A systemic investigation on the hydroxylation behavior of caustic magnesia and magnesia sinter

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Abstract

Caustic magnesia (CM) and magnesia sinter (MS or hard-burnt magnesia) are the main sources of MgO employed in industry. Both are obtained from the calcination of $Mg(OH)_2$ or $MgCO_3$, howeever, due to differences in their manufacture, they display significant distinct physical–chemical properties. MS is produced at temperatures above 1500 °C and shows large crystal size and low inner micro–meso pores content, whereas CM is attained at lower temperatures (600–900 °C) and has high specific surface area, micro–meso pores content and chemical reactivity. Their hydroxylation behavior is also different, as it takes MS several hours-days to react completely with water, while the CM reaction achieves total conversion after few minutes. Because of their technological importance, a deeper understanding of the processes involved in hydroxylation reactions and how particles' characteristics affect them is required. This study relates the characterization of MS and CM particles with their hydroxylation reactions in aqueous suspensions through thermogravimetry, X-ray diffraction, nitrogen adsorption, and scanning electron microscopy.
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1. Introduction

Magnesium oxide (MgO) or magnesia, is one of the most important raw materials for industrial processes and technological applications. It can be produced by two main commercial routes [1], namely calcination of brucite ($Mg(OH)_2$), produced from seawater or underground brine, and calcination of natural brucite or magnesite ($MgCO_3$).

1.1. MgO from seawater or brine brucite

Seawater naturally contains a 1–3.5 wt% portion of dissolved ionic species, such as Cl^-, $(SO_4)^{2-}$, Br^-, Na^+, K^+, Ca^{2+} and Mg^{2+} and by means of water evaporation, this salt concentration can be raised to above 50 wt%. After the selective precipitation of less soluble salts, such as $CaCO_3$

$(0.0004 \text{ g L}^{-1})$ and $CaSO_4$ (2.5 g L^{-1}), the resulting solution shows a higher content of highly soluble magnesium salts ($MgCl_2 = 540 \text{ g L}^{-1}$ and $MgSO_4 = 350 \text{ g L}^{-1}$) [1,2]. A similar system can be obtained through the injection of plain water into underground deposits of salt-rocks and brine recovering [1,2]. The next step is to treat Mg^{2+}-rich brine with an alkaline compound, as NaOH or CaO to precipitate $Mg(OH)_2$ (or brucite) according to the expression [1–3]

$$Mg^{2+} + 2Cl^- + Na^+ + OH^- \rightarrow Mg(OH)_2$$
$$\text{(Precipitate)} + NaCl_{\text{(Dissolved)}} \quad (1)$$
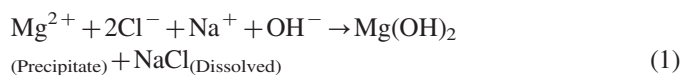
After washing, filtration and drying steps, $Mg(OH)_2$ is recovered and calcined in rotary kilns to produce MgO [4–8]

$$Mg(OH)_2 \overset{260-400\ ^\circ C}{\Longrightarrow} MgO + H_2O_{\text{(Gas)}} \quad (2)$$

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1.2. MgO from magnesite

Magnesite is a general name employed to describe an abundant family of magnesium carbonates and hydroxycarbonates (magnesite=$MgCO_3$; artinite=$MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$; nesquehonite=$MgCO_3 \cdot 3H_2O$; hydromagnesite=$4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$) found in many countries [1]. Due to its sedimentary origin, magnesite is usually found in open pits or low-depth deposits. Depending on the geological activity of the area, the magnesite ore may contain impurities (dolomite, talc, calcite, clay, and sand), which can be removed by filtration and separation standard processes. After milling and granulometric classification, magnesite is calcined in rotary kilns (700–1700 °C). During this thermal treatment, it undergoes decarbonation and produces MgO, according to the general expression [1,9,10]

$$MgCO_3 \overset{500-750\ ^oC}{\Longrightarrow} MgO + CO_{2(Gas)} \qquad (3)$$
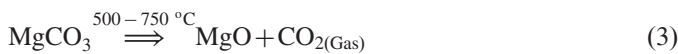
After these operations, grades of MgO content above 98–99% are used in the production of refractory bricks or castables, whereas those of lower MgO content are employed as pH correctors in soil and water treatments and as mineral supplement in animal and human feeding.

1.3. Production of different grades of polycrystalline MgO

The final step of routes 1.1 and 1.2 (expressions (2) and (3)) is a calcination process, through which the hydroxylated (brucite) or carbonated (magnesite) precursors are transformed into MgO. Depending on the conditions employed (final temperature, residence time, atmosphere, and impurities), different types of polycrystalline materials can be obtained [1,4–9]. The MgO grade known as *caustic magnesia* (CM) is produced through the rapid calcination of brucite or magnesite at temperatures of up to 800–900 °C in rotary and Herreshoff-type kilns [8,9,11]. During calcination, such precursors undergo a series of topotactic changes before their total conversion into MgO (Fig. 1) [4,5,6,7,12,13]. The loss of OH^- and $(CO_3)^{2-}$ ions (as H_2O and CO_2) causes a significant volumetric shrinkage in their crystalline lattices (particularly at the *c* axis), which increases density, and the withdrawal of gases generates microcraked porous surfaces. The external morphology of the freshly produced CM particles is similar to the shape of the precursor ones and, because of their high specific surface area (usually above 10 m^2 g^{-1}) and chemical reactivity, they can be employed in several chemical processes [8,9].

On the other hand, CM characteristics are unsuitable for uses that involve sintering for the production of dense parts, and a further processing is required. Therefore, CM particles are compacted into 10–30 mm beads (agglutinants, as carboximetil-cellulose, and sintering aids, B_2O_3 and Fe_2O_3, are often added previously [14,15]) and sintered at temperatures of 1500–1700 °C, for up to 1–3 h. After cooling, the compacts produced (whose relative density is above 90%) are crushed and classified in the desired granulometric range. As they show

very low porosity and chemical reactivity, they are called hard-burnt magnesia or *magnesia sinter* (MS) and are almost exclusively used in the production of refractory bricks and castables [1,14,16].

CM and MS have been the focus of many investigations for over half a century and an aspect that has drawn plenty of attention is their hydroxylation (or hydration) behavior [17–26]. Depending on the application aimed at, MgO hydroxylation can be either valuable or undesired and, in both cases, the knowledge of how this process occurs can be highly useful. The hydroxylation process must be efficient for the production of fertilizers [1,18], animal and human nutrition [1,27], water-treatment input [1,28], medicaments [1,27,28], fast-hardening Sorel and MgO-based cements [1,29–31] and anti-flame agents for polymer composites [32–34] and generates particles of controllable size distribution, specific surface area and shape at competitive costs. On the other hand, it must be avoided or at least minimized in applications to refractory [10,13,14,16,35–40] and abrasive [1] materials and optic and electronic devices.

1.4. General aspects of MgO hydroxylation

MgO hydroxylation is a dissolution–precipitation reaction (Eqs. ((1)–3)) [20–24,27]. In the presence of water, MgO surfaces initially become protonated and positively charged due to their strong ionic character, according to the following equation [23,24,37]:

$$MgO + H_2O \rightarrow MgOH^+ + OH^- \qquad (4)$$

The presence of positive charges enables the dissociation of the intermediate compound $MgOH^+$

$$MgOH^+ + OH^- \rightarrow Mg^{2+} + 2OH^- \qquad (5)$$

The low solubility of $Mg(OH)_2$ in pH levels that range from neutral to highly alkaline favors the precipitation of $Mg(OH)_2$ on the nearest MgO surfaces [3,22,27,28,41]

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2 \qquad (6)$$

The characteristics of the reacting medium (temperature and solid load) and the MgO source (single crystal or polycrystalline grains) affect the rates of steps 4–6 differently [14,16,18,22,25,26]. When the dissolution steps (expressions (4) and (5)) occur gradually (for instance, in very diluted suspensions of monocrystalline particles at temperatures below 20 °C), the precipitation (expression (6)) necessarily slows down and $Mg(OH)_2$ is formed orderly as a dense thin layer on the surface of the MgO particles [16,22,25,26,37,42]. This layer behaves as protective coating preventing further MgO dissolution and halting the process. Therefore, under such conditions, hydroxylation occurs along several days or weeks [30]. On the other hand, for high solid load suspensions of polycrystalline particles at temperatures above 20 °C, dissolution occurs more rapidly. Consequently, the massive and exothermic precipitation of $Mg(OH)_2$ particles generate a thick and porous brucite layer [11,12,16,25,43]. Because of the large density mismatch (ρ_{MgO}=3.5 g cm^{-3} and $\rho_{Mg(OH)_2}$=2.4