

THE EFFECT OF MAGNETIC FIELDS ON THE THERMAL REACTIONS OF NONTRONITE

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(Received 27 May 1982)

ABSTRACT

The removal of interlayer water from nontronite at $\sim 50\text{--}200^\circ\text{C}$ is found to be retarded in its later stages by magnetic fields of 5.2 kOe, although the elimination of hydroxyl water at $\sim 500\text{--}600^\circ\text{C}$ appears to be slightly enhanced by the field, the activation energy of this reaction being reduced by $\sim 6\text{ kcal mole}^{-1}$ and its DTA peak temperature lowered by 10°C by the action of the field. The formation at higher temperatures of anhydrous product phases (in air) or iron metal (under reducing conditions) is also retarded by the field, probably as a consequence of increased water retention, even up to 740°C , with the suppression of the subsequent transformations. Magnetic susceptibility measurements of reactant and products show that these results are not as would be predicted by existing theory.

INTRODUCTION

From time to time, studies have been reported of the effect of external magnetic fields on solid state reactions. From a theoretical viewpoint, it has been suggested that the influence of a magnetic field depends on the relative magnetic properties of the reactants and products; when a diamagnetic compound forms products which are less diamagnetic (or more paramagnetic), the reaction rate should be increased by the field, whereas the rate should be decreased where the products are more diamagnetic than the reactants [1]. The rate should be unchanged where the magnetic susceptibilities of the reactants and products are similar [1]. The reduction of transition metal oxides to their metals might have been expected to provide experimental verification of these principles, but the several reported studies [2–6] show unexpected and sometimes contradictory behaviour. Thus, thermogravimetric studies have indicated that the rates of hydrogen reduction of Fe_2O_3 [2], Fe_3O_4 [4], Co_3O_4 and CoO [4] are enhanced by magnetic fields of $\sim 0.5\text{--}4.5\text{ kOe}$, whereas hydrogen reduction of NiO is uninfluenced [5] and the reduction of FeO is retarded [3]. However, the use of in situ weight-loss measurements to study reactions having highly magnetic products has been questioned [6], and when an alternative dynamic evolved gas analysis method

was used to monitor the water produced during hydrogen reduction of NiO, Fe₂O₃ and Co₃O₄, no significant differences could be detected in the presence or absence of a magnetic field [6].

Another interesting result which cannot be explained by existing theory is an earlier observation that the rate of reduction of Fe₂O₃ by CO or CH₄ appears to be retarded by applied magnetic fields, in contrast to the enhancing effect on hydrogen reduction noted in the same study [2]. An explanation of this result [2] in terms of the increased attraction of the magnetised reacting powder for orthohydrogen (which has nuclear paramagnetic properties) has been criticised by Svare [7] and Peters [8], neither of whom, however, has produced an alternative explanation.

In addition to the reduction studies summarised above, occasional studies have been reported of the effect of magnetic fields on other types of solid state reaction. Thus, the rate of thermal decomposition of solid Ag₂C₂O₄ is reported to be decreased by a magnetic field of 1.1 kOe, whereas that of BaN₆ was increased by the field and the decomposition of AgN₃ was uninfluenced [9]. Presumably this odd assortment of compounds was chosen for study because of their reasonably low decomposition temperatures. The thermal decomposition of KMnO₄ is also reported to be influenced by magnetic fields of 0.75–1.0 kOe [10], but no unified theory is presently available to explain these isolated results.

The thermal decompositions of hydrous layer silicate minerals represent another class of solid state reaction which appears worthy of study under magnetic fields, since the thermal reactions of kaolinite are influenced by d.c. electric fields, which assist both the dehydroxylation step [11] and the higher-temperature reactions [12]. To ensure maximum interaction between the sample and the field, it was decided to make the present study on a mineral containing appreciable amounts of iron; the iron-rich montmorillonite (nontronite) which was chosen has the additional advantage of having been the subject of a previous thermal study [13], and is well characterised. The thermal reactions of ferric nontronite in air include (i) the loss of interlayer water at 40–200°C, (ii) loss of structural hydroxyl groups at 350–550°C, and (iii) higher-temperature structural rearrangements resulting in the ultimate formation of iron oxides and silica [13]. Reactions (i) and (ii) can conveniently be studied by thermogravimetry and since gross changes in the magnetic susceptibilities of the reactant and product are unlikely to occur, these TG measurements should not suffer from the limitations identified in the previous transition metal oxide reduction studies [6]. The higher-temperature reactions (iii) are best studied by techniques such as X-ray powder diffraction, IR and Mössbauer spectroscopy.

EXPERIMENTAL

The ferric nontronite, from Washington State, U.S.A., came from the New Zealand Geological Survey Collection (No. 39184) and has been fully described elsewhere [13]. The TG experiments were carried out using a silica spring balance from which was suspended a fine platinum wire and small platinum sample bucket. The whole assembly was enclosed in a fused silica tube, on the lower end of which was wound a bifilar nichrome microfurnace controlled by an RKC multistage programmable controller. Temperature measurement and control was by a Pt-13% Pt/Rh thermocouple inserted from the bottom of the tube in a fine fused silica sheath and located adjacent to the sample. The furnace assembly was encased in a fused silica water jacket which fitted snugly between the poles of a Newport Instruments electromagnet. The magnetic field was calibrated by a Hall probe and R.F.L. Model 505 gaussmeter. The furnace windings and water jacket were found not to exert any detectable magnetic shielding effect, neither was any difference detected in the field strength at the sample position when the furnace current was switched on. The TG experiments were made on 150 mg samples in air at heating rates of 2 and 10°C min⁻¹ to an upper temperature of 740°C at a field strength of 5.2 kOe. To avoid the effect of the small residual field present when the magnet was switched off, the zero-field control experiments were made with the thermobalance removed from the magnet. Experiments made on the empty sample bucket showed no magnetic contribution from either the bucket or the suspension assembly over the temperature range of the study (up to 740°C). As a cross-check on the silica spring balance results, non-field TG runs were also made under identical conditions in a Mettler model 21 thermal analyser. To complement the results, some DTA runs were also made, both in and out of the field, using the platinum DTA cell from a Mettler model 21 thermal analyser, inserted from the bottom of the furnace. Heating rates of 10 and 20°C min⁻¹ in air were used.

Semi-quantitative estimates of the various reaction phases were made by XRD using 10% aluminium powder as an internal standard; the results were for comparative purposes only and no attempt was made to relate the intensity ratios to absolute concentrations via calibration curves. The IR and Mössbauer spectra of the reacted materials were obtained as previously described [13]. The room-temperature magnetic susceptibilities of the unheated nontronite and of samples heated to 220 and 740°C were measured by the Faraday method using a Cahn electrobalance. The calibration substance was HgCo(CNS)₄, for which a gram susceptibility ψ_g of 16.44×10^{-6} at 20°C was assumed.

RESULTS AND DISCUSSION

Effect of magnetic fields on water elimination

Typical magnetised and non-magnetised TG curves for nontronite are shown in Fig. 1.

The slopes of both curves are similar to the corresponding curves obtained with the Mettler thermal analyser and suggest that the reaction mechanism is not significantly changed by the action of the field. However, in all experiments, the first weight-loss stage, corresponding to the loss of interlayer water [13], flattened out at a smaller value in the presence of the field, this difference being then carried through the subsequent dehydroxylation weight-loss step. Thus, the magnetic field appears to suppress the later stages of interlayer water loss, with the retention of some residual water even up to the maximum temperature of the present experiments. That the observed difference in final weight loss for field-on and field-off experiments is not simply an artifact caused by interaction of the sample with the field was established by independent weighing before and after each experiment; in all cases, the final weight loss of the field-on samples was less than the field-off by an average of 1.8% (taken over four field-on and four field-off experiments.) In a further experiment suggested by these results, the weight loss in the magnetic field was monitored at a heating rate of $2^{\circ}\text{C min}^{-1}$ up to the first plateau (220°C), at which temperature the field was switched off. An immediate weight loss was observed, but its magnitude ($\sim 0.5\%$) was insufficient to account for the difference between the field-on and field-off experi-

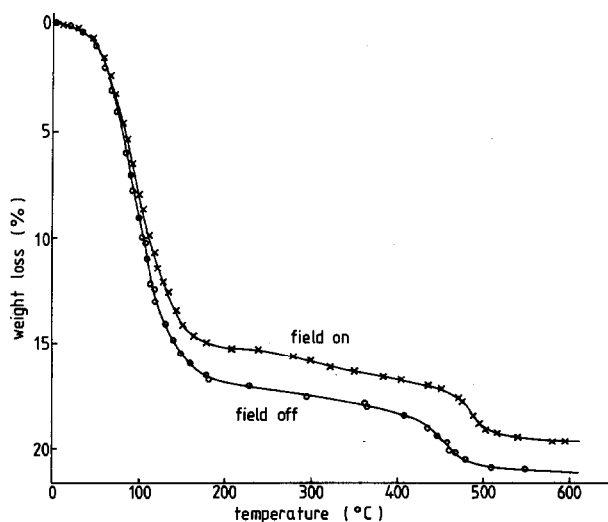


Fig. 1. Thermobalance curves for nontronite heated in air at $2^{\circ}\text{C min}^{-1}$ in the presence and absence of a magnetic field (5.2 kOe).

ments (Fig. 1). Continued heating at $2^{\circ}\text{C min}^{-1}$ produced a further small, gradual weight loss before the onset of dehydroxylation, the final weight loss after dehydroxylation being comparable with that of a field-off experiment. The weight change accompanying the removal of the field is not due to the change in magnetic force exerted on the paramagnetic sample by the field, since for this force to act, the sample must experience a magnetic field *gradient*; this is the principle underlying magnetic susceptibility measurements. The 18 cm diameter flat pole pieces of the magnet used here were specifically designed to provide a homogeneous field over a large volume and the homogeneity of the field was confirmed both by measurements using the Hall probe and by the identical weights recorded for nontronite samples at room temperature in the presence and absence of the field. Neither was the weight change noted in the interrupted-field experiment due to changes in the magnetic susceptibility of the sample, which will be shown later to be unchanged during this stage of the reaction; this result therefore appears to reflect a real field-dependent reaction process in the sample. The immediate effect of removing the field was, however, less marked than anticipated, possibly because the first plateau corresponds to two processes (the tail-end of interlayer dehydration and the onset of dehydroxylation), both of which may be influenced by the field to different degrees.

To further explore possible differences between the field-on and field-off

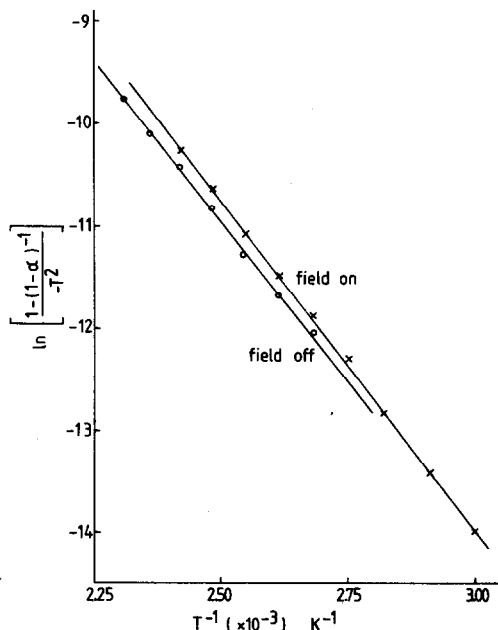


fig. 2. Arrhenius plots for interlayer water loss from nontronite in the presence and absence of a magnetic field (5.2 kOe), based on the second-order kinetic equation.

TG curves, kinetic analyses were made of the data obtained at $2^{\circ}\text{C min}^{-1}$ using the method of Coats and Redfern [14]. This treatment of dynamic TG data was appropriate for the present purpose since (i) the heating rate was reasonably slow and (ii) the aim was to detect *differences* in the sample behaviour under field-on and field-off conditions rather than to establish mechanistic details of the reaction. For this purpose, the interlayer dehydration and dehydroxylation reactions were treated independently, since the two reactions do not appear to overlap appreciably. Figure 2 shows Arrhenius plots for the interlayer water-loss data computed on the basis of a reaction order of 2.

Although second-order kinetics have no theoretical basis in solid-state chemistry, this equation best describes the experimental data and was therefore adopted. Figure 2 shows that the temperature dependence of the interlayer dehydration reaction rate ($12.5 \text{ kcal mole}^{-1}$) is unchanged by the magnetic field and the pre-exponential factor is only slightly changed (4.77 and 4.99 for the field-off and field-on experiments, respectively). In both the field-on and field-off experiments, the second-order expression adequately describes the TG data up to the point where the interlayer water-loss is about 92% complete. The kinetic results obtained using the silica-spring balance in the absence of the field compare well with those obtained independently using the Mettler thermobalance, which confirmed that this reaction is best described by a second-order expression, with a temperature dependence of $12.0 \text{ kcal mole}^{-1}$. These apparent activation energies are of the order reported for reactions involving protonic water movements such as protonic isotope exchange in $\alpha\text{-FeOOH}$ ($8.2 \text{ kcal mole}^{-1}$ [15]) and in boehmite, $\gamma\text{-AlOOH}$ ($15.7 \text{ kcal mole}^{-1}$ [16]).

The TG data for the higher-temperature dehydroxylation reaction were found to be fitted over a reasonable decomposition range by substituting $n = 0.5$ in the Coats and Redfern equation [14]; however, a better fit, up to a degree of reaction of 85% was given by a one-dimensional diffusion equation of the type

$$\alpha^2 = kT \quad (1)$$

where α is the fraction reacted. Although dehydroxylation processes in other clay minerals such as kaolinite are known to obey diffusion-controlled kinetic laws under reduced pressures or controlled water-vapour pressures [17], the success of a diffusion equation in describing the present kinetic results is not necessarily proof of a diffusion-controlled mechanism for nontronite dehydroxylation, particularly since the water-vapour pressure was not controlled here, and is best regarded as a convenient means of describing and comparing the TG data for this reaction.

Figure 3 shows the temperature dependence of dehydroxylation in the presence and absence of the magnetic field. The apparent activation energies derived from the slopes of Fig. 3 show a degree of field dependence, having a

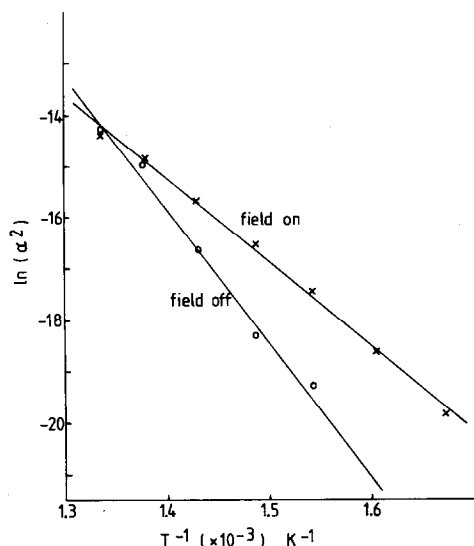


Fig. 3. Arrhenius plots for hydroxyl water loss from nontronite in the presence and absence of a magnetic field (5.2 kOe) based on the one-dimensional diffusion model.

mean value of $37.4 \text{ kcal mole}^{-1}$ for four experiments in the absence of the field and $31.1 \text{ kcal mole}^{-1}$ (mean of three runs) with the field on. These activation energy values are similar to those obtained independently using the Mettler thermobalance and are of the order of those reported for kaolinite dehydroxylation under reduced pressures ($43\text{--}51 \text{ kcal mole}^{-1}$ [17]). The pre-exponential factors calculated from the data of Fig. 3 are also slightly field-dependent, having mean values of 10.4 and 6.0 for the field-off and field-on cases, respectively. Thus, the TG kinetic results indicate that, although the magnetic field does not change the apparent dehydroxylation mechanism, small but probably significant changes are induced in the reaction kinetics which indicate that the reaction occurs more gradually and over a slightly wider temperature range in the presence of the magnetic field.

The validity of conclusions based on TG measurements depends on the magnetic properties of the samples remaining essentially unchanged during the course of the reaction. For this reason, magnetic susceptibility measurements of the original nontronite were compared with samples from which interlayer water had been removed and with dehydroxylated samples. To convert the as-measured gram susceptibility values, ψ_g , to molar susceptibilities, the molecular weight of nontronite was calculated on the basis of the unit formula $[\text{Si}_{4.3}\text{Al}_{0.57}][\text{Fe}_{1.95}^{\text{III}}\text{Mg}_{0.16}]\text{O}_{10}(\text{OH})_2(\frac{1}{2}\text{Ca, Na})_{0.33} \cdot 3.5 \text{ H}_2\text{O}$, derived from the chemical analysis of this material [13]. The molecular weights of the dehydrated materials were adjusted to take account of the loss of

appropriate amounts of water. The resulting molar susceptibility of nontronite, corrected for the diamagnetic contributions of the various ions, was 2.29×10^{-2} e.m.u. mole⁻¹, an identical value being obtained for samples dehydrated at 220°C. Samples dehydroxylated at 740°C showed a smaller susceptibility ($\psi_m = 1.59 \times 10^{-2}$ e.m.u. mole⁻¹), indicating that dehydroxylation causes the samples to become less paramagnetic. Two points emerge from these results: (i) the most obvious field-induced differences in the shapes of the TG curves, noted at ~ 100 – 200°C , cannot be attributed to changes in the magnetic properties of the samples at these temperatures and (ii) the possibility that susceptibility changes during dehydroxylation influence the TG measurements in this higher temperature range cannot be ruled out. For this reason, verification of the TG conclusions was sought by techniques which are not sensitive to changes in the magnetic properties. The susceptibility measurements yield further information about the iron species in the nontronite, since their effective magnetic moment, μ_{eff} , is related to the molar susceptibility by

$$\mu_{\text{eff}} = 2.84(\psi_m T)^{1/2} \quad (2)$$

where T is the absolute temperature. The effective magnetic moment thus calculated for the assumed nontronite unit and its dehydrated form is 7.4 Bohr magnetons, the value for dehydroxylated nontronite being 6.1 Bohr magnetons, or 3.8 and 3.1 Bohr magnetons per iron atom, respectively. These values are smaller than the spin-only values predicted for high-spin Fe^{3+} (~ 5.9 Bohr magnetons) and are consistent with a degree of iron-to-iron interaction in nontronite.

To investigate the possibility that the TG dehydroxylation results might be an artifact of susceptibility changes, a number of DTA measurements were also made in the presence and absence of the magnetic field. The DTA curves were as previously published for this sample [13], having two endotherms corresponding to the two water-loss reactions under consideration. The peak temperatures of these endotherms, determined from the point of intersection of tangents drawn to the sides of the peaks, showed systematic differences in the presence and absence of the field. At a heating rate of $10^\circ\text{C min}^{-1}$, the peak temperature corresponding to interlayer water loss without the field is 180°C (mean of three runs), whereas in the field it is 12°C lower; this difference is not significant, however, because of the scatter in these lower-temperature endotherms (standard deviation $\sigma_{n-1} = 6$ and 13°C in the presence and absence of the field, respectively). The peak temperatures of the higher-temperature endotherms also showed differences which appear to be more significant, being more reproducible ($\sigma_{n-1} = 2.3^\circ\text{C}$). In the absence of the field, the mean peak temperature was 545°C , being lowered to 535°C by the field. The result is consistent with a smearing-out of the reaction over a wider temperature range by the field, as indicated by the lowered TG activation energy, although the relatively crude DTA traces gave

no indication of any significant changes in the peak shapes under the influence of the magnetic field.

Effect of magnetic fields on product formation

According to a previous study [13], interlayer water loss is accompanied by a collapse of the basal spacing from 15.1 to 9.5 Å; the appearance of an X-ray reflection at 3.16 Å is also said [18] to be diagnostic of the dehydrated phase. Dehydroxylation is accompanied by a progressive intensity loss in these X-ray peaks and the growth of a hematite precursor phase (possibly maghemite [13]) with a characteristic X-ray reflection at 2.52 Å. As an indication of the degree to which the higher-temperature reactions had proceeded, the intensities of these three peaks were measured with respect to an aluminium powder standard, in samples heated rapidly to 740°C with the field on, held for 0.5 and 1.5 h and rapidly cooled in the presence of the field. In samples fired for 0.5 h, significant differences were not found in the phase intensity ratios of the magnetised and non-magnetised samples, but in the 1.5 h experiments, the intensity ratios of both the dehydrated phase and product phase showed small but statistically significant decreases in the presence of the magnetic field (Table 1). Since the thermal reactions are sequential (i.e. dehydration and dehydroxylation must always precede product phase formation), this result suggests that retardation of product formation by the field is a consequence of its retarding effect on the water elimination reactions. Thus, the retarding effect of the field on the early stages of water loss (Fig. 1) appears to influence all subsequent stages of the reaction, including the formation of high-temperature phases.

Further evidence of increased water retention at high temperatures in the magnetic field is found in the IR spectra of the isothermally heated samples,

TABLE 1
Effect of magnetic field (5.2 kOe) on the X-ray and IR parameters of nontronite samples heated in air at 740°C for 1.5 h

Measured parameter	Field off	Field on
X-Ray ratio <u>nontronite dehydrate (9.5 Å)</u> Al standard (2.34 Å)	1:1	0.85
X-Ray ratio <u>nontronite dehydrate (3.16 Å)</u> Al standard	0.62	0.52
X-Ray ratio <u>hematite precursor (2.52 Å)</u> Al standard	0.27	0.20
Intensity of 3440 cm ⁻¹ IR band (arbitrary units)	18.5	25.5

which all contain a broad band in the characteristic O–H stretching region ($3000\text{--}4000\text{ cm}^{-1}$). This band, centred at 3440 cm^{-1} is more characteristic of molecular water than of the hydroxyl group, which shows up as an additional sharp band at 3570 cm^{-1} in the unheated nontronite. Although quantitative IR measurements were not attempted, a semi-quantitative comparison of the relative amounts of residual water in the samples was derived from the intensity of the water band (Table 1) by making the measurements on KBr discs containing identical sample concentrations. As with the X-ray measurements, differences in the IR spectra of the 0.5 h samples were not statistically significant because of greater scatter, but the 1.5 h samples showed small but significant differences in water concentration, the samples reacted in the field containing consistently more water (Table 1). Apart from intensity differences in the water band, the IR spectra of all the field-on and field-off samples were identical. The Mössbauer spectra of the field-on and field-off samples were also identical, being resolvable into two pairs of ferric doublets, one of which has an isomer shift value (with respect to soft iron, Co/Rh source) of 0.39 mm s^{-1} and a quadrupole splitting of 1.69 mm s^{-1} , the parameters for the other doublet being I.S. = 0.40 , Q.S. = 1.02 mm s^{-1} . Thus, the field does not perturb the environment of the iron atoms sufficiently to be detected by this technique.

Effect of magnetic fields on reduction of nontronite

Since the most significant magnetic field effects so far reported in the literature have involved reduction reactions, a number of isothermal heating experiments were made at 740°C for 1.5 h in a flowing atmosphere of H_2/N_2 (5%:95%, flow rate 0.6 l min^{-1}). Under these conditions, this nontronite forms a small amount of iron metal [13] which was semiquantitatively estimated by XRD, again using aluminium powder as the internal standard. As with the air-fired samples, only small differences were detected between magnetised and non-magnetised samples, but in all cases the iron metal content was less in samples fired in the presence of the field. In all other respects, the XRD traces of the samples were identical.

CONCLUSIONS

The combined experimental evidence suggests that magnetic fields exert a small but significant effect on the water-loss reactions of nontronite in air. The low-temperature loss of interlayer water does not proceed as completely in the magnetic field as in its absence, an effect which follows through the subsequent reactions, interfering with the formation of anhydrous product

phases. Although the retention of molecular water is found by IR spectroscopy to be enhanced by the field even in samples fired at 740°C, the elimination of hydroxyl water appears to be slightly assisted by the field, the DTA peak temperature of this reaction being lowered by ~10°C and its activation energy reduced by ~6 kcal mole⁻¹. Neither of these results would have been predicted by existing theory [1]; the loss of interlayer water is not accompanied by a change in magnetic susceptibility, and on the basis of the theory should be unaffected by the field, whereas dehydroxylation results in the formation of a slightly less paramagnetic product and should therefore be slightly retarded by the field. On the same theoretical basis, the reduction of nontronite to metallic iron should be assisted by the field, but in practice is found to be slightly retarded. Thus, the thermal behaviour of nontronite in a magnetic field is evidently more complex than would be expected from existing theory.

ACKNOWLEDGEMENTS

We are indebted to Dr. J.W. Waters for the nontronite samples and to Prof. N.F. Curtis for the use of the Faraday electrobalance.

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