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Effect of Particle Size on Oxidation Reaction Kinetic Parameter of Cu_2O Powders

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Abstract The 0.4mol/L $CuSO_4$ liquor and 5mol/L NaOH liquor were prepared using $CuSO_4 \cdot 5H_2O$ and NaOH as raw materials. The Cu_2O powders were prepared using glucose as reducer and polyvinylpyrrolidone(PVP) as dispersant. The Cu_2O oxidation reaction DTA-TG-DTG curves were obtained by using SDT-2960 thermal analysis apparatus. The measurement condition was that temperature rise rate is 15℃/min and reducing gas is air. The oxidation reaction kinetic parameters of Cu_2O powders were calculated using DTA-TG-DTG curves data. The results indicate that the shapes of cuprous oxide powders were spherical, their particle sizes were respectively 100, 200, 1 000nm. Their apparent activation energy were respectively 164.38, 175.54, 282.65 KJ/mol, the apparent activation energy increases with increase of Cu_2O particle size. Their frequency factors were respectively 1.22×10^{13}, 1.40×10^{13}, 2.88×10^{20}. Their reaction progressions were respectively 1.02, 1.00, 0.96, the reaction progressions decrease with increase of Cu_2O particle size.

Key words Cu_2O, particle size, kinetic parameter, oxidation

Introduction

The great leader Comrade **Kim Il Sung** said.

“Scientists must conduct research on the production of stainless steel using raw material which is plentiful here, using a small amount of nickel or none at all, and then should also conduct research in the production of corrosion-resistant materials which can be used to replace stainless steel.”(“**KIM IL SUNG** WORKS” Vol. 37 P. 360)

The research about the physical and chemical properties of nano-particles and nano-materials is a hot topic in the nanotechnology scopes. But the research on the kinetic parameters of different particle size is very rare. Calculation methods of nonisothermal caloric analysis kinetics were plenty [1－5].

In this paper, oxidation reaction kinetic parameters of different Cu_2O particle size were studied by using Arrhenius formula. The oxidation reaction kinetic parameters of Cu_2O powders were calculated using DTA-TG-DTG curves data. The Cu_2O oxidation reaction kinetic parameters include apparent activation energy E, frequency factor A and reaction progression n.

1. Calculation Method

Arrhenius formula is as follows.

$$k = A\exp\left(-\frac{E}{RT}\right) \tag{1}$$

where k is the specific reaction rate constant, E is the apparent activation energy(J/mol), A is the frequency factor, R is the gas constant(J/(K·mol)), T is thermodynamic temperature(K).

In both sides of equation (1) logarithm were adopted, and then we can get following equation.

$$\ln k = -\frac{E}{RT} + \ln A \tag{2}$$

A straight line was obtained by the linear relation between lnk and $1/T$. E was obtained from the slope of the straight line, A was obtained from the intercept of lnk axis.

Where k is defined as:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \tag{3}$$

where t is time, α is the conversion rate, and n is the reaction progression. If the temperature rise rate is β, $\beta=dT/dt$. If $dt=dT/\beta$ is substituted into equation (3), equation (4) can be obtained.

$$\frac{d\alpha}{dT} = \frac{k(1-\alpha)^n}{\beta} \tag{4}$$

Namely

$$k = \frac{(d\alpha/dt)\beta}{(1-\alpha)^n} \tag{5}$$

By using equation (5), k can be possibly calculated.

Reaction progression n is obtained by calculation of the Kissinger peak shape factor [6].

Fig. 1 shows the exothermic peak of DTA curves, peak shape factor is defined as $I = a/b$, a and b are peak shape indexes, their sizes are shown in Fig. 1.

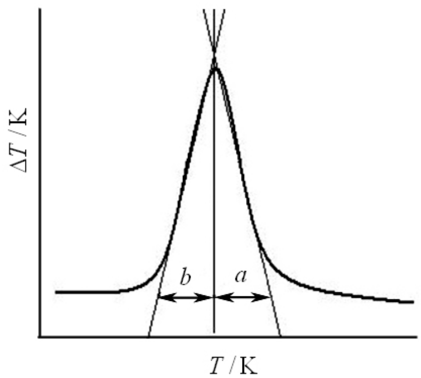


Fig. 1. Peak shape factor of the DTA curve

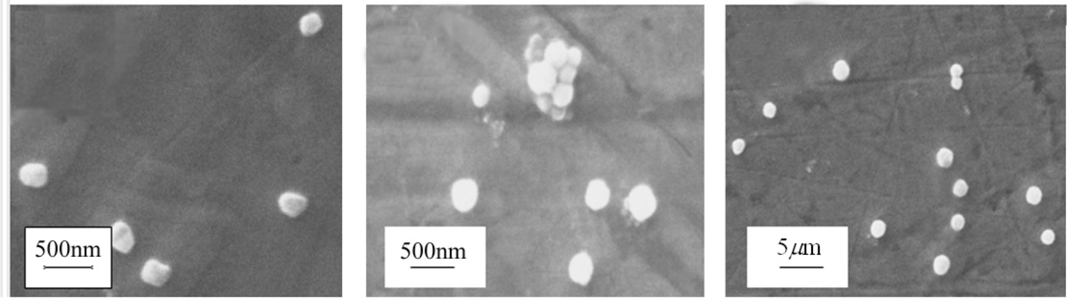
Firstly, finds the inflection point in the both sides of DTA curve peak-shaped. Secondly, makes tangent of passing DTA curve inflection point. Thirdly, makes lines parallel to longitudinal axis and passing the intersection of two tangents. Fourthly, makes lines parallel to horizontal axis, respectively with the two tangent intersections. The parallel line of horizontal axis is divided into two segments, these are respectively a and b. Reaction progression is defined as:

$$n = 1.26I1/2 \tag{6}$$

By the DTA curve, according to equation (6), the reaction progression n can be obtained. Using α, β, $d\alpha/dT$, n and equation (5), k is calculated.

2. Preparation and Characteristics of Cuprous Oxide Samples

0.4mol/L $CuSO_4$, 0.2 mol/L glucose and a little dispersant(PVP) mixed solution is preheated till appropriate temperature and the mixed solution is stirred. After that, 5mol/L NaOH solution is dropped at constant rate in that solution. Controlling pH value of the solution, reacts for 60 minutes. And then washes with distilled water and ethanol, centrifugates, dries, cuprous oxide powders are obtained. The samples is observd by SEM, the results are shown in Fig. 2.



a) b) c)

Fig. 2. SEM plots of different particle size Cu_2O

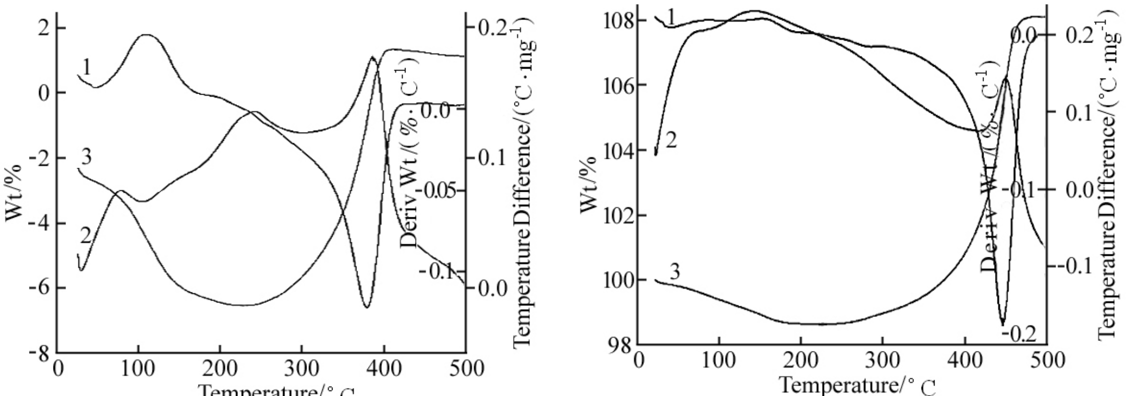
The reaction conditions are as follows: in case of sample a) stirring speed is 1 100r/min, pH of the reaction solution is 10.5, reaction temperature is 75℃, in case of sample b) stirring speed of is 1 500r/min, pH of the reaction solution is 12.88, reaction temperature is 75℃ and in case c) stirring speed is 1 200r/min, pH of the reaction solution is 12, reaction temperature is 80℃

Fig. 2 shows that the particle sizes of sample 1, 2, 3 are about 100, 200 and 1 000nm respectively.

3. Kinetics Calculation of Cu_2O Oxidation Reaction

The Cu_2O sample placed into platinum crucible was put in the "SDT-2960" thermal analysis system, made differential thermal analysis. The analysis condition is as follows: temperature rise rate is 15℃/min and reducing gas is air.

Fig. 3 shows DTA-TG-DTG curves of cuprous oxide oxidation reaction of different particle size.



a) b)

Fig. 3. DTA-TG-DTG curves of sample 1(a) and 3(b)

Fig. 3 shows that their initial oxidation reaction temperature, final oxidation reaction temperature and the DTA-TG-DTG curves peak temperature in cuprous oxide of different particle sizes were different.

Using DTA-TG-DTG curves data and equation (2), we calculated apparent activation energy *E* and frequency factors *A* in cuprous oxide of different size. Using the calculation results, relation curve between ln*k* and 1/*T* of cuprous oxide of different size was shown in Fig. 4.

Fig. 4 shows that relation between lnK and 1/*T* is linear and the oxidation reaction is Arrhenius type. By slope of the ln*k*~1/*T* relation graph, the apparent activation energy *E* of cuprous oxide of different sizes was obtained, frequency factors *A* were calculated by the intercept with the Kissinger method calculated the reaction progression *n*, the results were shown in table.

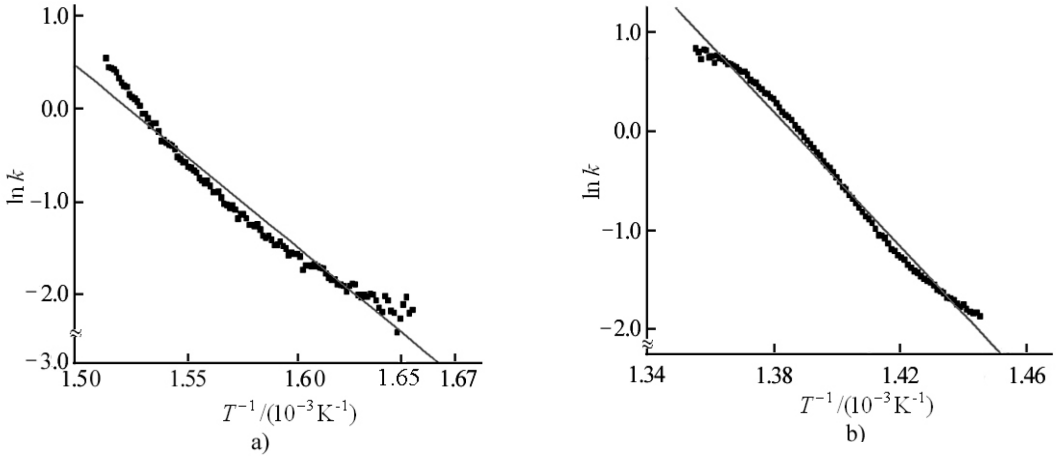


Fig. 4. Relation curve between ln*k* and 1/*T*

a) sample 1, b) sample 3

The table shows that apparent activation energy of oxidation reaction of cuprous oxide powders were respectively 164.38, 175.54, 282.65 kJ/mol respectively, the apparent activation energy increase with increasing of Cu_2O particle size; their frequency factors were respectively 1.22×10^{13}, 1.40×10^{13}, 2.88×10^{20}, the frequency factors increase with increasing of Cu_2O particle size; their reaction progressions were respectively 1.02, 1.00, 0.96, the reaction progressions decrease with Cu_2O particle size.

Table. Oxidation reaction kinetic parameters of cuprous oxide of different particle sizes

No.	Particle size/nm	Slope−E/R	*E*/(kJ · mol)	Intercept LnA	*A*	*n*
1	100	−19 772.07	164.38	30.13	1.22×10^{13}	1.02
2	200	−21 114.18	175.54	30.27	1.40×10^{13}	1.00
3	1 000	−33 996.57	282.65	47.11	2.88×10^{20}	0.96

Conclusion

The shapes of cuprous oxide powders were spherical, their particle sizes were 100, 200 and 1 000nm respectively. Their apparent activation energy were respectively 164.38, 175.54, 282.65 kJ/mol, the apparent activation energy increase with increasing of Cu_2O particle size.

Their frequency factors were respectively 1.22×10^{13}, 1.40×10^{13}, 2.88×10^{20}, the frequency factors increase with increasing of Cu_2O particle size. Their reaction progression were respectively 1.02, 1.00, 0.96, the reaction progressions decrease with increasing of Cu_2O particle size.

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