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EFFECT OF THERMAL DEHYDRATION ON SURFACE CHARACTERISTICS OF TITANIA GEL

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ABSTRACT

The surface properties of titania gel and its thermal dehydration products were investigated by nitrogen and water vapour sorption between 110 and 600°C. Structural and phase changes were studied by X-ray diffractometry and differential thermal analysis. Up to 200°C, samples were X-ray amorphous and formed anatase at 300, 450 and 600°C. The glow phenomenon is attributed to the conversion to anatase at 350°C.

Thermal dehydration of the gel between 110 and 300°C and 600°C led to the widening of the pore radii of the gel. At 450°C, marked steps appeared on the nitrogen isotherm, and was accompanied by a sharp increase in nitrogen uptake. The stepwise character is attributed to the presence of a certain porosity characteristic of the gel.

Heats of immersion in water depend mainly on the hydrophilic centres on the surface, whereas heats of immersion in cyclohexane are controlled by the micropore fraction of the gel.

INTRODUCTION

In a previous publication [1] the surface characteristics of titania gel and its thermal dehydration products, obtained from the addition of NH_4OH to $TiCl_3$ followed by oxidation of the precipitate by bubbling oxygen gas, were studied. In the present investigation the precipitate was oxidized with H_2O_2. An attempt was made to study the effect of the method of preparation on surface characteristics of the gel, since it has been reported that limited changes in pore volume could be obtained by changing the concentration [2] of the reagent used to prepare the gel or by changing the time [3], temperature [4], and conditions of its preparation.

MATERIALS AND METHODS

Materials

Titania gel was prepared [5] by the addition of concentrated ammonia solution to 200 ml of 15% $TiCl_3$ solution followed by 20 ml of 30% H_2O_2; the blue-black precipitate changed to white and the supernatant liquid acquired a faint yellow colour. The gel was filtered and dried at room temperature over P_2O_5 to constant weight.

Dehydration products were obtained by heating the titania gel between 110 and 600°C for 6 h in a small electrical tubular furnace at a rate of 2.5—3°C min^{-1}. The products are labelled by the letter T followed by the dehydration temperature, e.g. T200 indicates titania gel heated at 200°C for 6 h in air.

Measurements

Differential thermal analysis was carried out with α-alumina as an inert standard, a programme temperature controller "ether" transitrol type 996/2 to permit a linear rate of heating of 12°C min^{-1}, and a Cambridge Recorder Model "B" for recording temperature difference.

X-Ray diffraction patterns were obtained by means of a GEXR diffraction unit, Model XRD-6, using Cu$K\alpha$ radiation. The calculated d distances were compared with their relative intensities in ASTM cards [6].

Adsorption—desorption isotherms of nitrogen at —195°C were determined by using a conventional volumetric apparatus [7].

Water adsorption was determined gravimetrically at 35°C using a McBain-Bakr quartz spring balance with a sensitivity of about 25 mg^{-1}. The elongation of the balance was determined using a cathetometer that read to 0.01 mm.

H_i values were determined at 300 ± 0.05°C by means of a calorimeter thermostatted within ±0.002°C. Details of the calorimeter are described elsewhere [8]. At least two electrical calibrations were performed after each experiment, the agreement between these pairs always being better than 0.3%. All H_i values reported here are the result of at least two independent determinations.

RESULTS AND DISCUSSION

X-Ray diffraction (XRD) patterns of titania gel dehydrated up to 200°C were partially amorphous (showing no distinct peaks but very broad bands). Thermal treatment at 300, 450 and 600°C produced anatase, as shown in Fig. 1.

The DTA isotherm of titania gel exhibits an endothermic effect caused by dehydration at 190°C (Fig. 2), followed by a sharp exothermic effect, the glow phenomenon, at 350°C, due to the crystallization of the gel. The second exothermic effect at 550°C may be related to a complete transformation process of titanium oxyhydroxide to the oxide, viz. $TiO(OH)_2 \rightarrow TiO_2$, since the water content of T450 and T600 is 0.128 and 0.0%, respectively, as shown in Table 1. The reluctance of evolution of the last traces of water at about 450°C indicates that this is present in narrow pores of the gel.

Full adsorption—desorption cycles of nitrogen at —195°C, and water vapour at 35°C, were carried out on titania gel thermally treated between 110 and 600°C. As shown in Fig. 3, the nitrogen isotherm of T110 is mainly

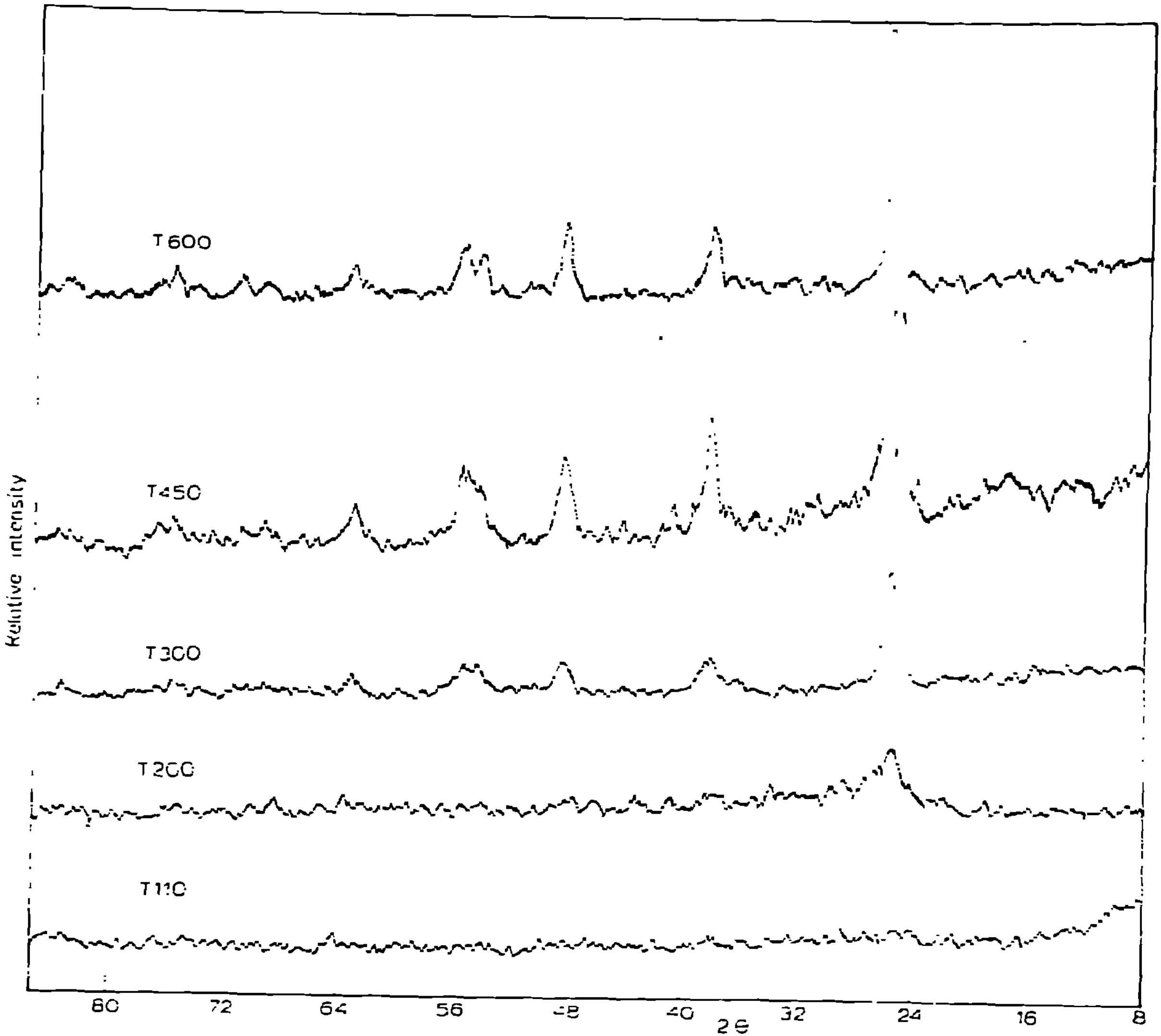

Fig. 1. X-Ray diffraction patterns of titania gel and its thermal dehydration products.

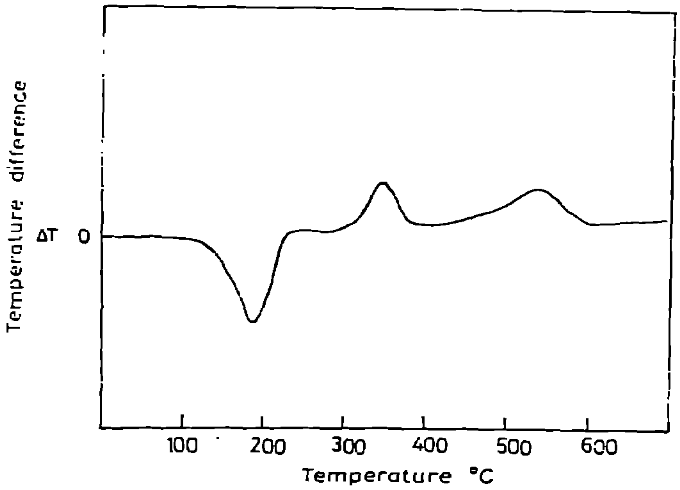

Fig. 2. Differential thermal analysis of titania gel.

TABLE 1

Some surface characteristics of titania gel (anatase modification)

Sample	$S_{BET}^{N_2}$ (m^2 g^{-1})	S_t (m^2 g^{-1})	$\bar{r}$ (Å)	C-BET constant	V_p (ml g^{-1})	H_2O adsorbed × 10^{-1} (g g^{-1})	H_i cal/g		Water content (%)
							C_6H_{12}	H_2O	
T110	140	139	15	58	0.1055	0.9660	0.4470	2.639	20.78
T200	124	120	31	19	0.1939	0.6309	0.3110	2.498	8.19
T300	112	105	32	45	0.1785	0.2238	0.2023	1.214	1.70
T450					0.9125	0.1258	0.9831	0.763	0.128
T600	68	65	33	21	0.1133	0.0581	0.0813	0.935	0.000

type I and those of T200, T300 and T600 are type II of the BDDT classification [9]; the T450 isotherm shows stepwise character. The T110 and T600 nitrogen isotherms are mainly reversible, those on T200 and T300 exhibit a hysteresis loop closed at $P/P_0 \sim 0.45$ and 0.6, respectively. The T450 nitrogen isotherm exhibits a hysteresis loop which was closed at $P/P_0 \sim 0.65$, and then reopened at the lowest P/P_0 attained in the measurement. Water adsorption isotherms (Fig. 4) are mainly type I of the BDDT classification and are reversible, except that of T200, which exhibits a hysteresis effect closing at $P/P_0 \sim 0.4$.

The nitrogen-specific surface areas of various samples were calculated by application of the BET equation in the P/P_0 range 0.05—0.35, and adopting the value of the molecular area of nitrogen as 16.2 Å^2 [10]. $S_{BET}^{N_2}$ areas are summarized in Table 1. Nitrogen uptake, expressed as V_p (ml g^{-1}), is also summarized in Table 1 and it is clear that V_p values increased with increase in temperature of thermal treatment up to 300°C, and reached a maximum value at 450°C, after which a sharp decrease was observed at 600°C.

The amount of water adsorbed (expressed in g g^{-1}), as calculated from the Dubinin equation [11], shows a gradual decrease with increase in dehydration temperature.

Analysis of the adsorption data was carried out using the V_l—t method. Evidence favours the argument [12] that the V_l—t area, denoted S_t, is identical to $S_{BET}^{N_2}$, provided a correct t curve is used in the analysis. A basic requirement is to have a t curve based on adsorbents with comparable heats of adsorption BET-C constants. This condition was fulfilled for nitrogen adsorption by using the t curve of de Boer and co-workers [13] for T110 and T300 samples and that of Mikhail et al. [14] for the others. A typical set of V_l—t plots for samples T110—T600 from nitrogen adsorption data is given in Fig. 5. The S_t values are summarized in Table 1.

After evolution of the water of hydration, the microporous character of the parent gel was converted to mesoporous character, as indicated from the average pore radius, $\bar{r}$, show in Table 1; thus the average pore radius of the parent sample was 15 Å, and after partial and complete dehydration it was found to be 33 Å. The stepwise character of the isotherm obtained at 450°C made analysis by the V_l—t method impossible. The high nitrogen uptake at

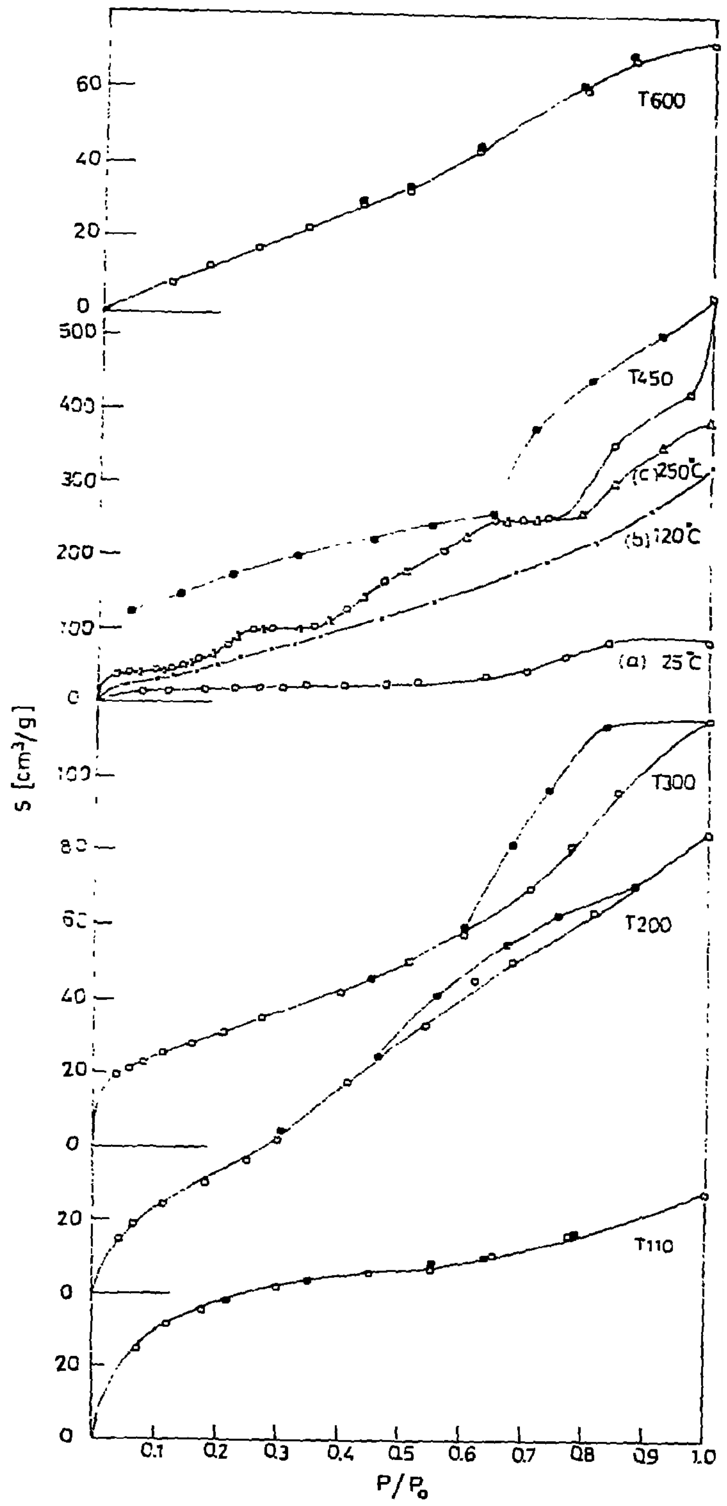

Fig. 3. Adsorption—desorption isotherms of nitrogen on titania gel and its thermal dehydration products. (a), (b), and (c) are nitrogen isotherms on T450 filled with nonane and partially evacuated at 25, 120, and 250°C.

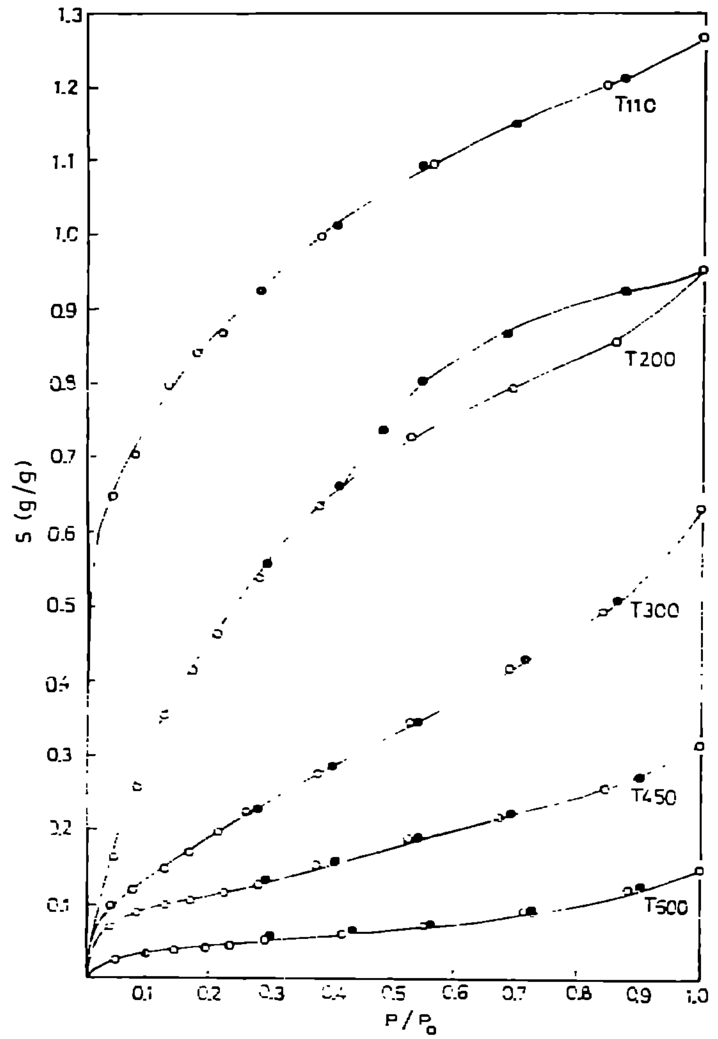

Fig. 4. Adsorption—desorption isotherms of water vapour on titania gel and its thermal dehydration products.

this temperature indicates that the sample is mainly porous. The porosity of this sample, T450, was tested by using Gregg and Langford's method [15], in which the evacuated sample, T450, was filled with nonane at −195°C. Nitrogen isotherms at −195°C were then carried out on the partially evacuated samples; these are represented in Fig. 3 (a, b and c). Isotherms (a) and (b) are mainly type II of the BDDT classification, no steps were observed on these two isotherms. After evacuation at a higher temperature, the isotherm restored the stepwise character, as shown in Fig. 3(c), but nitrogen uptake on this sample was still lower than the unfilled sample, especially at high P/P_0 values.

Stepwise multilayer adsorption isotherms are usually associated with adsorption on uniform non-porous surfaces; such isotherms have been noted for the adsorption of krypton on metal films [16], argon on highly graphitized carbon [17], on sintered powders [18,19], and on hexagonal boron

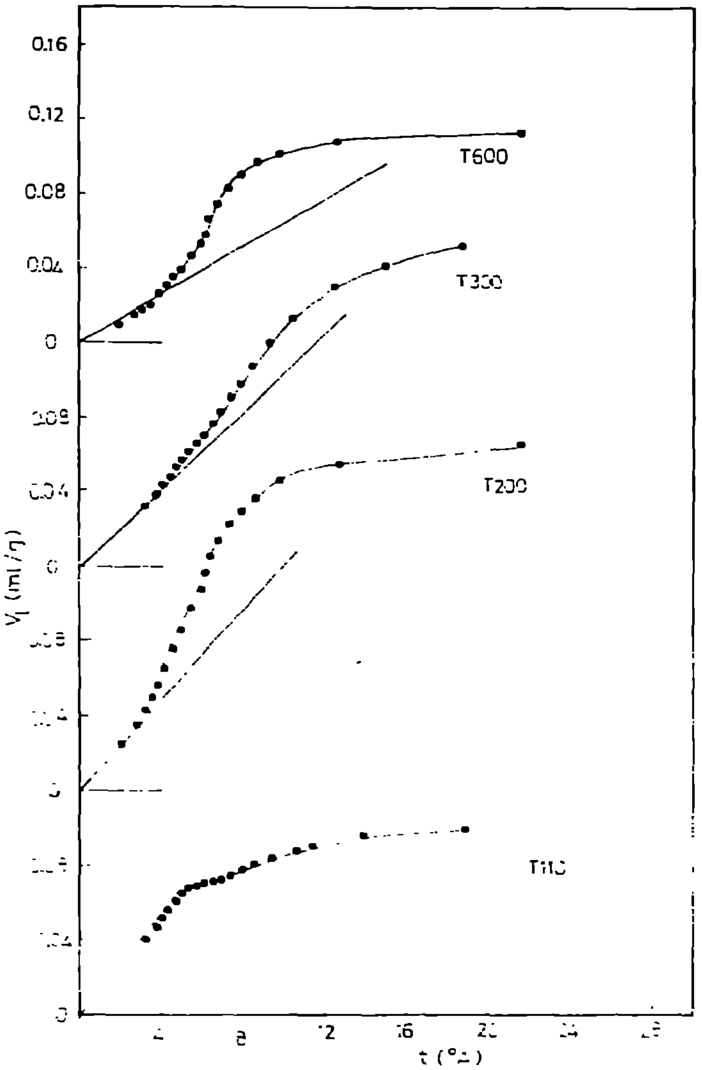

Fig. 5. V_l—t plots of titania gel and its thermal dehydration products from nitrogen adsorption data.

nitride [20]. There are other cases where steps in the isotherms result from phase transformation within the adsorbed layer [21].

Hill [22] and de Boer [23] were able to predict that the stepwise character would imply the presence of a few active sites, which are first saturated with the adsorbate molecules and, in so doing, render the surface homogeneous and allow condensation to take place at a particular pressure. The fewer these active sites, the stronger they are, and the more likely is two-dimensional condensation to take place at lower pressure. This may permit sufficient lateral interaction between the different molecules to compensate any thermal agitation on the surface.

In this connection, one can affirm that the active sites play no role in the appearance of the steps on the adsorption isotherm, as mentioned previously [22,23], since it is clear from Fig. 3(a and b) that the steps disappeared after filling the sample with nonane at —195° C. This indicates that the porosity character of the gel, and not the active steps on the gel surface, plays a major role in the appearance of the steps. The behaviour of TiO_2 with outgassing temperature is similar to that for SiO_2; the loss of physically adsorbed water is followed by chemically bonded surface hydroxyl groups. The removal of the latter is accompanied by a certain perforation in the gel surface in a well organized form to enhance the stepwise character on the isotherm.

It is worth noting that nitrogen adsorption at the temperature of liquid nitrogen should not give a two-dimensional condensation, since its critical temperature (63 K) is lower than that of liquid nitrogen. But de Boer [24] found that if the nitrogen molecules are adsorbed with their long axis perpendicular to the surface, i.e. mutually erected, then a subcritical two-dimensional gas would be formed, its two-dimensional critical temperature then being 92 K. In other words, the molecules of the gas should take up a special position during the process of adsorption in order to give a two-dimensional condensation.

Heats of immersion of titania gel obtained by thermal treatment in the temperature range 110—600° C were carried out at 35° C in both cyclohexane and water. Heats of immersion in cyclohexane, as shown in Table 1, run parallel with the extent of surface area measured by nitrogen adsorption. For cyclohexane as a non-polar wetting liquid, where only the dispersion forces are involved, the major factor is the presence of the micropores [25]. Results indicate that the pore structure of a solid is essential, and must be defined if results of heats of immersion in non-polar solvents are to be meaningful.

Heats of immersion of T110—T600 in water exhibit an almost constant value up to 200°C. This may be attributed to the fact that the removal of the physicosorbed water has a slight effect on heats of immersion. At 300 and 450° C a gradual decrease in the number of hydroxyl groups on the surface is accompanied by the gradual decrease in the heat evolved. The increase in the heat evolved at T600 may be basically due to the compensation between the marked decrease in the heat evolved as a result of complete depletion of hydroxyl groups at 600° C, and the increase in the heat evolved as a result of rehydration of the gel surface [26]. In other words, two main factors appreciably affect the heats of immersion of titania gel in water; these are: the interaction of water molecules with the hydroxyl groups, and rehydration of the dehydroxylated surface of the gel.

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