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**RAPID TEST METHODS FOR DETERMINATION
OF THE APPROXIMATE AVERAGE PORE
RADIUS, TOTAL PORE VOLUME AND
SURFACE AREA CONTAINED IN POROUS MATERIALS**

by

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AND
D. S. MONTGOMERY**

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W. D. Machin, * B. I. Parsons, ** and D. S. Montgomery***

SYNOPSIS

Rapid test methods are described for the determination of the average pore radius, the total pore volume and the surface area contained in catalyst pellets and granules. The measurements resulting from the application of these test methods to two alumina-silica catalysts are compared with the data calculated from the nitrogen absorption isotherm. Methods of estimating (a) the relative amounts of large and small pores, (b) the uniformity of the packing of the powder in pellets, and (c) the presence or absence of cracks in the pellet, are also discussed.

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PROCÉDÉ RAPIDES D'ANALYSE EN VUE DE LA DÉTERMINATION
DU RAYON MOYEN APPROXIMATIF DES PORES, DU VOLUME TOTAL
DES PORES ET DE LA SURFACE TOTALE DES MATIÈRES POREUSES

par

W.D. Machin*, B.I. Parsons** et D.S. Montgomery***

RÉSUMÉ

Le présent bulletin décrit des procédés rapides d'analyse en vue de la détermination du rayon moyen des pores, du volume total des pores et de la surface totale de contact au sein de boulettes et de granules utilisées comme agents catalyseurs. Il établit la comparaison entre les résultats de l'application de ces procédés d'analyse à deux catalyseurs d'alumine-silice et les données calculées à partir de l'isotherme d'absorption de l'azote. Ce bulletin traite aussi des méthodes d'évaluation (a) des quantités relatives de petites et de grosses pores, (b) de l'uniformité du tassement de la poudre au sein des boulettes et (c) de la présence ou de l'absence de fissures dans les boulettes.

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INTRODUCTION

In the course of the development work on the preparation of new and improved porous substrates for catalysts, it became apparent that the slowest phase of the investigation was the examination of the pore characteristics of the samples. To accelerate the investigation, methods were required for rapid determination of the average pore radius, total pore volume and surface area, contained in porous material. In the present bulletin are described the laboratory test methods for determining these properties, that were evolved from a background of published results, (1, 2) incorporating short-cut procedures suggested by laboratory experience.

These measurements, together with the qualitative inferences that can be drawn from observations made in the course of these measurements, have proved invaluable as a preliminary means of estimating the relative merit of a large number of samples. The methods and techniques are presented in a general form, for use with pellets or granules of alumina, silica, or any similar porous material.

EXPERIMENTAL

The tests described below are intended for use on medium-sized pieces of catalyst. Experience has shown that the best results

are obtained with granules, pellets or extrusions of about $1/8$ to $1/4$ in. diameter.

Procedure for the Determination of the Total Pore Volume

Place a weighed amount of catalyst in a beaker containing distilled water. Boil the sample for several minutes; then allow the water and pellets to cool to room temperature. After two hours, or overnight, remove the pellets from the water and dry them superficially with filter paper or Kleenex. (The superficial moisture is considered to be removed from the pellets when they do not stick together.) Reweigh the pellets and calculate the pore volume from the change in weight and the density of the water at the temperature of the experiment. This operation should be performed quickly to prevent errors due to evaporation of the liquid.

In some instances, water cannot be used as the immersion liquid since it may cause the pellets to disintegrate. Under these circumstances benzene or carbon tetrachloride may be used. The more volatile the liquid, the greater is the possibility of errors as the result of evaporation.

Procedures for the Determination of the Average Pore Radius

Two separate procedures have been developed to measure the average radius of the pores present in a pellet. Both methods are based on the fact that the penetration of a liquid into a cylindrical

pore is related to the surface tension and the viscosity of the liquid. (2) Expressed mathematically, the relationship is:

$$r = \frac{2 v X^2}{St} \left[\frac{r}{r-a} \right]^4 10^8$$

where: r is the average pore radius in Å,
 v is the viscosity of the liquid in cgs units,
 S is the surface tension of the liquid in cgs units,
 X is the distance in cm the liquid travels through the pellet in t seconds, and
 a is a constant characteristic of the liquid.

The derivation of this equation is outlined in an appendix at the end of this bulletin. The quantity "a" is a correction introduced to allow for the presence of a single adsorbed layer of the liquid on the pore wall. It is the thickness of one adsorbed layer in angstrom units. For the two liquids used in this investigation, aniline and water, the values "a" are approximately 5Å and 2Å respectively. (3, 4)

This equation can be rearranged to the form:

$$\frac{2v}{S} \frac{X^2}{t} 10^8 = r \left[\frac{r-a}{r} \right]^4,$$

where all the quantities on the left hand side can be measured experimentally. Using such a rearrangement in conjunction with the

experimental data, the pore radius can be determined from a graph of

$$r \left[\frac{r - a}{r} \right]^4 \text{ vs. } r$$

Typical graphs of these quantities are shown in Figures 1 and 2.

The two methods for estimating the pore radius differ only in detail and are described below.

1. Capillary Rise Method - Macro Pore Radius

This method is best suited to right circular cylindrical pellets which have flat, or only slightly convex, ends. A diagram for this determination is shown in Figure 3.

The measurement is begun by touching the horizontal bottom plane surface of a single pellet to the surface of the liquid. Care must be taken to prevent the pellet from dipping into the liquid beyond the level of the bottom face. To accomplish this the relative levels of the liquid and pellet are adjusted so that surface tension effects can be made to just hold the liquid in contact with the lower face or edge of the piece of catalyst. If this adjustment of the relative levels is not made with considerable care, the meniscus of the liquid creeps up beyond the level of the lower face of the pellet and introduces an error into the origin, or basal, plane from which the rate of capillary rise is measured.

Experience has shown that a reasonably simple means of

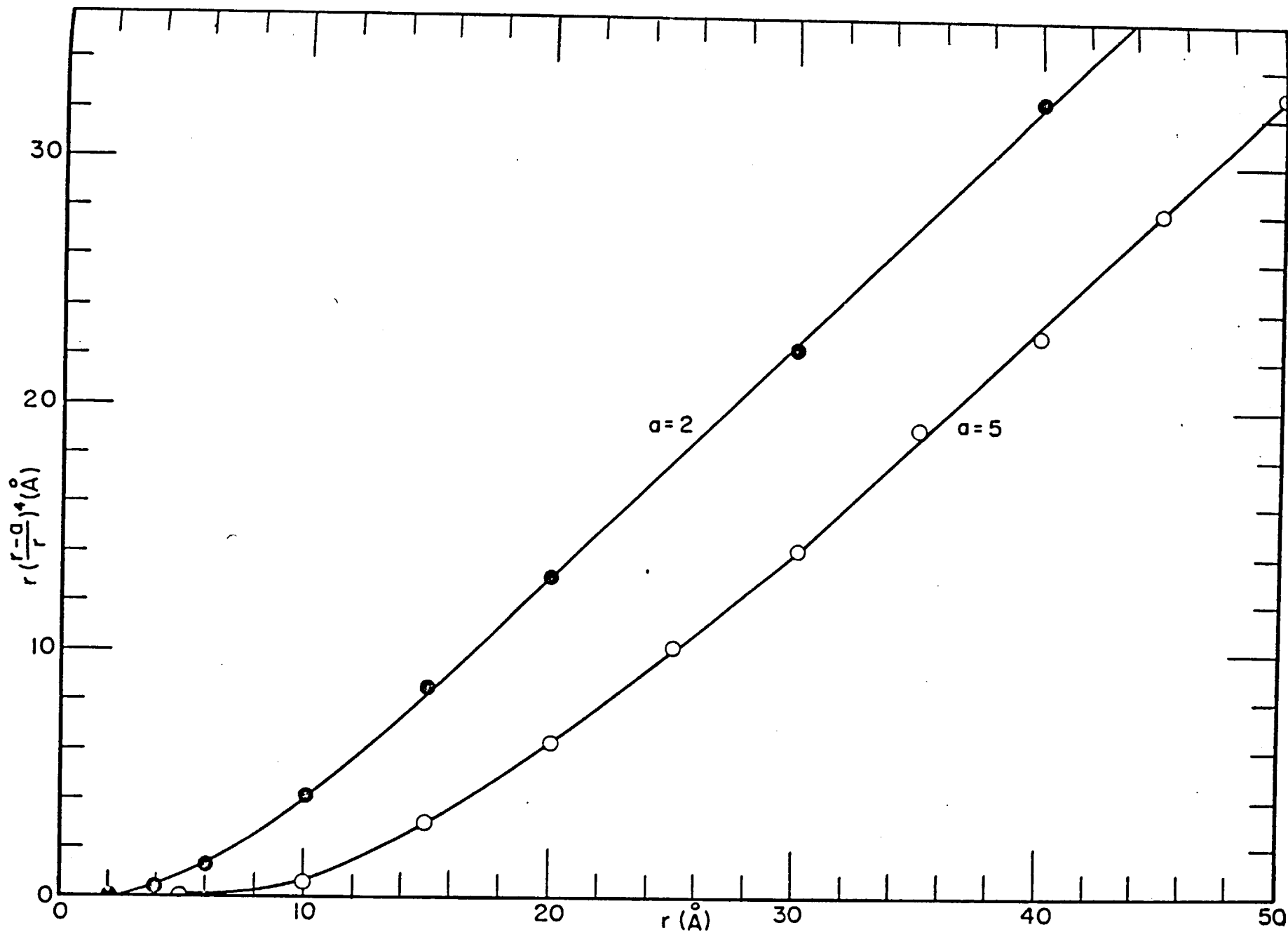


FIGURE 1 - GRAPH OF $r\left(\frac{r-a}{r}\right)^4$ vs. r RANGE 0 TO 50 Å

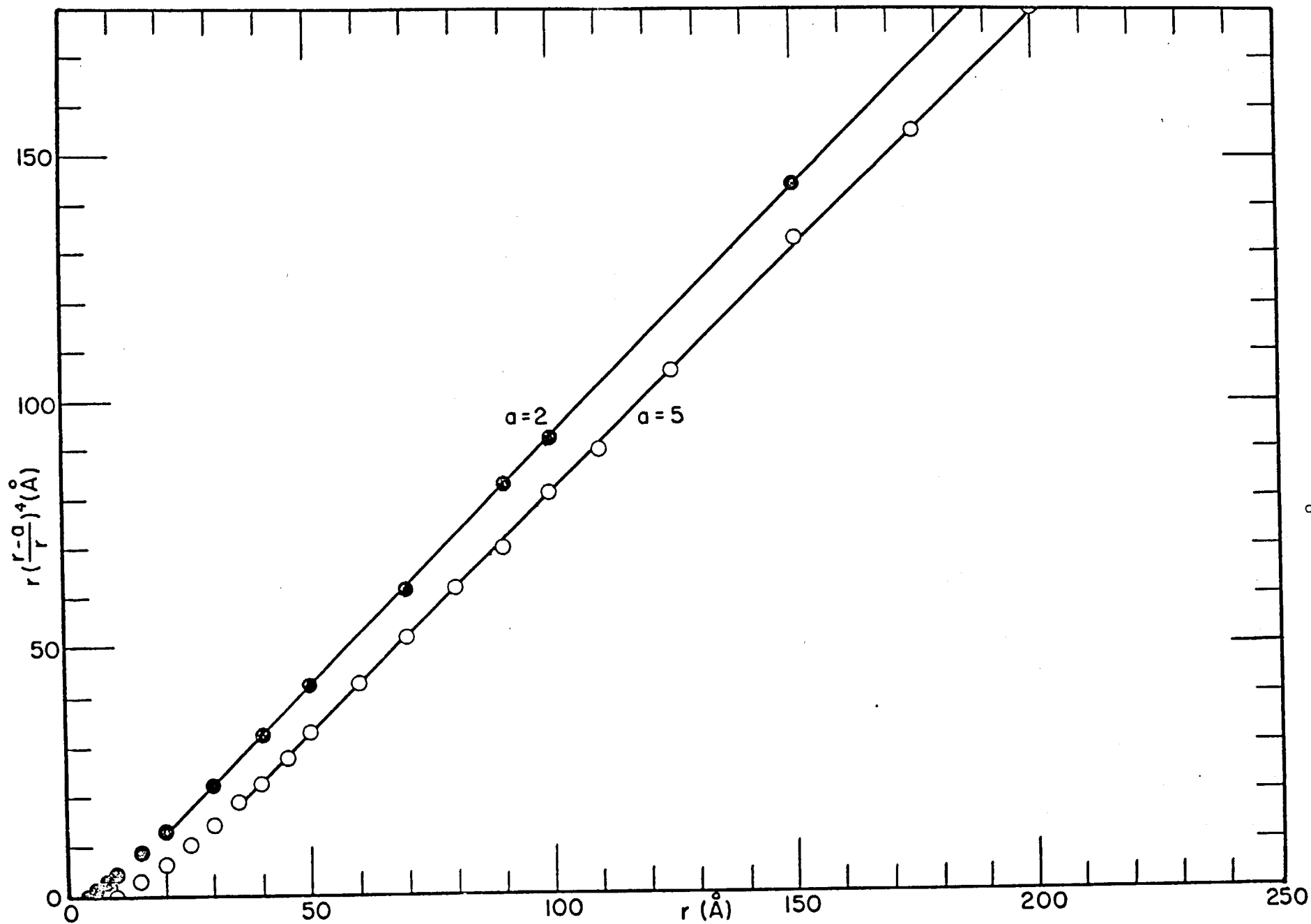


FIGURE 2 - GRAPH OF $r \left(\frac{r-a}{r}\right)^4$ vs. r RANGE 30 TO 250 Å

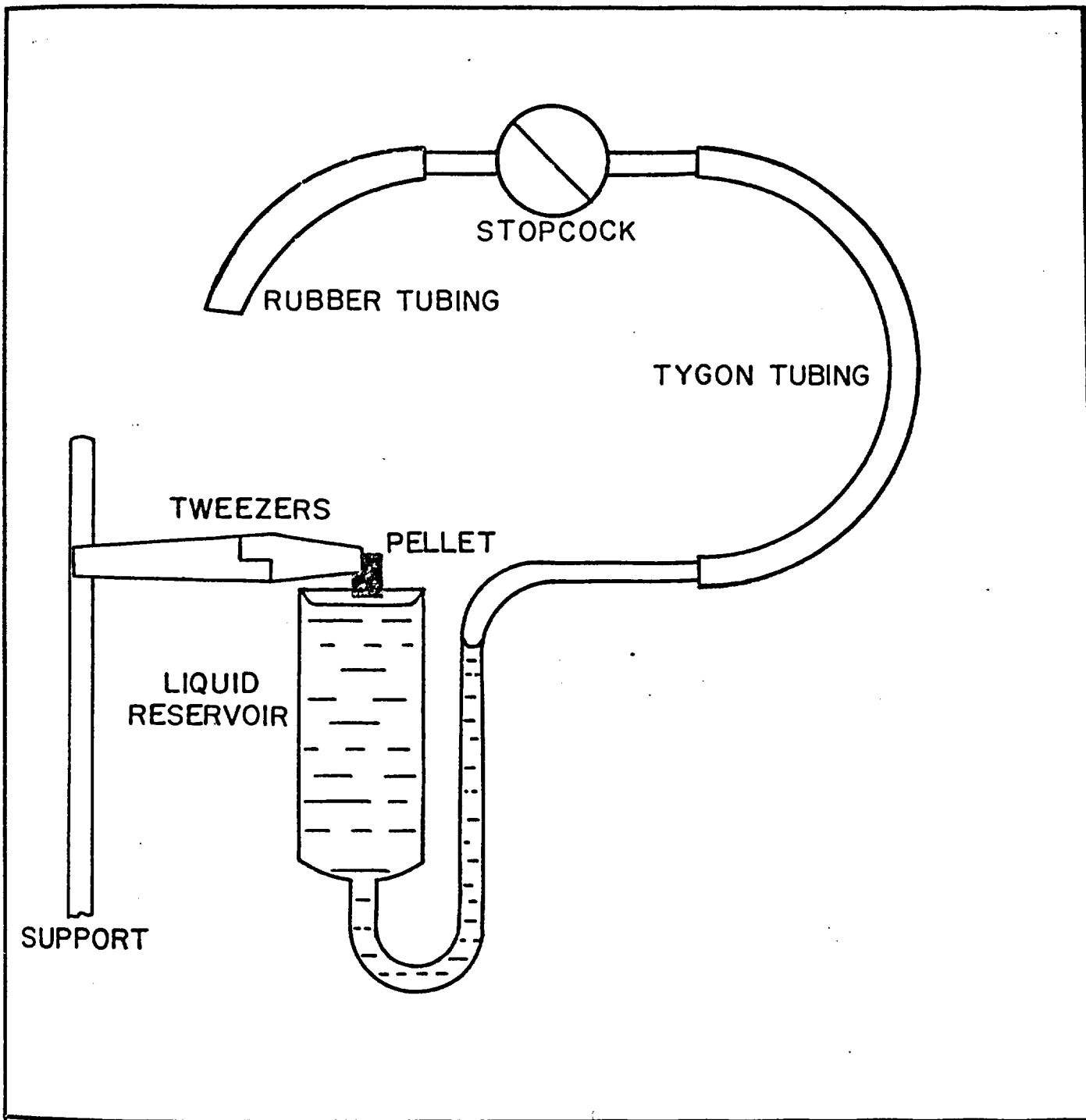


FIGURE 3- APPARATUS FOR THE DETERMINATION OF THE MACRO PORE RADIUS

obtaining a reproducible basal plane is to suspend the pellet slightly above the liquid and to have the bottom face wetted by liquid that is suspended above the hydrostatic liquid level in the reservoir by capillary forces. The adjustment of the relative levels can be made in the following way: Hold the pellet in tweezers mounted in a laboratory clamp just above the centre of the reservoir. Raise the liquid level by gently blowing into the connecting tubing until the liquid is 1 to 2 mm below the bottom of the pellet; then close the stopcock. Pinch the tubing until the liquid touches the bottom of the pellet momentarily, and then allow the liquid level in the reservoir to fall back to its previous level below the lower face of the pellet. (Small adjustments in the level of the liquid are best made by means of a pinch clamp attached to the tubing.)

The time is measured from the instant the liquid wets the lower surface until the liquid reaches the top of the pellet. The pore radius is calculated from the equations referred to previously, where the quantity X is the length of the pellet. The temperature of the liquid should also be noted, to relate the surface tension and the viscosity of the liquid to the conditions of the experiment.

Under certain circumstances, such as where there is present an impervious disc through the centre of the pellet as the result of non-uniform packing of the powder, it may be desirable to turn the pellet on its side for the measurement. In these cases, because of the curvature of the wall of the pellet, it is necessary to estimate a

correction for the depth to which the pellet is immersed in the liquid, before substituting the measured diameter for the quantity X in the calculations.

2. Total Immersion Method - Micro Pore Radius

In this technique the pellet is totally immersed in water or some other suitable liquid. The penetration of the liquid into the pore structure is indicated by the evolution of air bubbles from the pellet.

The method is as follows: Drop a pellet into a test tube of the liquid and start a stopwatch. Stop the measurement of time as soon as the rate of evolution of the bubbles is greatly reduced. A large number of experiments with a wide variety of samples have shown that, on the average, there is a period of time in the beginning of the measurement when the rate of bubbling is high and more or less uniform. When virtually all of the trapped air has been forced out of the pellet the bubbling rate decreases rapidly, and it is at this point that the measurement of the time is stopped. The length, X, through which the liquid has passed is taken as one-half the minimum diameter of the pellet. The temperature of the liquid should be noted, as mentioned in the macro pore determination, to calculate the viscosity and surface tension of the liquid for the conditions of the experiment.

Calculation of the Surface Area

The surface area contained in the pores of the catalyst pellet

or granule is calculated from the equation:

$$A = \frac{2V}{r} 10^4,$$

where A is the surface area in m^2/gm ,
 V is the total pore volume in cm^3/gm , and
 r is the immersion pore radius in \AA units.

RESULTS

The results of experiments, using both the rapid test methods and the slower quantitative techniques of nitrogen adsorption and high pressure porosimetry, are shown in Table 1. For purposes of comparison two catalysts were tested, namely: $1/8 \times 1/8$ in. pellets of cobalt molybdate on alumina, designated as type H760, manufactured by the Union Oil Co., Los Angeles; and $1/8$ in. diameter extrusions of type S cobalt molybdate on alumina, manufactured by the National Aluminate Corporation, Chicago.

DISCUSSION

The rapid method for the determination of the total pore volume gave results in close agreement with other more complicated methods. For the two samples of catalyst pellets tested, the total pore volume as measured with water is within five percent of the sum of the micro pore volume, as measured by the adsorption of nitrogen, and the macro pore volume as determined by mercury porosimetry method. This is, therefore, a very useful procedure for rapidly determining the total pore volume of catalyst pellets.

TABLE 1

Summary of Results

Sample	Nitrogen Adsorption Method			Rapid Test Methods				
	Micro pore volume cm ³ / gm	Average pore radius • Å	Surface area m ² / gm	Macro pore volume* cm ³ / gm	Total pore volume cm ³ / gm	Immersion pore radius • Å	Capillary Rise pore radius • Å	Surface area m ² / gm
Union Oil) # H-760)	0.323	24.5(0) 22.0(S) 25.0(BJH)	229(BET) 239(BET)	0.05	0.396 0.388	20.3 19.2	50.5 39.4 47.0 50.4	390 330
Nalcat) Type S)	0.416	32.5(0) 35.0(S) 35.0(BJH)	222(BET)	0.04	0.470 0.469	39.6 32.6 38.8	81 54	254

(0) Average pore radius calculated by the method of Oulton. (5)

(S) Average pore radius calculated by the method of Shull. (5)

(BJH) Average pore radius calculated by the method of Barratt, Joyner and Halenda. (5)

(BET) Surface area calculated from the Brunauer, Emmett and Teller equation. (5, 6).

* The macro pore volume, i. e. the volume of the pores with radii greater than 100 Å, was determined by the method of high pressure mercury porosimetry. A full report of this technique is in preparation.

The two procedures that were evolved in the present investigation for determining the pore radius, namely the capillary rise technique and the total immersion method, do not agree with each other nor with the pore radius determined by nitrogen adsorption. The nitrogen adsorption method gives the average radius of all pores, both in the micro and macro pore ranges. On the other hand, the capillary rise technique is greatly influenced by the very large pores or cracks in the direction of the capillary rise. Water may rise rapidly through these large cracks to the top surface of the pellet, by-passing the small pores. The average pore radius calculated by this method is therefore profoundly influenced by the presence of macro pores.

The total immersion method, on the other hand, is little influenced by the macro pores and is, in the main, a measure of the micro pore radius. The time required for the liquid to penetrate the large pores is very short in comparison with the length of time required for the immersion liquid to force out the air entrained in the micro pore system. The large, or macro, pores appear to act simply as channels for the air to escape from the micro pores in the interior. Extreme cases of very hard-pressed pellets containing few or no macro pores occasionally show peculiar characteristics, because the trapped air cannot escape freely. The air may not begin to bubble out of the pellet for several minutes, or the flow may stop temporarily and then begin again. In such cases every effort must

be made to use, for the calculation of the pore radius, only the actual time of evolution of the gas.

The difference in the pore radius, as determined by the capillary rise and total immersion techniques, gives an indication of the upper and lower limits of the pore radius distribution in a pellet. The surface area calculated from the average immersion pore radius therefore tends to give an upper limit of surface area, and thus a value higher than that determined by nitrogen adsorption.

Qualitative information on the relative amounts of macro and micro pore volume within a pellet can be obtained by observing the colour changes in the pellet at the end of the experiment. When the pellets are removed from the apparatus at the end of the measurement, they are usually darkened in appearance because of the presence of liquid at the surface. If the pellet returns to its original "dry" appearance within a few minutes after removal from the apparatus, then it can be inferred that there are many unfilled micro pores left in the pellet. If it changes in appearance slowly, or not at all, then there are very few unfilled micro pores.

The capillary rise test will also give some information about the packing of the powder in a pellet. For example, many cylindrical tablets, particularly those manufactured commercially, have a thin non-porous disc across the centre section, due primarily to the non-uniform packing of the powder in the die. When such a disc is present the liquid rises up to it at a uniform rate, then slows down or

stops altogether. Such variations should be taken into account in assessing the quality of a pellet.

The surface areas of the pellets reported in the last column of Table 1 were calculated from the total pore volume and the immersion pore radius. The area figures do not agree with the measurements made by the adsorption of nitrogen, but they do give an indication of the order of magnitude of the surface involved. For many purposes an estimate of the magnitude is all that is required and the approximate techniques described herein are quite adequate.

With background experience and proper selection the rapid methods of measurement of pore volume and pore radius give an excellent means of quickly determining pore characteristics of a material with a satisfactory degree of accuracy for many purposes. Their main usefulness is for the rapid comparison of similar materials or for relative measurements on pellets prepared by methods which vary slightly.

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APPENDIX 1. - Derivation of the Equation Used to Determine the Average Pore Radius

The pressure difference across a spherically curved surface is given by the equation:

$$P = \frac{2S}{r} \quad (\text{Reference 7}) \dots\dots\dots 1)$$

where P is the pressure difference in dynes/cm²,
 S is the surface tension in dynes/cm, and
 r is the radius in cm of curvature of the meniscus.

Poiseuille's equation for the flow of liquid through a cylindrical tube is:

$$v = \frac{\pi P r^4 t}{8VX} \quad (\text{Reference 8}) \dots\dots\dots 2)$$

where v is the viscosity of the liquid in poises,
 P is the driving pressure in dynes/cm²,
 r is the radius of the tube in cm,
 t is the time in seconds required to force V cm³
of liquid through the capillary, and
 X is the length of the capillary in cm.

For the usual applications of the Poiseuille equation, the quantity r , the pore radius, is relatively large and the accuracy of

the calculation is unaffected by the presence of an adsorbed layer of liquid on the walls. In this particular case, however, adsorption measurements on the catalysts made with nitrogen (1) indicate that the average pore radius is of the order of 25 to 30 Å. The thickness of the adsorbed liquid film is estimated to be about 5 Å, which corresponds to 10 to 20% of the quantity to be calculated. It was felt that a reasonable approximation to the correction required for the application of the equation at these radii could be made by subtracting the thickness of the film from the value for the radius, i. e. substituting for r the quantity $r - a$, where "a" is the thickness of the adsorbed layer.

Poiseuille's equation then becomes:

$$v = \frac{\pi P (r - a)^4 t}{8 V X} \dots\dots\dots 3)$$

The combination of equations 1 and 3 gives:

$$v = \frac{\pi (r - a)^4 t}{8 V X} \cdot \frac{2S}{r}$$

but $V = \pi r^2 X$

$$\therefore v = \frac{\pi (r - a)^4 t}{8 \pi r^2 X^2} \cdot \frac{2S}{r}$$

Rearrangement gives:

the calculation is unaffected by the presence of an adsorbed layer of

$$r = \frac{4v}{S} \cdot \frac{X^2}{t} \cdot \left[\frac{r}{r-a} \right]^4 \text{ in centimetres.}$$

The tortuosity factor (2) for most porous materials is $\sqrt{2}$. As X, the length of the pellet, appears in the equation as a squared term, the radius becomes

$$r = \frac{2v}{S} \cdot \frac{X^2}{t} \cdot \left[\frac{r}{r-a} \right]^4 \cdot 10^8 \text{ in angstroms,}$$

where the term 10^8 converts the radius from centimetres to angstrom units.

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