Thermochimica Acta, 113 (1987) 87–94
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

KINETIC INVESTIGATION OF THE SORPTION OF WATER BY LITHIUM HYDROXIDE

JOAN DE PABLO *

Departamento Química, ETSEIB (UPC), Diagonal 647, E-08028 Barcelona (Spain)

JAN ANDERSSON and MICHEL AZOULAY

Department of Physical Chemistry, The Royal Institute of Technology,
S-100 44 Stockholm (Sweden)

(Received 28 July 1986)

ABSTRACT

The mechanism for the rehydration reaction LiOH (s) + H_2O (g) = LiOH·H_2O (s) was investigated by using thermogravimetry under controlled water vapour pressure. The mechanism has been explained as resulting from the formation of capillary condensed water and the formation of an impenetrable hydrate layer which stops the reaction at 0.5 mole of H_2O per mole of LiOH. Scanning electron microscopy and X-ray diffractometry confirm this interpretation.

INTRODUCTION

Salt hydrates have been proposed to be used as heat storage media in chemical heat pumps [1]. A selection of suitable salt hydrates can be made from their thermodynamic properties [2], e.g., the theoretical temperature difference between the hot and cold reservoir and the energy density within the working temperature range. However, other kinds of limitation exist which cannot easily be scrutinized. An important limitation operates at the particle level, which is especially important for processes where the sorption is accompanied by a structural transformation. This is thus inherent to the salt hydrate–water vapour reaction. A survey of the literature indicates that sorption kinetics is a poorly investigated topic [3–17]. It is being increasingly recognized that more basic knowledge is required for a more direct application of the chemical heat pump.

In a previous paper [16], we have established the dynamic criteria for salt hydrates with regard to their suitability for chemical heat pumping. The

---

* To whom correspondence should be addressed.

0040-6031/87/$03.50 © 1987 Elsevier Science Publishers B.V.

present work tries to demonstrate that basic kinetic knowledge of these reactions is necessary. We decided to investigate the sorption kinetics for the following reaction:

$$\mathrm{LiOH\ (s) + H_2O\ (g) = LiOH \cdot H_2O\ (s)}$$

which has very interesting thermodynamic properties, energy density 0.70 kWh kg^{-1} anhydride, as well as a proper temperature interval. Equilibrium data have been recently determined [18]. Furthermore, complete crystal structures have been determined for LiOH [19] and $LiOH \cdot H_2O$ [20].

The work reported in this paper involved the use of thermogravimetry, scanning electron microscope and X-ray diffractometry.

EXPERIMENTAL

Materials

Crystalline $LiOH \cdot H_2O$ (Merck p.a.) powders were classified by sieving, and the fraction in the range 100–125 μm was used. The compound was crystallographically identified as $LiOH \cdot H_2O$ and used without further purification.

Experimental procedure

Sorption studies were performed mainly by means of thermogravimetry under controlled water vapour pressure according to the cold-point method [21]. The instrumental set up is well suited for kinetic experiments in both isothermal and temperature scanning modes.

Instrumentation

The thermogravimetry equipment used, which consists of a McBain quartz spring balance, is described elsewhere [22,23]. X-ray diffractograms were taken by means of a Siemens Kristalloflex 4. Microstructural studies were carried out by using a Philips 500 scanning electron microscope.

RESULTS

Kinetics studies by thermogravimetry

Temperature scanning experiments

Water vapour pressure was kept constant at 6 torr during these experiments and the temperature was scanned from 20 to 60°C and vice versa at

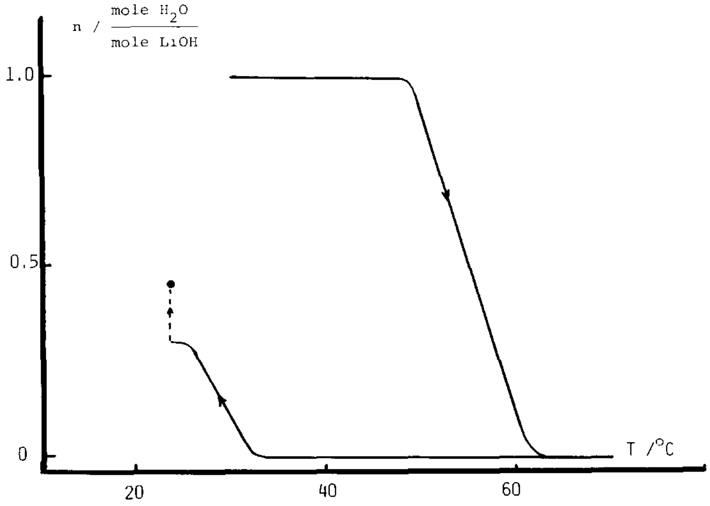

Fig. 1. Thermogram for an incomplete dehydration–rehydration cycle at 6.7 torr. Scanning rate 12°C h^{-1}. Particle size 0.100–0.125 mm. The dashed line of the rehydration branch refers to isothermal conditions for 9 h.

12°C h^{-1}. Figure 1 shows the results and it can be seen that the rehydration process is not complete, even under isothermal conditions for 9 h (dashed line). This behaviour was not modified by increasing the water vapour pressure.

Isothermal experiments

Isothermal experiments were carried out in order to check the possibility of completely rehydrating LiOH anhydride. The isothermal dehydrations were always performed at 6 torr at 47°C and the sorption progress curves were obtained at various pressures. Typical progress curves are illustrated in Fig. 2. It is noteworthy that, after a short induction period, the reaction proceeds quickly up to 0.5 mole of H_2O per mole of LiOH, but after 72 h at these conditions an increase of only 0.1 mol of water was observed.

In order to get more information, reaction rates were calculated from the slope of the linear parts of the progress curves, and were plotted versus pressure at 47°C (Fig. 3). It is interesting that the reaction rate isotherm does not intersect the pressure axis at the equilibrium pressure which is added in the plot, the observed deviation is about 7 torr. Similar results have been obtained previously [16]. Some rehydrations were carried out at 25 and 40°C. These results showed that LiOH can only be rehydrated partially and it was never possible to rehydrate more than 0.65 mol of H_2O per mol of LiOH, even after rehydrating for one week.

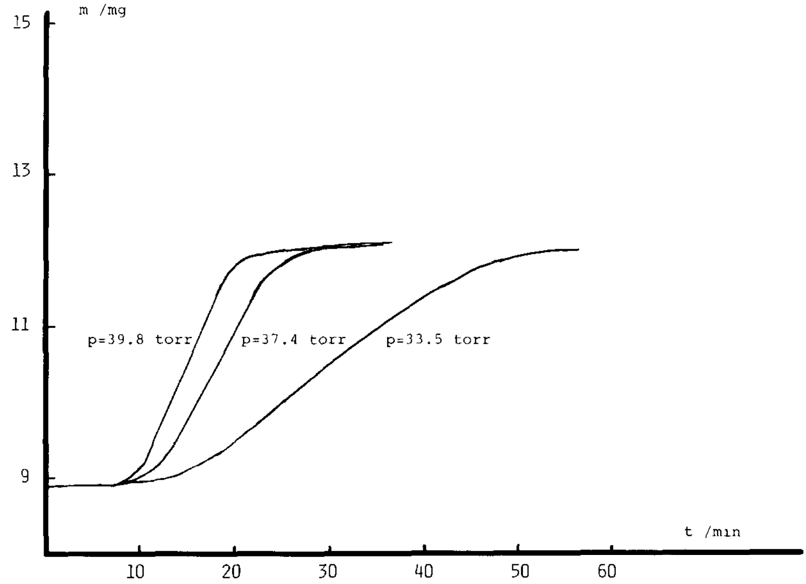

Fig. 2. Rehydration curves at 47 °C and different water vapour pressures. Particle size 0.100–0.125 mm.

Phase analysis of the reaction products

LiOH obtained from LiOH · H_2O at 6 torr and in vacuum was crystallographically characterized by its X-ray powder diffractogram. The X-ray

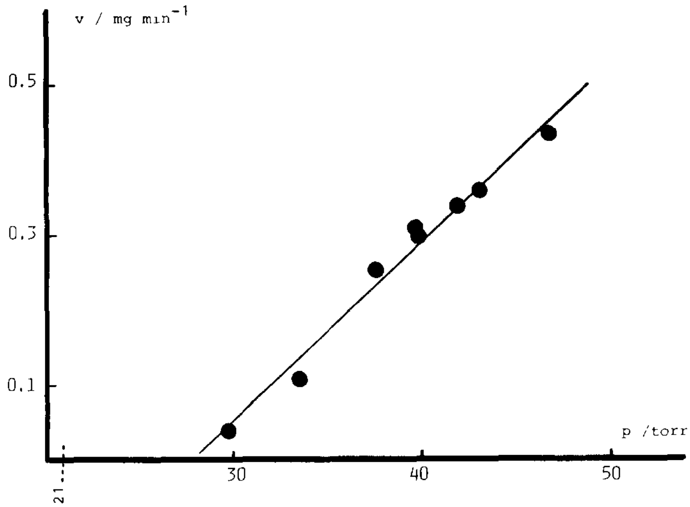

Fig. 3. Reaction rate isotherm versus vapour pressure at 47 °C. Particle size 0.100–0.125 mm.

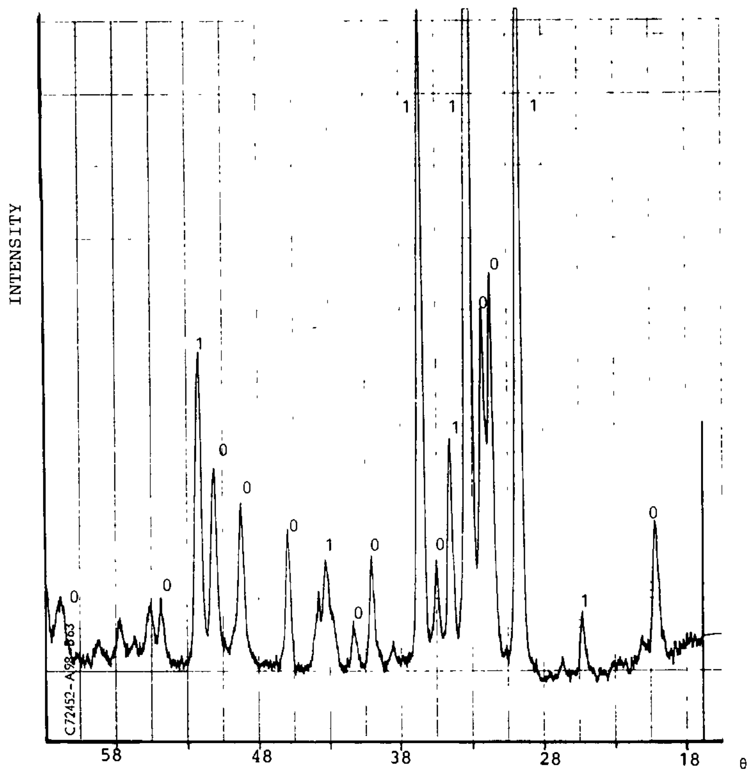

Fig. 4. X-ray diffractogram of rehydrated lithium hydroxide. Scanning rate 2.5° min^{-1}. (1) Characteristic reflections of $LiOH \cdot H_2O$. (0) Characteristic reflections of LiOH.

diffractogram of the rehydrated product is shown in Fig. 4. This diffractogram shows the characteristic reflections of $LiOH \cdot H_2O$ [20] and LiOH [19]. All these experiments were carried out at constant temperature and water vapour pressure.

Microstructural analysis

Scanning electron microscope examinations of rehydrated lithium hydroxide were made in the magnification range 320–5000 × . Figure 5 (a) shows a microphotograph of the rehydrated particle; it should be noted that the external shape remains unchanged and the surface is very compact. The other microphotograph (Fig. 5 (b)) shows the particle cross section, which reveals the internal microstructure of the same product. The presence of cracks and pores can be observed.

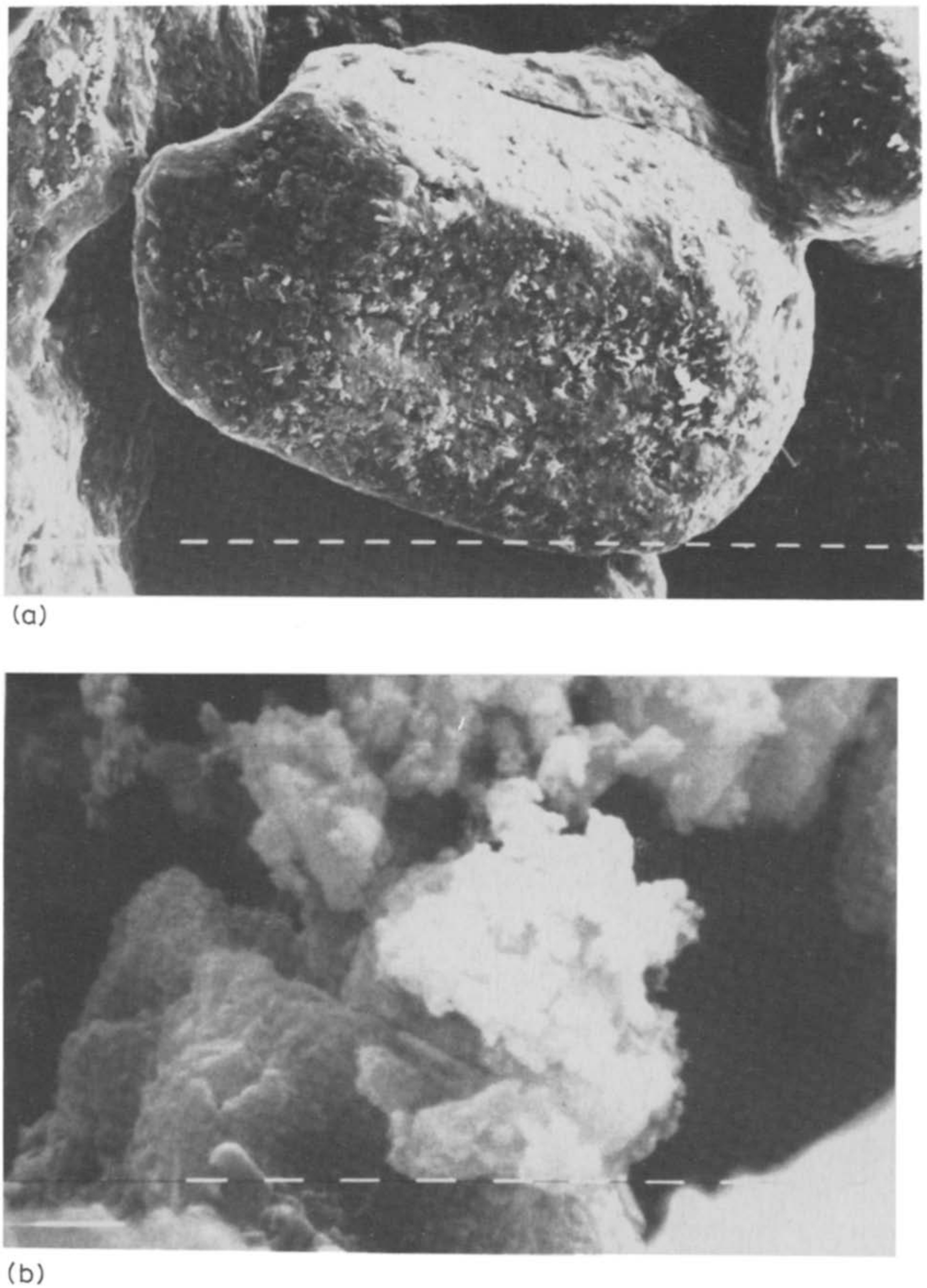

Fig. 5. Scanning electron micrographs showing: (a) rehydrated particle shape (320×); (b) a sectioned rehydrated particle (5000×).

DISCUSSION

The rehydration of LiOH is not complete at the conditions of temperature and pressure studied in this work. This result indicates that it is necessary to take into account the kinetic properties of the salt hydrates which are to be used in a chemical heat pump.

The rehydration mechanism of salt hydrates consists of several intermediate steps. The first one is always adsorption of water onto the surface. As discussed elsewhere [16], when the water vapour pressure is high enough, there is capillary condensation which facilitates the structural transformation. Figure 4b indicates the formation of pores and cracks in the anhydride during dehydration which facilitate at the beginning of the reaction. This explains the inhibition domain appearing in Fig. 2 where capillary condensation is absent.

Thermogravimetry and X-ray results show that it is not possible to rehydrate LiOH completely even after several cycles. This experimental finding can be understood as follows: the initial rapid rehydration is confined to surface layers; additional rehydration should occur through the lithium hydroxide monohydrate layers at the surface, and it seems to be impenetrable to water vapour, at least during one week of rehydration.

The formation of an impenetrable layer in some rehydrations can be related to the different molar volume changes between the two phases. In the present case the molar volume change is 40%, which is enough to form this impenetrable layer. In other complete rehydrations which can be explained by a similar mechanism (e.g., CaC_2O_4 [6], $BaCl_2 \cdot H_2O$ [16] and $Mn(HCO_2)_2$ [13]), there is a change of less than 15%.

ACKNOWLEDGEMENT

This work was supported by The Swedish Natural Science Research Council.

REFERENCES

1 G. Wettermark (Ed.), Proceedings of the International Seminar on Thermochemical Energy Storage, Swedish Council for Building Research, Stockholm, 1980.
2 E.A. Brunberg, The Tepidus Storage System, German-Swedish Workshop on Thermochemical Energy Storage and Absorption Heat Pump Technology, Stockholm, 1980.
3 A. Bielanski and F.C. Tompkins, Trans. Faraday Soc., 46 (1950) 1072.
4 R.M. Dell and S.W. Weller, Trans. Faraday Soc., 55 (12) (1959) 2203.
5 P. Barret and R. Thiard, C.R. Acad. Sci., Ser. C, 260 (1965) 2823.
6 N. Gerard, G. Watelle-Marion and A. Thrierr-Sorel, Bull. Soc. Chim. Fr., 5 (1967) 1788.
7 M. Trollier and B. Guilhot, C.R. Acad. Sci., Ser. C, 281 (1975) 27.

8 M. Trollier and B. Guilhot, Bull. Soc. Chim. Fr., (1977) 1.
9 S. El and D. Hamad, Thermochim. Acta, 17 (1976) 85.
10 B. Beden, A. Cointot, M.J. Croissant and G. Valensi, Kinetics in Heterogeneous Chemical Systems, Elsevier, Amsterdam, 1975.
11 J. Andersson, M. Azoulay and J. de Pablo, Thermochim. Acta, 91 (1985) 223.
12 T.B. Flanagan, Can. J. Chem., 44 (1966) 2941.
13 R.C. Eckhardt, P.M. Fichte and T.B. Flanagan, Trans. Faraday Soc., 67 (1970) 1143.
14 P.M. Fichte and T.B. Flanagan, Trans. Faraday Soc., 67 (1971) 1467.
15 M.L. Franklin and T.B. Flanagan, J. Chem. Soc., Dalton Trans., (1972) 192.
16 J. Andersson, M. Azoulay and J. de Pablo, Thermochim. Acta, 70 (1983) 291.
17 M.A. Stanish and D.D. Perlmutter, AIChE J., 30 (1984) 56.
18 E.A. Brunberg, The Royal Institute of Technology, Stockholm, to be published.
19 ASTM LiOH card No. 4-0708.
20 ASTM $LiOH \cdot H_2O$ card No. 1-1062.
21 A. Tiselius and S. Brohult, Z. Phys. Chem., Abt. A: 168 (1935) 248.
22 F. Lavanant, Thesis, Dijon University, 1963.
23 M. Lallemant, Thesis, Dijon University, 1974.