange probability, number of replicas and initial temperature, thereby obtaining the initial temperature sequence. The marker M is used to indicate the potential energy surface and the reaction heat and the reaction energy barrier are used to express the potential energy surface of the model. According to Formula 1 and Formula 4, the M(13,25) model is taken as an example to obtain the corresponding equilibrium constants, as shown in Table 1 below. It can be seen from the analysis of the data in the Table that the logarithmic equilibrium constant obtained from the direct simulation method is close to that from the replica exchange dynamics simulation method, which indicates that the replica exchange dynamics simulation method can correctly simulate the law of material change of the chemical elemental reaction process. At the same time, the replica exchange dynamics simulation method can reach convergence within 3 ns, which is far lower than the convergence time of the direct simulation method. The above research results show that the replica exchange dynamics simulation method can greatly improve the simulation speed and have better convergence. For the solution system, the solution model system MS (-3, 25) model is taken as an example to obtain the corresponding equilibrium constants, as shown in Table 2 below.

Table 1: Logarithmic equilibrium constant

Direct simulation			Copy exchange dynamics simulation			
T	Ln(K)	t_c(ps)	T	Ln(K)	t_c(ps)	Ln (K_r)
1500	1.63	800	1500	1.48	250	1.45
2500	0.71	200	2525	0.69	250	0.7
3500	0.52	35	3468	0.48	250	0.39
4500	0.43	10	4506	0.42	250	0.31

Table 2: Logarithmic equilibrium constant

Direct simulation			Copy exchange dynamics simulation			
T	Ln(K)	t_c(ps)	T	Ln(K)	t_c(ps)	Ln (K_r)
1500	1.52	4000	1500	1.52	1200	1.43
2500	0.79	200	2525	0.79	1200	0.76
3500	0.45	25	3468	0.45	1200	0.41
4500	0.28	10	4506	0.28	1200	0.37

It can be seen from the analysis in Table 2 that the logarithmic equilibrium constant obtained from the direct simulation method is consistent with that from the replica exchange dynamics simulation method. In fact, there is no interacting gravity between the solvent molecule and the reactant molecule and the theoretical equilibrium constant should be consistent with the gas-phase equilibrium constant, which indicates that the replica exchange dynamics simulation method is of good applicability to the prediction of solution systems.

3.2 Simulation of Microscopic Reaction Process of Chemical Elements

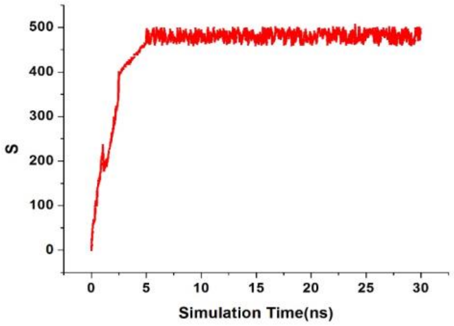
In order to verify the feasibility of the simulation method, the paper sets two working conditions, namely, with and without the addition of structural-directing agent. The Nose-Hoover method is adopted for the temperature control and the simulation system involves a total of 1000 phosphoric acid monomers, aluminum hydroxide monomers and water molecules. The temperature rises to 326.85 °C and the sampling is conducted at 2 nanoseconds and 20 nanoseconds after the balance. It can be seen from the sampling results that the polymerization reaction has already occurred in the monomer at 20ns. In order to express the gel characteristics of the polymerization, a structural factor parameter is introduced and the expression is as follows:

$$S = \frac{1}{2}\int dr(\nabla\rho(r)^2)$$

In this formula: ρ-- average solute density;

The larger the density gradient factor S, the greater the crystallization degree of the polymerization gel. The time-varying law of the density gradient factor S before 20 ns can be obtained from the simulation, as is shown in Figure 5. It can be seen from the above Figure that there is almost no change in the density gradient factor of the reaction system at about 6ns and the equilibrium has already been reached. The number of rings of the polymerization gel can reflect the structural characteristics of the micelle. Therefore, the correlation between the number of rings and the time in the paper is shown in Figure 6. As can be seen from the Figure, the polymerization process is a process in which the number of rings increases gradually. With the increase of time, the tricyclic and pentacyclic rings with poor bond energy stability gradually disappear and the number of rings with excellent stability gradually increases until occupying the dominant position.

The early growth stage of the aluminum phosphate added with the structure-directing agent is affected. The sampling is conducted on the simulation of 2ns and the sampling results are analyzed. It can be found that the polymerization has already occurred in the monomer at 2ns. The comparison of crystallization rate and disappearing rate with and without the addition of structure-directing agent is shown in Figure 6 and Figure 7. After the addition of the structure-directing agent, the polymerization rate between aluminum monomers slows down significantly and the effect of the structure-directing agent is summarized in two aspects. The first aspect is to reduce the chemical crystal concentration in the reaction and accelerate the polymerization rate. The other aspect is to hinder the formation of other gel clusters and ensure the dilution of the chemical reaction system.



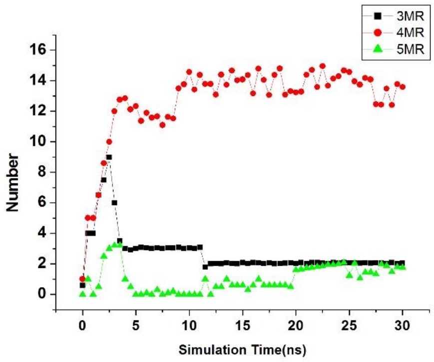


Figure 5: Density gradient factor S evolution process *Figure 6: The correlation between ring number and time*

4. Conclusion

This paper takes the aluminum phosphate as the research object, combines quantum chemistry, reaction kinetics and computer simulation technology to study the microscopic crystallization mechanism of chemical elements. The main conclusions are as follows:

(1) The ReaxFF reaction kinetic method parameters of a specific system are developed. By studying the heat capacity change under multiple temperature conditions, the use temperature in the model is slightly higher than the ultimate temperature to ensure the simulation efficiency and simulation accuracy.

(2) The performance law of the structure-directing agent in the initial stage of the polymerization of aluminum phosphate is determined. The structure-directing agent can not only reduce the concentration of chemical crystals in the reaction and accelerate the polymerization rate, but also hinder the formation of other gel clusters, ensure the dilution of the chemical reaction system and have a structural guiding effect on hydrogen bond interaction.

(3) The simulation test conditions of reaction kinetics are optimized. Based on the replica exchange dynamics the simulation parameters of the reaction force field are optimized and this method is used for the initial simulation of the zeolite system. The simulation results show that the simulated temperature is reduced to approximately equal to the experimental temperature, which optimized the test conditions under the premise of ensuring the accuracy and speed of the simulation.

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