Research Article

Morphology Effect on the Kinetic Parameters and Surface Thermodynamic Properties of Ag_3PO_4 Micro-/Nanocrystals

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Considerable effort has been exerted using theoretical calculations to determine solid surface energies. Nanomaterials with high surface energy depending on morphology and size exhibit enhanced reactivity. Thus, investigating the effects of morphology, size, and nanostructure on the surface energies and kinetics of nanomaterials is important. This study determined the surface energies of silver phosphate (Ag_3PO_4) micro-/nanocrystals and their kinetic parameters when reacting with HNO_3 by using microcalorimetry. This study also discussed rationally combined thermochemical cycle, transition state theory, basic theory of chemical thermodynamics with thermokinetic principle, morphology dependence of reaction kinetics, and surface thermodynamic properties. Results show that the molar surface enthalpy, molar surface entropy, molar surface Gibbs free energy, and molar surface energy of cubic Ag_3PO_4 micro-/nanocrystals are larger than those of rhombic dodecahedral Ag_3PO_4 micro-/nanocrystals. Compared with rhombic dodecahedral Ag_3PO_4 , cubic Ag_3PO_4 with high surface energy exhibits higher reaction rate and lower activation energy, activation Gibbs free energy, activation enthalpy, and activation entropy. These results indicate that cubic Ag_3PO_4 micro-/nanocrystals can overcome small energy barrier faster than rhombic dodecahedral Ag_3PO_4 micro-/nanocrystals and thus require lower activation energy.

1. Introduction

Nanomaterials that exhibit high specific surface effect differ from massive materials in terms of physical and chemical properties [1, 2]. Du et al. [3] explained that the specific surface effect, surface heat capacity, and specific surface energy of nanomaterials cannot be neglected. The overall thermodynamic property of nanoparticles comprises surface and bulk phases [3–9]. Surface thermodynamic properties are the intuitive expression of the special structure-activity relationship of nanomaterial surface, which significantly affects many physical/chemical reactions, including chemical thermodynamics [3, 4], chemical kinetics [5], catalysis [10–13], sense [11], adsorption [14], phase transition [15], and electrochemistry of nanomaterials [16]. Theoretical calculation results showed that nanomaterials with different sizes and

facets have different surface energies [17–19] and that the reactivity of nanomaterials depends on surface energy [11, 12]. Studying the surface thermodynamic property of nanomaterials and the structure-function relationship between reaction dynamics and size, morphology, and structure is valuable to understand the nature of chemical reactions.

Calorimetry [7, 8, 20, 21], contact angle [22], Young modulus [23, 24], balance crystal shape [3, 25], zero creep, and field-emission microscopic method [26] are common methods of measuring solid surface energy. Hulett [27, 28] reported that the surface energies of BaSO_4 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ obtained using the Ostwald-Freundlich formula are within $1000\text{--}3000\text{ mJ}\cdot\text{m}^{-2}$. However, Tang et al. [29–32] discovered that results obtained using the Ostwald-Freundlich formula for nanoparticles with far higher solubility than common crystals contradict with experimental facts. Thus, Tang et al.

[31, 32] measured the surface energy of inorganic insoluble salt indirectly through crystal growth or dissolution kinetics. Methods commonly used in Young modulus (e.g., tearing) and other methods involving compression, solubilization, high-temperature dissolution, or lowering of melting point produce high and even applied stress-covered surface energies. Hence, theoretical calculation is preferred to measure solid surface energy [23]. Nevertheless, theoretical calculation often deviates from the practical ideal model and from many hypotheses. Real surfaces with abundant atom ladders and unsaturated bonds, as well as those with unstable thermodynamics, tend to absorb water [7], gas molecules, and surfactant [11, 12]; undergo surface atom reconstruction and aggregation; or even form a protective film layer. The surface energies of these complicated real surfaces are extremely difficult to theoretically calculate. Experimental measurement still faces several challenges. Different experimental methods provide significantly different values for the surface energies of the same material [33]; researchers using the same experimental method also obtain varying results [34, 35]. A universal method to determine surface energy has yet to be developed. Developing a scientific and universal experimental method to measure the surface energy of nanomaterials is a pressing need in the scientific endeavors on solid surface and in other disciplines.

The visible-light-driven Ag_3PO_4 photocatalyst has become popular since its introduction in 2010 [36, 37]. Scientists calculated the surface energies of different facets of Ag_3PO_4 on the basis of the relationship between included angle of crystal faces and Miller index [38]. Other researchers performed the same calculation by using density functional theory [39]. Studying the structure-function relationship between the surface energy of micro-/nanomaterial Ag_3PO_4 and size, morphology, and structure is valuable to understand the natures of chemical reactions. However, the surface energy of this material was rarely calculated using experimental methods. The present study determined the surface energies of Ag_3PO_4 micro-/nanocrystals with cubic and rhombic dodecahedral morphologies and their kinetic parameters when reacting with HNO_3 by using microcalorimetry. This study also discussed rationally combined thermochemical cycle, transition state theory, basic theory of chemical thermodynamics with thermokinetic principle, morphology dependence of reaction kinetics, and surface thermodynamic properties.

2. Experiments

2.1. Materials. Analytical-grade sodium dihydrogen phosphate dihydrate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$), disodium phosphate dodecahydrate ($\text{NaH}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$), silver nitrate (AgNO_3), ammonium hydroxide ($\text{NH}_3 \cdot \text{H}_2\text{O}$), potassium chloride (KCl), and nitric acid were purchased from Sinopharm Chemical Reagent Co. Ltd. and used without further purification. Deionized water with a resistivity of $18.2 \text{ M}\Omega \cdot \text{cm}$ was used in all experiments.

2.2. Characterization. The morphology of the sample was examined under a field-emission scanning electron microscope (Zeiss SUPRA 55 Sapphire, Germany). The X-ray diffraction (XRD) pattern was recorded on an X-ray powder

diffractometer (Philips PW 1710 with $\text{Cu K}\alpha$ radiation, $\lambda = 1.5406 \text{ \AA}$, Holland). Trace amounts of the sample were measured on a XPE analytic balance (Mettler Toledo, Switzerland). Calorimetric experiments were performed using a microcalorimeter (RD496L, Mianyang CP Thermal Analysis Instrument Co., Ltd., China) under constant temperature and pressure.

2.3. Calorimetric Experiment. Rhombic dodecahedrons, cubes, and bulk Ag_3PO_4 were prepared by a simple ion-exchange method at room temperature [40]. The microcalorimeter was calibrated by Joule effect, and its calorimetric constant was $(69.91 \pm 0.56) \mu\text{V} \cdot \text{mW}^{-1}$ at 298.15 K . The dissolution enthalpy of KCl in deionized water (1:1110, $m_{\text{KCl}}/m_{\text{de-water}}$) was $(17.792 \pm 0.029) \text{ kJ} \cdot \text{mol}^{-1}$. This value agrees with the previously published value of (17.524 ± 0.028) [41]. This agreement indicates that the calorimetric system is accurate and reliable.

A small glass tube containing 1.0 mL of 0.36 M HNO_3 solution was placed above a 15 mL glass tube charged with 1.500 mg of Ag_3PO_4 samples (bulk or the obtained nanocubes). Simultaneously with the establishment of equilibrium, the small glass tube with HNO_3 solution was pushed down. The in situ thermodynamic and kinetic information for this reaction was recorded using the microcalorimeter.

2.4. Establishment of Chemical Reaction Kinetic Models for Cubic and Rhombic Dodecahedron Ag_3PO_4 Micro-/Nanocrystals. The specific surface area and specific surface energy of the reactant increase after being refined; thus, the mean molar energy of the refined reactant is higher than that of the corresponding bulk reactant. If the reactant particle size is insignificant to the mean energy of the activated molecules, then the difference between the mean molecular activation energy of 1 M of nanoparticles and mean energy of 1 mol super-refined reactant is the chemical activation energy of the nanomaterial [42]. Figure 1 shows the transition state theory [8, 42, 43]. In the same chemical reaction, the reactant experiences the same transition state to the final state. Therefore, the apparent activation energy of nanoparticles E_a is the difference between the activation energy of corresponding bulk material [$E_a(\text{bulk})$] and the molar surface energy of nanoparticles (E_m^S):

$$E_a(\text{nano}) = E_a(\text{bulk}) - E_m^S. \quad (1)$$

If the dispersion phase in heterogeneous reaction has only one reactant and others belong to the continuous phase, then the relationship between surface energy and apparent activation energy for cubic nanoparticles without inner bores can be expressed as

$$E_a(\text{nano}) = E_a(\text{bulk}) - E_m^S = E_a(\text{bulk}) - \frac{4\sigma M}{\rho l}, \quad (2)$$

where σ , M , ρ , and l are the surface tension, molar mass, density, and particle size (length of cube edge) of the cubic nanoparticle reactant, respectively. Equation (2) provides that the apparent activation energy in the chemical reaction of the nanomaterials is proportional to the particle size of the reactant.

FIGURE 1: Schematic of relationship between surface energy and apparent activation energy.

If the heterogeneous reaction follows Arrhenius Law, substituting (2) into it yields the Arrhenius equation of the nanocube:

$$k = A \exp \left[-\frac{E_a^b}{RT} + \frac{4\sigma M}{RT\rho l} \right]. \quad (3)$$

Similarly, the Arrhenius equation of dodecahedron is obtained:

$$k = A \exp \left[-\frac{E_a^b}{RT} + \frac{\sqrt{6}\sigma M}{RT\rho l} \right], \quad (4)$$

where T is the reaction temperature, k is the reaction rate constant, and A is the preexponential factor.

Substituting the logarithm on both sides of (4), we obtain the following:

Cube:

$$\ln k = \ln A - \frac{E_a^b}{RT} + \frac{4\sigma M}{RT\rho l}. \quad (5)$$

Dodecahedron:

$$\ln k = \ln A - \frac{E_a^b}{RT} + \frac{\sqrt{6}\sigma M}{RT\rho l}. \quad (6)$$

Therefore, when the particle size is larger than 10 nm, the surface tension slightly changes and can be viewed as a constant [43]. On the basis of (5) and (6), the logarithm of the reaction rate constant is inversely proportional to the particle size of the reactant.

2.5. Acquisition of Dynamic Parameters of Ag_3PO_4 Reacting with HNO_3 . The thermodynamic equation of reversible chemical reaction under constant temperature and pressure can be expressed as [44]

$$\ln \left[\frac{1}{H_\infty} \frac{dH_i}{dt} \right] = \ln k + n \ln \left[1 - \frac{H_i}{H_\infty} \right], \quad (7)$$

where H_∞ is the enthalpy change during the whole reaction and may be directly obtained by microcalorimetry, dH_i/dt is the enthalpy change rate, k (s^{-1}) is the reaction rate constant expressed by conversion rate, and H_i is the enthalpy change at reaction time t . k can be calculated from the linear regression of thermodynamic data:

$$\ln k = \ln A - \frac{E_a}{RT} \quad (8)$$

$$\Delta G_\#^\theta = RT \ln \left[\frac{RT}{N_A h k} \right] \quad (9)$$

$$\ln \frac{k}{T} = \ln \frac{k_B}{h} + \frac{\Delta S_\#^\theta}{R} - \frac{\Delta H_\#^\theta}{RT}, \quad (10)$$

where N_A is Avogadro's constant, k_B is Boltzmann's constant, h is Planck's constant, and R is the molar gas constant. The diagram of $1/T$ was drawn with $\ln k$. E_a and A were calculated using (8). $\Delta G_\#^\theta$, $\Delta H_\#^\theta$, and $\Delta S_\#^\theta$ were calculated from (9) and (10).

2.6. Theoretical Derivation of Molar Surface Gibbs Free Energy, Molar Surface Enthalpy, Molar Surface Entropy, and Molar Surface Energy. The molar Gibbs free energy of chemical reaction of nanosystem consists of bulk phase ($\Delta_r G_m^B$) and surface phase ($\Delta_r G_m^S$) [8, 42]:

$$\Delta_r G_m(\text{nano}) = \Delta_r G_m^B + \Delta_r G_m^S. \quad (11)$$

The molar Gibbs free energy of the bulk chemical reaction nearly exhibits bulk phase. The bulk phase of the nanosystem is similar to that of bulk:

$$\Delta_r G_m^B = \Delta_r G_m(\text{bulk}), \quad (12)$$

where $\Delta_r G_m(\text{bulk})$ is the molar Gibbs free energy of the same chemical reaction bulk material.

Therefore, the molar Gibbs free energy difference between the nanosystem and the bulk lies in the molar surface Gibbs free energy of the nanomaterial (excessive Gibbs free energy compared with bulk material). Substituting (12) into (11), we obtain

$$\Delta_r G_m^S = \Delta_r G_m(\text{nano}) - \Delta_r G_m(\text{bulk}). \quad (13)$$

On the basis of (13), the thermochemical cycles of nano- and bulk Ag_3PO_4 were designed (Figure 2). The thermodynamic functions of nano- and bulk Ag_3PO_4 reactions with HNO_3 were tested. The thermodynamic function of nano- Ag_3PO_4 conversion into the bulk one was calculated on the basis of their difference.

On the basis of (12), the chemical reaction for the molar surface Gibbs of Ag_3PO_4 micro-/nanocrystals with a net reaction of $\text{Ag}_3\text{PO}_4(\text{nano}) \rightarrow \text{Ag}_3\text{PO}_4(\text{bulk})$ is

$$\begin{aligned} \Delta_r G_m^\theta &= \Delta_r G_m^\theta(\text{Ag}_3\text{PO}_4, \text{nano}) \\ &\quad - \Delta_r G_m^\theta(\text{Ag}_3\text{PO}_4, \text{bulk}) \\ &= \Delta_r G_m^S(\text{Ag}_3\text{PO}_4, \text{nano}) \\ &= -G_m^S(\text{Ag}_3\text{PO}_4, \text{nano}), \end{aligned} \quad (14)$$

FIGURE 2: Thermochemical cycle of nano- and bulk Ag_3PO_4 reacting with HNO_3 .

where $\Delta G_m^\theta(\text{Ag}_3\text{PO}_4, \text{ nano})$ and $\Delta G_m^\theta(\text{Ag}_3\text{PO}_4, \text{ bulk})$ are the standard molar Gibbs free energies of the reactions of Ag_3PO_4 micro-/nanocrystals and bulk Ag_3PO_4 with HNO_3 , respectively; $\Delta G_m^S(\text{Ag}_3\text{PO}_4, \text{ nano})$ and $G_m^S(\text{Ag}_3\text{PO}_4, \text{ nano})$ are the molar reaction surface Gibbs free energy and molar surface Gibbs free energy, respectively.

In accordance with transition state theory, the relationship between reaction rate constants of Ag_3PO_4 micro-/nanocrystals reaction system and bulk Ag_3PO_4 reaction system and the Gibbs free energy can be expressed as [8, 45]

$$\begin{aligned} \Delta_r G_m^\theta(\text{Ag}_3\text{PO}_4, \text{ nano}) - \Delta_r G_m^\theta(\text{Ag}_3\text{PO}_4, \text{ bulk}) \\ = \Delta_r G_\ddagger^\theta(\text{bulk}) - \Delta_r G_\ddagger^\theta(\text{nano}) \\ = RT(\ln k_{\text{bulk}} - \ln k_{\text{nano}}), \end{aligned} \quad (15)$$

where $\Delta_r G_\ddagger^\theta$ and k are the activation Gibbs free energy and rate constant of Ag_3PO_4 chemical reaction.

On the basis of (14) and (15),

$$\begin{aligned} G_m^S(\text{Ag}_3\text{PO}_4, \text{ nano}) &= -\Delta_r G_m^S(\text{Ag}_3\text{PO}_4, \text{ nano}) \\ &= -RT(\ln k_{\text{bulk}} - \ln k_{\text{nano}}). \end{aligned} \quad (16)$$

Similarly, $\Delta H_\ddagger^\theta$ can be calculated from (10). Molar surface enthalpy can be deduced from transition state theory:

$$\begin{aligned} \Delta_r H_m^S &= \Delta_r H_m^\theta(\text{nano}) - \Delta_r H_m^\theta(\text{bulk}) \\ &= \Delta_r H_\ddagger^\theta(\text{bulk}) - \Delta_r H_\ddagger^\theta(\text{nano}) \\ \Delta_r H_m^S &= H_m(\text{Ag}_3\text{PO}_4, \text{ nano}) - H_m(\text{Ag}_3\text{PO}_4, \text{ bulk}) \\ &= -H_m^S(\text{Ag}_3\text{PO}_4), \end{aligned} \quad (17)$$

where $\Delta_r H_m^S$, $\Delta_r H_m^\theta$, $\Delta_r H_\ddagger^\theta$, and H_m^S are the molar surface reaction enthalpy, molar reaction enthalpy, molar activation enthalpy, and molar surface enthalpy of Ag_3PO_4 chemical reaction, respectively.

Similarly, molar surface entropy can be deduced from transition state theory:

$$\begin{aligned} \Delta_r S_m^S &= \Delta_r S_m^\theta(\text{nano}) - \Delta_r S_m^\theta(\text{bulk}) \\ &= \Delta_r S_\ddagger^\theta(\text{bulk}) - \Delta_r S_\ddagger^\theta(\text{nano}) \\ \Delta_r S_m^S &= S_m(\text{Ag}_3\text{PO}_4, \text{ nano}) - S_m(\text{Ag}_3\text{PO}_4, \text{ bulk}) \\ &= -S_m^S(\text{Ag}_3\text{PO}_4), \end{aligned} \quad (18)$$

where $\Delta_r S_m^S$, $\Delta_r S_m^\theta$, $\Delta_r S_\ddagger^\theta$, and S_m^S are the molar surface reaction entropy, molar reaction entropy, molar activation entropy, and molar surface entropy of Ag_3PO_4 chemical reaction, respectively.

Apparent activation energy refers to the total energy needed for the material to overcome activation. The essential difference between Ag_3PO_4 micro-/nanocrystals and bulk Ag_3PO_4 is the high specific surface effect of the surface phase. After the same transition state to the final state in the same chemical reaction (Figure 1), the surface energy of the nanosystem surface phase (E_m^S) is the energy difference between the nano-reaction system and the bulk reaction system. The molar surface energy in the manuscript cited reference [8] which deduced in our published paper. Its correct form is [8]. Consider

$$\begin{aligned} \Delta E_m^S &= E(\text{nano}) - E(\text{bulk}) = E_a(\text{bulk}) - E_a(\text{nano}) \\ \Delta_r E_m^S &= E_m(\text{Ag}_3\text{PO}_4, \text{ nano}) - E_m(\text{Ag}_3\text{PO}_4, \text{ bulk}) \\ &= -E_m^S(\text{Ag}_3\text{PO}_4), \end{aligned} \quad (19)$$

where ΔE_m^S , E_a , and E_m are the molar surface reaction energy, activation energy, and molar surface energy of Ag_3PO_4 chemical reaction, respectively.

3. Results and Discussion

3.1. Product Characterization. Figures 3(a)–3(c) show the SEM images of Ag_3PO_4 micro-/nanocrystals. Cubic Ag_3PO_4 has six (100) faces, clear and sharp edges and angles, and smooth surfaces; the mean particle size is (695.9 ± 100.2) nm. Figure 3(b) is the rhombic dodecahedral Ag_3PO_4 with 12 rhombus (110) faces. White spots are scattered on the surfaces; the mean particle size is (647.1 ± 91.8) nm. Figure 3(c) shows the SEM image of the irregularly shaped Ag_3PO_4 that forms the bulk of the substance; its mean particle size is (6.9 ± 3.9) μm .

Figure 4 shows the XRD pattern of the bulk, rhombic dodecahedral, and cubic Ag_3PO_4 . All diffraction peaks in Figure 4 agree with those of Ag_3PO_4 with the standard calorie JPCDS (06-0505). No other impurity peak is observed. Moreover, the full width at half maximum of all diffraction peaks is narrow, indicating purity and good crystallinity of the prepared samples.

3.2. Effect of Morphology on the Chemical Reaction Rate Constant of Ag_3PO_4 Micro-/Nanocrystals. Linear regression was

FIGURE 3: SEM images of cubic (a), rhombic dodecahedral (b), and bulk (c) Ag_3PO_4 micro-/nanocrystals.

FIGURE 4: XRD patterns of bulk (a), rhombic dodecahedral (b), and cubic (c) Ag_3PO_4 micro-/nanocrystals.

performed using the original thermodynamics data obtained from (7), and the reaction rate constants of Ag_3PO_4 and HNO_3 under varying temperatures were obtained (Table 1).

The curves shown in Figure 5 were drawn on the basis of the reaction rate constants of Ag_3PO_4 with HNO_3 and the reciprocal of temperature in Table 1.

Figure 5 shows that the reaction rate is proportional to temperature when the particle size is fixed. Compared with bulk Ag_3PO_4 , the super-refined materials have significantly more particles of the surface phase. Particles of the surface phase account for a large proportion of the total particles. Atoms of the surface phase have uneven stresses, unsaturated force field, and dangling bonds, which lead to high surface energy. This result explains the faster reaction rate of Ag_3PO_4 micro-/nanocrystals than bulk Ag_3PO_4 . As the temperature increases, the surface turbulence and surface energy of Ag_3PO_4 micro-/nanocrystals increase; consequently, the chemical reaction increases. The effect of morphology on the reaction rate shows that cubic Ag_3PO_4 has higher reaction rate than dodecahedral Ag_3PO_4 .

FIGURE 5: Effect of morphology on the reaction rate constant of Ag_3PO_4 micro-/nanocrystals with HNO_3 .

TABLE 1: Reaction rate constant of Ag_3PO_4 micro-/nanocrystals with HNO_3 .

T (K)	298.15	303.15	308.15	313.15	318.15
$k \cdot 10^{-3}$ (s^{-1})					
Cube	3.37	3.53	3.77	3.99	4.17
Rhombic dodecahedra	3.25	3.44	3.64	3.86	4.08
Bulk	2.95	3.25	3.48	3.71	3.98

3.3. Effect of Morphology on the Activation Energy, Activation Gibbs Free Energy, Activation Enthalpy, and Activation Entropy of Ag_3PO_4 Micro-/Nanocrystals. Linear regression of logarithmic reaction rate constant and temperature reciprocal (slope and intercept in Figure 4) was performed using (8), and the E_a of the Ag_3PO_4 micro-/nanocrystals reaction was obtained. The $\Delta G^\theta_\#$ of the Ag_3PO_4 micro-/nanocrystals reaction was calculated using (9). The $\Delta H^\theta_\#$ and $\Delta S^\theta_\#$ of

TABLE 2: Activation energy, activation Gibbs free energy, activation enthalpy, and activation entropy of Ag_3PO_4 micro-/nanocrystals.

Ag_3PO_4 Micro-/nanocrystals	T (K)	$\Delta G_{\ddagger}^{\theta}$ ($\text{kJ}\cdot\text{mol}^{-1}$)	E_a ($\text{kJ}\cdot\text{mol}^{-1}$)	$\Delta H_{\ddagger}^{\theta}$ ($\text{kJ}\cdot\text{mol}^{-1}$)	$\Delta S_{\ddagger}^{\theta}$ ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)
Cube	298.15	87.132	8.653	6.093	-271.831
	303.15	88.518			
	308.15	89.852			
	313.15	91.204			
	318.15	92.585			
Rhombic dodecahedra	298.15	87.222	8.990	6.430	-270.987
	303.15	88.583			
	308.15	89.941			
	313.15	91.290			
	318.15	92.643			
Bulk	298.15	87.462	11.548	8.988	-263.123
	303.15	88.726			
	308.15	90.056			
	313.15	91.393			
	318.15	92.708

FIGURE 6: Morphology effect on the activation Gibbs free energy of Ag_3PO_4 micro-/nanocrystals.

the Ag_3PO_4 micro-/nanocrystals reaction were calculated using (10). Results are listed in Table 2.

As shown in Table 1, the activation energy, activation Gibbs free energy (as shown in Figure 6), activation enthalpy, and activation entropy of Ag_3PO_4 micro-/nanocrystals decrease with decreasing particle size. Surface atoms are in metastable state because of the high specific surface effect of micro-/nanomaterials. The nanosystem has higher potential energy than the bulk system because of high specific surface effect. Transition state theory states that the nanosystem has to overcome smaller energy barrier than the bulk system to reach the same transition state. Therefore, smaller particles

TABLE 3: Surface Gibbs free energy of Ag_3PO_4 micro-/nanocrystals.

T (K)	298.15	303.15	308.15	313.15	318.15
G^S ($\text{kJ}\cdot\text{mol}^{-1}$)					
Cube	0.330	0.208	0.205	0.189	0.123
Rhombic dodecahedra	0.240	0.143	0.115	0.103	0.066

require less activation energy. The effect of morphology on E_a , $\Delta G_{\ddagger}^{\theta}$, $\Delta H_{\ddagger}^{\theta}$, and $\Delta S_{\ddagger}^{\theta}$ demonstrates that cubic Ag_3PO_4 overcomes smaller energy barrier than dodecahedral Ag_3PO_4 in the same reaction. Thus, cubic Ag_3PO_4 requires less activation energy than dodecahedral Ag_3PO_4 .

3.4. Effect of Morphology on the Surface Gibbs Free Energy of Ag_3PO_4 Micro-/Nanocrystals. Combining (14)–(16), we calculated the surface Gibbs free energy of Ag_3PO_4 micro-/nanocrystals on the basis of the activation Gibbs free energy listed in Table 3.

The molar surface Gibbs free energy of Ag_3PO_4 micro-/nanocrystals (G_m^S) under different temperatures is shown in Figure 7. Cubic Ag_3PO_4 has higher G_m^S than rhombic dodecahedral Ag_3PO_4 . Both conditions are inversely proportional to temperature. The uneven stress on the atoms of the surface phase intensifies with increasing reaction temperature. The thermal motion of nanoparticles also intensifies with the increase in unsaturated force field and dangling bonds. The widening particle space weakens their interaction and decreases the surface tension of nanomaterials, thereby reducing the surface Gibbs free energy.

3.5. Effect of Morphology on the Molar Surface Enthalpy, Molar Surface Entropy, and Molar Surface Energy of Ag_3PO_4 Micro-/Nanocrystals. The H_m^S , S_m^S , and E_m^S of Ag_3PO_4 micro-/nanocrystals were calculated using (17), (18), and (19), respectively.

TABLE 4: Morphology effect on the surface enthalpy, surface entropy, and surface energy of Ag_3PO_4 micro-/nanocrystals.

Surface energies	Ag_3PO_4 micro-/nanocrystals	
	Cube	Rhombic dodecahedron
H_m^S ($\text{kJ}\cdot\text{mol}^{-1}$)	2.895	2.558
S_m^S ($\text{kJ}\cdot\text{mol}^{-1}$)	8.708	7.864
E_m^S ($\text{kJ}\cdot\text{mol}^{-1}$)	2.895	2.558

FIGURE 7: Morphology effect on surface Gibbs free energy of Ag_3PO_4 micro-/nanocrystals.

Table 4 shows that cubic Ag_3PO_4 micro-/nanocrystals have higher H_m^S , S_m^S , and E_m^S than rhombic dodecahedral Ag_3PO_4 . This result agrees with that on surface Gibbs free energy. Molar surface energy is the sum of the kinetic energy, potential energy, and chemical energy of surface phase particles. After super-refinement of the material, atoms of the surface phase suffer from uneven stress, display unsaturated force field, and possess dangling bonds because of strong specific surface effect. Consequently, the interaction of nanoparticles is enhanced. This phenomenon explains why micro-/nanomaterials have high kinetic energy and potential energy.

4. Conclusion

This study determined the surface energies of Ag_3PO_4 micro-/nanocrystals and their kinetic parameters when reacting with HNO_3 by using microcalorimetry. It also discussed rationally combined thermochemical cycle, transition state theory, basic theory of chemical thermodynamics with thermokinetic principle, morphology dependence of reaction kinetics, and surface thermodynamic properties. Results show that the molar surface enthalpy, molar surface entropy, molar surface Gibbs free energy, and molar surface energy of cubic Ag_3PO_4 micro-/nanocrystals are larger than those of

rhombic dodecahedral Ag_3PO_4 micro-/nanocrystals. Compared with rhombic dodecahedral Ag_3PO_4 , cubic Ag_3PO_4 with high surface energy exhibits higher reaction rate and lower activation energy, activation Gibbs free energy, activation enthalpy, and activation entropy. These results indicate that cubic Ag_3PO_4 micro-/nanocrystals possess a much higher reactivity and it is more easily activated than rhombic dodecahedral Ag_3PO_4 micro-/nanocrystals. This paper presents a novel facile approach to study the surface thermodynamic property of nanomaterials and the structure-function relationship between reaction dynamics and size, morphology, and structure.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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