

Note

Thermal decomposition of brucite, $\text{Mg}(\text{OH})_2$: a ^{25}Mg MAS NMR study

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Abstract

^{25}Mg NMR spectra for unheated and thermally decomposed brucite are reported. The spectra support a model of coherent growth of MgO in small domains, followed by coalescence into crystallites.

The thermal decomposition reactions of inorganic magnesium compounds have been extensively studied, because of the technical importance of the final product, MgO , as a refractory or, in its sintered form, as an engineering ceramic. One of the most extensively studied of these reactions is that of brucite, for which three different reaction mechanisms have been proposed, as reviewed by Green [1].

(i) The homogeneous mechanism, involving condensation of hydroxyl groups on the upper surface of the brucite layer with those on the lower surface of the adjacent layer. The anhydrous product, a highly defective oxide, subsequently collapses to cubic MgO . Experimental evidence for this mechanism in terms of a shrinkage in the c axis was cited by Goodman [2], but ruled out in a more recent electron optical study [3].

(ii) The inhomogeneous mechanism, in which protons and Mg^{2+} counter-migrate to “donor” and “acceptor” regions respectively, the acceptor regions becoming MgO and the donor regions becoming pores from which water is lost. Such migration of Mg^{2+} via a defect or spinel structure implies the formation of an intermediate phase containing non-octahedral Mg sites [4]; these were subsequently shown to be an artifact resulting from the presence of Fe impurities [5].

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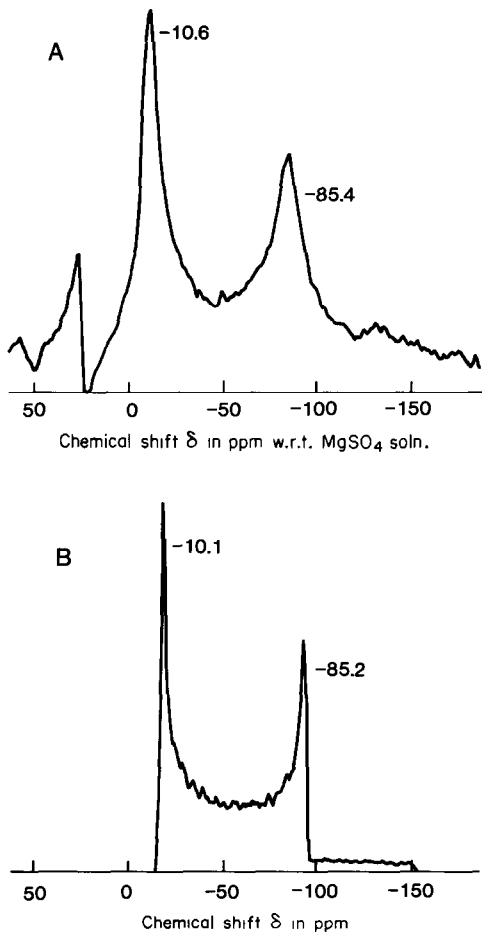


Fig. 1. (A) ^{25}Mg MAS NMR spectrum of polycrystalline BDH brucite, processed using 60 Hz gaussian line broadening. (B) Simulation of brucite spectrum, using parameters as in text.

(iii) The nucleation and growth mechanism, in which MgO microcrystals with an expanded cubic lattice form coherently within the brucite matrix and gradually assume the normal MgO lattice parameter as heating progresses. A recent TEM study [3] seems to support this conclusion.

In a previous ^{25}Mg NMR study of several inorganic compounds [6], brucite was found to have a very broad resonance which was most conveniently observed by static-echo methods. By spinning polycrystalline brucite at 19.5–20 kHz in a 3.5 mm Doty MAS probe at 11.7 T in a Varian Unity 500 spectrometer, we have acquired a much sharper ^{25}Mg MAS NMR spectrum (Fig. 1A) which shows a typical second-order quadrupolar lineshape. For this spectrum, 560 000 transients were acquired at

30.584 MHz using a 90° (solids) pulse of $3 \mu\text{s}$ with a recycle delay time of 0.3 s. Chemical shifts are quoted with respect to a saturated solution of MgSO_4 .

Spectral simulation of this resonance, using the parameters reported for single-crystal brucite by Bastow [7] (nuclear quadrupole coupling $e^2qQ/h = 3.056$ MHz, electric field gradient (EFG) tensor asymmetry parameter = 0) shows a satisfactory degree of similarity with the observed spectrum, which can however be improved by setting e^2qQ/h to 3.15 MHz, with a gaussian line broadening of 60 Hz (Fig. 1B). The simulated spectrum indicates a value of 14.1 ppm for the chemical shift of brucite after correction for EFG effects.

The small resonance at about 29 ppm has a similar chemical shift to that reported for MgO [6]; although X-ray powder diffraction (XRD) indicates

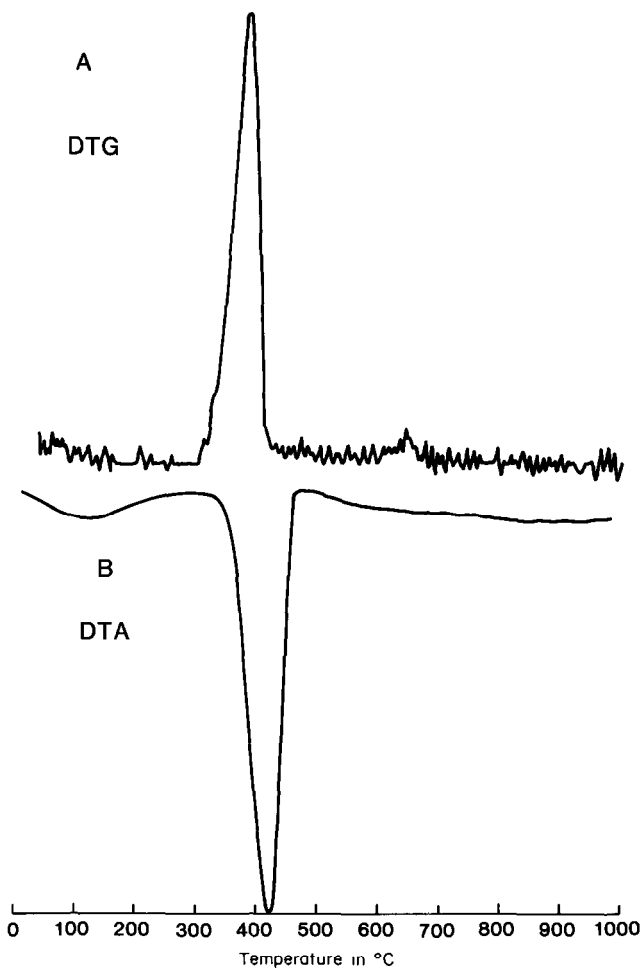


Fig. 2. Thermal analysis traces of BDH brucite at a heating rate of $10^\circ\text{C min}^{-1}$.

this brucite sample (BDH reagent grade) to be free of all such impurities except a very small trace of basic magnesium carbonate, it is possible that the NMR is more sensitive to MgO impurities than is XRD. Basic magnesium carbonate has a quite different spectrum [8], none of the features of which can be distinguished in the present brucite spectra.

Thermal analysis of the present brucite in Ar (1.5 ml min^{-1} ; heating rate of $10^\circ\text{C min}^{-1}$) shows it to decompose to MgO at $350\text{--}400^\circ\text{C}$ with a mass loss of 29.4% (Fig. 2). XRD shows that at 350°C , the sample consists of a mixture of brucite and MgO, which by 400°C has been completely converted to MgO of small particle size.

The ^{25}Mg MAS NMR spectra of brucite samples heated to various temperatures for 15 min (Fig. 3) closely follow the X-ray results, and

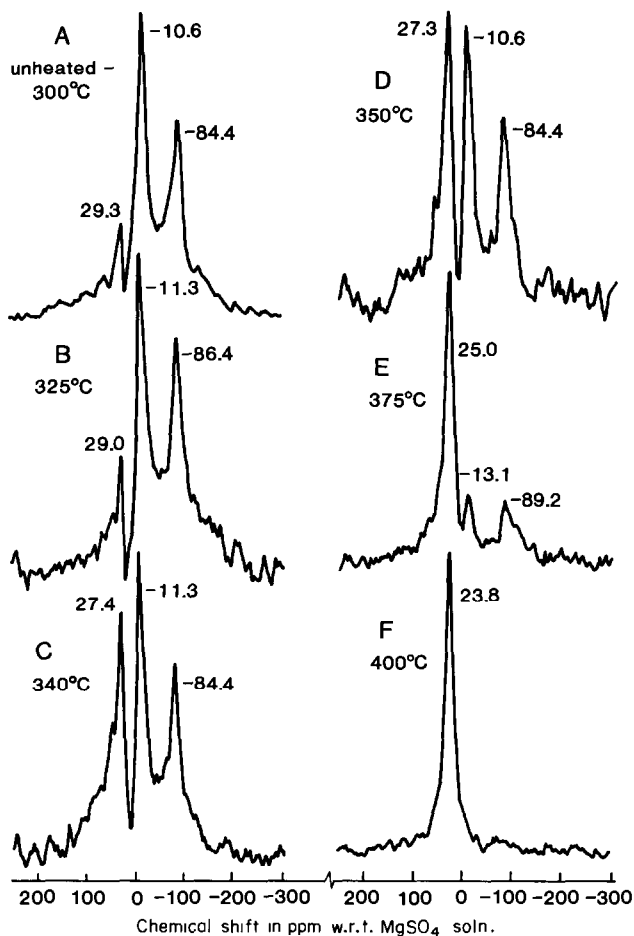


Fig. 3. ^{25}Mg MAS NMR spectra of brucite, heated to various temperatures. Spectra processed using 200 Hz gaussian line broadening.

indicate a smooth transition between brucite and MgO. Below 300°C, the spectra are typically those of brucite (Fig. 3, curve A), with no indication of distortions in the Mg coordination sphere due to the formation of non-cubic intermediates such as might be expected if the inhomogeneous mechanism was operating. At 325°C, the spectrum consists of the brucite resonances, with a slight increase in the resonance at about 29 ppm, (Fig. 3, curve B), suggesting the appearance of incipient MgO with a chemical shift only slightly different from that of well-crystallized MgO [6]. This MgO resonance increases in intensity upon heating to higher temperatures (Fig. 3, curves C and D), with a concomitant decrease in the brucite resonances. The MgO chemical shift moves slowly upfield with increasing degree of reaction, possibly as a consequence of increases in the size of the MgO domains forming in the brucite lattice. By 400°C, the spectrum consists solely of the single, fairly broad MgO peak (Fig. 3, curve F). Thus, the transformation from brucite to MgO appears to occur directly, without significant formation of intermediate phases detectable by ²⁵Mg MAS NMR, as would be expected if an inhomogeneous reaction mechanism was operating. There is, however, some indication of possible spectral intensity in the region 44–60 ppm, present as a broad shoulder or a tail in the samples in which reaction is just starting (Fig. 3, curve B) or partially completed (Fig. 3, curve C). Although this is the spectral region in which 4-coordinated Mg occurs, as in spinel (MgAl₂O₄) [6], the present spectra do not constitute clear evidence for the formation of a spinel-like reaction intermediate. Neither is there NMR evidence that the initially formed MgO (as opposed to the phase present in the starting material) is particularly defect, as would be a consequence of the homogeneous mechanism.

The present results, including the changes in the MgO chemical shift with increasing reaction, are thus more consistent with the coherent growth of MgO in small domains within the brucite lattice, as suggested by recent TEM studies [3]. These then coalesce into crystallites with sufficient long-range order to be detected as MgO by X-ray diffraction.

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