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SOME PHYSICAL MEASUREMENTS ON CATALYSTS AND THEIR SIGNIFICANCE

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The large scale use of catalysts in commercial processes has undergone remarkable expansion the past decade. Along with this the manufacture of catalysts has become a major industrial activity. It is conceded that knowledge of the surface chemistry of catalytic processes is of critical importance and considerable effort is being extended in this direction. However, knowledge of the catalyst's physical structure is essential for a complete understanding of catalyst function.

Measurements to determine the physical structure of catalysts are significant in that catalyst deterioration on use and regeneration may be followed, the effect of process variables on catalysts may be determined, and the relative importance of various factors in catalyst preparation and treatment may be determined. In addition to this the economics of a process often hinge on the catalyst or catalyst life.

It is the purpose of this paper to describe some methods used for the determination of surface area and pore volume. These two physical properties of catalysts are extremely valuable in the determination of an optimum catalyst as a criteria for the reproducible production of catalysts, in forming a basis for comparison of catalysts, etc.

The Brunauer, Emmett, Teller (B.E.T.) method (1) is considered the most accurate for surface area and pore volume measurements. This is essentially a low temperature-high vacuum method that entails covering the catalyst with a single layer of gas molecules, calculating the molecules necessary to accomplish this, and determining the surface area from known physical constants of the gas used. Nitrogen is the gas most generally used and the temperature of adsorption is -196°C. Pore volume is also determined by this method; it is calculated from desorption data. B.E.T. nitrogen adsorption-desorption requires rather elaborate apparatus and is very time consuming. About two days is required for a surface area measurement and a week is required for pore volume measurements. The methods described below circumvent these disadvantages.

AROMATIC ADSORBANCY INDEX METHOD (4,5) SURFACE AREA DETERMINATION.

I. REAGENTS AND APPARATUS

Aromatic Adsorbancy Index Solution. This is a 30% (by volume) toluene and 70% (by volume) iso-octane solution. These chemicals should be reagent grade and water free.

Adsorbancy Vessel. Figure 1 shows a diagram of this vessel. A series of those were made from 50 ml. distilling flasks. A two-way stopcock is attached to the delivery arm of the flasks. The annular space between the ground glass socket insert and the walls of the flask is 1/16". The end of this insert should not extend below the neck of the flask. These restrictions are essential to efficient cleaning of the adsorbancy vessel. A ground-glass ball joint stopper to fit the socket is also needed.

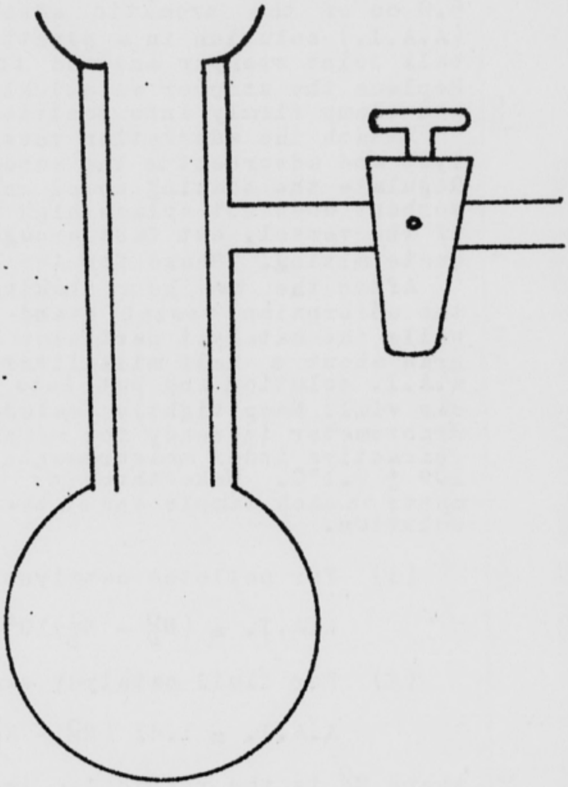
Refractometer. All refractive index measurements are made at 20° ± 0.1°C and are read to the fourth decimal place.

Automatic shaking device.

II. PROCEDURE

Dry the catalyst, whether pelleted or fluidized, in a muffle oven over night. The drying temperature is dictated by the catalyst reaction temperature. Cool in a desiccator.

Weigh a clean, dry adsorption vessel on an analytical balance. For a pelleted catalyst weigh 3.50 ± 0.01 grams of the dried catalyst into the vessel; for a fluidized catalyst weigh 2.50 ± 0.01 grams. Clamp a greased, ball joint stopper on to the vessel and evacuate through the stopcock with a vacuum pump for ten minutes. All effort must be made to minimize contact time of the



AROMATIC ADSORBANCY INDEX

REACTION VESSEL

FIGURE 1

catalyst sample with the atmosphere.

Open the stopcock of the adsorption vessel briefly to reduce the vacuum and facilitate removal of the ball joint stopper. With 5.0 cc of the aromatic adsorbancy index (A.A.I.) solution in a pipette, remove the ball joint stopper and add the adsorbent. Replace the stopper as quickly as possible and clamp firmly into position.

Attach the adsorption vessel with catalyst and adsorbent to the automatic shaker. Regulate the shaking speed so that the adsorbent does not splash high into the neck of the vessel, but fast enough to give adequate mixing. Shake for two hours.

After the two hour shaking period, let the adsorption vessel stand five minutes while the catalyst particles settle. Withdraw about a half milliliter of the clear A.A.I. solution and put into a small screw cap vial. Keep tightly sealed until the refractometer is ready for measurement. All refractive index measurements are made at 20° ± 0.1°C. Make three or four measurements on each sample and on the A.A.I. stock solution.

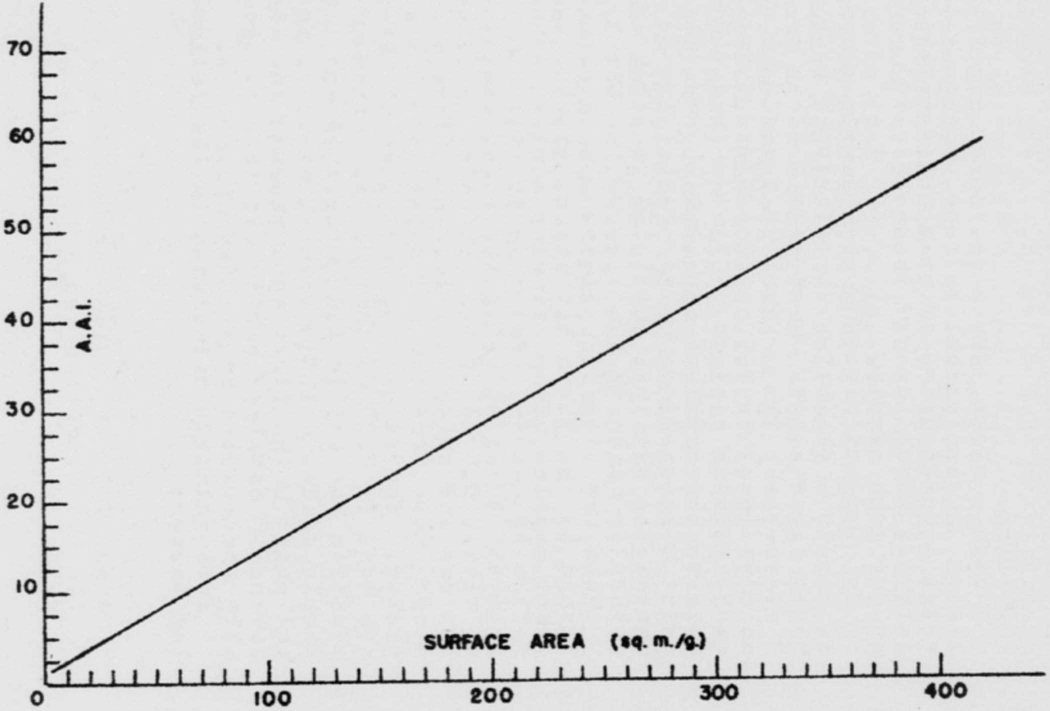
(1) For pelleted catalyst samples:

$$\text{A.A.I.} = (N_D^0 - N_D^1)10^4$$

(2) For fluid catalyst samples:

$$\text{A.A.I.} = 1.41\,(N_D^0 - N_D^1)10^4 - 1.1$$

where N_D^0 is the refractive index of 20°C of the A.A.I. stock solution; N_D^1 is the refractive index at 20°C after adsorption; (1.41) and (1.1) are correction factors for the change in sample size. The surface area in sq. m./gram is obtained from the calculated A.A.I. value by reference to the calibration curve, Figure 2.



AROMATIC ADSORBANCY INDEX (A.A.I.) vs. SURFACE AREA

FIGURE 2

WATER TITRATION METHOD (3)
PORE VOLUME MEASUREMENTS

I. PROCEDURE.

Weigh a clean, dry 2 oz. screw cap bottle on an analytical balance. Accurately weigh about 5 grams of oven dried catalyst into it. About three of these should be made up for each sample.

The first titration on each sample series is merely to establish the titration range. To the first sample add distilled water from a micro-buret (10 cc buret graduated in 0.02 cc divisions) in 0.5 cc increments. After each addition replace the lid and shake well. Observe the catalyst appearance. The end-point is reached when the last addition of water causes the catalyst particles to stick together or adhere to the sides of the bottle.

When the titration limit has been established by the first titration, titrate the other samples of a particular series in the following manner. Add enough distilled water from the buret to bring the first addition to within 0.5 cc of the end point. Replace the cap and shake well for about five minutes to make sure the end point has not been passed. The succeeding additions of water are made in 0.05 cc increments. After each addition the bottle lid is replaced and the sample shaken well for several minutes. The end-point is the first appearance of any adherence of catalyst particles; this is usually accompanied by a shiny appearance.

Pore volume is calculated in the following manner:

Pore Volume in cc/gram = V/W
where V is the volume of water used for the titration and W is the sample weight.

DISCUSSION

The Harshaw Chemical Company submitted four catalyst samples for evaluation together with their B.E.T. data for surface area and pore volume. The reliability of the methods described herein has been based on the comparative data given in Table I.

From Table I it may be seen that the comparative data of the A.A.I. and B.E.T. methods for surface area is very good. The A.A.I. values are within ± 5 sq.m./g. of the B.E.T. values. The four catalyst samples of this table include both pelleted and fluidized catalysts. The reproducibility of the A.A.I. method is shown in Table II; the precision is ± 5 sq.m./gram. Total time for an analysis by the A.A.I. method is about three hours; actual working time about an hour. Another advantage of this method is that a group of samples may be done simultaneously whereas only one (requiring about eight hours) may be done at a time with the B.E.T. method. The A.A.I. method is dependent on refractive index measurements; accuracy of these measurementments to ± 0.0002 units is mandatory. The calibration curve for this method, Figure 2, was taken from the Kellogg paper(5).

Comparative values of the water titration and B.E.T. methods for pore volume determination are also given in Table I. The water titration values are within ± 0.06 cc/gram of the B.E.T. values. The excellent reproducibility of the water titration method is shown in Table III. The precision is well within ± 0.01 cc/gram. Herein lies the value of the method. Although the values will not be equivalent to B.E.T. values, with the excellent precision of the water titration method trends in pore volume change can easily be followed. Analysis time by this method is about an hour compared to a week by the B.E.T. nitrogen adsorption-desorption method.

In Table I comparative values are also given for a carbon tetrachloride-cetane method (2) of pore volume measurement. The data are not in good agreement with the B.E.T. values. The method was not considered satisfactory for pore volume measurements.

The main advantage of the A.A.I. method and water titration method is the time required for analysis. Both methods greatly reduce analysis time and have the additional advantage that a number of samples may be determined simultaneously. The distinct advantage of the B.E.T. method is that, from the data

TABLE I

COMPARISON OF METHODS

Harshaw Catalyst Sample	Pore Volume (c.c./g.)			Surface Area (sq.m./g.)	
	B.E.T.	Water Titration	CCl_4-Cetane	B.E.T.	A.A.I.
1	0.30	0.39	0.08	14.3	14
2	0.45	0.40	0.40	160	165
3	0.37	0.33	0.22	61	56
4	0.42	0.35	0.30	150	147

TABLE II

REPRODUCIBILITY OF A.A.I. METHOD*

I	II	III	IV	V
200	94	179	14	300
200	94	164	14	330
200	94	164	14	
200	94	164		
		164		
		156		

*Values are surface area in sq.m./gram.

TABLE III

REPRODUCIBILITY OF WATER TITRATION METHOD*

I	II	III	IV
0.419	0.391	0.468	0.325
0.417	0.389	0.467	0.326
0.417		0.463	
0.416		0.461	
0.417		0.455	
0.414		0.456	
0.418			
0.418			
0.415			
0.416			
0.419			

required for surface area and pore volume, pore size distribution calculations can be made. Measurements of this type are also valuable in catalyst evaluation.

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*Values are pore volume in cc/gram.