JOURNAL OF CATALYSIS 13, 43-52 (1969)

The Porous Structure of Self-Supporting Pressed Silica Discs

II. Nitrogen Adsorption Studies

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Received June 7, 1968; revised September 30, 1968

The nitrogen sorption isotherms of a range of silica powders and gels prepared by controlled processes from an Aerosil silica have been determined at 77°K. The results confirm that the pressed self-supporting oxide discs commonly used in infrared studies are microporous to a degree that significantly alters their adsorptive properties.

Analysis of the isotherms by the *t*-plot method shows that in general it is not possible to obtain quantitative information about the microporous structure by adsorption methods alone.

INTRODUCTION

As the discussion in the preceding paper indicates, the spectroscopic data may be rationalized on the basis that "rehydration" and mechanical pressing produce porous, gellike, materials from the corresponding powdered solids. In order to obtain additional information about the porosity of all the samples studied, their nitrogen adsorption isotherms were determined at 77°K and the results analyzed so as to give information especially about pores of molecular dimensions.

EXPERIMENTAL

The apparatus and techniques used were identical to those described by Lippens *et al.* (*1*) and the reader is consequently referred to this work for the detailed experimental procedure employed here. The samples studied were prepared in precisely the same manner as described in Part I (preceding paper). The calculations for obtaining the adsorption data from the experimental measurements were carried out on the Atlas Computer of the University of Manchester.

NITROGEN GAS ADSORPTION—SOME FUNDAMENTAL CONSIDERATIONS

For adsorption at constant temperature onto a planar surface, at any particular equilibrium gas-phase pressure (p) the experimentally measured surface coverage per gram of adsorbent is given by the equation

$$\Gamma_a = \gamma\Gamma_p \tag{1}$$

where Γ_p is the surface coverage per unit area of the solid at pressure p and γ is a quantity coefficient per unit mass (in this simplest case the specific surface area of the adsorbent).

It should be remembered that at constant temperature

$$\Gamma_p = f(p) \tag{2}$$

in such a way that for first-layer adsorption $f(p)$ will be dependent on specific adsorbate–adsorbent interactions. It follows that chemically different solids may well exhibit different adsorption isotherms in the original or submonolayer region. One of the three fundamental assumptions of the Universal *t*-plot method of de Boer *et al.* (*2*) is that, after the first adsorbed layer is completed, these specific interactions are sufficiently shielded by the layer of absorbed gas for Γ_p to become equivalent for a large number of chemically different planar solids at equal equilibrium pressures. Consequently, in the supramonolayer region, the ratio of the respective Γ_a values for any two such planar solids at the same equilibrium gas-phase pressure and temperature is the ratio of their specific surface areas. The other two fundamental assumptions of the universal method are that application of the BET equation to the nitrogen adsorption isotherm determined at 77°K gives the true surface area of a planar solid and also that the mean thickness (*t*) of one adsorbed nitrogen layer is 3.5 Å. These last two assumptions enable one to convert the adsorption isotherm determined with a truly planar solid into a master or universal relationship between the mean thickness of the adsorbed nitrogen layer and the equilibrium gas-phase pressure. Thus the universal *t*-plot method only enables one to obtain quantitative information concerning the porosity of porous adsorbents of different chemical composition from the master solid, from the supramonolayer regions of their nitrogen adsorption isotherms.

If one compares two planar solids of identical chemical composition then the ratio of their respective Γ_p's determined at constant temperature and equal equilibrium gas-phase pressures will be constant over the entire equilibrium pressure range. An equivalent statement is that planar solids of identical chemical composition exhibit identical adsorption isotherms under identical experimental conditions.

Considering now a solid that contains pores of dimensions of the same order of size as the adsorbate molecule (i.e., micropores), then their presence in the adsorbent leads to an enhancement of the adsorption isotherm in the submonolayer region as compared to that obtained with a chemically identical planar solid. In this case the measured surface coverage Γ_a becomes Γ'_a and may now be written using a similar formalism as before

$$\Gamma'_a = \alpha\Gamma_m + \beta\Gamma'_p \qquad (3)$$

where Γ_m is the surface coverage per unit area of the microporous region of the sample and α, the respective unit mass quantity coefficient; β and Γ'_p refer only to the planar regions of the solid surface. For solids containing a range of pore sizes and shapes the generalized equation describing the total adsorption per unit mass (Γ'_b) is now given by

$$\Gamma'_b = \Sigma\alpha_i\Gamma_i + \beta\Gamma'_p \qquad (4)$$

where α_i and Γ_i are the respective unit mass quantity coefficient and unit area coverage in the ith pore type present in the adsorbent and β and Γ'_p again refer only to the planar regions of the solid's surface.

In practice the universal *t*-plot method involves plotting over the whole supramonolayer equilibrium pressure range the isobarically equivalent values of Γ'_b against $3.54\ \Gamma_a/\gamma$ obtained from the master curve. The resulting *t* plot consists of a series of intersecting straight lines. The gradients of each of these lines are related—but not always in a straightforward manner—to the unit mass quantity coefficients in Eq. (4) and the values of $3.54\ \Gamma_a/\gamma$ at which the gradient of such *t* plots change are related to the dimensions of the pores present in the sample. Hence the tremendous usefulness of the universal *t*-plot method. However, another great practical advantage of the *t*-plot type of method in general is that, because it is essentially a comparative method of presenting adsorption data, the experimenter is able to see which regions of the adsorption isotherms he obtains are affected by the porosity of the adsorbents under study.

In the present study the most relevant equations are (3) and (4). In this case, the relevant *t* values must be determined on a master solid of identical chemical composition to the porous adsorbent under investigation. Even taking this precaution, however, it seems to us to be impossible to obtain unambiguous quantitative information as to small pore structure from adsorption isotherms alone since the porous sample under investigation may contain more than one type or size of pore that contributes to the adsorption observed at any one equilibrium pressure. Referring to Eq. (4), it can be seen that since one can only measure Γ'_b experimentally, then one cannot *a priori* obtain discrete solutions for each of the necessary α_i quantity coefficients.

The object of our own nitrogen sorption studies as reported here was to obtain information about the *changes* in porosity that are caused in the two parent materials (namely, R.A.2 and U.A.3) when they were subjected to the treatments outlined in the previous paper. Consequently, we have deliberately chosen as the two master curves the nitrogen adsorption isotherms of R.A.2 and U.A.3. In general, as the results show mechanical pressing and hydrothermal treatment tend to increase the effective microporosity of the samples and enhance their nitrogen adsorption isotherms in their original region as compared to their respective masters, whereas thermal treatment alone tends to decrease their microporosity and so conversely diminish their relative adsorption in the original region. Although we have adhered to the *t*-plot method of presentation as that which most clearly reveals the changes in porosity caused by the treatments used, the precise values of the statistical thickness (*t*) used on the *t* axes do not have the same absolute significance as those presented by de Boer *et al.* (*2*) for the universal *t* curve. Should any of the isotherms presented be used to obtain a generally applicable master curve for fully hydroxylated silicas then perhaps that shown in Fig. 10 corresponds most closely to that which is required since the cor-

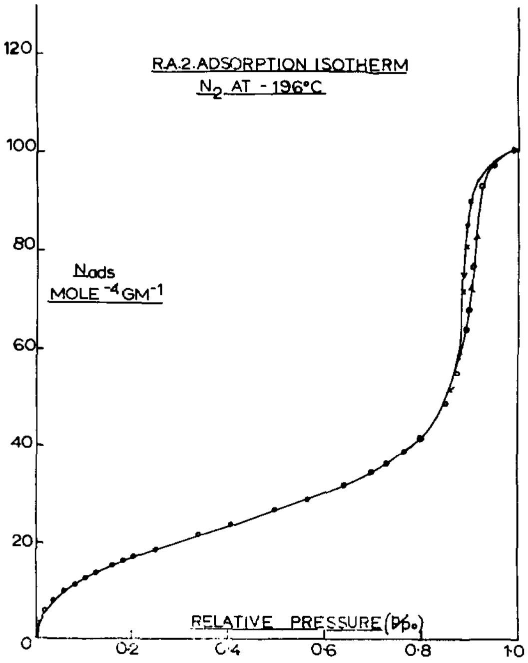

Fig. 1. Nitrogen adsorption isotherm of R.A.2 powder at −196°C.

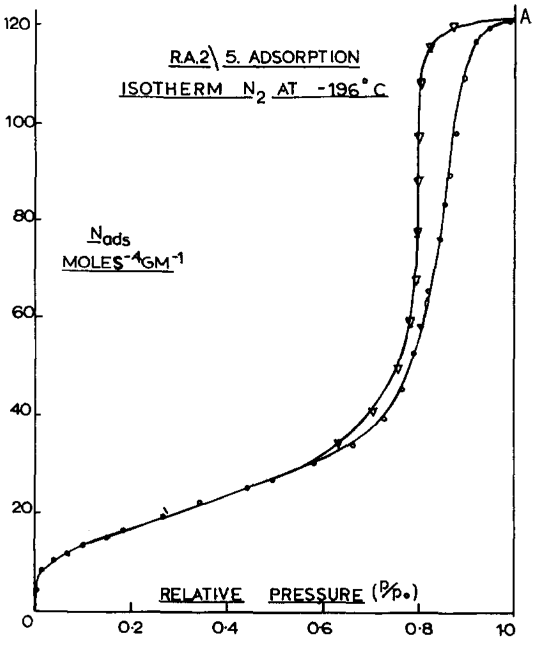

Fig. 2. Nitrogen adsorption isotherm of R.A.2/5 pressed disc at −196°C.

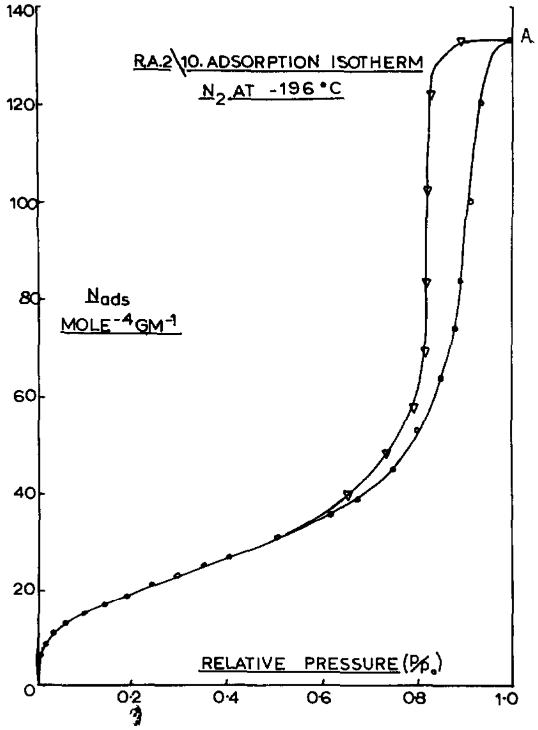

Fig. 3. Nitrogen adsorption isotherm of an R.A.2/10 pressed disc at −196°C.

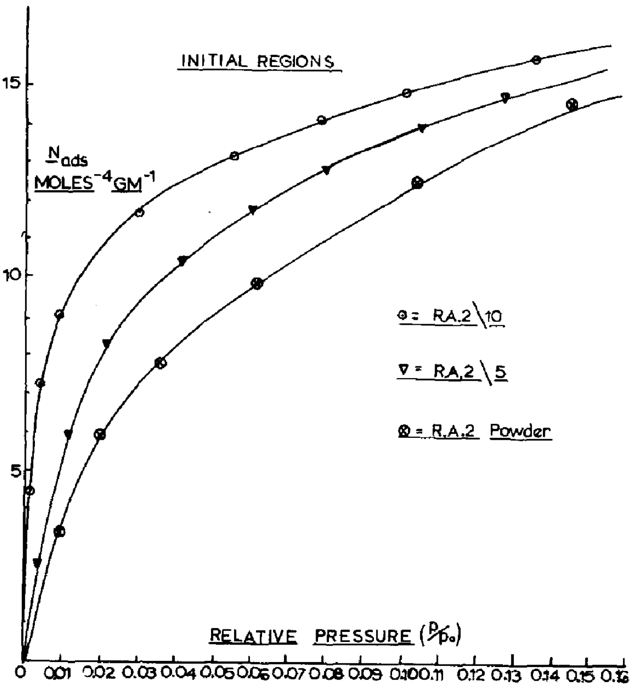

FIG. 4. The initial regions of the N_2 adsorption isotherms of R.A.2 powder, R.A.2/5, and R.A.2/10

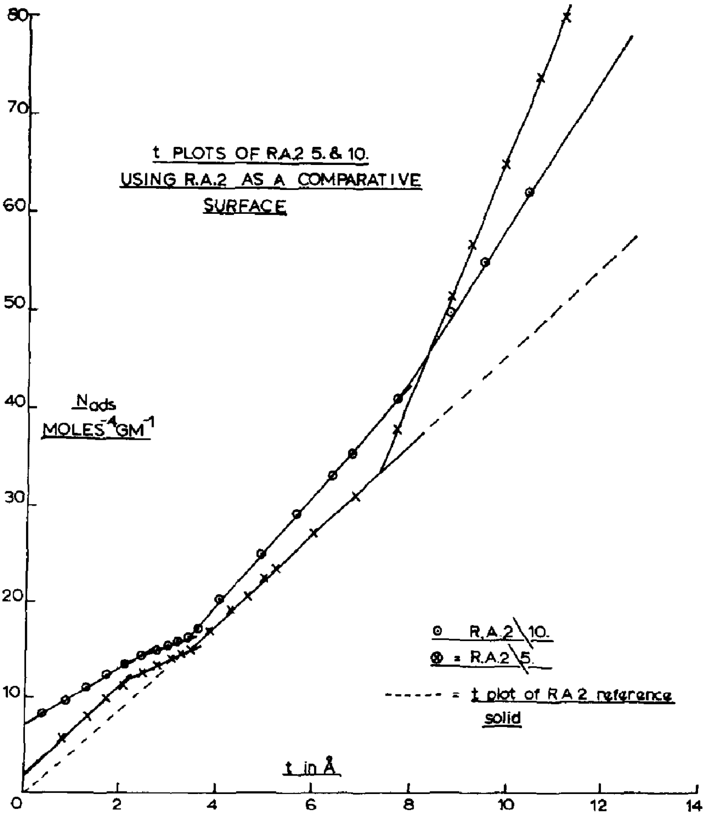

FIG. 5. The t plots for R.A.2/5 and R.A.2/10 using R.A.2 powder as a comparative surface.

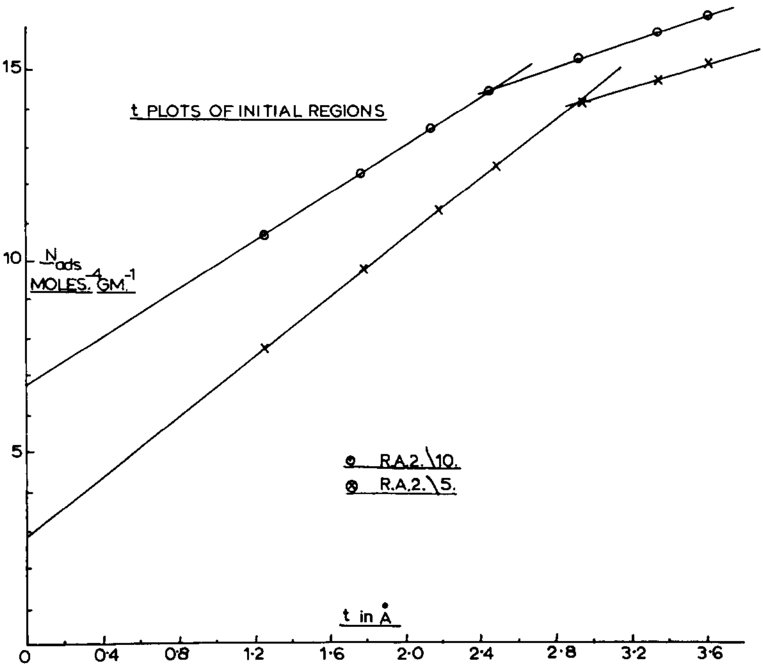

Fig. 6. The initial regions of the *t* plots for R.A.2/5 and R.A.2/10.

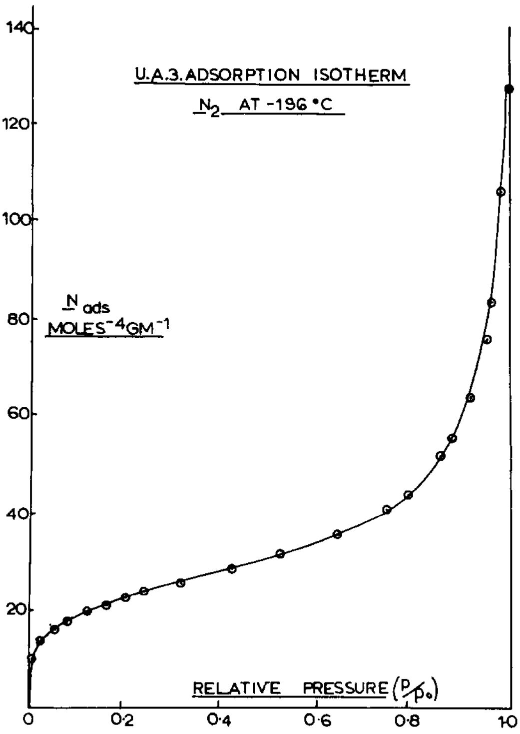

Fig. 7. The nitrogen adsorption isotherm of U.A.3 powder at −196°C.

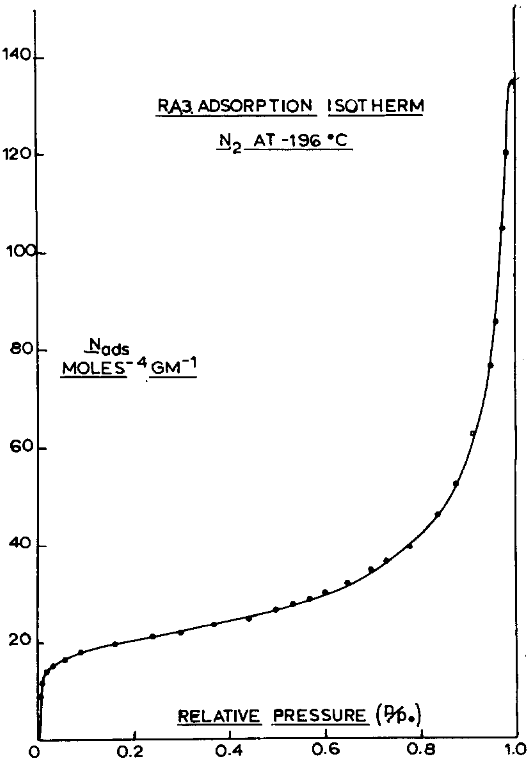

Fig. 8. The nitrogen adsorption isotherm of R.A3. powder at −196°C.

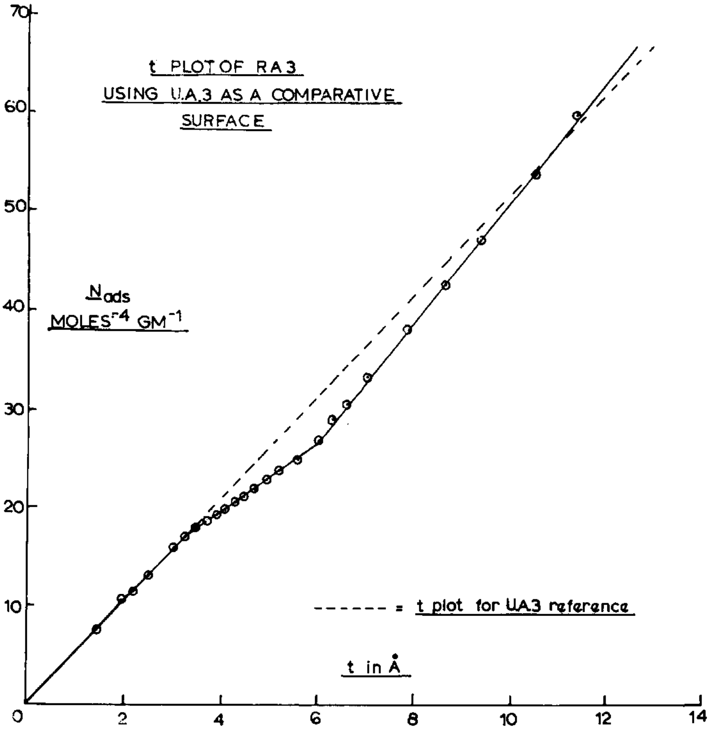

Fig. 9. The *t* plot of R.A.3. using U.A.3 as a comparative surface.

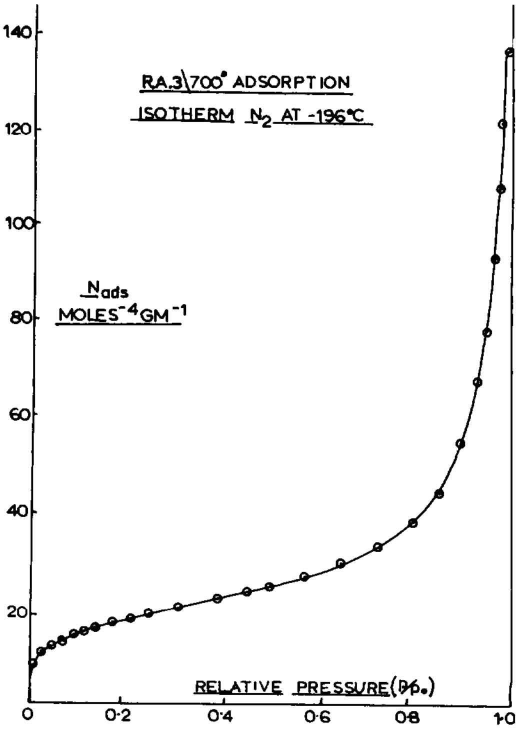

Fig. 10. The nitrogen adsorption isotherm of R.A.3/700 powder at −196°C.

responding adsorbent is virtually equivalent to a fully hydroxylated wide-pore silica gel.

Results and Discussions

Figures 1, 2, and 3 show the nitrogen adsorption isotherms of R.A.2/5 and R.A.2/10, respectively, after evacuation at 25°C. All these isotherms are typical of those obtained with gellike adsorbents. Figure 4 shows the initial or original regions of these isotherms on an expanded scale. Pressing the specimens has caused an increased adsorption in the initial region of the isotherm. The respective *t* plots shown in Figs. 5 and 6 also show very clearly (compare reference plot 2, for example) that the pressed specimens are microporous relative to the parent solid R.A.2.

The desorption hysteresis exhibited at high relative pressure by R.A.2/5 and R.A.2/10 confirms the result obtained by Zwietering (*3*). The shape of the hysteresis loops indicate that the pressed specimens contain a mixture of type A and type E pores according to the classification suggested by de Boer (*4*). Application of the Kelvin

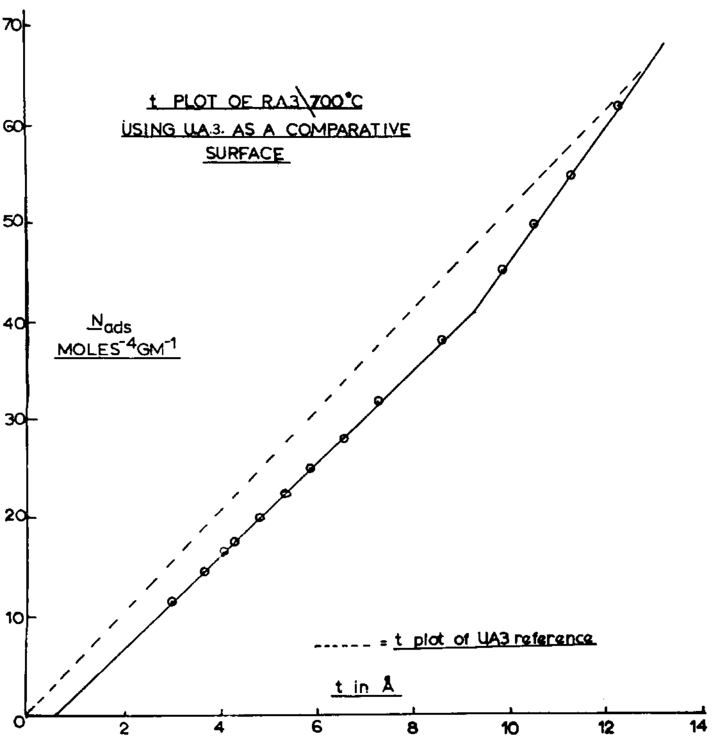

FIG. 11. The *t* plot for R.A.3/700 powder using U.A.3 as a comparative surface.

equation to the desorption branches of the isotherms shown in Figs. 1, 2, and 3 yields a mean macropore radius of about 90 Å for R.A.2 and about 40 Å for R.A.2/5 and R.A.2/10.

The total void volume of the pressed discs is given by the total volume of nitrogen in milliliters of liquid that is required to attain point (A) on the isotherms. Assuming that the adsorbed nitrogen has the same density as liquid nitrogen the total void volume of R.A.2/10 is 0.54 ml/g and for R.A.2/5 it is 0.50 ml/g. It proved possible to check this calculation by a purely mechanical method, which consisted of measuring the thickness and diameter of weighed discs of R.A.2/10 by means of a micrometer. Assuming that the silica had a density of 2.32 g/ml (β-cristobalite) this mechanical method gave a void volume of 0.54 (±0.02) ml/g.

THE POROUS STRUCTURE OF R.A.3, R.A.3/700, R.R.A.3/700, AND U.A.3/5

The adsorption isotherms of U.A.3 and R.A.3 and the *t* plot for the latter sample are shown in Figs. 7, 8, and 9, respectively. The changes in slope in the initial region of the *t* plot are again evidence that this rehydrated material is microporous, compared to the reference solid U.A.3. Figures 10 and 11 show the adsorption isotherms and *t* plot, respectively, for R.A.3/700. The results indicate that heating the rehydrated gellike material R.A.3 to 700°C has greatly reduced the microporosity of the sample. The adsorption isotherm obtained with R.R.A.3/700. (i.e., R.A.3/700 that has been rehydrated in liquid water at 95°C) is identical with that obtained for R.A.3/700. That is to say that the hydrothermal treatment (rehydration) of a gel that has been thermally set (R.A.3/700) produces no measurable change in the nitrogen adsorption isotherm.

Figures 12 and 13 show the adsorption isotherm and *t* plot for U.A.3/5 (a sample of U.A.3 that has been mechanically compressed at 5 tons/cm^2). The adsorption isotherm of the pressed sample deviates from that of the reference solid U.A.3 (see Fig. 7) only at high relative pressures, where type A macropore hysteresis is (*4*) indicated.

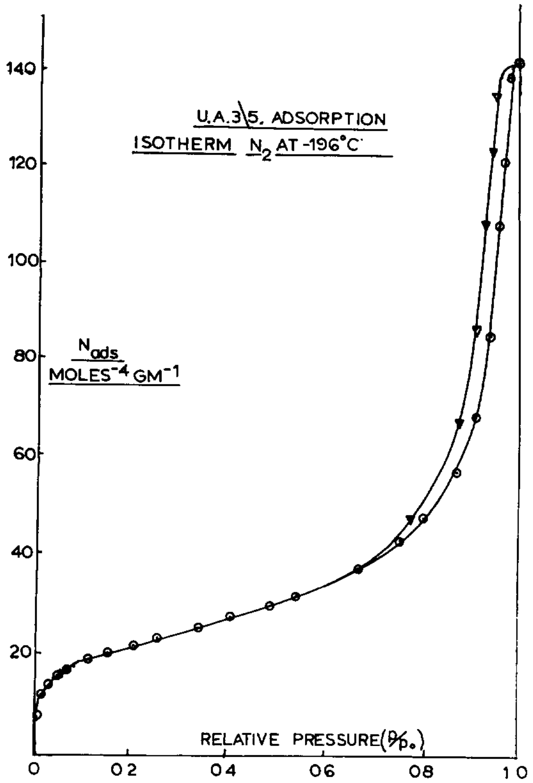

Fig. 12. The nitrogen adsorption isotherm of a U.A.3/5 pressed disc at −196°C.

The mean pore radius calculated from the Kelvin equation corresponds to about 80 Å.

At first sight the adsorption isotherm obtained from this mechanically compressed sample suggests that it does not contain any pores of molecular dimensions and that aggregating the sample during the pressing process has caused no decrease in the specific surface area of the solid. Common sense suggests that neither of these conclusions is tenable, especially the latter. When a comparison of the spectra for U.A.3 and U.A.3/5 shown in the preceding paper is made this discrepancy becomes even more obvious (see also Table 1 of the preceding paper).

One possible explanation is that U.A.3/5 is indeed microporous, but the sample possess a micropore and intermediate pore structure which enhances the nitrogen adsorption at all relative pressures up to the onset of macropore filling by an amount equivalent to the loss in surface coverage caused by the loss in external or planar surface area that occurs when U.A.3 is mechanically aggregated.

This explanation rests on the fact that the surface coverage of any adsorbate at any particular equilibrium gas-phase activity is a measure of the sum of the surface coverages on each type of surface domain present in the adsorbent [see Eq. (*4*)]. That is to say that the fundamental tenet mentioned previously on which all isotherm analysis methods for interpreting microporosity intermediate porosity are based—namely, that solids of identical chemical composition and porosity possess identical adsorption isotherms—is insufficient. The corollary of this postulate must also be correct for such methods to be valid, namely, that solids of identical chemical composition but different porosity should exhibit different adsorption isotherms.

The identity of the adsorption isotherms exhibited by U.A.3. and U.A.3/5 would thus appear to be a case where this latter condition is not obeyed. Therefore, in this case as in all others, analysis of pore structure by gas adsorption methods alone cannot yield absolutely *quantitative* information as to micropore or intermediate pore size or volume as has recently been suggested (*6*). Corroborating information from other techniques such as measurements of the heat of adsorption is always required. Nonetheless, nonlinearity in the initial region of a t versus V_{ads} (N_{ads}) plot may always be accepted as an indication that significant microporosity is present in the sample as compared to the master solid.

In the general context of infrared studies of adsorption on self-supporting pressed discs, the presence of pores of molecular dimensions in the discs is important since they lead to markedly enhanced adsorption at low relative pressures, i.e., in the crucial submonolayer region. For example, at a relative pressure of 0.01 the surface coverage of nitrogen on R.A.2 corresponds to about 0.3 of a BET monolayer but on R.A.2/10 the coverage is almost double this value (see Fig. 4).

It is also relevant here to stress that the term micropore is a relative expression and is dependent solely on the size of the adsorb-

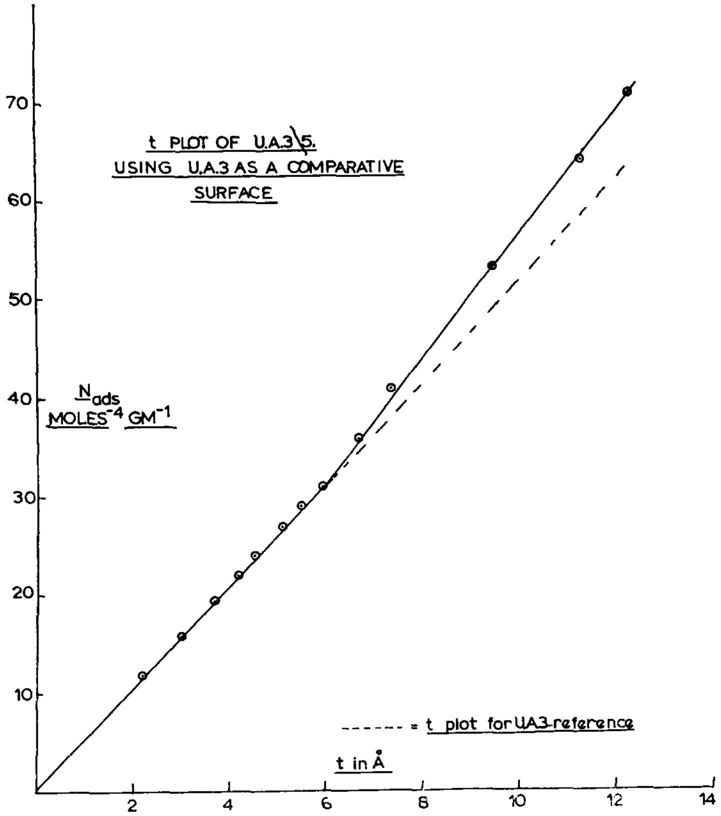

FIG. 13. The *t* plot for R.A.3/5 using U.A.3 as a comparative surface.

ate molecule. It is noticeable that the breaks in the original regions of the *t* plots both in the present work and in previous studies by other workers (*2*) occur at a statistical thickness near about 3.5 Å. Using nitrogen as the adsorbate this is not an altogether unexpected result since adsorption in those pores with diameters greater than two monolayer thicknesses of adsorbed nitrogen will not be cooperative and consequently there will be no relative enhancement of the adsorption in the submonolayer region.

The micropores in the powdered samples examined almost certainly correspond to those regions just above the points of primary crystallite contact within the larger spheroidal aggregates and also at the fewer interaggregate junctions present in the adsorbent. Compressing the sample by either mechanical or hydrotensile forces leads to a marked increased in the number of such contacts and so to an increase in the effective microporosity. Similarly, hydrothermal treatment, which increases the number of crystallites per aggregate will also tend to increase the effective microporosity. The changes in intensity of the 3650(2690) cm^{-1} adsorption band are also in agreement with this interpretation since there is a consistent correlation between the changes in the absorption intensity of this residual band and the increased microporosity indicated by the gas adsorption results. Indeed, considering that the infrared results reflect changes in those regions within the sample where the primary crystallites are in contact whereas the adsorption data are a measure of where they do not, the correlation between the two sets of results may be taken as a fair indication that both the interpretation of the infrared spectroscopic results is correct and also that the "soft-fruit" model for the structure of silicas is correct.

Finally, the size of the macropores present in the samples (at least 90-Å diameter) is so large that they are unlikely to produce any significant change in the kinetics of any catalytic reaction under study by infrared spectroscopic methods involving pressed discs (*5*) although the presence of the small molecular size pores may under some circumstances lead to significant alternations in the observed kinetics of heterogeneous reactions.

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