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# EFFECTS OF THERMAL TREATMENT ON THE SURFACE PROPERTIES OF A WIDE PORE SILICA GEL*

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## ABSTRACT

A mesoporous silica gel Davidson 59 was thermally treated in vacuo, in the temperature range 20–1000°C. Effects of thermal treatment on the water contents, nitrogen surface areas, pore structure and heats of immersion in water were investigated and discussed. The temperatures selected were 20, 110, 200, 290, 380, 480, 510 and 1000°C. These temperatures were found to cover all the various textural changes resulting from the heat effect.

It could be shown that the heats of immersion in water depend primarily on the water content of the sample and are proportional, at least qualitatively to the number of hydroxyl groups on the surface and their availability for interaction with liquid water. The interesting result obtained is that a second factor is involved, namely the pore structure of the adsorbent. A qualitative parallelism exists between the normalized heat of immersion per unit area, and the average pore radius. Apparently the packing of water molecules in narrow pores leads to a decrease in the heat of immersion due to repulsion between the permanent dipoles of the molecules. In narrower pores, the heat of immersion in water is smaller than in wide pores.

## INTRODUCTION

In defining the physical state of an oxide surface, it has been recently indicated[1, 2] that the pore structure represents an important part of the surface character because of the variable pore dimensions, and both the accessibility and adsorption energies involved.

For the heat of immersion of magnesia in cyclohexane, it has been demonstrated that micropores can have a significant effect in enhancing the heat per unit area, whereas the reverse effect is obtained for the heat of immersion of silica gel in water[2]. In the latter case it could be shown that the sample with the highest proportion of micropores yields the minimum heat of immersion normalized per unit area. The

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differences between the cyclohexane results and the water results could be interpreted to be due to the non-polar character of cyclohexane molecules and the strongly polar character of the water molecules. In the former case, the forces between the adsorbate molecules are mainly dispersion, and the heat increases in narrower pores, while for the latter case (i.e., water) the repulsion between oriented permanent dipoles on the surface leads to a decrease in the heat in narrower pores.

In a continuation of these studies, the present investigation deals with the heat of immersion in water of a mesoporous silica gel, namely Davidson 59, which has been supplied by the Davidson Division of W. R. Grace and Company, U.S.A. Thermal treatment of the parent material affects the molecular water and hydroxyl population on the surface, as well as the specific area and pore structure. These parameters were investigated to show the comparative effects of the chemistry of the surface (hydroxyl population) and the geometry of the surface (pore structure) on the heats of immersion in water. The induced properties due to thermal treatment would permit this study to cover a wide range of both hydroxyl content and pore structure.

## EXPERIMENTAL AND MATERIALS

The heat of immersion ($h_i$) values were determined at 35 ± 0.05°C by means of a thermostated calorimeter, the temperature of which could be kept constant to within ± 0.002°C during the experimental run. Details of the calorimeter were described elsewhere[3]. At least two electrical calibrations were performed after each experiment, the agreement between these pairs is always better than 0.3%. All the $h_i$ values reported are the result of at least two independent determinations. The accuracy of the data is ± 2% for the lowest surface area sample but considerably better for the other samples.

TABLE I

WATER CONTENT AND NUMBER OF SILANOL GROUPS OF DAVIDSON 59 SAMPLES

| *Sample* | *Water loss* C *(g $H_2O$/g) $10^2$* | *Water content (g $H_2O$/g) $10^2$* | $N_{-OH}/100 Å^2$ |
|---|---|---|---|
| ID(20) | 4.45 | 4.09 | (7.8)[a] |
| ID(110) | 5.80 | 2.74 | (5.8)[a] |
| ID(200) | 6.18 | 2.36 | 4.9 |
| ID(290) | 6.65 | 1.89 | 4.6 |
| ID(380) | 6.79 | 1.75 | 3.2 |
| ID(480) | 6.90 | 1.64 | 3.1 |
| ID(510) | 7.32 | 1.22 | 0.1 |
| ID(1000) | 8.52 | 0.00 | 0.0 |

[a] The number of silanol groups, calculated on the basis of the total water loss including capillary condensed and adsorbed water.

Silica gel Davidson 59 was evacuated at temperatures ranging from room temperature to 1000°C for four hours. The selected temperatures were 20, 110, 200, 290, 380, 480, 510 and 1000°C. These samples are designated as ID(20), ID(110), ID(200), ID(290), ID(380), ID(480), ID(510) and ID(1000), respectively. The preheating temperatures being indicated between parentheses.

Water contents of the different silica samples were calculated, and from the percentage loss of water at each temperature and assuming that the loss of water is completed at 1000°C, the number of silanol groups could be calculated. Water contents and the number of silanol groups are summarized in Table 1.

## RESULTS AND DISCUSSION

Silica gel Davidson 59 dehydrates upon heating at different temperatures ranging from room temperature to 1000°C and all the water is assumed to be lost at 1000°C. At any temperature, the loss of molecular water starts from the lowest temperature up to 300°C and involves also some dehydroxylation at temperatures above 200°C. At temperatures above 300°C, the dehydration of the silica sample is mainly due to the interconversion of the silanol groups to siloxane bridges with the evolution of some last traces of molecular water. An essential preliminary was the assessment of both the extent of the surface of all the Davidson 59 samples and their pore structures, as obtained from the adsorption of nitrogen at liquid nitrogen temperature.

### *Specific surface areas from nitrogen adsorption*

Areas were derived by applying the BET equation to the adsorption isotherms of nitrogen in the conventional range of relative pressure ($P/P_0$ = 0.05–0.35), and by adopting the value of 16.2Å$^2$ for the molecular area of nitrogen. The adsorption–desorption isotherms on all samples are type II of Brunauer's classification, and all

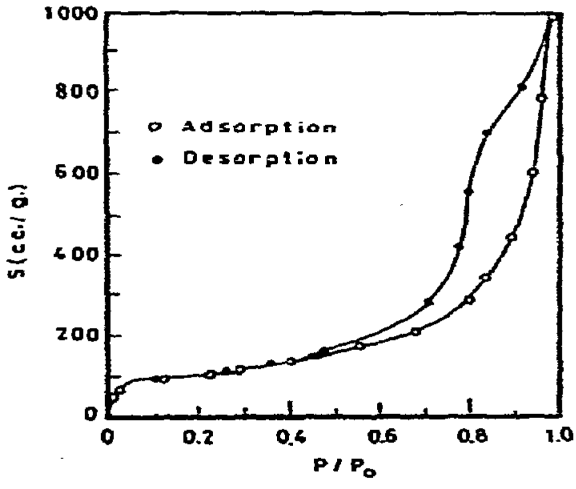

Fig. 1. Adsorption–desorption isotherm of nitrogen on ID (480)

are characterized by hysteresis loops which close at some intermediate pressure. A typical isotherm is shown in Fig. 1 for the sample ID(480).

The porous character of the various samples was detected by both the $V_t$–$t$ plots of de Boer et al.[5], and by the $n_S$–$n_R$ method, recently developed by Mikhail and Cadenhead[6]. Both methods gave essentially the same information. The $n_S$–$n_R$ plots are shown in Fig. 2. As shown in Fig. 2, for all the samples prepared from room temperature to 1000°C, the initial linear region (with slope equals to one) is followed by an upward deviation, indicating the presence of only mesopores in all samples investigated, although of variable size, as will be shown shortly.

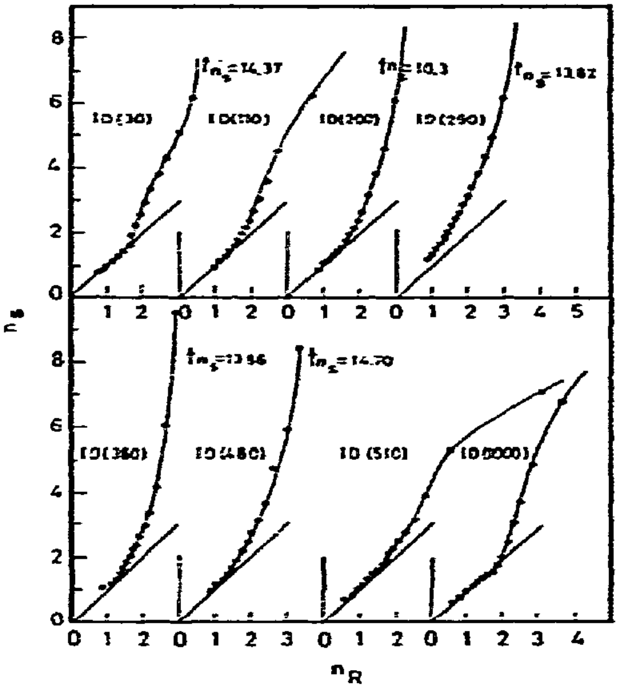

Fig. 2. $n_S$–$n_R$ plots for nitrogen adsorption on Davidson 59 samples.

TABLE 2

SPECIFIC SURFACE AREAS OF DAVIDSON 59 SAMPLES

| *Sample* | *$S_{BET}$ ($m^2 g^{-1}$)* | *$S_t$ ($m^2 g^{-1}$)* | *BET-C constant* |
|---|---|---|---|
| ID(20) | 348.6 | 337.0 | ∞ |
| ID(110) | 318.0 | 287.0 | 133 |
| ID(200) | 322.0 | 280.0 | ∞ |
| ID(290) | 272.0 | 305.0 | ∞ |
| ID(380) | 363.1 | 330.0 | ∞ |
| ID(480) | 348.6 | 335.0 | ∞ |
| ID(510) | 382.6 | 397.0 | 30 |
| ID(1000) | 272.4 | 278.0 | 32 |

### *Pore structure analysis*

The analysis for the surfaces and volumes associated with mesopores was carried out using the "corrected modelless method"[7]. The analysis was based on the desorption branches of the isotherms and was continued downward to the closure points of the hysteresis loops. Mesopore analysis was carried out adopting the parallel plate model, which was found to satisfy the criteria for correct analysis[7].

The cumulative surfaces ($S_W^{PP}$, m$^2$ g$^{-1}$) and the cumulative volumes ($V^{PP}$, ml g$^{-1}$) associated with mesopores are summarized in columns (3) and (4) of Table 3.

An average pore radius was also calculated by the relation ($\bar{r} = 2V_P/S_{BET}$), where $V_P$ is the total pore volume (ml g$^{-1}$) and $S_{BET}$ is the specific surface area (m$^2$ g$^{-1}$). The values are shown in column 7 of Table 3.

TABLE 3

SURFACES AREAS AND PORE VOLUMES LOCATED IN MESO-PORES

| *1* | *2* | *3* | *4* | *5* | *6* | *7* |
|---|---|---|---|---|---|---|
| *Sample* | *$N_2$ $S_{BET}$ (m$^2$ g$^{-1}$)* | *$S_W^{PP}$ (m$^2$ g$^{-1}$)* | *$V_W^{PP}$ (ml g$^{-1}$)* | *$V_P$ (ml g$^{-1}$)* | $\frac{S_W^{PP}}{S_{BET}}$ | *Average pore radius r(Å)* |
| ID(20) | 348.6 | 331.4 | 1.20 | 1.80 | 0.95 | 103 |
| ID(110) | 318.0 | 314.9 | 1.21 | 1.68 | 0.99 | 106 |
| ID(200) | 321.0 | 357.0 | 1.11 | 1.88 | 1.11 | 116 |
| ID(290) | 272.0 | 264.8 | 0.90 | 2.24 | 0.97 | 164 |
| ID(380) | 363.1 | 359.5 | 1.16 | 1.21 | 0.99 | 99 |
| ID(480) | 348.1 | 367.1 | 1.16 | 1.84 | 1.06 | 105 |
| ID(510) | 382.6 | 384.9 | 1.21 | 1.24 | 1.01 | 65 |
| ID(1000) | 272.4 | 295.9 | 1.18 | 1.53 | 1.09 | 112 |

### *The number of silanol groups*

The number of silanol groups per unit area of the surface shows a gradual decrease with rise of temperature up to 1000[8].

Some studies[9] on a fully hydroxylated silica sample emphasize that the number of silanol groups ($N_{-OH}$/100Å$^2$) will not exceed the number of silicon atoms per unit area, as determined by crystallographic data[9, 10], assuming that each silicon atom coming to the surface binds only one hydroxyl group. Therefore, the minimum values obtained for different crystalline and amorphous silicas are 4.2–5.7 OH/100 Å$^2$.

Upon heating Davidson 59 at temperatures below 200°C, the number of silanol groups, as calculated by thermogravimetry, are larger than those postulated basically on crystallographic data. This is due to the fact, that the number of silanol groups were calculated from the total water loss including the loss of molecular water present in the pore system of the sample. These values ($N_{-OH}$/100 Å$^2$) are represented between parentheses in Table 1.

### *Heats of immersion*

Heats of immersion were measured using water as a wetting liquid. Figure 3 shows the variation of the integral heat of immersion and the water content of these samples, both as functions of temperature. The integral heat of immersion shows an almost constant value from room temperature up to 200°C, followed by a marked rise of the heat, leading to a maximum at 290°C. With further dehydration, the heat of immersion decreases, showing a shoulder in the range of 380–480°C, followed by a gradual decrease of the heat to 1000°C.

The almost constant heat of immersion in the temperature range (20–200°C) might be due to a compensation effect of two factors operating in opposite directions, namely the desorption of molecular water (cf. Fig. 3) overlapping with the sharp decrease in the number of silanol groups. The first factor could cause an increase in the

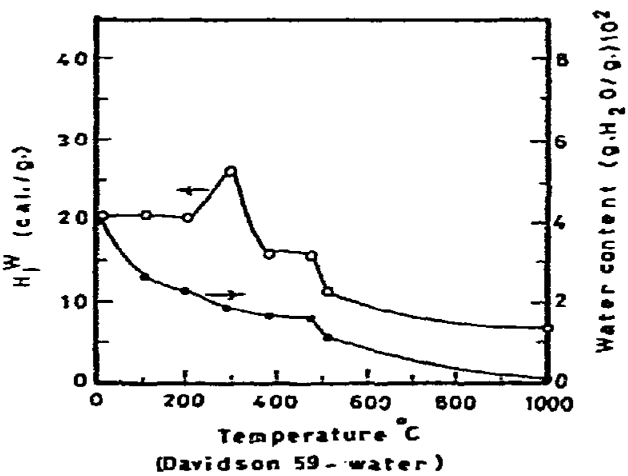

Fig. 3. Variation of the heat of immersion in water, $H_I^W$ (cal g$^{-1}$), and the water content as a function of temperature of thermal treatment.

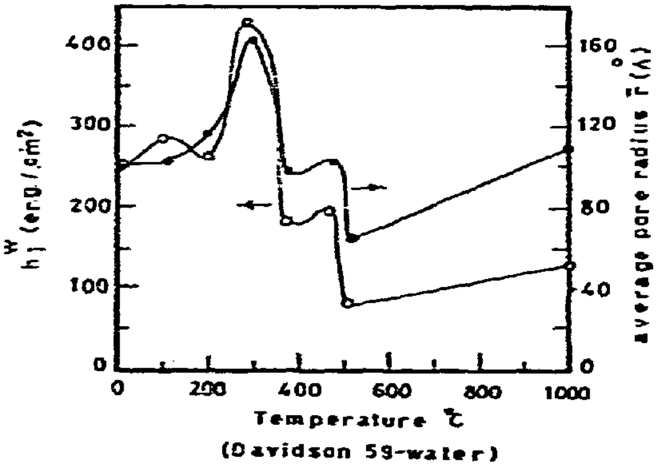

Fig. 4. Variation of the heat of immersion in water, $h_I^W$ (erg cm$^{-2}$), and the number of silanol groups with temperature of thermal treatment.

TABLE 4

HEATS OF IMMERSION OF DAVIDSON 59 IN WATER

| *Sample* | $S_{BET}^{N_2}$ | $H_i^w$ (cal $g^{-1}$) | $h_i^w$ (erg $cm^{-2}$) | Water content ($g H_2O/g$) $10^2$ | $N_{-OH}/100 Å^2$ |
|---|---|---|---|---|---|
| ID(20) | 348.6 | 21.15 | 253.6 | 4.09 | 7.8 |
| ID(110) | 318.0 | 21.91 | 288.0 | 2.74 | 5.8 |
| ID(200) | 322.0 | 20.54 | 266.7 | 2.36 | 4.9 |
| ID(290) | 272.4 | 27.48 | 430.0 | 1.89 | 4.6 |
| ID(380) | 363.1 | 16.06 | 184.9 | 1.75 | 3.2 |
| ID(480) | 348.1 | 16.44 | 197.1 | 1.64 | 3.1 |
| ID(510) | 382.1 | 13.52 | 079.4 | 1.22 | 0.1 |
| ID(1000) | 272.4 | 08.16 | 175.3 | 0.00 | 0.0 |

interaction between the adsorbate water molecules and the exposed silanol groups on the surface, whereas the second factor could be associated with a decrease in the heat of immersion. The sharp increase in the heat of immersion around 290°C is mostly attributed to a rehydration of the partly siloxaned surface.

The shoulder located in the 380–480° temperature range, may be due to the fact that these two samples contain almost the same number of silanol groups. The slower rate for dehydroxylation in the temperature range 380–480° could be explained on the basis of some spectroscopic investigations[11, 12] which indicate the removal of the surface hydroxyls bounded by mutual hydrogen bonds at temperatures up to 400°C, beyond which the dehydroxylation process becomes slower, mainly because of the increase in the mean distances between neighbouring free (non-interacting) hydroxyl groups on the surface of the silica sample.

Figure 4 shows the variation of the water heat values, normalized to unit area on the surface and the number of silanol groups both as functions of the dehydra-

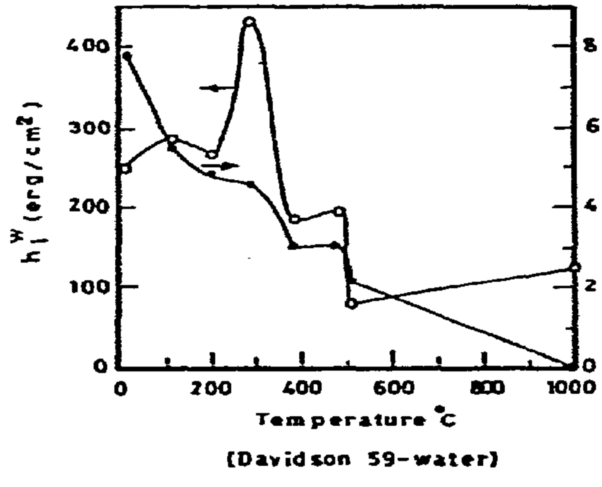

Fig. 5. Variation of the heat of immersion in water, $h_i^w$ (erg $cm^{-2}$) and the average pore radius with temperature of thermal treatment.

tion temperature. As pointed out earlier, the number of silanol groups decreases rapidly over the range 200–400°C, and continues to decrease at a slower rate.

Figure 5 shows the variation of the heat of immersion, $h_i^w$ (erg $cm^{-2}$), and the average pore radius as parameters of the pretreatment temperature, and they show essentially the same behaviour, indicating the strong dependence of the heat of immersion on the pore size. The presence of the maximum located around 290°C, which was attributed to the rehydration of some suitably oriented siloxane bridges on the surface, is also associated with a marked increase in the average pore radius of the sample. Also, the other minor peak (or shoulder) located around 480°C, in which the heat values run parallel to the hydroxyl content of the surface, show noticeable dependence on the average pore radius as well. In Figure 5, the general trend is that the normalized heat values per unit area run remarkably parallel to the average pore radius.

The results obtained in this investigation indicate therefore, that while the chemistry of the silica surface (i.e., degree of hydroxylation), plays a significant role in determining the heat of immersion in water, the geometry of the surface, and in particular its pore structure, play a major role as well. The results confirm the previously reached conclusions[2, 13], that the heat of immersion in water is higher in wide pores. Apparently repulsion between the permanent dipoles of the water molecules is enhanced in narrower pores, and this would lead to a decrease in the heat of immersion, especially when a definite orientation of the water molecules takes place on the surface, with similar poles oriented in the same directions. Work is still going on to confirm these views.

The situation with a non-polar molecule is totally different, e.g., in the case of immersional heats in cyclohexane, when the forces are mainly dispersion, and the heats were found to be enhanced in narrower pores.

## REFERENCES

1 R. Sh. Mikhail, S. Nashed and A. M. Khalil, *Discuss. Faraday Soc.*, 52 (1971) 187.
2 R. Sh. Mikhail, A. M. Khalil and S. Nashed, *J. Appl. Chem. Biotechnol.*, 27 (1977) 17.
3 R. I. Razouk, *J. Phys. Chem.*, 45 (1941) 179.
4 J. H. de Boer and J. M. Vleeskens, *Proc. K. Ned. Akad. Wet.*, B 60 (1957) 45; B 60 (1957) 54; B 60 (1957) 24; B 61 (1958) 2; B 61 (1958) 58.
5 B. C. Lippens, B. G. Linsen and J. H. de Boer, *J. Catal.*, 3 (1964) 32.
B. C. Lippens and J. H. de Boer, *J. Catal.*, 4 (1965) 329.
6 R. Sh. Mikhail and D. A. Cadenhead, *J. Colloid Interface Sci.*, 62 (1977) 375.
7 S. Brunauer, R. Sh. Mikhail and E. E. Bodor, *J. Colloid Interface Sci.*, 74 (1967) 451.
8 L. T. Zhuravlev and A. V. Kiselev, in D. E. Everett and R. H. Ottewill (Eds.), Proceedings of the *International Symposium of Surface Area Determination, Bristol, 1969*, Butterworths, London, pp. 155–160.
9 S. P. Zhadnov and A. V. Kiselev, *Zh. Fiz. Khim.*, 31 (1959) 2213.
10 W. Stobber, *Kolloid Z.*, 145 (1956) 17.
11 A. V. Kiselev and V. I. Lygin, *Usp. Khim.*, 31 (1962) 361.
12 R. M. Donald, *J. Phys. Chem.*, 62 (1958) 1168.
13 A. M. Khalil, *Ph.D. Thesis*, Ain Shams University, Egypt, 1976.