

Determination of Zeolite Contents of Zeolitic Catalysts from Vaporization Measurements

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A vaporization technique has been devised to measure amounts of liquids strongly adsorbed by crystalline zeolites. It consists of adding a suitable liquid such as benzene to a weighed catalyst sample, then monitoring sample weight versus time as excess benzene is vaporized in a stream of dry nitrogen at room temperature. Since vaporization rates are a sensitive function of pore diameter, such measurements provide a method for the determination of zeolite contents of zeolitic catalysts that contain other porous solids. Vaporization of benzene has been measured for a variety of porous solids that include A-, X-, Y-, and L-zeolites, mordenite, and amorphous solids such as silica, alumina and silica-alumina gels.

INTRODUCTION

Crystalline zeolites strongly adsorb molecules that are small enough to penetrate their crystal lattices; in fact, adsorption measurements of a variety of molecules have been used to determine intracrystalline volumes of pure zeolites (1). In principle it should also be possible to utilize adsorption measurements of suitable liquids to determine zeolite contents in mixtures of zeolites with other solids. However, this type of measurement cannot be used for this purpose when the nonzeolitic components consist of high-surface area solids that also adsorb comparable amounts of liquid at the relative pressures (>0.1) that are commonly used to fill intracrystalline cavities in zeolites. The relative pressure could, of course, be lowered until adsorption by the nonzeolitic component becomes negligible but the adsorption process now becomes too time consuming to be useful as a routine tool for the determination of zeolite contents. It has been found, however, that this goal can be conveniently attained by utilizing a simple vaporization technique to determine the amount of liquid adsorbed only by the crystalline zeolite. The technique it-

self and results that illustrate its application are described below.

EXPERIMENTAL DETAILS

Vaporization measurements are carried out as follows. A glass sample tube (Fig. 1) is weighed after it is capped with a rubber septum (which will protect the sample from atmospheric moisture and carbon dioxide). Enough catalyst sample is added (2-5 g) to fill roughly one third the length of the tube, the tube is recapped with the rubber septum, and the filled sample tube is reweighed to obtain the dry sample weight. The rubber cap is removed, a suitable liquid such as benzene (1-2 cc) is added, the cap is replaced, and a stream of dry nitrogen (50 cc/min) passed downward through the wet catalyst sample. The nitrogen is introduced by means of a hypodermic needle that pierces the rubber septum. After the catalyst sample has been swept with the nitrogen stream for 1 hr, the capped sample tube is disconnected from the nitrogen supply, reweighed, then reconnected to the nitrogen supply. Weighings are repeated at hourly intervals (except for the overnight interval) until a 20 hr vaporization process has been com-

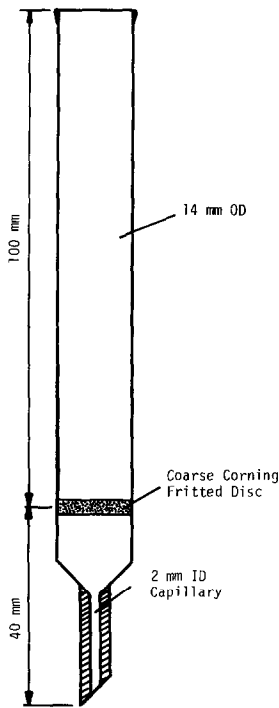


FIG. 1. Pyrex tube for adsorption measurements.

pleted. The weight of liquid retained by 100 g of dry sample is calculated and plotted versus time to give vaporization curves as illustrated in Figs. 2 and 3;

weight retention at 20 hr is used as an index of zeolite content. Catalyst samples are calcined at least 2 hr in air at 500°C directly before the vaporization measurements. It is convenient to have a bank of sample tubes attached to separate rotometers supplied by a nitrogen manifold (at 10 psig) so that as many as six catalyst samples can be monitored during a given 20 hr period. The sample tube bank can be set up in a hood to dispose of hydrocarbon vapors.

The crystalline zeolites and other porous solids used in this study were as follows: MS-A-3 cracking catalyst (through 100 mesh, 25% Al_2O_3) from American Cyanamid Co.; Grades 70 and 950 silica gels (60 to 200 mesh) from Davison Chemical Division, Grace Co.; sodium form of Y-zeolite (SK-40 powder), sodium form of X-zeolite (SK-20 powder), sodium form of A-zeolite (4A powder), and potassium-sodium form of L-zeolite powder from Linde Division, Union Carbide Corp.; and sodium and hydrogen forms of mordenite (Na- and H-Zeolon powder) from Norton Co.

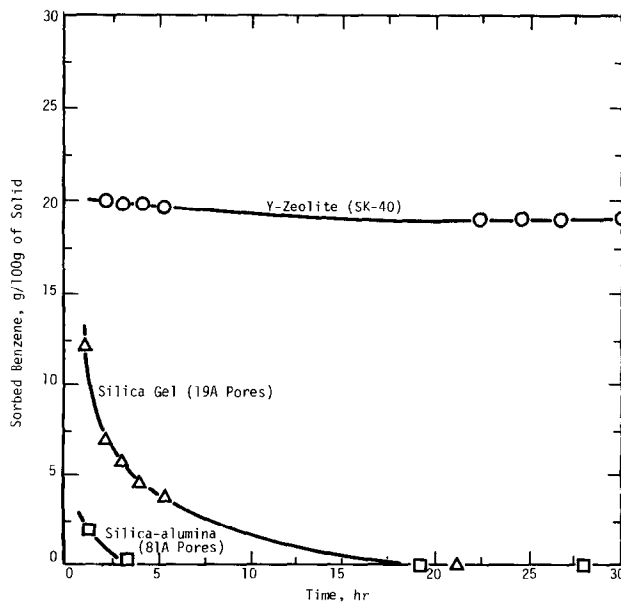


FIG. 2. Vaporization of benzene at 25°C from Y-zeolite and from nonzeolitic porous solids.

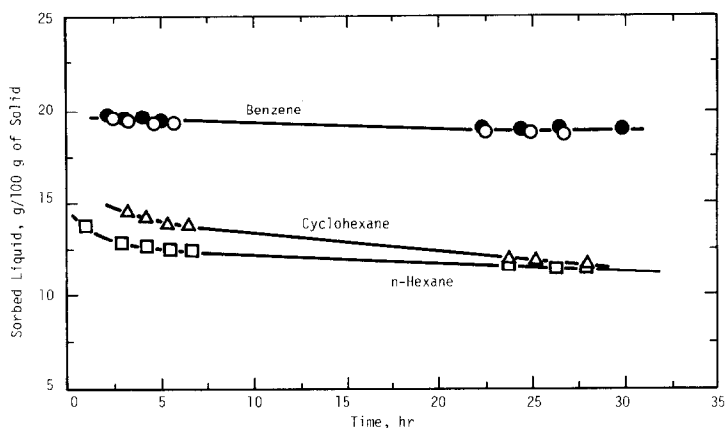


FIG. 3. Vaporization of C_6 hydrocarbons from Y-zeolite at 25°C.

The benzene, cyclohexane and *n*-hexane were Pure Grade products from Phillips Petroleum Co.

RESULTS AND DISCUSSION

Vaporization measurements of benzene from a crystalline zeolite (Y-zeolite, Na form) and from three amorphous solids are listed in Table 1. To prevent overcrowding, only three sets of data are plotted in Fig. 2. These results show that benzene readily vaporizes in flowing nitrogen from the amorphous solids since it is completely removed after 20 hr of sweeping at room temperature. In the case of the Y-zeolite, however, 19.0 g of benzene/100 g of zeolite are still retained after 20 hr of sweeping; vaporization has vir-

tually ceased because of the low vapor pressure of the benzene that remains adsorbed by the Y-zeolite.

The decrease in vaporization rate that occurs after removal of excess liquid from porous solids is a general phenomenon that arises because of the lowering of the vapor pressure of liquids in small pores. The vapor pressure p of a liquid in a cylindrical pore of diameter d at the absolute temperature T can be calculated by means of the Kelvin equation:

$$\ln p/p_0 = \frac{-4\gamma V \cos \theta}{d RT},$$

where p_0 is vapor pressure of the bulk liquid, γ is surface tension, V is molar volume, and θ is contact angle. It can be seen that our experimental data (Table 1) are consistent with the predictions of the Kelvin equation (Table 2). Vaporization rates are highest in the case of the solids having large pore diameters (81 and 104 Å). Though the vaporization rate is extremely low after 20 hr in the case of Y-zeolite, it is measurable and amounts to a loss of 1 mg of benzene/hr (which corresponds to a vapor pressure of 0.08 Torr). According to the Kelvin equation, the diameter that corresponds to a vapor pressure lowering of this extent is 6 Å—surprisingly close to the actual 7.4 Å pore openings in Y-zeolite. This agreement

TABLE 1
VAPORIZATION OF BENZENE FROM POROUS SOLIDS AT 25°C

Solid	Pore diam (Å)	Adsorbed benzene ^a (g/100 g)			
		(hr): 2	4	20	24
Silica-alumina	81	1.9	0.1	0.1	0.0
Silica gel	19	7.0	4.6	0.0	0.0
	104	28.9	0.2	0.0	0.0
Y-zeolite	7.4	19.9	19.7	19.0	18.9

^a Benzene retained after sweeping the indicated times in flowing nitrogen (50 cc/min).

TABLE 2
VAPOR PRESSURES AND VAPORIZATION RATES OF
BENZENE CONDENSED IN MICROPORES
AT 25°C

Pore diam (Å)	Vapor pressure ^a (Torr)	Vaporization rate ^b (g/hr)
∞	95	1.20
100	63	0.79
50	42	0.53
10	1.6	0.02

^a Calculated by means of the Kelvin equation.

^b Assuming saturation at a nitrogen flow rate of 50 cc/min.

is surprising because the 6 Å value is obtained by mathematical extrapolation to a region in which the concepts of meniscus and surface tension become meaningless.

The vaporization behavior for Y-zeolite shown in Fig. 2 appears to be followed by all "large pore" zeolites; i.e., by zeolites with pore openings formed by 12-membered rings of oxide ions that are accessible to benzene. Amounts of benzene retained after 20 hr of vaporization are listed in Table 4 for several crystalline zeolites. Adsorbed benzene is expressed in cubic centimeters per gram (assuming that the density of adsorbed benzene is the same as that of liquid benzene at 25°C) so that these values can be compared to corresponding intracrystalline volumes derived from previous studies. The accessible pore volume in the X- and Y-zeolites arises from a three-dimensional network of supercages, that in mordenite and L-zeolite from parallel channels. Benzene cannot penetrate the small pore openings in A-zeolite. Pore volumes derived from benzene vaporization measurements for the "large pore" zeolites are appreciably lower than those reported in previous work. At least part of this difference probably arises because of partial removal of adsorbed benzene during the 20 hr vaporization period. It is also possible that the packing of benzene molecules adsorbed in zeolite

TABLE 3
VAPORIZATION OF BENZENE FROM ACID-TREATED
MORDENITE AT 25°C

Treatment	Al content (% wt)	Adsorbed benzene ^a (g/100 g)
None ^b	4.2	0.4
Boiled in 2 M HCl, 3 hr	3.7	5.6
Extracted with 12 M HCl, 4 hr	3.1	4.2
96 hr	1.2	1.9

^a Benzene retained after sweeping with nitrogen for 20 hr.

^b Consists of sodium form of synthetic mordenite.

pores is different than that in the normal liquid state.

The differentiation between crystalline zeolites and amorphous solids that is possible by means of the vaporization technique is potentially useful in a variety of studies involving zeolitic catalysts. Since simultaneous measurements of several catalyst samples can easily be carried out, this technique is well suited for monitoring progressive changes in zeolite content. Areas of application include zeolite synthesis, aging of zeolitic cracking catalysts, and variations in catalyst pretreatment. One such application is illustrated by Table 3 which lists results obtained for mordenite samples that were subjected to varying degrees of acid treatment. These

TABLE 4
VAPORIZATION OF BENZENE FROM ZEOLITES
AT 25°C

Zeolite	Adsorbed benzene ^a (cc/g)	Accessible volume ^b (cc/g)
X-zeolite, Na form	0.22	0.30 (2)
Y-zeolite, Na form	0.21	0.29 (1)
A-zeolite, Na form	0.00	0.00 (1)
Mordenite, H form	0.07	0.11 (3)
L-zeolite, K + Na form	0.08	0.15 (4)

^a Benzene retained after sweeping in nitrogen for 20 hr.

^b Former work; references are italicized.

data show that the lattice of the original sodium form of modenite becomes accessible when this zeolite is boiled in 2 *M* HCl. More drastic treatment with 12 *M* HCl removes aluminum and lowers benzene retention.

Zeolite contents of commercial cracking catalysts are not generally made available by catalyst manufacturers but they can easily be estimated by means of the same vaporization technique. Benzene retentions after 20 hr of sweeping vary from 1 to 3 g/100 g of sample for this class of catalysts. The corresponding zeolite contents would therefore range from 5 to 15%wt, assuming that the zeolite components consist of X- or Y-zeolites.

Other liquids such as cyclohexane and *n*-hexane, which have volatilities close to that of benzene, exhibit similar vaporization behavior (Fig. 3) and can also be used for the determination of zeolite contents. By using molecules that differ in size, the

vaporization technique can also be used to differentiate between contents of "small pore" zeolites (e.g., A-zeolite) and "large pore" zeolites (e.g., Y-zeolite). For example, *n*-hexane can be used to determine total content of both types of zeolites; benzene can be used to determine large pore zeolites only.

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