Thermal analysis of the Mg(OH)$_2$ dehydroxylation process at high pressures

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## ARTICLE INFO

ABSTRACT

Magnesium hydroxide (Mg(OH)$_2$) is widely used in different applications, including as a magnesium oxide precursor. Therefore, understanding the different physicochemical properties as a function of pressure is important. In this work, a systematic thermal analysis was performed at high pressure using differential scanning calorimetry. The dehydroxylation enthalpy (ΔH) of Mg(OH)$_2$ was determined at different pressures. The results showed that between atmospheric pressure and a pressure of 500 psi, ΔH increases due to a reaction equilibrium shift. However, at pressures higher than 500 psi, ΔH decreases significantly. At these high pressures, the reaction occurs at temperatures above the critical temperature, resulting in the production of overheated steam.

1. Introduction

There are many natural and synthetic layered hydroxides with important environmental, biological and industrial applications. These materials are used as catalysts, catalyst supports, ion exchangers and sorbents, among others [1,2]. Brucite (Mg(OH)$_2$) is often considered to possess the ideal structure of a layered hydroxide. Mg(OH)$_2$ is a layered hydroxide comprising two antiparallel hydroxyl sheets surrounding the basal MgO plane. The Mg ions are located in a hexagonal close packing position [3].

Mg(OH)$_2$ is an important material that has been commonly used in many different fields, including as a flame retardant in polymers [4–6], in antibacterial and biological applications [7,8], as membranes for gas separation [9,10] and as an acidic waste neutralizer in environment protection and papermaking industry [11]. In addition, it serves as the most important magnesium oxide (MgO, periclase) precursor [12]. The dehydroxylation reaction of Mg(OH)$_2$ to MgO is as follows:

$$\text{Mg(OH)}_{2(s)} \xrightarrow{300-330\ ^\circ C} \text{MgO}_{(s)} + \text{H}_2\text{O}_{(v)} \tag{1}$$
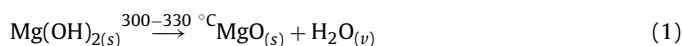
In recent years, considerable research has been devoted to understanding this dehydroxylation reaction [12–18]. In the literature, there are reports of the kinetics of Mg(OH)$_2$ thermal decomposition data, and it is clearly evident that the Mg(OH)$_2$ dehydroxylation process is dependent on different physicochemical factors. However, the effect of high pressures, a very important factor especially in many industrial applications, has not been previously analyzed. Therefore, the aim of this work was to analyze the Mg(OH)$_2$ dehydroxylation process at high pressures using differential scanning calorimetry (DSC).

2. Experimental

Commercial magnesium hydroxide (Mg(OH)$_2$, Aldrich) was used without further purification. X-ray diffraction (XRD) characterization was performed using a D-5000 Siemens X-ray Diffractometer with a Co anode tube. The nitrogen adsorption–desorption isotherm and BET surface area analyses were determined with a Bel-Japan Minisorp II, employing a multipoint technique. Prior to this analysis, the sample was degassed at room temperature for 24 h in a vacuum. The BET surface area was found to be 4.2 m^2/g, and the adsorption–desorption curve provided no evidence for porosity (data not shown).

High pressure differential scanning calorimetry (DSC) experiments were carried out using a pressure differential scanning calorimetry (PDSC) equipment from instruments specialists incorporated. Samples were heated from room temperature to 500 °C at a ramp rate of 10 °C/min in an increasingly pressured N$_2$ atmosphere (atmospheric to 850 psi). Some of the PDSC products were further analyzed using XRD. The crystal size was calculated using the Debye–Scherrer equation [19].

3. Results and discussion

Pressure differential scanning calorimetry (PDSC). Fig. 1 shows the PDSC curves obtained from the Mg(OH)$_2$ that was subjected

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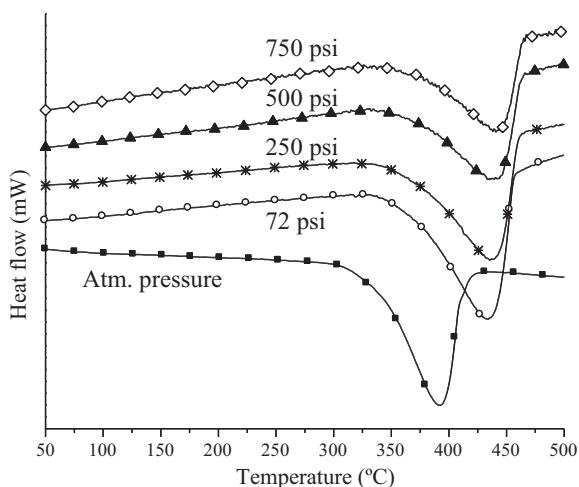E-mail address: pfeiffer@iim.unam.mx

Fig. 1. DSC analyses of the Mg(OH)$_2$ sample performed at different pressures, using N$_2$ as pressurizing gas.

Fig. 3. Variation of the ΔH value as a function of the temperature, for the Mg(OH)$_2$ dehydroxylation process.

to different pressures. The sample exposed to atmospheric pressure presented no change between room temperature and 300 °C, as expected. A well-defined endothermic peak was obtained at 333.3 °C, corresponding to the onset temperature of Mg(OH)$_2$ dehydroxylation. Although this process could be associated with reaction (1), the entire Mg(OH)$_2$ dehydroxylation process, as measured by DSC, consists of the following two different phenomena: first, the Mg(OH)$_2$ dehydroxylation reaction, and second, the consequent H$_2$O vaporization.

When the experiments were performed at higher pressures, the Mg(OH)$_2$ dehydroxylation endothermic peak shifted to higher temperatures. For example, the onset temperature at atmospheric pressure was 333.3 °C, but the same onset temperature was increased to 385.9 °C when the pressure was raised to 850 psi (a temperature shift of 52.6 °C). This effect can be explained by analyzing the relationship between the decomposition process and the pressure and temperature. In fact, according to the Clausius–Clapeyron equation (Eq. (2), [20]), plotting the ln(P) against the 1/T plot yields a linear relationship. Fig. 2 shows that our data follow this linear behavior.

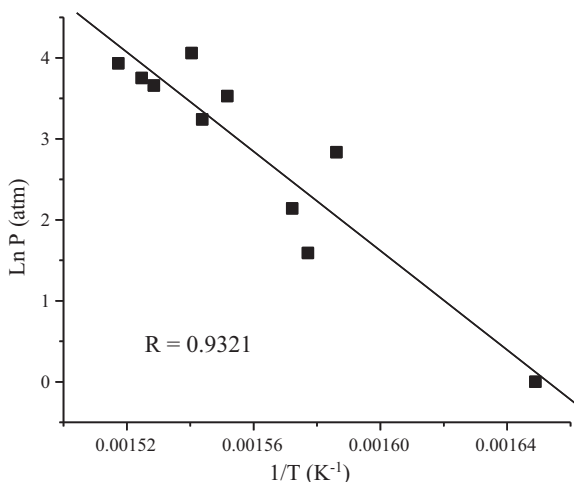$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}; \quad \ln(P) = -\left(\frac{\Delta H}{RT}\right) \qquad (2)$$

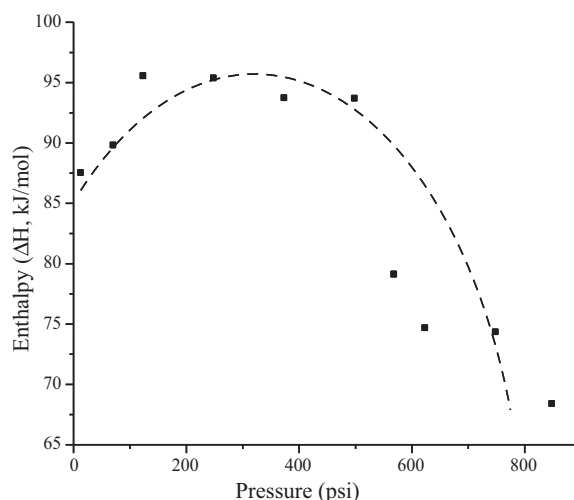**Fig. 2.** Clausius–Clapeyron plot of the Mg(OH)$_2$ dehydroxylation process as a function of the pressure.

The measured enthalpy (ΔH) obtained from the PDSC thermograms varied significantly between the samples (Fig. 3). The ΔH value obtained at atmospheric pressure was 87.5 kJ/mol. This value is in line with those previously reported for ΔH, which vary between 72.5 and 84.5 kJ/mol [13]. However, when the pressure was increased (from 72 to 500 psi), ΔH increased as well, stabilizing near 93–95 kJ/mol. Finally, when the pressure was increased to 850 psi, ΔH decreased significantly to 68.3 kJ/mol. Hence, to explain this behavior, the following factors must be considered: (1) the Mg(OH)$_2$ dehydroxylation reaction mechanism, and consequently; and (2) the H$_2$O equilibrium vapor pressure and the critical conditions.

It should be mentioned that as the critical conditions (temperature and pressure) are approached, the properties of the H$_2$O vapor and liquid phases approach each other, resulting in only one phase at the critical point: a homogeneous supercritical fluid. Additionally, if the temperature and pressure approach the critical conditions, then the heat of vaporization tends to zero. The heat of vaporization becomes zero at the critical conditions, and beyond this point, there is no distinction between the two phases. In this case, the supercritical point of water occurs above 374 °C and 3205 psi [21]. It should be noted that the experiments performed here did not reach this critical pressure condition. However, as mentioned previously, the pressure–temperature effect must induce a partial reduction on the vaporization heat, which contributes to the total value of ΔH obtained using PDSC. Additionally, it should be mentioned that the reaction temperature is fortuitously very close to the H$_2$O critical temperature (T_c), near 370–380 °C.

Summarizing the PDSC results, the ΔH measurements show two different effects. At relatively low pressures ($\leq$500 psi), the decomposition reaction occurs at temperatures lower than the Tc (374 °C), and the obtained value for ΔH corresponds to the combination of the Mg(OH)$_2$ decomposition reaction and the H$_2$O evaporation process. However, when the pressure is higher than 500 psi, the reaction process occurs at temperatures higher than the Tc. Therefore, the heat of vaporization must decrease considerably, thus producing over heated steam.

Finally, to investigate whether the increased pressure subjected to the samples during the PDSC experiments modified the structure of the powder, structural characterization of the PDSC products was performed using XRD. Fig. 4 shows the XRD patterns of selected PDSC products (Fig. 4A) as well as two different Mg(OH)$_2$ samples (Fig. 4B), the original sample and a Mg(OH)$_2$ sample pressurized at 850 psi for 48 h at 30 °C. As can be seen, neither the Mg(OH)$_2$
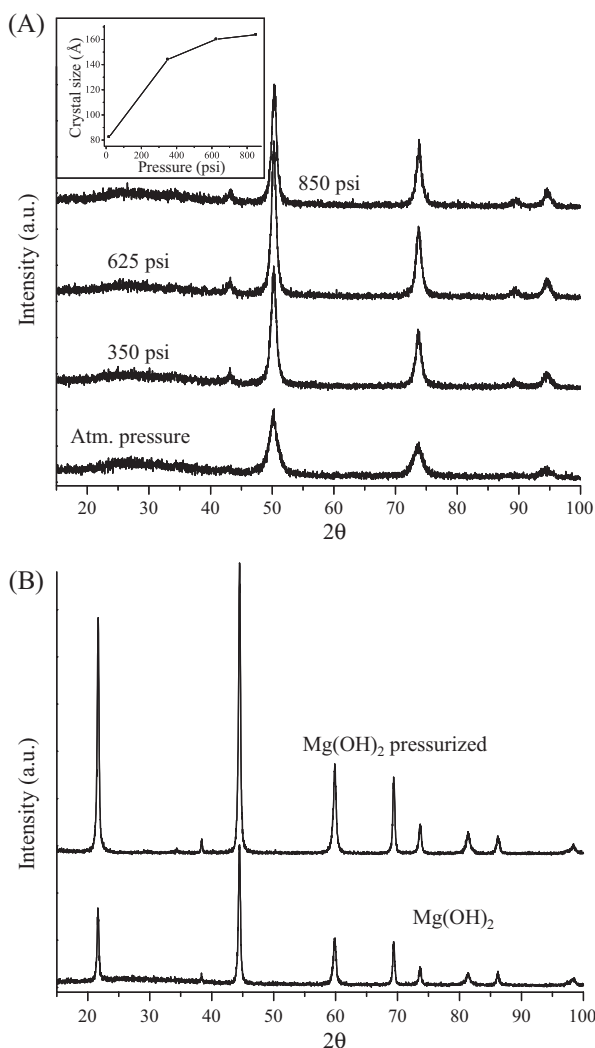
Fig. 4. XRD patterns of some PDSC products (A), and Mg(OH)$_2$ original and pressurized at 850 psi samples (B).

samples nor the MgO products underwent any significant structural change. The only observed change is in the crystal size of MgO, which was found to increase with increasing pressure (see inset of Fig. 4A). These results are in agreement with the previous discussion concerning energy variation, supporting that the Mg(OH)$_2$ and MgO crystal structures did not vary with temperature or pressure.

4. Conclusions

DSC experiments performed at high pressures showed that Mg(OH)$_2$ dehydroxylation enthalpy depends on two different processes. When the pressure was increased from atmospheric pressure to 500 psi, the ΔH values increased from 87.5 to 95 kJ/mol. This can be explained in terms of the reaction equilibrium shift. In contrast, when the thermal experiments were performed at pressures higher than 500 psi, the ΔH values decreased significantly

to 68.3 kJ/mol at 850 psi. This behavior can be explained based on the H$_2$O equilibrium vapor pressure and its critical conditions. As the critical conditions (temperature and pressure) are approached, the properties of the H$_2$O vapor and liquid phases approach each other, resulting in only one phase at the critical point: a homogeneous supercritical fluid. At the critical condition, the heat of vaporization tends to zero. Therefore, the ΔH values measured by DSC correspond to both the Mg(OH)$_2$ dehydroxylation and the H$_2$O evaporation.

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