JOURNAL OF
Materials
CHEMISTRY

Determination of the kinetics of crystallisation of gibbsite using time resolved *in situ* energy dispersive powder X-ray diffraction†

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Received 15th June 2000, Accepted 18th July 2000
First published as an Advanced Article on the web 4th September 2000

Time resolved *in situ* powder X-ray diffraction has been used to study the kinetics of crystallisation of gibbsite from supersaturated synthetic Bayer liquors as a function of temperature and hydroxide ion concentration. It was found that the crystallisation data was best described in terms of the Avrami–Erofe'ev kinetic model. This analysis indicated a two-dimensional growth mechanism with a deceleratory nucleation rate.

Introduction

In situ monitoring of chemical reactions can provide valuable insights into the kinetics and mechanisms of the processes occurring. This kind of information is just not available by studying solid state reactions using more conventional *ex situ* studies. Recently, the development of high flux synchrotron X-ray and neutron sources has led to the use of *in situ* diffraction in such studies becoming much more routine. In particular energy dispersive synchrotron X-ray diffraction (EDXRD), which uses polychromatic radiation and an energy discriminating detector, has yielded valuable kinetic and mechanistic information. For example, we have used *in situ* EDXRD techniques to: study intercalation reactions of metal dichalcogenide host lattices,[1,2] provide evidence for staging and selectivity in ion exchange reactions of layered double hydroxides,[3–5] reveal the existence of intermediate phases in the crystallisation of gallophosphates[6,7] and elucidate the mechanism of formation of mesoporous silicates.[8,9] Comprehensive reviews have recently been published on the application of *in situ* techniques to sol–gel syntheses and the crystallisation of microporous materials.[10,11]

Aluminium hydroxide is a naturally occurring mineral with four structural modifications: gibbsite,[12,13] bayerite,[14–16] nordstrandite[17–19] and doyleite.[20] Gibbsite (γ-Al(OH)$_3$) is an industrially important material being a major intermediate in the Bayer process for the extraction of alumina from bauxite. Although this process has been in use for over 100 years the mechanism for the crystallisation of gibbsite is still unclear. As a consequence of this there have been numerous studies into the crystallisation utilising a variety of experimental techniques including ^{27}Al NMR,[21–24] IR and small angle X-ray scattering[25,26] and molecular modelling.[27]

In situ X-ray diffraction has previously been used to study the crystallisation of aluminium hydroxide.[28] This study looked at the factors affecting the polymorph of aluminium hydroxide which crystallised from highly caustic solutions but was unable to provide any kinetic data. It was found that only gibbsite was obtained if gibbsite was used as the source of aluminium or if the solution was seeded prior to crystallisation with either gibbsite or bayerite. However if aluminium metal was used then a mixture of gibbsite and bayerite crystallised from the liquor.

In this paper we describe the use of time resolved *in situ* energy dispersive X-ray diffraction to study the kinetics and mechanism of the crystallisation of gibbsite from supersaturated sodium aluminate solutions.

Experimental

Synthesis

Supersaturated solutions of sodium aluminate were prepared by the dissolution of aluminium wire into sodium hydroxide at 80 °C. Two sets of experiments were performed using either 3.77 M or 6 M NaOH and a Na : Al molar ratio of 1.37. The crystallisation of gibbsite from 10 mL of solution was monitored at 65, 80 and 90 °C in each case.

Diffraction experiments

Time resolved *in situ* X-ray diffraction studies were performed using the energy dispersive powder diffraction method on Station 16.4 of the UK Synchrotron Radiation Source (SRS) at the Daresbury Laboratory, UK using an experimental setup which has been described elsewhere.[29,30] In a typical experiment individual spectra were collected with an acquisition time of either 120 or 300 s and a fixed detector angle (2θ) of 4.2°. This geometrical setting allows the detector to sample Bragg reflections in the *d*-spacing range 8.5–2 Å. This range is such that it will permit Bragg reflections due to all the polymorphs of aluminium hydroxide to be monitored simultaneously.

Results and discussion

The *in situ* diffraction experiments were carried out on each of the six liquors and in each case the 002 (4.85 Å, 34.88 keV), 110 (4.38 Å, 38.62 keV), 200 (4.33 Å, 39.07 keV) and some higher order Bragg reflections of gibbsite were observed to grow in smoothly after an initial induction period. A typical energy dispersive X-ray diffraction pattern of gibbsite with an acquisition time of 300 s is shown in Fig. 1 and the course of a typical crystallisation run is shown as a 3D stack plot in Fig. 2, from which it can be seen that only Bragg reflections due to gibbsite are observed throughout the whole growth process. The high background profile is due to diffuse scatter from the cell and sample through which the beam passes. The higher order Bragg reflections were of insufficient intensity to be used in the kinetic analysis. Experiments using a higher fixed detector angle of 8.0° 2θ were also performed but again the observed reflections were too weak to be used in the kinetic analysis. In each experiment gibbsite was the only crystalline

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†Electronic supplementary information (ESI) available: raw data for α *vs.* t plot. See http://www.rsc.org/suppdata/jm/b0/b005198p/

DOI: 10.1039/b005198p

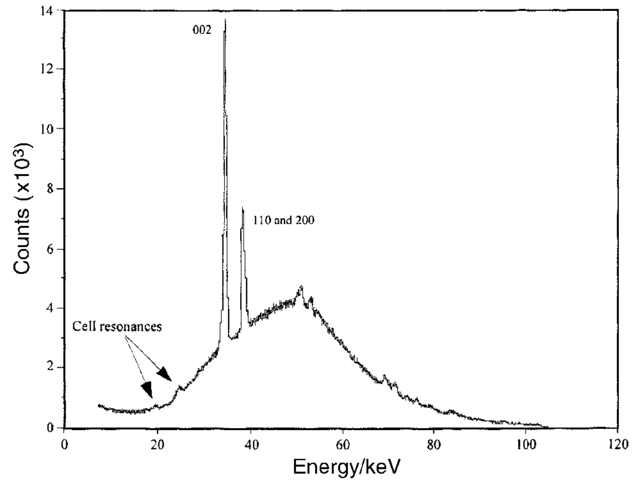

Fig. 1 Energy dispersive powder X-ray diffraction spectrum of a 500 mg sample of gibbsite stirred in 10 cm^{-3} of water. Total data collection time was 300 s and the detector angle, $2\theta = 4.2°$.

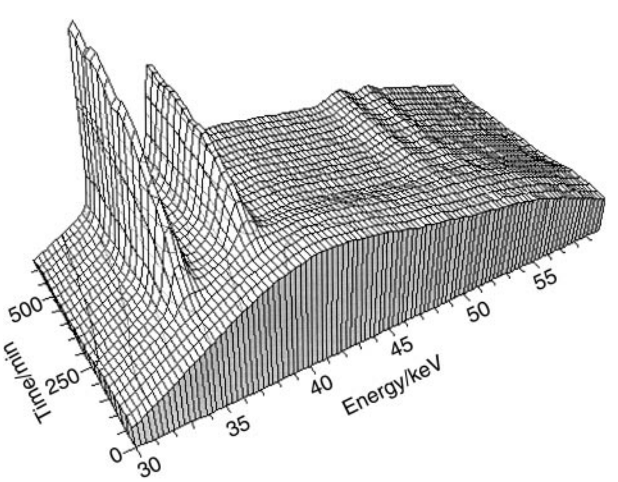

Fig. 2 Three-dimensional plot showing the time evolution of the growth of gibbsite from a caustic liquor containing 3.77 M NaOH and a Na : Al molar ratio of 1.37 at 80 °C.

phase observed though a standard sample containing a mixture of gibbsite and bayerite showed that it was possible to resolve the 00*l* reflections of these polymorphs.

Kinetic analysis of the growth rates of the observed diffraction peaks was performed by integration of the peak intensity in the individual spectra using a Gaussian fitting routine.[31] The value of the extent of reaction, α at any time, t, can be calculated from the growth of a new Bragg reflection (*hkl*) as defined by eqn. (1)

$$\alpha_{hkl}(t) = \left(\frac{I_{hkl}(t)}{I_{hkl}(t_\infty)}\right) \qquad (1)$$

where $I_{hkl}(t)$ represents the integrated intensity of a reflection (*hkl*) at time, t, and $I_{hkl}(t_\infty)$ is the integrated intensity when the reaction is complete. The errors on the integrated intensities, and therefore the extent of reaction, are small and contained with the data points.

Analysis of the extent of reaction data for the different Bragg reflections in each run shows that the α–time curves are superimposable within experimental error as shown in Fig. 3(a). This indicates that once the growth nuclei have formed the relative growth rates are the same for the different reflections implying that the crystal morphology does not change. If the α-curves for the crystallisation from solutions at different temperatures and starting concentrations are compared in the form of a reduced time plot then they are all superimposable within experimental error as shown in Fig. 3(b). This suggests that the mechanism of crystallisation is the same in each case regardless of temperature or initial concentration.

One of the most widely used treatments of solid state kinetics are the schemes proposed by Avrami and Erofe'ev.[32–35] The Avrami–Erofe'ev relationship assumes that a solid state transformation proceeds by a nucleation-and-growth mechanism and takes into account the coalescence and ingestion of other nuclei as the new phase grows. Nucleation is assumed to be random, that is if the entire sample is divided into small equal volumes, then the probability of a nucleus forming in each element in unit time is the same. The generalised theory also assumes isotropic growth (equivalent growth in all three crystallographic directions) and that the number of potential nucleation sites are limited. The general functional form is given by eqn. (2)

$$\alpha(t) = 1 - \exp\{-(k_{\mathrm{obs}}t)^m\} \qquad (2)$$

where: $3 \leqslant m \leqslant 4$ for three-dimensional growth; $2 \leqslant m \leqslant 3$ for two-dimensional growth or $1 \leqslant m \leqslant 2$ for one-dimensional growth. This equation has successfully been applied to a variety of solid state processes including decompositions,[36] phase transformations,[37] crystallisations[38] and intercalation reactions.[2] For these systems it was generally found to be most applicable for the range $0.15 < \alpha < 0.5$.

Data for the crystallisation of gibbsite were fitted to the Avrami–Erofe'ev equation and it was found that it gave a good fit for α values up to approximately 0.6. A typical α *versus* time curve is shown in Fig. 4 along with the corresponding Sharp–Hancock plot.[36] This analysis allows the determination of a rate constant and reaction exponent for each crystallisation run. The kinetic data are summarised in Table 1 from which it can be seen that the exponents lie in the range 0.9–1.8 which following the analysis of

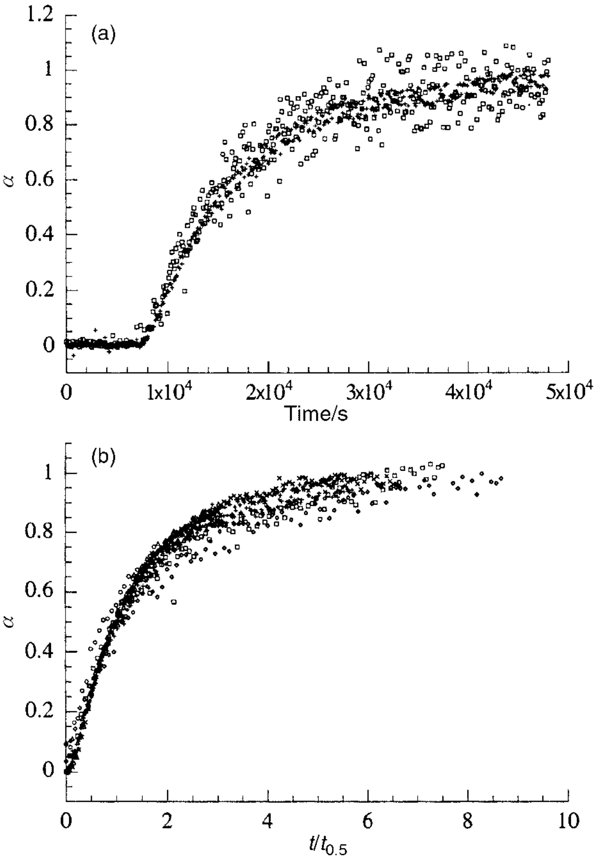

Fig. 3 (a) Comparison of the extent of reaction *versus* time curves for the growth of the 001 (+) and 110 (□) reflections of gibbsite from a supersaturated sodium aluminate solution at 65 °C. (b) Plot of extent of reaction against reduced time ($t/t_{0.5}$) for the crystallisations from 3.77 M NaOH at 65 °C (+), 80 °C (△), 90 °C (○) and from 6 M NaOH at 65 °C (□), 80 °C (*), 90 °C (×).

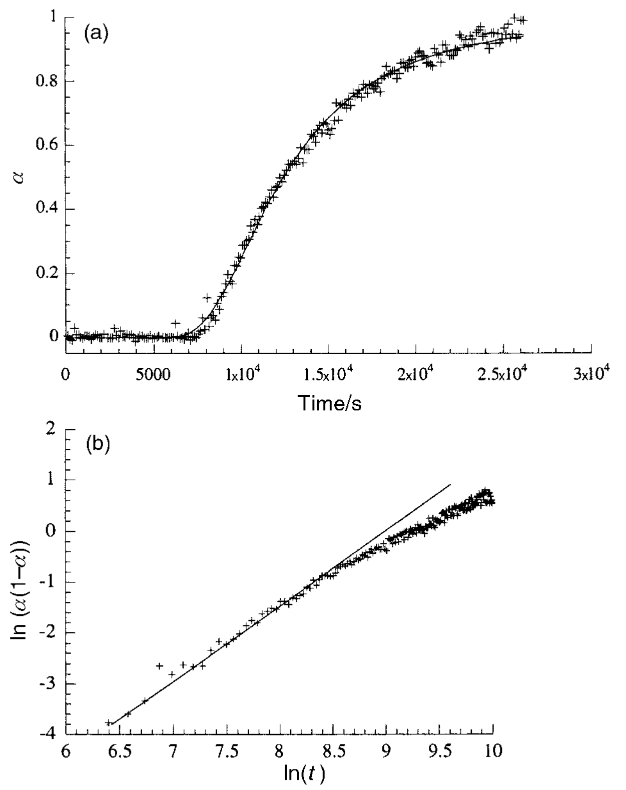

Fig. 4 (a) Plot of α *versus* time for the crystallisation of gibbsite from a supersaturated sodium aluminate solution (3.77 M NaOH) at 65 °C. The data has been fitted to the Avrami–Erofe'ev rate equation [eqn. (2)]. (b) Sharp–Hancock plot for the same data.

Hulbert is indicative of a two-dimensional diffusion controlled growth process with a deceleratory nucleation rate.[39] This mechanism would appear to be reasonable given the layered nature of the crystal structure of gibbsite and that as the crystallisation proceeds the decreasing supersaturation of the solution will lead to a decreasing rate of nucleation.

One of the problems with the crystallisation of gibbsite is the difficulty in obtaining reproducible induction periods before the onset of growth. This is perhaps not surprising given the complex nature of the solutions and the fact that, due to the constraints of beamtime, data were collected over several visits to the SRS. Small variations in factors such as speed of stirring and even the ampoule used may lead to variations in the rate of formation of the initial growth nuclei. However, once the growth had been initiated the data were reproducible. In order to overcome these problems a subsequent study has been performed in which seeded crystal growth of gibbsite is monitored in the same way. This data will be published elsewhere.[40]

Summary of the kinetic and mechanistic information

Time resolved *in situ* EDXRD experiments have revealed considerable kinetic and mechanistic information on the crystallisation of gibbsite from supersaturated sodium aluminate solutions. It was found that the data could be satisfactorily fitted by Avrami–Erofe'ev kinetics with data indicating a two-dimensional growth mechanism with a deceleratory nucleation rate. The rate of crystallisation was found to vary both as a function of temperature and initial level of supersaturation.

Table 1 Kinetic parameters for the crystallisation of gibbsite obtained by least square fitting to the Avrami–Erofe'ev rate equation eqn. (2)]

[NaOH]/mol dm^{-3}	T/°C	m	k/s^{-1}
3.77	65	1.31	1.06×10^{-4}
3.77	80	1.50	1.58×10^{-4}
3.77	90	0.96	2.51×10^{-4}
6.00	65	1.12	1.89×10^{-4}
6.00	80	0.97	2.14×10^{-4}
6.00	90	1.82	4.17×10^{-4}

Acknowledgements

We thank Professor Gordon Parkinson for helpful discussions and the Leverhulme Trust for financial support. The EPSRC is acknowledged for financial support and for provision of facilities at Daresbury Laboratory.

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