JOURNAL OF CATALYSIS 68, 223–226 (1981)

Adjustment of an Adsorbent's Macropore Volume

A new technique is presented which enables macropore volume of adsorbent to be reduced, while keeping micropore volume intact. "Hydral," basic aluminum chloride, is particularly effective for the present purpose.

INTRODUCTION

Solid catalyst and adsorbent have both micropores and macropores. Active sites are located in the micropores, while the macropores connect the active sites with the external flow. Both reactants and adsorbates reach the active sites in the micropores through the macropores so that the pore-size distribution is very important. In the catalyst reactions, the rates of which are controlled by internal pore diffusion, wider and shorter macropores with less diffusion resistance are suitable for faster reaction rates. In practical separation processes by selective adsorption the apparent selectivity decreases with the increasing macropore volume, because adsorbates adsorbed selectivity in the micropores are usually contaminated with adsorbates in the macropores.

In manufacturing solid catalysts and adsorbents, the control of the pore-size distribution is rather limited although to a certain extent this can be done. In the present paper, a new method for reducing macropore volume is presented.

EXPERIMENTAL

Adsorbent. Faujasite crystalline aluminosilicate having a SiO_2/Al_2O_3 ratio of 4.8 (Zeolite Y) was pelleted into spherical pellets of 1–2 mm diameter with bentonite as a binder. The binder content is 15 wt% of the pellet.

Measurement of macropore disitribution. The macropore distribution was measured by the pressured mercury (*1–4*) method, using a porosimeter from Carlo Erba, Italy. The maximum mercury pressure was 1500 kg/cm^2 so that the macropores down to 50 Å in radius were measured.

Measurement of micropore distribution. The micropore data were obtained by N_2 adsorption, using a Carlo Erba Sorptmat. The calculation was made according to the method of Barrett *et al.* (*5*) which was improved by Cranston and Inkley (*6*). An adsorption branch of the nitrogen isotherm was used.

Impregnation. The materials used for the impregnation are shown in Table 1. The adsorbents were calcined at 500°C for 2 h, and were impregnated with these foreign materials. The excess liquid phase was discarded. The impregnated adsorbent was dried and calcined at about 300°C for 2 h.

Benzene adsorption. The mixture of benzene and *n*-heptane (50:50 in weight) was adsorbed by the adsorbent in a flask at 50°C. After 2 h, the liquid was sampled and subjected to analyses by gas chromatography. By postulating that *n*-heptane is not adsorbed, the adsorption capacity was calculated by

$$C = F(1 - F_7/R_7)/S,$$

where C is the amount of benzene adsorbed per adsorbent, S is the amount of adsorbent, F is the amount of adsorbate, F_7 is the weight percentage of *n*-heptane in the adsorbate before the adsorption, R_7 is the weight percentage of *n*-heptane in adsorbate after the adsorption.

The adsorption capacity thus obtained agreed with that obtained by the following

0021-9517/81/030223-04$02.00/0

TABLE 1

Impregnation Materials

Name	Main component	Concentration (%)	Producer	Remarks
Snowtex-20	Silicasol	20	Nissan Chemicals	Particle size 10–20 nm
Snowtex-30	Silicasol	30	Nissan Chemicals	Particle size 10–20 nm
Snowtex-N	Silicasol	20	Nissan Chemicals	With basic stabilizer
Snowtex-O	Silicasol	20	Nissan Chemicals	Pure silicasol
PAC-250A	$[Al_2(OH)_3Cl_3]x$	20	Taki Chemicals	pH 2.7
Hydral	$[Al_2(OH)_5Cl]x$	32	Taki Chemicals	
Bitaseal-1500	$SiO_2 \cdot nH_2O$	20	Taki Chemicals	Average particle size 18 nm
Aluminasol-200	Aluminasol	11	Nissan Chemicals	Particle size 140 × 10 nm
Potassium silicate	Potassium silicate	27	Wako Chemicals	EP
Acoram	Alkanalamine complex of aluminum hydrogen phosphate	30	Taki Chemicals	P_2O_5: 19% Al_2O_3: 4%

method. After the adsorption of benzene on the adsorbent, excess benzene in liquid phase was drained, and the adsorbent was purged with dry nitrogen until the concentration of benzene in purge nitrogen became negligible. These operations were carried out at 50°C. The temperature of the adsorbent was raised to 400°C and the benzene desorbed was collected. Thus the assumption that *n*-heptane is not adsorbed by the adsorbent in the presence of benzene at 50°C seems to be valid.

RESULTS AND DISCUSSIONS

The macropore volume of adsorbents impregnated with various foreign materials is shown in Table 2. The macropore volume between 100 and 75,000 Å in radius is decreased, except for adsorbents impregnated with Aluminasol or Bitaseal. The increase of macropore volume seems to be due to the formation of new pores around the skin of the adsorbent pellets. Hydral is very effective in reducing the macropore volume.

The effect of the amount of Hydral on

TABLE 2

Macropore Volume of the Impregnated Adsorbents

No.	Impregnation materials	Macropore (100–75,000 Å in radius) (ml/g)[a]
A	None	0.35
B	Snowtex-20	0.28
C	Snowtex-30	0.27
D	Snowtex-N	0.29
E	Snowtex-O	0.29
F	PAC-250A	0.25
G	Hydral	0.14
H	Bitaseal-1500	>0.4
I	Potassium silicate	0.29
J	Acoram	0.23
K	Aluminasol	0.37

Note. Weight increase of adsorbent by the impregnation is approximately 20%.

[a] Based on adsorbent before impregnation.

TABLE 3

Effect of the Amount of Hydral

	Hydral concentration[a] (wt%)			
	0	2	5	12
Macropore (ml/g) of 100–75,000 Å in radius[b]	0.30	0.27	0.21	0.09
Benzene adsorption[c] g/100 g	14.2	13.9	13.9	13.1

[a] As Al_2O_3 relative to adsorbent before impregnation.

[b] Relative to the weight of adsorbent after the impregnation.

[c] Relative to the weight of adsorbent before the impregnation.

macropore volume is shown in Table 3. With the increasing amount of Hydral the macropore volume decreases remarkably, while the decrease of adsorption capacity is only slight. This result suggests that macropores are selectively plugged with Hydral, while active sites in micropores remained almost intact. Hydral is too bulky to plug a micropore.

The pore volume measured by the nitrogen adsorption isotherm is shown in Fig. 1 and Table 4. The pore distribution between 150 and 50 Å in radius was measured by both the pressured mercury method and the nitrogen adsorption method. The agreement between the two methods in the range between 150 and 50 Å in radius is excellent. By the impregnation, the volume of pores larger than 100 Å in radius decreases noticeably, while the volume of pores between 7 and 100 Å in radius increases. This increase of the transitional pores is due to the formation of new pores in the old macropores. The total pores between 7 and 75,000 Å in radius, which adsorbates fill nonselectively, are reduced by 30%.

The micropore volume is calculated as follows. The amount of nitrogen adsorbed at relative nitrogen pressure of 0.058 (*6*), which corresponds to the pore of 7 Å in radius, is read from nitrogen adsorption isotherm. This quantity V is a sum of nitrogen condensed in micropores less than 7 Å in radius, V_c, and nitrogen adsorbed on the surface of pores larger than 7 Å in radius, V_A. From the curve of adsorption thickness versus relative pressure, the adsorption thickness at the relative pressure of 0.058 is read to be 3.6 Å (*6*). Assuming cylindrical pores, the surface area of the pores larger than 7 Å in radius is calculated. V_A is estimated by multiplying the adsorption thickness by both the surface area and density of the adsorbed nitrogen, 0.808 g/ml (*7*). V_c is obtained by subtracting V_A from V. Finally micropore volume is obtained by dividing V_c by the nitrogen density 0.808 g/ml. The micropore thus estimated is presented in Table 4. The micropore volume of the impregnated adsorbent is 0.21 ml/g (based on impregnated

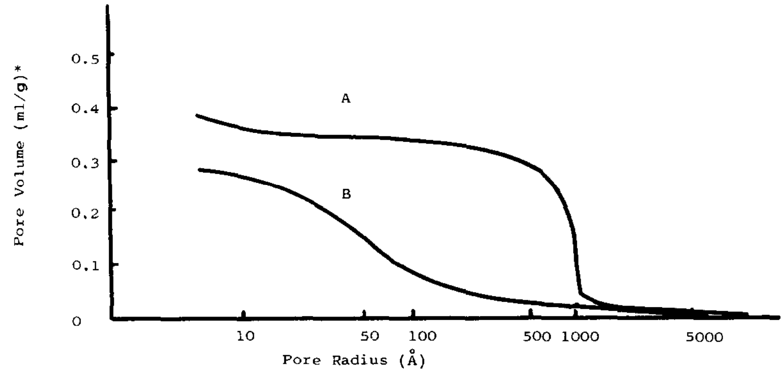

FIG. 1. Reduction of pore volume with Hydral (relative to impregnated adsorbent): (A) unimpregnated; (B) impregnated with Hydral (12 wt% as Al_2O_3).

TABLE 4

Pores of the Adsorbent Impregnated with Hydral

	Bentonite-bonded Y-Zeolite	
	Prior to impregnation	Impregnation[a]
Pore volume ml/g[b]		
100–75,000 Å radius	0.35	0.1
7–100 Å	0.04	0.17
7 Å >	0.24	0.21
Benzene adsorption[b] g/100 g	14.0	12.3

[a] 12 wt% as Al_2O_3.

[b] Relative to impregnated adsorbent.

pellet), which corresponds to 88% of the pore volume of the unimpregnated pellet. The weight increase during the impregnation being 12%, the present figures show that the micropore volume has not changed during the impregnation. This is also supported by the fact that benzene adsorbtion by the impregnated adsorbent is 88% of that of unimpregnated adsorbent.

In summary, a new method is presented which enables one to reduce effectively the macropore volume of a Y-Zeolite adsorbent pellet, while keeping intact the micropores where active sites are located.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to Toray Industries, Inc., for permission to publish this paper, and M. Kihara for his skillfull assistance in experiments.

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Received June 23, 1980; revised October 2, 1980