shown. However the microstructure, and its relation to the macrostructure, are not resolved. As the resolution of our instrument is 20 nm it is clearly impossible to do this. However, as the voids and cracks are visible in the scanning electron micrographs, they are not formed by the ion-milling procedure. Thus the ion-milling technique and scanning electron microscopy complement each other.

Cumulative pore volumes obtained by nitrogen desorption at 77°K and by mercury porosimetry are shown in Fig. 6. The nitrogen data were calculated from isotherms using Dollimore and Heal's method B (*9*). The mercury data were calculated assuming a constant contact angle of 130°. Fine pore radii of 3 to 4 nm are confirmed and there is a pore volume of at least 0.16 cm^3/g of pores with radii greater than 10 nm. This confirms the microscopic observation of many large voids.

The results reported in this note show that ion-milling may be used to advantage to examine the structure of practical alumina pellets. Much of the structure may be examined in a single specimen in the absence of debris and artifacts caused by pressure. The method appears promising for the examination of many catalyst materials, and complements both dispersion work and examination by scanning electron microscopy.

ACKNOWLEDGMENTS

We thank A. G. Wikjord and C. F. Musick for determining the nitrogen desorption isotherms, and R. G. Duncan for obtaining the porosimetry data.

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Received October 5, 1971

Volumetric Nitrogen Pore Volume Analysis

INTRODUCTION

Surface area and pore volume are two critical parameters in the characterization of catalysts. Of these parameters surface area is most readily determined by rapid one-point techniques, and one of the most useful of these involves a continuous flow system. Pore volume determinations, however, particularly for the higher pore volumes, are tedious because adsorption at high values of relative pressure (P/P_0) approaches the required equilibrium value sluggishly (*1*). For example, samples which yield equilibrium value in minutes at $P/P_0 = 0.1$ to 0.3 may take many hours to attain equilibrium of $P/P_0 = 0.967$. In this paper we describe a flow technique similar in principle to other dynamic methods (*2–4*), which avoids the long delay. Properly carried out, this technique enables a determination of micropore volume (defined herein as the volume of pores between 14 and 600 Å diam determined by the Kelvin equation (*5*) in eight or more samples per day. This is much faster than with standard techniques such as those using automated devices for isotherm determination (*6*). In essence a flow method at atmospheric pressure with a N_2:He stream (96.7% N_2) is utilized to establish the amount adsorbed at $P/P_0 = 0.967$ when the sample is at liquid nitrogen temperature. Equilibration is accelerated by a brief pressurization, and the amount adsorbed is determined by measuring the volume of gas evolved when the sample is warmed to room temperature. In practice this procedure yields the micropore volume as defined. Cross-checks show that errors due to hysteresis, variations in liquid nitrogen temperature, etc., are small and that this method is reliable to ±5% for samples ranging in pore volume from 0.05 to 3.0 cm^3/g.

EXPERIMENTAL METHODS

The chief novelty of the present apparatus is the use of simple volumetric vessels to determine volume of gas desorbed and the use of a single gas mixture to fill the desired pores. The flow system is simple to build and operate. The adsorption cell, a 6 in. U-tube made from ⅜ in. stainless-steel tubing, holds catalyst samples of 0.2 to 5.0 g. Following catalyst pretreatment, described below, flow of the N_2–He mixture is established over the catalyst. Gas flow rates are regulated with a needle valve and measured with a rotameter tube and are routinely checked with a soap-film flow meter. Nitrogen desorbed from the sample is determined volumetrically by collecting the gas over a saturated sodium chloride solution.

Standard Gas

A N_2–He gas mixture containing 96.7% N_2 and 3.3% He was purchased with analysis from the Matheson Chemical Co. The concentration of nitrogen should be 96.7 ± 0.15%.

Procedure

The adsorption tube containing glass wool plugs is tared and 0.5 ml of sample is charged to the tube; this size sample is generally adequate if the pore volume is in the range of 0.05 to 3.0 cm^3/g. The small plugs of glass wool in each leg of the sample U-tube prevent loss of sample during the test. The sample tube is attached to the degassing system (vacuum pump). Heating at 400°C for 0.5 hr is suitable for drying most silica or alumina samples without altering the surface and pore volume characteristics. Degassing under vacuum is faster than degassing under a flow of dry helium. When degassing is complete, the sample tube plus sample is weighed to get the gross dry weight. Net sample weight is thus obtained by subtracting the tare weight from the gross dry weight. The sample tube is then attached to the adsorption system and the N_2–He mixture flow rate is set at 30 ml/min with a sample inlet pressure of 10 psig as indicated on the second stage of a two-stage regulator. The sample is cooled to liquid nitrogen temperature to condense nitrogen in the pores at atmospheric pressure. When the pores are nearly filled, as evidenced by the gas flow returning to normal, the sample tube is closed at the exit end and the tube is pressurized to 10 psig for 20 min to accelerate equilibration. When the pores are completely filled, the pressure is reduced to atmospheric and the N_2–He mixture is allowed to flow over the sample until the flow rate returns to normal. This usually requires about 4 min. With this flow, the pores greater than 600 Å in diameter have been emptied and a partial pressure of N_2 in the sample tube equivalent to 0.967 relative pressure has been established. The flow of nitrogen over the sample is stopped. The sample tube is connected to the gas collection system and the liquid nitrogen trap is removed from the sample tube. Desorption starts when the cold trap is removed. Then the amount of adsorbed nitrogen is determined by completely desorbing the gas at room temperature with the aid of a water bath at 25°C, collecting it over a saturated sodium chloride brine solution, and measuring it volumetrically. The quantity of gas collected is converted to the corresponding amount of liquid nitrogen and thus to the pore volume (dry sample basis) in cm^3/g with the following formula:

$$\text{pore vol} = \frac{Vn(P_t/760) \times [273/(273+t)] \times K}{\text{Sample wt (g)}},$$

where

- Vn Volume of gas desorbed − system blank which is determined by exactly the same procedure except that the sample tube contains only the glass wool plugs.
- P_t Barometric pressure at temperature t corrected for the vapor pressure of the brine.
- t Room temperature (°C)
- K Factor for converting ml(STP) of gaseous nitrogen at room temperature to ml of liquid nitrogen at the temperature of the liquid nitrogen coolant.

A diagram of the apparatus is included as Fig. 1.

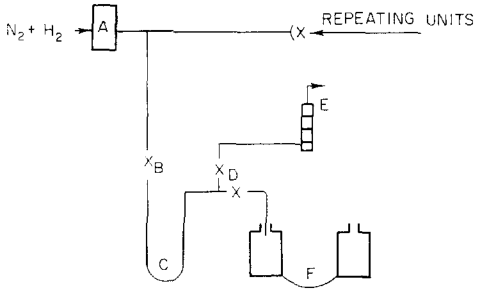

FIG. 1. Schematic drawing of flow apparatus: (A) Two-stage regulator; (B) needle valve; (C) sample tube; (D) gate valves; (E) flow meter; (F) leveling bottles.

RESULTS AND DISCUSSION

Data obtained by this method are precise and compare favorably with results on an automated device for isotherm determination at 0.967 relative pressure (14–600 Å diam pores). A comparison of data obtained (dry sample basis) by the two methods is shown in Table 1.

This method was developed specifically for use in high pore volume (>1.0 cm^3/g) solids since the time required to determine a single pore volume with the automated instrument or with the standard manual technique (*6*, *7*) is about 3 hr while with the described volumetric method, with an 8 unit manifold, 8 samples can be easily analyzed in this period of time. Even though the method was developed to determine pore volumes of high pore volume materials, it is equally useful for the analysis of materials having very low pore volumes (e.g., 0.05 cm^3/g). In the latter case a larger sample should be used.

For a variety of catalysts, pores with diameters ranging from 14 to 600 Å (corresponding to a P/P_0 of 0.967) are most related to catalytic activity, thus dictating

TABLE 1

	Pore vol (cm^3/g; dry basis)	
Sample	Automated isotherm (6)	Volumetric method
Silica–alumina	0.83	0.86
	0.82	0.83
	0.82	0.84
	0.45	0.46
	0.33	0.31
	0.31	0.32
Silica	1.7	1.8
	2.2	2.1
	2.4	2.3
	2.6	2.4
	2.2	2.3
	2.0	2.0
	1.6	1.7
	3.0	2.9
	1.9	1.8
	2.8	2.7
Metal sponge	0.03	0.03
	0.05	0.06
Alumina	0.35	0.35
	0.77	0.79

our choice of relative pressure. For P/P_0 used in these studies cross checks reveal that hysteresis effects are trivial.

This method may be usable for measurements of pores in other ranges of diameters by varying the composition of the N_2:He stream, i.e., P/P_0. Checks should be made, however, to assure that the adsorption–desorption occurring during pressurization at such relative pressures does not introduce hysteresis effects which can spoil agreement with traditional evaluation methods.

ACKNOWLEDGMENTS

The authors thank Dr. P. H. Emmett and Dr. R. J. Kokes for suggesting this method and for helpful discussions during its development.

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Received October 19, 1971

Remarks on the Reduction–Oxidation Mechanism of Sulfur Dioxide Oxidation on Vanadium Catalyst

NOMENCLATURE

A_1	frequency factor [g-mole/(hr)(atm)(g catalyst)]
A_2	parameter in Eq. (12)
E_1	activation energy (cal/g-mole)
E_2	parameter in Eq. (12)(cal/g-mole)
k	rate constant [g-mole/(hr)(atm)(g catalyst)]
K	equilibrium constant defined as $K = c_{V^{4+}}^2 p_{SO_3}/c_{V^{5+}}^2 p_{SO_2}$
$c_{V^{4+}}$, $c_{V^{5+}}$	concentration of vanadium in oxidation state +4 or +5
K_p	equilibrium constant of sulfur dioxide oxidation defined by partial pressures ($atm^{-1/2}$)
p_i	partial pressures of species i (atm)
r_0	initial reaction rate [g-mole/(hr)(g catalyst)]
r	reaction rate [g-mole/(hr)(g catalyst)]
$\hat{r}$	calculated reaction rate [g-mole/(hr)(g catalyst)]
R	gas constant [cal(mole)(°K)]
T	absolute temperature (°K)

I. INTRODUCTION

In 1964 Mars and Maessen (*1*) proposed an reduction–oxidation mechanism for the catalytic oxidation of sulfur dioxide on potassium–vanadium oxide catalyst. Since that time, this mechanism has been the subject of many studies (*2–5*). Mars and Maessen (*1*) assumed that the catalytic oxidation of sulfur dioxide proceeds via the following reaction steps:

$$SO_2 + 2V^{5+} + O^{2-} \rightleftarrows SO_3 + 2V^{4+}, \qquad (1)$$

$$\tfrac{1}{2} O_2 + 2V^{4+} \rightleftarrows 2V^{5+} + O^{2-}. \qquad (2)$$

They further assumed that the surface reaction described by Eq. (1) is fast compared to the reduction–oxidation reaction of Eq. (2), and that the reduction–oxidation reaction is rate controlling. In continuation of this original work Mars and Maessen (*2*) studied the oxidation reaction on a sodium–potassium–vanadium catalyst and found that the reaction rate can also be described by the above mechanism.