

AN *IN SITU* KINETIC STUDY OF THE DEHYDRATION OF BRUCITE USING SYNCHROTRON X-RAY POWDER DIFFRACTION

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ABSTRACT

The dehydration kinetics of brucite were studied *in situ* by synchrotron X-ray powder diffraction (XRPD) in the temperature range 320–370 °C. The sequence of XRD spectra clearly reveals that the phase transformation of brucite into periclase occurs with increasing temperature up to 600 °C under ambient pressure. Our results show that there is a positive temperature dependence of the reaction rate k . Elevated temperatures will be conducive to the dehydration process. The obtained n values suggest that the reaction mechanism is a one-dimensional diffusion of the water molecules with an instantaneous nucleation. The influence of temperature on the reaction rate is well described by the Arrhenius equation, which yields an apparent activation energy E_a of 386 ± 12 kJ/mol and frequency factor A of $1.14 \times 10^{29} \text{ s}^{-1}$. The activation energy is influenced by factors such as grain size, shape, temperature, gas atmosphere, and surrounding water.

Keywords: high temperature, brucite, X-ray diffraction, dehydration, kinetics.

INTRODUCTION

Brucite, $\text{Mg}(\text{OH})_2$, is one of the most widely used inorganic materials, with many applications in industry (Kumari *et al.* 2009, Pilarska *et al.* 2017, Yousefi *et al.* 2017). Because of its structural and chemical simplicity, brucite serves as a useful prototype for hydrous and layer minerals. At ambient pressure and high temperature, brucite decomposes to periclase (MgO) and water (H_2O) and the dehydration reaction can be

written as $\text{Mg}(\text{OH})_2(\text{s}) = \text{MgO}(\text{s}) + \text{H}_2\text{O}(\text{l})$. In recent decades the kinetics of thermal decomposition of brucite have been extensively studied (Turner *et al.* 1963, Gordon & Kingery 1967, Lonvik 1978, Bhatti & Dyer 1984, Halikia *et al.* 1998, Su *et al.* 2008, Nahdi *et al.* 2009, Hollingbery & Hull 2010, Tritschack *et al.* 2014). However, the kinetic parameters, particularly the measured activation energies, are substantially different and there is no general agreement on the mechanism of thermal decomposition. Therefore,

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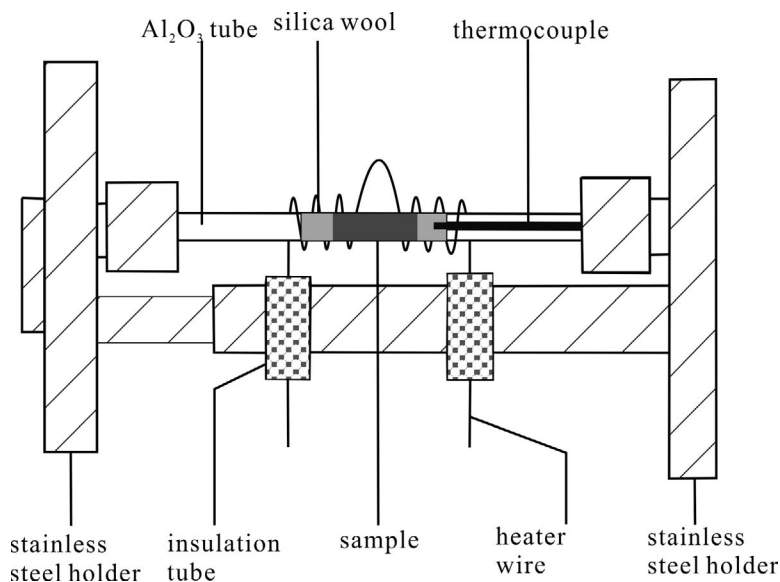


Fig. 1. Cell assembly used for the *in situ* X-ray powder diffraction study at high temperature.

further studies of the dehydration kinetics of brucite using other methods, such as X-ray powder diffraction (XRPD), should be conducted to confirm the previous results.

In the present work, we measured the kinetics of dehydration of brucite *in situ* at high temperature with synchrotron radiation. New experimental data from high time-resolved X-ray powder diffraction study have been acquired. The kinetic analysis using the classical Avrami models yields parameters useful for the interpretation of the reaction mechanism and allows the calculation of the apparent activation energy.

EXPERIMENTAL METHODS

The selected starting material in this study was reagent-grade magnesium hydroxide [$\text{Mg}(\text{OH})_2$], which was commercially obtained from Alfa Aesar Chemical Ltd. (China). The grain size of the sample was in the range of 5–10 μm . X-ray fluorescence (XRF) analysis was performed using an ARLAD-VANT XP+ scanning wavelength dispersive X-ray fluorescence spectrometer, which was manufactured by Thermo Electron Corporation in the United States. The results showed that the powdered sample of synthetic brucite has an average chemical composition of MgO (64.36%), SiO_2 (3.19%), CaO (0.70%), Cl (0.32%), Fe_2O_3 (0.17%), and Al_2O_3 (0.15%) by weight.

In situ high-temperature X-ray powder diffraction (XRPD) measurements of brucite were carried out using synchrotron radiation at beamline BL14B1 of the Shanghai Synchrotron Radiation Facility (SSRF, Shanghai, China). A prominent advantage of the synchrotron-based technique is its very high photon flux and high stability, which is necessary for *in situ* real time studies at non-ambient conditions (Yang *et al.* 2015). The energy and the spot size of the X-ray beam were 18 keV and 0.2 mm(*H*) $\times$ 0.3 mm(*V*), using a wavelength of 0.6887 Å. The sample signal was collected by a MARCCD area detector, which provides a large surface of detection, high resolution, wide dynamic range, and fast readings for kinetic experiments.

The high-temperature cell assembly used for the *in situ* measurements is presented in Figure 1. The brucite sample was loaded into an Al_2O_3 capillary tube with a diameter of ~ 1 mm; some silica wool was placed at both sides of the sample to prevent it from moving. Kanthal heating wire was uniformly wrapped around the outside of the Al_2O_3 tube to avoid temperature gradients. A *K*-type thermocouple (diameter of 0.6 mm) was closely attached to the silica wool surface for accurate temperature measurements.

In our study, two sets of experiments were carried out under atmospheric pressure. In the first experiments, the high-temperature phase transition of brucite was studied at a constant heating rate of 10 $^\circ\text{C}/\text{min}$ over a temperature range of 25 to 600 $^\circ\text{C}$. In addition, time-resolved isothermal runs for the dehydration

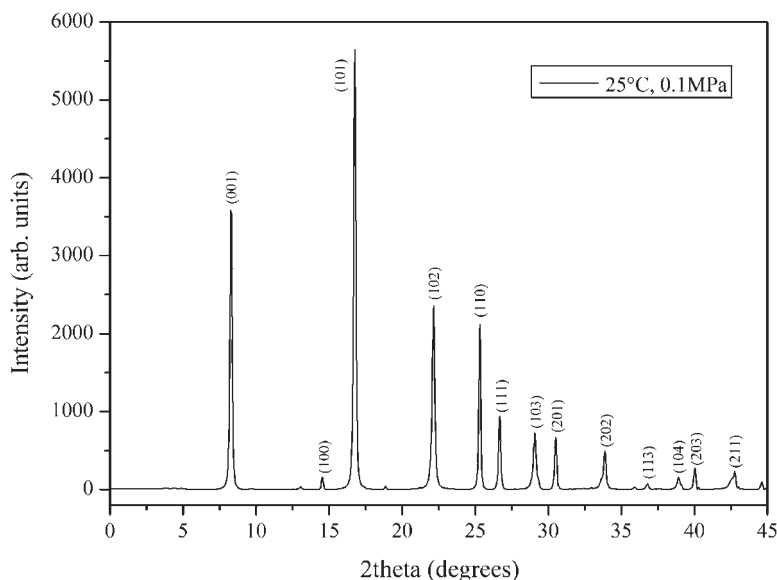


FIG. 2. The XRD pattern of the starting sample of brucite acquired at ambient conditions.

kinetics of brucite were performed at temperatures of 320, 330, 340, 350, 360, and 370 °C, which is similar to the previous kinetic study of gypsum dehydration reported by Liu *et al* (2015). At each isothermal condition, the first measurement was immediately done once the desired temperature was achieved, which was then held constant throughout the experiment. During transition the counting time for each diffraction pattern was 60 s and patterns were collected every 0.5–4 min at each temperature from 320 to 370 °C, with an interval of 10 °C.

In this work, the dehydration process was analyzed in terms of the classical Avrami kinetic equation describing nucleation and growth processes (Avrami 1939, 1940, 1941). The relationship between transformed fraction $X(t)$ and time (t) takes the form

$$X(t) = 1 - \exp(-kt^n) \quad (1)$$

and after linearization, it gives

$$\ln \ln \left[\frac{1}{1 - X(t)} \right] = \ln k + n \ln t \quad (2)$$

where k is the rate constant in s^{-n} and n the exponent dependent on the reaction mechanism. We can extract the exponent n from the slope and the reaction rate k from the intercept $n \ln k$ in the corresponding $\ln \ln[1/(1 - X(t))]$ versus $\ln t$ plot. It is assumed that the theoretical n value varies from 0.5 to 4 for the Avrami equation and it may also provide information on the nucleation type and the crystal growth geometry (Cahn 1956, Christian 1975).

Following the Arrhenius equation, Equation 3, the temperature-dependent reaction rate k was used to calculate the apparent activation energy E_a from the slope, and the pre-exponential factor A from the intercept in the linear plot of $\ln k$ versus $1/T$

$$k = A \exp \left(-\frac{E_a}{RT} \right) \quad (3)$$

where R is the gas constant and T is the absolute temperature in Kelvin. Writing Equation 3 in logarithmic form:

$$\ln k = \ln A - \frac{E_a}{RT} \quad (4)$$

Therefore, the plot of $\ln k$ versus $1/T$ gives a slope of $-E_a/R$ and an intercept of $\ln A$.

RESULTS AND DISCUSSION

Figure 2 shows the X-ray diffractogram of brucite at ambient conditions. The diffraction lines are attributed to the planes (001), (100), (101), (102), (110), (111), (103), (201), (202), (113), (104), (203), and (211) of well-crystallized $Mg(OH)_2$. Based on the XRD pattern in this study, the ambient unit-cell parameters for brucite are determined to be $a = 3.141 \text{ \AA}$, $b = 3.141 \text{ \AA}$, $c = 4.761 \text{ \AA}$, $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$, which are in good agreement with the published crystal structure data (Yu *et al.* 2011). As reported in the literature, the dehydration of brucite initially produces periclase and H_2O at about 573–603

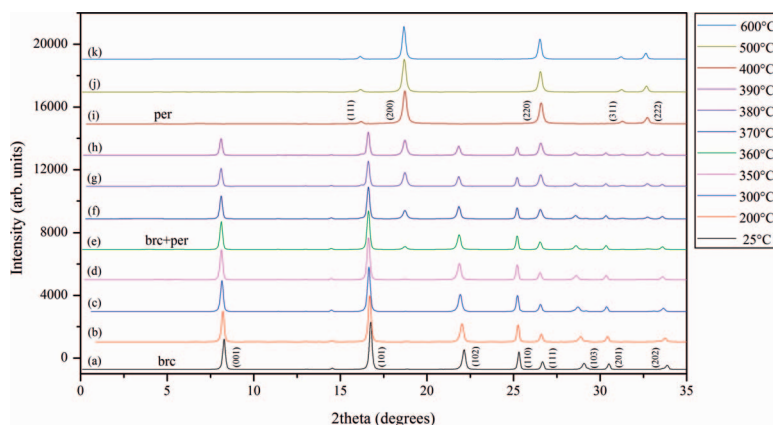
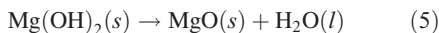


FIG. 3. Selected X-ray diffraction patterns of brucite obtained in this study up to 600 °C. Abbreviations: bru - brucite, per - periclase.

K and ambient pressure (Ball & Taylor 1961, Nahdi *et al.* 2009, Pfeiffer 2011) and the chemical reaction can be represented as:



A typical XRD spectral change during the *in situ* heating experiment was used to identify the diffractometric fingerprints of each phase occurring in the dehydration process up to 600 °C, as shown in Figure 3. We can see that no significant dehydration of brucite was observed at 25–350 °C (Fig. 3a–d). Upon heating, the peaks (001), (101), (102), (110), (103), (201), and (202) started to decrease in intensity due to the further breakdown of brucite from 360 to 390 °C (Fig. 3e–h). A new diffraction peak (200) appeared at $2\theta = 18.7^\circ$ as the temperature increased to 360 °C, indicating the onset of a phase transformation in brucite (Fig. 3e). With a further increase of temperature to 400 °C, the peaks (200), (220), and (222) continually increased in intensity, and two weak peaks, (111) and (311), were also observed (Fig. 3e–i). The diffraction intensities of the (200), (220), (222), (111), and (311) peaks almost persisted to a higher temperature, as seen from the diffraction patterns at 500 and 600 °C. However, these diffraction peaks assigned to brucite fully disappeared at 400 °C, reflecting a complete phase transformation. After that, no new peaks appeared or disappeared when temperature was elevated from 400 to 600 °C (Fig. 3i–k), implying that the new phase identified as periclase (MgO) remained stable in the present temperature range.

High temperature *in situ* X-ray experiments of the dehydration kinetics of brucite were performed at temperatures of 320, 330, 340, 350, 360, and 370 °C. A typical sequence of X-ray diffraction patterns with

increasing time as for the example at 350 °C is displayed in Figure 4, and the relatively strong (101) and (001) diffraction lines located at $2\theta = 16.6^\circ$ and 8.1° were selected to monitor the transformation of brucite to periclase. We can see that the (101) and (001) diffraction peaks remarkably decreased in intensity with time before and after dehydration, which is attributed to the continuous reduction of hydroxyl molecules in the crystal structure of brucite. These obvious changes also indicate an increasing dehydration degree at this isothermal condition.

The plots of $\ln[1/(1 - X(t))]$ versus $\ln(t)$ for six rounds of dehydration kinetics experiments are presented in Figure 5a–f. All the obtained k and n values, including the corresponding correlation value R^2 , for each isothermal experiment are listed in Table 1. It can be seen that all the experimental data take on a good linear relationship and the two straight lines for $2\theta = 16.6^\circ$ and 8.1° are approximately parallel due to the high precision of the measured data. Based on the intercept of the fitted straight line, the calculated dehydration rate k of brucite increases from 9.90×10^{-6} to $4.18 \times 10^{-3} \text{ s}^{-n}$ with increasing temperature from 320 to 370 °C, which shows a positive dependence of dehydration rate on temperature during the phase transformation. The Avrami exponents n are derived from the slope of plots of $\ln[1/(1 - X(t))]$ against $\ln(t)$ and linear least-square fits to these data give values of n in the range 1.09–1.30 for the six kinetic experiments, thus indicating almost the same reaction mechanism. These results point to the formation of periclase being controlled by the diffusion-controlled growth process, following rapid saturation of crystal nucleation sites (Christian 1975). Therefore, it is concluded that the dehydration of brucite should be dominated by an instant nucleation and one-dimensional diffusion-controlled growth.

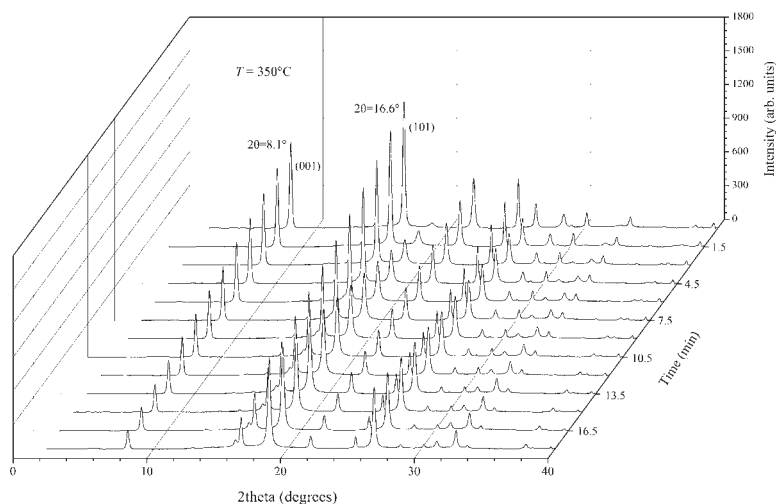


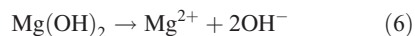
FIG 4. A typical sequence of X-ray diffraction patterns of brucite as a function of time at 350 °C during dehydration. The (001) and (101) peaks used to estimate the extent of transformation are indexed.

Rate constants k obtained from the various isothermal experiments were plotted against temperature as $\ln k$ versus $1/T$, as shown in Figure 6. The negative slope of the straight line also indicates a positive temperature dependence of the dehydration rate, which is in accordance with the results obtained by the kinetic analysis. Based on Equation 4, the Arrhenius relation provides an empirical activation energy E_a of 386 ± 12 kJ/mol and frequency factor A of $1.14 \times 10^{29} \text{ s}^{-1}$ with a regression coefficient of 0.989. It is obvious that, within the temperature range, $\ln k$ is linearly dependent on $1/T$, clearly indicating the occurrence of a single mechanism of dehydration.

The activation energy for the dehydration of brucite obtained in this study is almost in agreement with the E_a value of 372 kJ/mol given by Mu & Perlmutter (1981). However, this resulting E_a value in air is markedly larger than that of 121 kJ/mol obtained in vacuum at 550–663 K (Gordon & Kingery 1966, 1967). As reported earlier, Nahdi *et al.* (2009) gave an E_a value of 188 ± 10 kJ/mol for the dehydroxylation of brucite studied under water vapor pressure, and an E_a value of 166–173 kJ/mol was also calculated for the thermal dehydration of brucite in vacuum and under isothermal conditions (Lvov *et al.* 1998, Lvov & Ugolkov 2004), which were lower than that determined in our work (386 ± 12 kJ/mol). It is noteworthy that a significant disagreement in the E_a value is observed in the case of powder decomposition in air and in vacuum, though again, the compared results for powder decomposition in the presence of N_2 are in good agreement. These discrepancies can be attributed to the specific features of temperature distribution in powders dehydrated in vacuum. Additionally, other factors such

as sample size, sample preparation, and heating rate very likely affect the results.

As for the dehydration of brucite at elevated temperatures, the chemical bonds between Mg^{2+} and OH^- first break at the initial stage of dehydration, which can be simply written as



After that, the formation and migration of water molecules proceeds, followed by diffusion out of the crystal structure with increasing temperature. As noted earlier, donor and acceptor regions develop in the brucite crystal during the dehydration, and migration of magnesium and hydrogen ions occurs in opposite directions. The acceptor regions become MgO crystals and hydrogen ions combine with hydroxyl ions to form water molecules (Ball & Taylor 1961, Brindley 1963). It is also possible that the counter-migration of cations away from reaction zones such as external surfaces and grain boundaries leads to the formation of pores which would facilitate the loss of water (Taylor 1962). The dehydration of brucite involving proton migration and water formation can therefore be represented as



At a higher temperature, the O–H bond is more easily destroyed under the action of high energy, and as a result dehydration reactions (6) and (7) will be promoted.

CONCLUSIONS

The dehydration kinetics of brucite were investigated *in situ* using time-resolved synchrotron X-ray

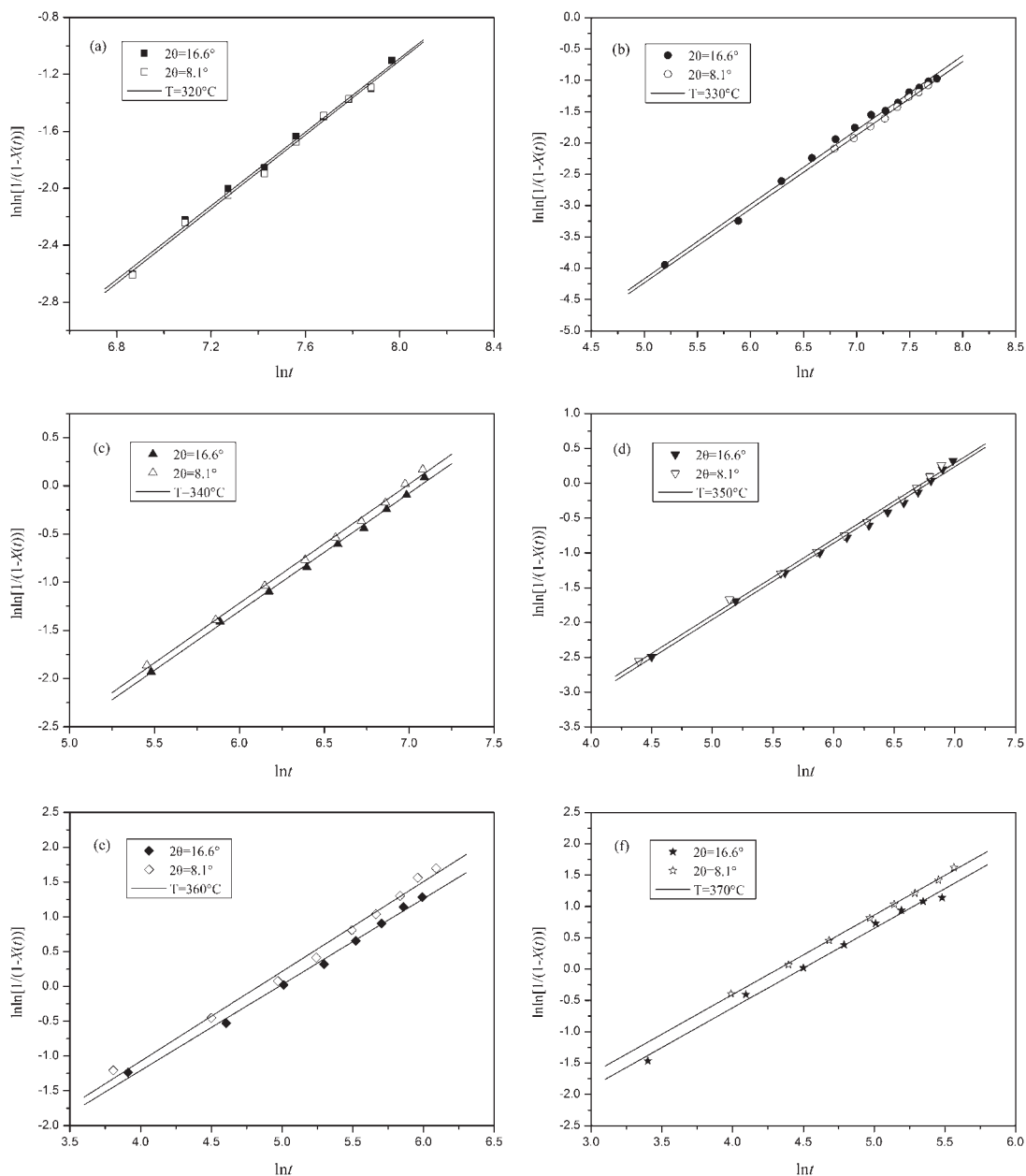


FIG. 5. Plots of $\ln[1/(1-X(t))]$ versus $\ln t$ corresponding to diffraction peaks at $2\theta = 8.1$ and 16.6° for the isothermal kinetic experiments (a–f). The slope of the regression line (n) is related to the order of the reaction.

powder diffraction (XRPD) in the temperature range 320–370 °C. Based on the Avrami kinetic model, the analysis of the transformation-time data at isothermal conditions shows that temperature elevation can accelerate the dehydration rate of brucite from 9.90×10^{-6} to $4.18 \times 10^{-3} \text{ s}^{-n}$ under the action of higher

energy, thus indicating a positive dependence of reaction rate on temperature. The obtained n values of 1.09–1.30 suggest that the reaction mechanism is characterized by instantaneous nucleation and diffusion-controlled growth, and that the rate-limiting step of the reaction is one-dimensional diffusion. The

TABLE 1. CALCULATED n AND k VALUES FOR THE DEHYDRATION REACTION OF BRUCITE

	T (°C)	n	$\ln k$	k (s ⁻ⁿ)	R^2	E_a (kJ/mol)
$2\theta = 16.6^\circ$	320	1.29(±0.04)	-11.44(±0.28)	1.07×10^{-5}	0.994	386 ± 12
	330	1.19(±0.02)	-10.11(±0.17)	4.08×10^{-5}	0.995	
	340	1.22(±0.02)	-8.65(±0.13)	1.75×10^{-4}	0.998	
	350	1.10(±0.02)	-7.45(±0.14)	5.83×10^{-4}	0.995	
	360	1.23(±0.03)	-6.15(±0.17)	2.14×10^{-3}	0.995	
	370	1.27(±0.04)	-5.69(±0.20)	3.38×10^{-3}	0.992	
$2\theta = 8.1^\circ$	320	1.30(±0.04)	-11.52(±0.28)	9.90×10^{-6}	0.994	
	330	1.18(±0.04)	-10.12(±0.26)	4.04×10^{-5}	0.994	
	340	1.24(±0.02)	-8.64(±0.14)	1.77×10^{-4}	0.998	
	350	1.09(±0.02)	-7.36(±0.13)	6.35×10^{-4}	0.996	
	360	1.29(±0.04)	-6.24(±0.23)	1.96×10^{-3}	0.991	
	370	1.27(±0.02)	-5.48(±0.09)	4.18×10^{-3}	0.999	

R^2 indicates the correlation factor for the fitting.

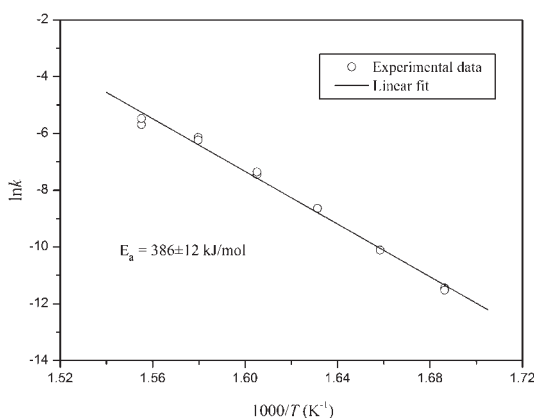


FIG. 6. Arrhenius plot of $\ln k$ against $1/T$ for calculation of the apparent activation energy of the dehydration reaction.

calculated apparent activation energy E_a and frequency factor A are 386 ± 12 kJ/mol and 1.14×10^{29} s⁻¹, respectively. With regard to the considerably different values of E_a obtained by various experimental methods, attention should be paid to important factors such as grain size, crystallinity, and shape, as well as environmental controls such as temperature, water-vapor pressure, gas atmosphere, and the presence of surrounding water.

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REFERENCES

- AVRAMI, M. (1939) Kinetics of phase change. I General theory. *Journal of Chemical Physics* **7**, 1103–1112.
- AVRAMI, M. (1940) Kinetics of phase change. II Transformation time relations for random distribution of nuclei. *Journal of Chemical Physics* **8**, 212–224.
- AVRAMI, M. (1941) Granulation, phase change, and microstructure kinetics of phase change. III. *Journal of Chemical Physics* **9**, 177–184.
- BALL, M.C. & TAYLOR, H.F.W. (1961) The dehydration of brucite. *Mineralogical Magazine* **32**, 754–766.
- BHATTI, A. & DYER, D.D. (1984) Decomposition kinetics of magnesium hydroxide using DTA. *Thermochimica Acta* **78**, 55–62.
- BRINDLEY, G.W. (1963) Crystallographic aspects of some decomposition and recrystallization reactions. *Progress in Ceramic Science* **3**, 1–55.
- CAHN, J.W. (1956) The kinetics of grain boundary nucleated reactions. *Acta Metallurgica* **4**, 449–459.
- CHRISTIAN, J.W. (1975) *The theory of transformations in metals and alloys: Equilibrium and general kinetic theory*. Pergamon Press, Oxford, England.
- GORDON, R.S. & KINGERY, W.D. (1966) Thermal decomposition of brucite: I, Electron and optical microscope studies. *Journal of the American Ceramic Society* **49**, 654–660.
- GORDON, R.S. & KINGERY, W.D. (1967) Thermal decomposition of brucite: II, Kinetics of decomposition in vacuum. *Journal of the American Ceramic Society* **50**, 8–14.
- HALIKIA, I., NEOU-SYNGOUNA, P., & KOLITSA, D. (1998) Isothermal kinetic analysis of the thermal decomposition

- of magnesium hydroxide using thermogravimetric data. *Thermochimica Acta* **320**, 75–88.
- HOLLINGBERY, L.A. & HULL, T.R. (2010) The thermal decomposition of huntite and hydromagnesite – a review. *Thermochimica Acta* **509**, 1–11.
- KUMARI, L., LI, W.Z., VANNOY, C.H., LEBLANC, R.M., & WANG, D.Z. (2009) Synthesis, characterization and optical properties of $\text{Mg}(\text{OH})_2$ micro-/nanostructure and its conversion to MgO . *Ceramics International* **35**, 3355–3364.
- LIU, C.J., ZHENG, H.F., & WANG, D.J. (2015) The dehydration kinetics of gypsum at high pressure and high temperature. *High Pressure Research* **35**, 273–281.
- LONVIK, K. (1978) An experimental investigation of the thermal decomposition of brucite by thermosoniometry. *Thermochimica Acta* **27**, 27–44.
- LVOV, B.V. & UGOLKOV, V.L. (2004) Kinetics and mechanism of free-surface decomposition of group II A and II B hydroxides analyzed thermogravimetrically by the third-law method. *Thermochimica Acta* **413**, 7–15.
- LVOV, B.V., NOVICHKIN, A.V., & DYAKOV, A.O. (1998) Mechanism of thermal decomposition of magnesium hydroxide. *Thermochimica Acta* **315**, 135–143.
- MU, J. & PERLMUTTER, D.D. (1981) Thermal decomposition of carbonates, carboxylates, oxalates, acetates, formates, and hydroxides. *Thermochimica Acta* **49**, 207–218.
- NAHDI, K., ROUQUEROL, F., & AYADI, M.T. (2009) $\text{Mg}(\text{OH})_2$ dehydroxylation: A kinetic study by controlled rate thermal analysis (CRTA). *Solid State Sciences* **11**, 1028–1034.
- PFEIFFER, H. (2011) Thermal analysis of the $\text{Mg}(\text{OH})_2$ dehydroxylation process at high pressures. *Thermochimica Acta* **525**, 180–182.
- PILARSKA, A.A., KLAPISZEWSKI, L., & JESIONOWSKI, T. (2017) Recent development in the synthesis, modification and application of $\text{Mg}(\text{OH})_2$ and MgO : A review. *Powder Technology* **319**, 373–407.
- SU, D., JIANG, N., SPENCE, J.C.H., HE, F., & PETUSKEY, W.T. (2008) On the dehydration mechanism of $\text{Mg}(\text{OH})_2$ by a high-energy electron beam. *Journal of Applied Physics* **104**, 063514.
- TAYLOR, H.F.W. (1962) Homogeneous and inhomogeneous mechanism in the dehydroxylation of Minerals. *Clay Minerals* **5**, 45–55.
- TRITTSCHACK, R., GROBET, B., & BRODARD, P. (2014) Kinetics of the chrysotile and brucite dehydroxylation reaction: a combined non-isothermal/isothermal thermogravimetric analysis and high-temperature X-ray powder diffraction study. *Physics and Chemistry of Minerals* **41**, 197–214.
- TURNER, R.C., HOFFMAN, I., & CHEN, D. (1963) Thermogravimetry of the dehydration of $\text{Mg}(\text{OH})_2$. *Canadian Journal of Chemistry* **41**, 243–251.
- YANG, T.Y., WEN, W., YIN, G.Z., LI, X.L., GAO, M., GU, Y.L., LI, L., LIU, Y., LIN, H., ZHANG, X.M., ZHAO, B., LIU, T.K., YANG, Y.G., LI, Z., ZHOU, X.T., & GAO, X.Y. (2015) Introduction of the X-ray diffraction beamline of SSRF. *Nuclear Science and Techniques* **26**, 020101.
- YOUSEFI, S., GHASEMI, B., TAJALLY, M., & ASGHARI, A. (2017) Optical properties of MgO and $\text{Mg}(\text{OH})_2$ nanostructures synthesized by a chemical precipitation method using impure brine. *Journal of Alloys and Compounds* **711**, 512–529.
- YU, J.S., LEI, X.R., ZHANG, J.H., & WU, H.D. (2011) *Identification Handbook for Mineral X-ray Powder*. Huazhong University of Science and Technology Press, Wuhan, China.

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