

Preparation of bismuth subcarbonate by liquid ball-milling transformation method from bismuth oxide

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Abstract: In order to solve the problems of environment pollution and high cost in traditional process of bismuth subcarbonate preparation, a new process using ball-milling transformation method from NH_4HCO_3 and Bi_2O_3 was proposed. Additionally, the kinetics of bismuth subcarbonate preparation was studied. Effects of reaction temperature, particle size of bismuth oxide, solid-to-liquid ratio and concentrations of ammonium bicarbonate on the conversion rate of bismuth oxide were studied. The results indicate that the conversion rate of bismuth oxide significantly increased under the conditions of higher temperature, smaller particle size, higher concentration of ammonium bicarbonate and smaller solid-to-liquid ratio. The XRD and ICP-AES analyses show that the purity of product is high. The reaction kinetics with activation energy of 9.783 kJ/mol was analyzed by shrinking core model, and the whole transformation process is controlled by solid product layer diffusion. A semi-empirical kinetics equation was obtained to describe the conversion process.

Key words: bismuth oxide; ball-milling transformation; bismuth subcarbonate; kinetics; shrinking core model

1 Introduction

Bismuth is a green and non-toxic metal. Since SILLÉN, a Swedish scientists, discovered the Sillén phase compound with layered structure by $(\text{Bi}_2\text{O}_2)^{2+}$ layers and the layers of X (X involving halogen, carbonate and other ionic groups) arranged alternately for the first time in 1942, bismuth subnitrate and bismuth subcarbonate as the deep-processing products of bismuth, which are of all Sillén phase compounds [1,2], have been widely applied in medical field, analytical reagents and bismuth compounds preparation [3–6]. The commercial route for the production of bismuth subcarbonate used bismuth nitrate as raw material, which was prepared by bismuth and nitric acid, and then bismuth compound was synthesized by the hydrolytic reactions of bismuth nitrate. A large amount of toxic gases and nitrogen dioxide were generated in this process, and it also has the shortcomings of consuming mass of acid and alkali reagents, having a long process and environmental pollution. CHEN et al [7] prepared bismuth subcarbonate nanoparticles by water-in-oil microemulsion-assisted hydrothermal process. DONG et al [8] studied rose-like

monodisperse bismuth subcarbonate synthesized by one-pot template-free method. CHENG et al [9] investigated bismuth subcarbonate nanomaterials synthesized by shape-controlled. CAO et al [10] used hydrothermal preparation means to prepare $(\text{BiO})_2\text{CO}_3$ with persimmon-like microstructure. These processes all have a long process as well as complicated device and high cost.

XIA et al [11] prepared $\alpha\text{-Bi}_2\text{O}_3$ through low-temperature oxidation process, and the results demonstrated that bismuth oxide was stable. The reaction conversion rate of bismuth oxide and ammonium bicarbonate solution was low in the natural state. Mechanical activation can accelerate the chemical reaction [12,13] due to the grain refinement and the lattice energy and defects increasing, so it has been widely used in materials preparing [14,15] and metallurgical process enhancing [16]. Zirconia ball is known to be a strong active medium in the milling process by surface friction and impact on the material, and it has been a intensified method for increasing the reaction conversion [17,18].

In this work, a new process using bismuth oxide and ammonium bicarbonate as raw materials to prepare

bismuth subcarbonate was proposed by liquid ball-milling transformation method. The new process could avoid to yielding NO_x toxic gases which was an inevitable by-product in the traditional process, and the mother solution from ball-milling process can be recycled after being treated, so it is a environment-friendly process. In the present work, the effects of temperature, particle size of Bi_2O_3 , solid-to-liquid ratio and concentration of ammonium bicarbonate on the conversion rate of Bi_2O_3 were interpreted, and reaction kinetics was analyzed.

2 Experimental

2.1 Materials

The bismuth oxide used in this experiment was provided by Jingtang Bismuth Company, Hunan Province, China. The chemical composition is listed in Table 1. The sample is a high-purity product and the content of Bi_2O_3 is 99.951%. NH_4NCO_3 used for reacting with Bi_2O_3 is analytical grade.

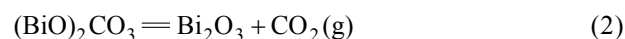
Table 1 Chemical composition of bismuth oxide (mass fraction, %)

Bi_2O_3	K(Na)	Cu	Ca	Fe	Si	Al	Sb
99.951	0.0008	0.0001	0.0033	0.0100	0.0025	0.0012	0.0016

2.2 Methods

The conversion experiments were carried out in a 1000 mL spherical glass reactor equipped with a mechanical stirrer and a temperature control unit, and activation medium was zirconia ball of 1 cm in diameter. 200 mL of solution containing specific NH_4HCO_3 was charged into the reactor. When the desired stirring speed and reaction temperature achieved their set values, the solid Bi_2O_3 was added into the reactor, and this moment was defined as the experiment start time. After the predetermined experimental time, the sample solution was taken out to filter and dry at 60 °C for 48 h.

A certain amount (m_1) of dried product was charged in an alumina crucible. After the total mass was measured, the crucible with sample was settled in the hot zone of the electric furnace to calcine the sample at 500 °C for 2 h. Yellow bismuth oxide powder was got after being calcined, and it was cooled to room temperature in a desiccator and then it was weighed (m_2). The conversion rate of bismuth oxide was calculated based on the mass difference before and after calcination. Related possible reactions were as follows:



Bi_2O_3 and HCO_3^- could react sufficiently under

ball-milling [19], and products were $(\text{BiO})_2\text{CO}_3$ and OH^- . The conversion rate of Bi_2O_3 was calculated by the following equation:

$$R = \frac{466(m_1 - m_2)}{44m_2} \times 100\% \quad (3)$$

where R is the conversion rate of Bi_2O_3 ; m_1 and m_2 are the masses of sample before and after calcined respectively.

3 Results and discussion

3.1 Effect of operation parameters on conversion rate of Bi_2O_3

The factors that might influence the conversion rate of Bi_2O_3 including ammonium bicarbonate concentration, the ratio of solid-to-liquid, reaction temperature and particle size of Bi_2O_3 were studied.

3.1.1 Effect of reaction temperature

The effect of temperature on conversion was investigated in the range from 282 to 323 K, at NH_4HCO_3 concentration 2 mol/L, particle size of Bi_2O_3 0.061–0.074 mm and solid-to-liquid 1:50. The relationship between conversion rate of Bi_2O_3 and reaction temperature is shown in Fig. 1(a).

As shown in Fig. 1(a), the conversion rate increases obviously with time and temperature increasing. The final conversion rate of Bi_2O_3 increases from 87.08% to 93.38% when the temperature changes from 282 to 303 K. Nevertheless, the conversion rate drops with temperature growing when the reaction temperature is over 303 K. The final conversion rate downs to 73.38% at 323 K. It can be explained that the reaction kinetics was accelerated by high temperature, but at the meanwhile, ammonium bicarbonate was decomposed to ammonia due to the high temperature [20,21], so actual concentrate of ammonium bicarbonate was reduced.

3.1.2 Effect of particle size of Bi_2O_3

The experiments were conducted in the particle size range of 0.026–0.038 mm to 0.250–0.180 mm, maintaining the ammonium bicarbonate concentrate at 2 mol/L, temperature at 293 K, and solid-to-liquid ratio at 1:50. The relationship between conversion rate of Bi_2O_3 and particle size of Bi_2O_3 is shown in Fig. 1(b).

As can be seen from Fig. 1(b), the conversion rate of Bi_2O_3 increases as the particle size of Bi_2O_3 decreases. When the particle size decreases from 0.250–0.180 mm to 0.026–0.038 mm, the final conversion rate correspondingly increases from 81.85% to 93.46%. Reducing the size of Bi_2O_3 particle is equivalent to increase the reaction surface. The gap is not obvious due to the little difference of particle size, but a small particle size has a positive effect on conversion rate.

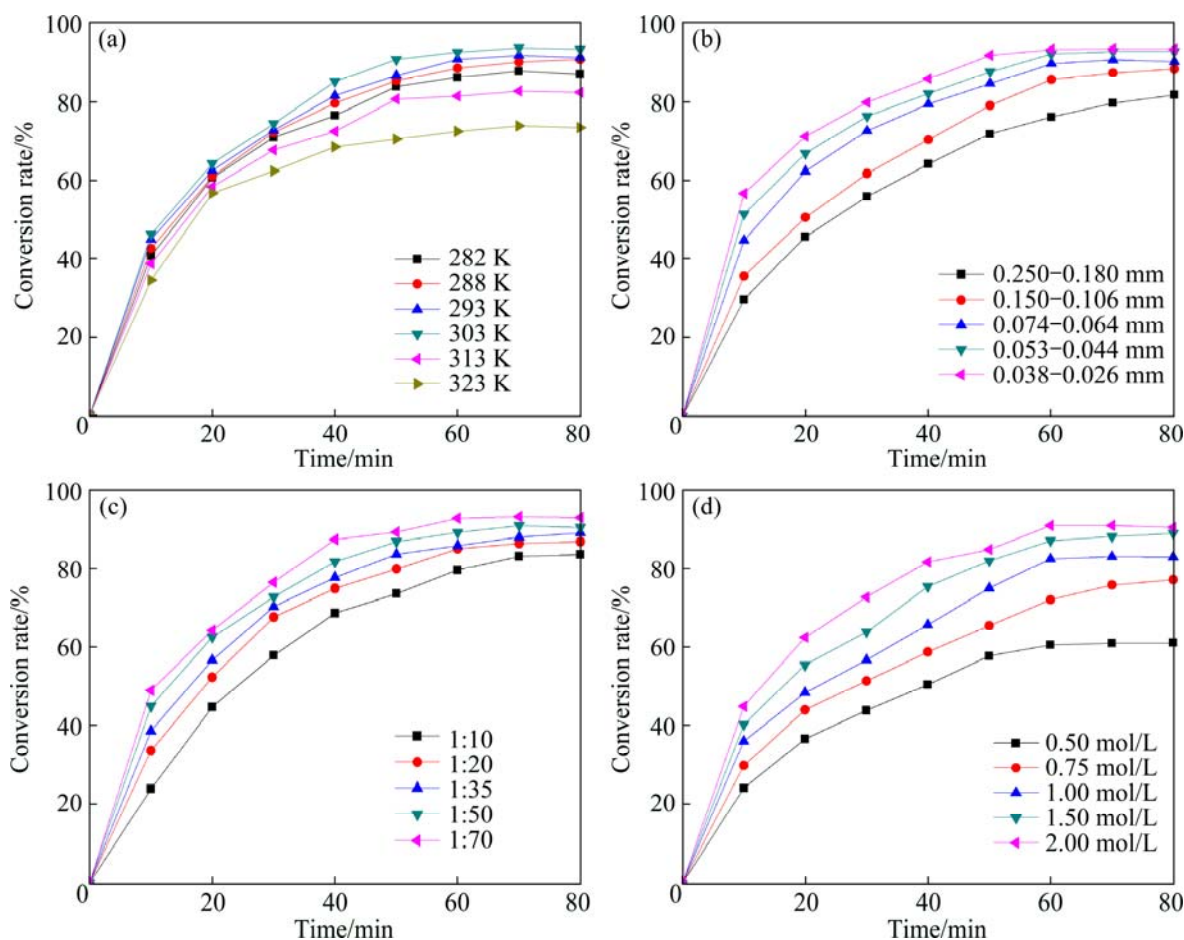


Fig. 1 Effects of operation parameters on conversion rate: (a) Temperature; (b) Particle size; (c) Solid-to-liquid ratio; (d) Ammonium bicarbonate concentration

3.1.3 Effect of solid-to-liquid ratio

The effect of solid-to-liquid ratio was investigated by running experiments using the solid-to-liquid ratio in the range from 1:10 to 1:70, when the temperature was 293 K, concentration of particle size of Bi_2O_3 was 0.061–0.074 mm and ammonium bicarbonate was 2 mol/L. The relationship between conversion rate of Bi_2O_3 and solid-to-liquid ratio is shown in Fig. 1(c).

When the solid-to-liquid ratio increases from 1:10 to 1:70, the final conversion rate of Bi_2O_3 increases from 83.45% to 92.86%. This indicates that increasing solid-to-liquid ratio could enhance the conversion rate of Bi_2O_3 . There is no significant change on the conversion of Bi_2O_3 with solid-to-liquid ratio increasing further. This can be explained that the ammonium bicarbonate is excess compared with calculated amount for the conversion of Bi_2O_3 .

3.1.4 Effect of ammonium bicarbonate concentration

The object of the experiments is to observe the influence of ammonium bicarbonate concentration on the conversion rate of Bi_2O_3 . These experiments were carried out at 293 K with solid-to-liquid ratio of 1:50 and

particle size of Bi_2O_3 of 0.061–0.074 mm. The concentration of ammonium bicarbonate was changed from 0.5 mol/L to 2 mol/L. The experimental results are shown in Fig. 1(d).

As shown in Fig. 1(d), the conversion rate of Bi_2O_3 increases quickly with the concentration of ammonium bicarbonate increasing. For concentration of NH_4HCO_3 increasing from 0.5 mol/L to 2 mol/L, the final conversion rate increases from 61.04% to 90.37%. This illustrates that the concentration of ammonium bicarbonate has a remarkable effect on conversion rate of Bi_2O_3 , because according to the mass action law, increasing the concentration of reactants could accelerate the reaction rate.

3.2 Characterization of product

The bismuth subcarbonate was obtained under the following conditions: solid-to-liquid ratio 1: 50, particle size of Bi_2O_3 0.061–0.074 mm, concentration of ammonium bicarbonate 2 mol/L and temperature 293 K. XRD, SEM and ICP-AES analyses of the product are presented in Fig. 2, Fig. 3 and Table 2, respectively.

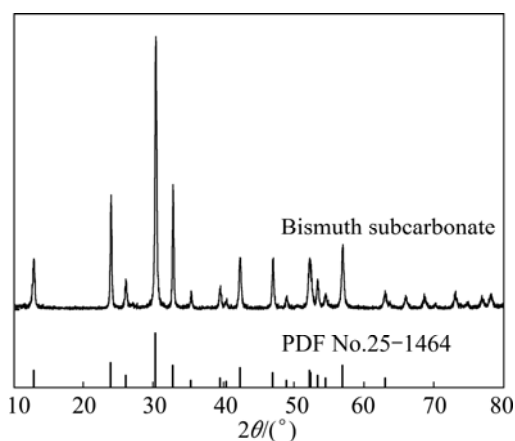


Fig. 2 XRD patterns of bismuth subcarbonate

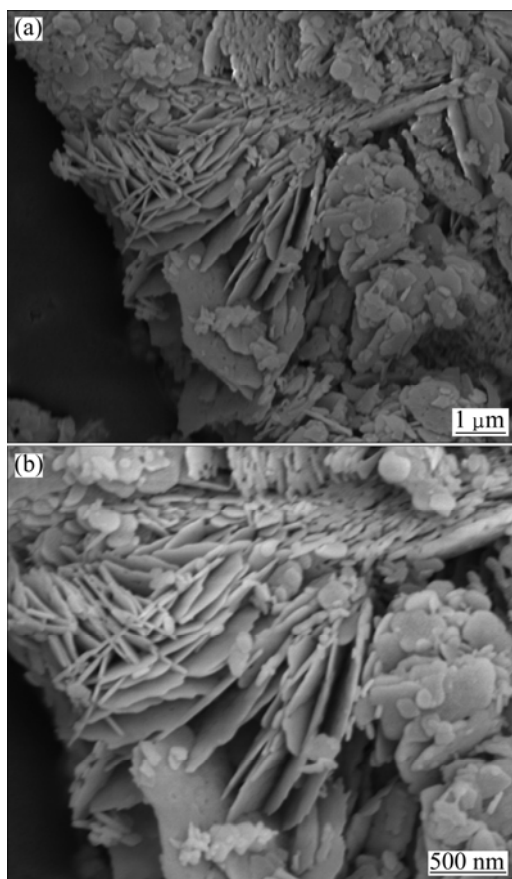


Fig. 3 SEM images of bismuth subcarbonate at different magnifications

Comparing the XRD pattern with the JCPDS files, it illustrates that almost all the peaks of product are identified as bismuth subcarbonate (JCPDS card, No.25-1464), and the impurity can be identified as bismuth oxide (JCPDS card, No.65-2366). SEM images of product illustrate that the morphology is nearly flaky.

As shown in Table 2, the contents of all impurities involving S, Sb, Sn, P, Fe, Ca, Na and Mg are lower than 0.02%, and the total amount of impurity is below 0.1%.

This illustrates that the product has a high purity and less impurity enters the product in preparation process.

Table 2 Chemical composition of bismuth subcarbonate (mass fraction, %)

Bi	S	Sb	Sn	P
86.89	0.010	0.005	0.001	0.001
Fe	Ca	Na	Mg	
0.001	0.022	0.020	0.008	

3.3 Kinetic analysis

The reaction process of Bi_2O_3 could be explained by a shrinking core model [22]. If the reaction rate is controlled by diffusion through a product layer, the kinetics equation is as follows [23,24]:

$$1 - \frac{2}{3}R - (1-R)^{\frac{2}{3}} = k_d t \quad (4)$$

If the reaction is controlled by a surface reaction, the kinetics equation is as follows [25]:

$$1 - (1-R)^{\frac{2}{3}} = k_r t \quad (5)$$

where R is the reacted fraction; t is the reaction time; k_d and k_r are the rate constants, respectively.

Equation (4) or (5) reveals that if the diffusion through the product layer or the surface reaction controls reactions rate, there must be a linear relationship between the $1 - (2/3)R - (1-R)^{2/3}$ or $1 - (1-R)^{2/3}$ and time. The slope is the apparent rate constant k_d or k_r .

The results of the analysis including the correlation coefficient (r^2) are shown in Table 3. As can be seen from Table 3, the diffusion controlled model fits better in two models. Using the apparent rate constant (k_d) obtained by Eq. (4), the Arrhenius plot is obtained (Fig. 4(a)). The activation energy is calculated to be 9.8138 kJ/mol. This value clearly confirms that this process was controlled by the diffusion through a product layer [26].

Table 3 Correlation coefficient (r^2) of two kinetics models at different temperatures

T/K	r^2	
	$1 - (1-R)^{1/3}$	$1 - (2/3)R - (1-R)^{2/3}$
282	0.9230	0.9824
288	0.9115	0.9694
293	0.9426	0.9890
303	0.9392	0.9762

A series of well-fitted plots of $1 - (2/3)R - (1-R)^{2/3}$ versus time at different temperatures, particle sizes, solid-to-liquid ratios, ammonium bicarbonate

concentrations are given in Fig. 5.

In order to determine the effect of temperature, particle size, solid-to-liquid ratio (ρ), concentration of ammonium bicarbonate on the reaction kinetics, the following semi-empirical model was established [27]:

$$1-(2/3)R-(1-R)^{2/3}=k_0C_{\text{NH}_4\text{HCO}_3}^aD^b\rho^c\exp[-E/(RT)]t \quad (6)$$

where T is the temperature; $C_{\text{NH}_4\text{HCO}_3}$ is the concentration of ammonium bicarbonate; D is the particle size; k_0 is the apparent reaction rate coefficient; and E is the activation energy.

To different ammonium bicarbonate concentrations, when other parameters maintain constant, Eq. (6) could be written as

$$1-(2/3)R-(1-R)^{2/3}=K_1C_{\text{NH}_4\text{HCO}_3}^at \quad (7)$$

$$\ln\{d[1-(2/3)R-(1-R)^{2/3}]/dt\}=\ln K_1+a\ln C_{\text{NH}_4\text{HCO}_3} \quad (8)$$

where $\{d[1-(2/3)R-(1-R)^{2/3}]/dt\}$ is the slope of the straight lines corresponding to different ammonium bicarbonate concentrations in Fig. 4(d). The values of $\ln\{d[1-(2/3)R-(1-R)^{2/3}]/dt\}$ versus $\ln C_{\text{NH}_4\text{HCO}_3}$ are

plotted to form a straight line, and from the slope, it is calculated $a=0.82683$. In a similar way the empirical reaction orders obtained for particle size and solid-to-liquid ratio are -0.36567 and 0.24977 , respectively, as shown in Fig. 5.

Substituting the values of a , b , c and E into Eq. (6), the value of k_0 is calculated to be about 0.0018274 when using the equation to fit different straight lines in Fig. 4. So, the kinetics equation was established as follows: $1-(2/3)R-(1-R)^{2/3}=0.0018274C_{\text{NH}_4\text{HCO}_3}^{0.82683}D^{-0.36567}\rho^{0.24977}\exp[-9.8138/(RT)]t$.

4 Conclusions

1) The results show that temperature, particle size, solid-to-liquid ratio and concentration of ammonium bicarbonate have favorable influence on the conversion rate of Bi_2O_3 . Small particle size and solid-to-liquid ratio, large concentration of ammonium and high temperature below 303 K will increase the conversion rate.

2) The conversion rate of Bi_2O_3 is controlled by the diffusion through the ash layer around the shrinking unreacted core and the activation energy is calculated to

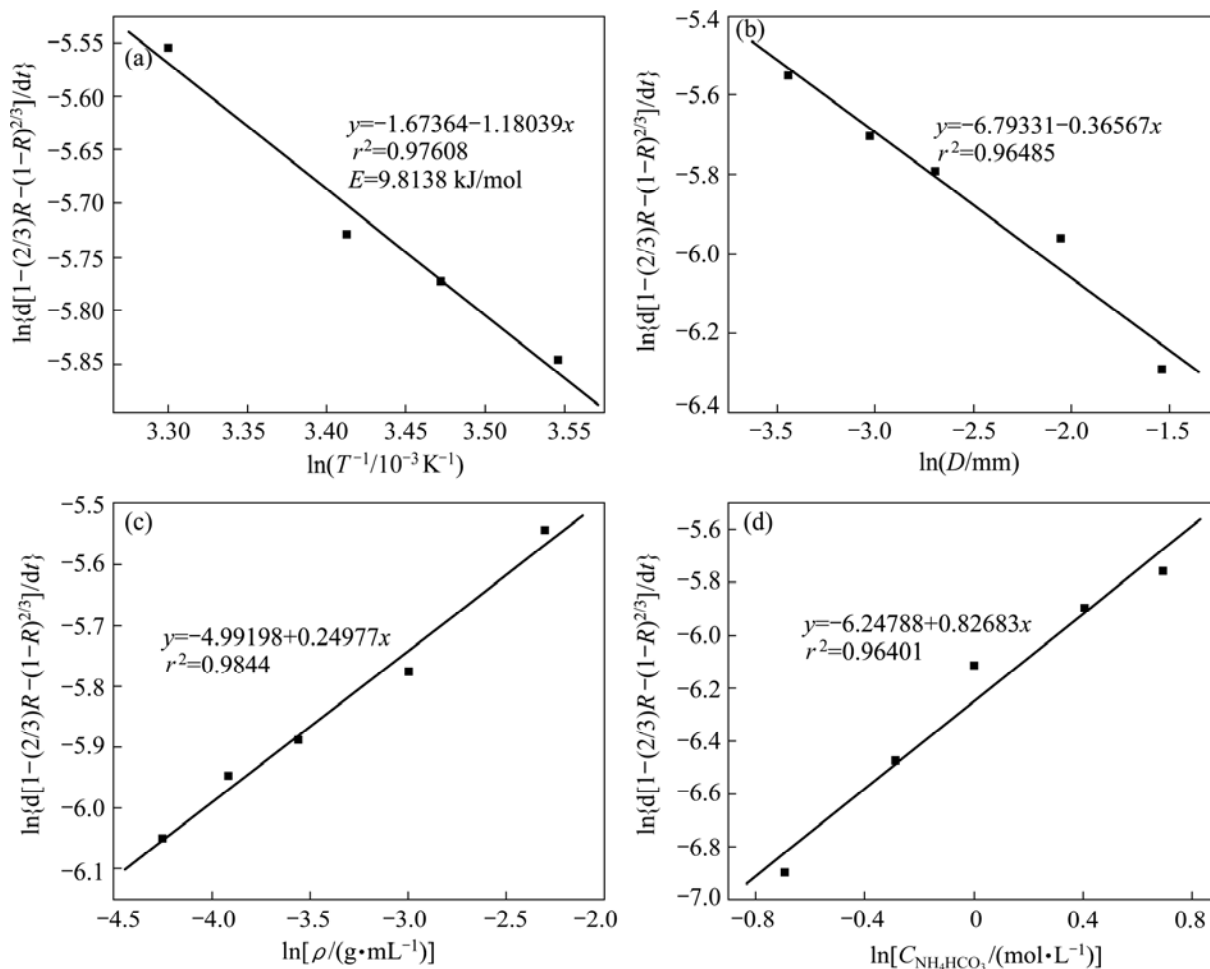


Fig. 4 Plots of $\ln\{d[1-(2/3)R-(1-R)^{2/3}]/dt\}$ versus $1/T$, $\ln \rho$, $\ln D$, $\ln C_{\text{NH}_4\text{HCO}_3}$

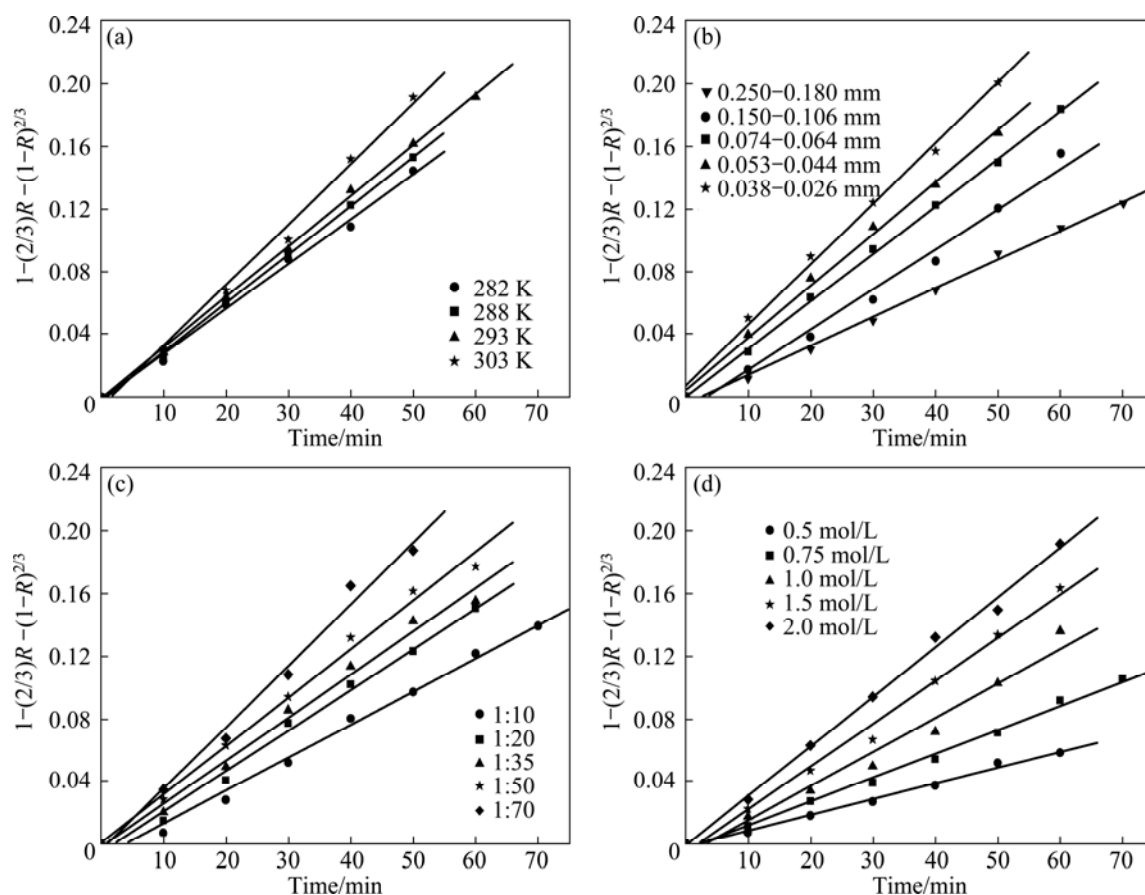


Fig. 5 Plots of t versus $1-(2/3)R-(1-R)^{2/3}$ at different operation parameters: (a) Temperature; (b) Particle size; (c) Solid-to-liquid ratio; (d) Ammonium bicarbonate concentration

be 9.8138 kJ/mol.

3) The reaction kinetics could be described by the following equation:

$$1-(2/3)R-(1-R)^{2/3}=0.0018274C_{\text{NH}_4\text{HCO}_3}^{0.82683}D^{-0.36567}\cdot\rho^{0.24977}\exp[-9.8138/(RT)]t.$$

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液相球磨法由氧化铋制备次碳酸铋的动力学

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摘 要:为解决传统次碳酸铋生产过程中成本高和环境污染问题, 提出采用液相球磨法由氧化铋制备次碳酸铋的新工艺, 研究用碳酸氢氨和氧化铋制备次碳酸铋反应过程的动力学, 考察反应温度、氧化铋粒度、液固比以及碳酸氢氨浓度对氧化铋转化率的影响。结果表明, 在 9~30 °C 的范围内, 升高反应温度、减小氧化铋粉末的粒度、扩大液固比以及提高碳酸氢氨浓度均有利于氧化铋转化率的提高。对反应产物的表征分析表明, 产品的纯度较高、杂质少; SEM 结果显示产品次碳酸铋主要呈针棒状形态。反应过程受产物层的扩散控制, 可用未反应收缩核模型描述, 反应的表现活化能为 9.783 kJ/mol, 同时获得了描述反应过程的半经验动力学方程。

关键词: 氧化铋; 球磨转化; 次碳酸铋; 动力学; 收缩核模型

(Edited by Xiang-qun LI)