Thermochimica Acta, 29 (1979) 277–282

GRAVIMETRIC STUDIES OF AGEING IN MICROPOROUS ZIRCONIA GELS

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ABSTRACT

The work reported in this paper demonstrates the use of the gravimetric techniques to characterize the irreversible textural changes in a hydrous oxide system. A series of microporous zirconia gels were prepared under strictly controlled conditions in the aqueous medium. The porosities of the gels have been characterized by the studies of the nitrogen and water adsorption isotherms. The water sorption isotherms indicated an ageing phenomenon demonstrated by the negative low pressure hysteresis.

Further, the hydrous gels which were initially outgassed at 298K (at 10^{-4} torr for 48 h) showed, on subsequent exposure to water vapour, an enhanced desorption (>30%) in excess of the total amount sorbed.

The mechanism of this ageing process is not obvious, but it is suggested that the loss in weight induced by almost saturated water vapour arises from the withdrawal of the molecular water present within the elementary particles of the hydrous oxide gels. The removal of the sorbed water results in the closure of micropores.

INTRODUCTION

The term "ageing" has been used, in the domain of hydrous oxides, to indicate all those irreversible structural (refs. 1,2) and textural (refs. 2,3) changes which occur after floculation or gelation. Ageing processes in different hydrous oxide systems (eg. Alumina, Silica, Chromia) have been investigated (refs. 2,4), and three distinct mechanisms have been identifed : (a) condensation polymerization (b) aggregation-cementation and (c) crystallization. Water plays a key role in all these ageing mechanisms (refs. 2,4).

In this paper we report the ageing of microporous hydrous zirconia gels with special emphasis on the role of water. We shall, however, confine ourselves here to only the textural changes in the gels. Gravimetric method has been used to study

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the sorption of water vapour, the results of which give a deeper understanding of the ageing processes.

EXPERIMENTAL

Preparation of microporous zirconia gels.

A series of microporous zirconia gels has been prepared at different pH values under strictly controlled conditions (ref. 5), using zirconyl chloride (20g in 400 cm^3 deionized water) as the starting material and ammonia gas (5000 $cm^3\ h^{-1}$) as the precipitant. After the completion of gelation, the gels were frozen at 77K (for 24 h), a process suggested by Rijnten (ref. 6) for obtaining finely divided zirconia gels, following the procedure earlier reported by Van der Geissen (ref. 7). The gels were then thawed at room temperature, washed free of impurities (eg. NH_4^+, Cl^-), filtered and subsequently dried under vacuum at 25°C.

Nitrogen adsorption

Nitrogen adsorption isotherms were determined volumetrically at 77K by means of a refined apparatus (ref. 8), based on the design of Harris and Sing (ref.9). Equilibrium pressures were measured on a mercury manometer with the aid of a cathetometer (to ± 0.002 cm).

Water sorption isotherms

Water sorption isotherms were obtained gravimetrically (ref. 8), using a McBain-Bakr fused quartz helical spring balance with a sensitivity $\pm 10^{-5}$ g. The spring was thermostated at 26.5 ± 0.05°C and the zirconia gel samples were maintained at 25°C. The extension of the spring was monitored by a cathetometer (to ± 0.002 cm). Equilibrium pressures were measured with a Bell and Howell (type 4-353) pressure transducer gauge (to $\pm 6.2 \times 10^{-3}$ torr). Before exposure to any water vapour, the samples were outgassed ($P<10^{-4}$ torr, for at least 36 h) at 25°C. Outgassing was considered complete when the sample under vacuum ($<10^{-4}$ torr) indicated no more weight loss for a further outgassing period of 24 h.

RESULTS AND DISCUSSION

Typical water vapour isotherms have been represented in figures 1 (a and b) and 2. The common feature of all the water isotherms is that they represent Type I in the BDDT classification, indicating microporosity. The microporous nature (pore diameter < 2nm) of these gels has been confirmed by the nitrogen adsorption studies (refs. 5,10) on the solids.

The water isotherms obtained on the solids outgassed at 25°C showed that at low relative pressures the desorption branch crossed over the sorption branch and gave rise to a negative low pressure hysteresis. In one case (fig. 2) this cross-over took place at such a low relative pressure that the plots alone were no sufficient to illustrate its significance. A better representation is in

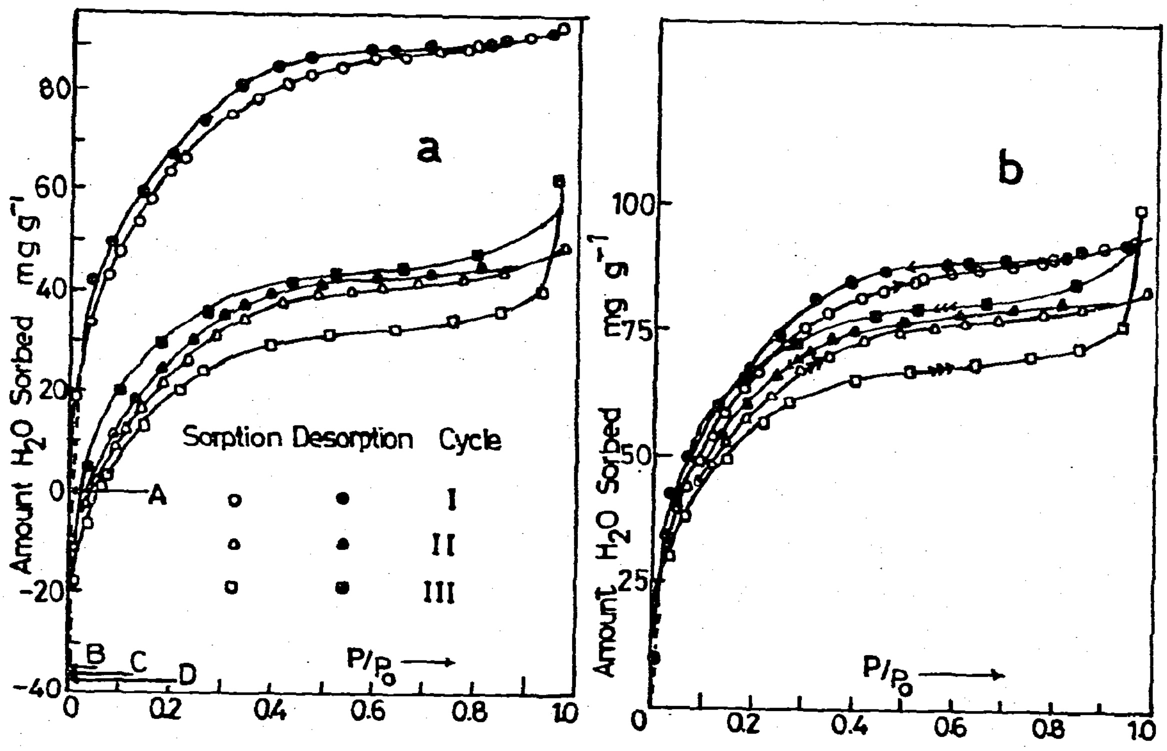

FIGURE 1 : Water Sorption Isotherms on Gel ARZr10. (a) Three are consecutive runs with relative origin for each cycle. A, B and C are the beginning of the first, second and third cycle respectively. (b) Three are consecutive runs ; zero of each run is the same.

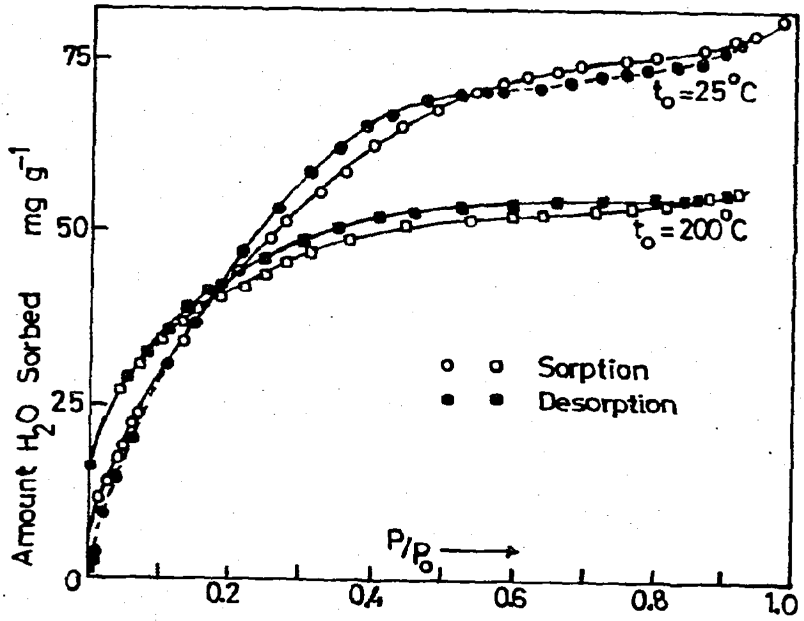

FIGURE 2 : Water Sorption Isotherms on Gel ARZr9 outgassed at 25 and 200°C respectively. (t_o refers to the outgassing temperature)

table 1, where the final desorbed amounts have been compared.

TABLE 1

Comparison of conditions of preparation and results of studies of sorption and ageing of hydroux zirconia gels.

SAMPLE	pH of Gelation	Outgassing temp °C	Micropore volume V_p cm^3 g^{-1}		Final point of desorption of water isotherms		
					Outgassing		Amount Retained mg g^{-1}
			N_2	H_2O	Time h	Pressure torr	
ARZr9	9.0	25	0.124	0.075	32	10^{-4}	-26.0
		200	0.056	0.056	16	10^{-4}	16.17
ARZr5	7.0	25	0.119	0.110	48	10^{-4}	-30.0
		200	0.042	0.050	48	10^{-4}	16.48
ARZr10	5.0	25 (I)	0.093	0.091	16	10^{-4}	-35.8
		25 (II)	-	0.082	56	5×10^{-5}	-1.23
		25 (III)	-	0.075	56	5×10^{-5}	-1.03
		200	0.030	-	-	-	-

a) Negative amount of water retained in column 8 indicates ageing effects.
b) In the case of ARZr10, three consecutive water isotherms are indicated.

The solids, outgassed over a long period at 25°C, on subsequent exposure to water vapour at the same temperature showed an enhanced desorption in excess of the total amount sorbed (Table 1). This anomalous behaviour is due to an ageing process. The gel showing the maximum weight loss on desorption has been studied in three consecutive water sorption-desorption cycles (at 25°C). In figure 1 (a) the arrow at A depicts the start of the first run, which reached desorption equilibrium at B. Point B forms the zero point of the second run, whose desorption equilibrium occurs at C and similarly D is the final desorption equilibrium for the third run. In figure 1 (b) these isotherms have been plotted, maintaining the same zero in each case. This approach demonstrated the relative change in the pore volumes after each cycle was completed. Though the limiting value of the negative hysteresis at the end of the first cycle in all the three samples is *ca.* 30 mg.g^{-1} (table 1), it fell sharply to only *ca.* 1 mg.g^{-1} in the subsequent runs with ARZr10.

The mechanism of this ageing process is not obvious, but it is suggested that the loss in weight induced by exposure to almost saturated water vapour, arises from the withdrawal of molecular water present within the elementary particles of the hydrous oxide gels. It should be noted that all the gels studied here were frozen at liquid nitrogen temperature, following precipitation, thus terminating any further polymerization occurring in the gel and leading to the formation of discrete particles. This procedure inevitably leads to the retention of water within the elementary particles, water which would normally not be removed on outgassing at low temperature (25°C). Exposure of these outgassed solids to water vapour allowed the latter to enter the narrow pores already present in the solid and leads to the generation of branching pores, through which entrapped water molecules could be desorbed at very low relative pressures.

Evidence for this proposed ageing process is provided by the successive broadening of the hysteresis loops (Fig. 1). This demonstrated a pronounced retention effect, probably caused by the creation or extension of the pore system in the primary particles. This, on one hand, increases the accessibility to the entrapped water molecules and, on the other hand, increases the retention of the sorption because of the narrower width of the pores.

Further evidence in favour of this ageing mechanism may be summarised as follows :

1) In the formation of hydrous zirconia gels (refs. 5,6),the lower the pH, the smaller is the extent of polymerization and hence the greater the amount of hydrogen bonded and coordinated water around each basic tetrameric unit of the zirconia gel network. This explains the observation that the net loss of weight, at the end of each sorption-desorption cycle performed on solids outgassed at 25°C, is greater the lower the pH at which the sample is prepared and decreases as the pH of precipitation is increased (Table 1). The thermogravimetric studies also showed a similar relationship between the weight loss by the samples during a corresponding thermal treatment (25°→ 200°C) and their pH of precipitation.

2) The ageing effect is almost totally eliminated as the outgassing temperature of the solids is increased up to 200°C. The sorption-desorption cycles on these samples showed no negative hysteresis after raising the temperature to 200°C such thermal treatment is sufficient to enable the removal of almost all the internal water and, hence, to diminish the possibility of ageing caused by exposure to water vapour.

It has been clearly demonstrated (refs. 2,4,11) with other hydrous oxide systems that amorphous products age very rapidly when dried and re-exposed to water vapour. The successive loss of pore volume in ARZr10, as is evident from Figure 1b, may be explicable by the mechanism of ageing process, partly by the removal of small particles but mainly by the closure of micropores (refs. 4,12). Studies with other similar hydrous oxide systems (refs. 4,12) indicate that the mechanism of micropore closure, is even more applicable when large quantities of water are evolved during low temperature heat treatment of poorly ordered hydrous oxides. All the solids reported here meet these requirements.

While both ARZr10 and ARZr5 gels show very good agreement between the pore volume accessible to water ($V_{p(H_2O)}$) and nitrogen ($v_{p(N_2)}$) as demonstrated in

Table 1, ARZr9 appears to be the exception. This anomalous decrease in $V_{p(H_2O)}$ may also be explained by the above-mentioned mechanism of micropore closure. The negative hysteresis at higher relative pressure (Fig. 2) supports this view. When heated to 200°C the $V_{p(H_2O)}$ and $V_{p(N_2)}$ are again in excellent agreement, demonstrating that the presence of initial residual water plays a key role in the ageing process.

CONCLUSION

Water plays a key role in the ageing mechanisms fo microporous hydrous zirconia gels. Two types of ageing processes have been identified : a) the extension of the microporous network to facilitate the withdrawal of trapped water molecules and b) closure of the micropores in a poorly ordered hydrous oxide system. The relative magnitude of the two apparently opposing processes depends on the solids (their pre-history, water content, stability of the micropore system) and the temperature to which the samples have been outgassed. The presence of sorbed water in the initial solid renders stability to the micropores in the poorly ordered hydrous oxides. Gravimetric sorption measurement has provided an important tool in the investigation of the precise textural changes occuring in the microporous hydrous zirconia gel system.

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