Sorption of Water and Polar-Nonpolar Organic Vapors on Microporous Chromia*

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High surface area, narrow particle size distribution chromia was investigated for its microporosity. Adsorption studies with argon, water vapor, methanol, isopropanol, butane, isobutane, neopentane, and heptane indicated alternative approaches to the determination of micropore volume.

High surface area chromia is usually amorphous and microporous. Chromia is known to catalyze a variety of chemical reactions of industrial importance. An excellent summary of catalytic and chemisorptive properties of chromia has been given by Burwell et al.[1].

Chemisorptive properties of a catalyst are of vital importance in heterogeneous catalysis since they provide information regarding the catalytically active sites on the catalyst surface as well as the reaction mechanisms. On the other hand, physical and structural properties such as surface area, pore structure and size distribution also play a dominant role in their proper utilization. For example, the recent works of Rollmann and Walsh[2] and Chen et al.[3] show that the latter properties of zeolitic catalysts not only determine the selectivity in hydrocarbon conversion but also affect coking tendencies and aging rates. Their work also shows that shape selective catalysis is being exploited in a number of reactions of industrial importance. Therefore, any progress made in evaluation of physical and structural properties of catalysts especially with regard to pore size and shape would be valuable and welcome.

Previous studies of Zettlemoyer and his co-workers[4-6] with chromia derived from the dehydration of chromium(III) hydrous oxide particles of narrow size distribution, prepared by the sulfate process of Matijević[7-9], showed that the relative uniform morphology of the original hydrous oxide played a significant role in producing uniform micro and mesopores. It was also shown that chromia samples became highly microporous upon heat treatment at 450 °C under vacuum. Siddiq and Zettlemoyer[6] also showed that this chromia attains the

highest degree of microporosity (highest equivalent surface or pore volume) if activation is carried out at the same temperature but in an inert environment such as that provided by argon or nitrogen.

In this study we have exploited the size and configuration of water, and of a number of polar and nonpolar organic vapors, to probe the structural characteristics of the microporous chromia. The vapor sorption isotherms of argon, water, methanol, isopropanol, butane, isobutane, neopentane, and heptane were measured and analyzed by the α_s-plots method of Sing[10,11], MP method of Brunauer and his workers[12-13], as well as by the B-Point method and BET approach. The surface properties of the chromia, intercomparison of various methods of microporosity evaluation, and uniformity of the micropores were investigated.

EXPERIMENTAL

1. *Sample Preparation.* Chromia samples of narrow particle size distribution were prepared on a multigram scale by employing the aforementioned sulfate process of Matijević[8,9]. The detailed preparation procedure and results of preliminary characterization of various chromia samples with regard to composition, particle size distribution, and impurity level, etc., can be found in reference 4. Sample B3 of Series B[4] was used throughout this investigation; this sample had 0.5% sulfur (as sulfate) as the chief impurity and had a mean particle size of 0.41 μm.

2. *Activation Conditions.* Hydrous oxide samples were activated by evacuation under a vacuum of $2—5 \times 10^{-6}$ Torr for 60 hours. Microporous chromia samples were obtained by heat treatment of this hydrous oxide sample according to procedure C of reference 6: the above room temperature activation of hydrous oxide was followed by heat treatment at 450 °C under 100 Torr argon for 16 hours.

3. *Adsorption Isotherms.* Adsorption isotherms of argon at liquid nitrogen temperature and of water, methanol, and isopropanol at 25 °C were measured by volumetric and gravimetric techniques (both apparatus' employed greased stopcocks), respectively. The details on the foregoing can be found in reference 4. Studies with hydrocarbons (butane, isobutane, neopentane, and heptane), however required a »grease-free« adsorption apparatus. This apparatus was constructed of a quartz spring balance (Worden Quartz Company, Houston, Texas) of 100 mg (1000 mm extension) total loading capacity, high vacuum glass-metal valves having Viton O-rings as the vacuum seal (Mass-Vac Inc., Billerica, Massachussets), and a quartz hangdown tube which had a Teflon and glass threaded vacuum fitting (Ace Glass Inc., Vineland New Jersey). Pumping, pressure and vacuum measuring equipments were of same design as described earlier[4]. All hydrocarbon isotherms were measured gravimetrically at 0 °C.

RESULTS AND DISCUSSION

A. *Sorption of Water and Alcohols.* — The smaller molecular size and strong polar character of water can be expected to yield greater penetrating power than argon. Hovewer, one of the major disadvantages in the use of water, as can be expected, is its specificity for chromia[1]. Nonetheless, water was used to establish the extent of availability of internal surface due to micropores. The same reasoning can be advanced for the use of methanol and isopropanol.

The sorption isotherms of water, methanol, and isopropanol were Type I, confirming the pronounced microporous character of 450 °C argon activated chromia. The results derived from the isotherms by BET and B-point methods are summarized in Table I; irreversible adsorbed amounts of each vapor are also tabulated. In addition, similar results derived from adsorption of argon on similarly activated chromia are also given therein for comparison purposes. The irreversibility and mechanisms of adsorption of these vapors will be a

Sorption Characteristics of Water, Methanol, Isopropanol and Argon on Microporous Chromia (B3) Activated at 450 °C in 100 Torr Argon

Adsorbate	»Monolayer« Capacity mg/g		C_{BET}	Surface Areas* m²/g		Irreversible Adsorbed Amount	
	BET	B-point		BET	B-point	mg/g	molecules**/nm
Water	60.2	72.0	276	211.3	252.7	30.1	4
Methanol	45.1	55.0	221	152.5	186.1	23.9	1.8
Isopropanol	46.5	50.5	215	163.2	177.3	29.6	1.2
Argon	89.0	98.8	223	225.3	249.9	0	0

Sorption isotherms of water, methanol, and isopropanol were measured at 25 °C, and argon isotherm was measured at liquid nitrogen temperature.

* Based on cross-sectional areas of 1.06, 21.0, 3.5, and 1.68 nm² per molecule for water, methanol, isopropanol, and argon, respectively.

** Calculated on the basis of B-point surface area of argon.

subject of another paper; here we will be mainly concerned with their pore filling characteristics.

Referring to Table I, the equality of the water and argon surface areas is noteworthy and interesting. Three other results are evident. First, activation in argon instead of vacuum (of the order of 5×10^{-6} Torr) prevented the extensive oxidation of chromia which otherwise yields a partially crystallized chromia of low surface area as reported by Siddiq and Zettlemoyer[6]. Second, the probability of the presence of smaller micropores than available to argon is very minimal. This is an important result, because it also suggests the absence of any activated entry into the micropores[14], due to differences in the temperature of adsorption measurements of water (25 °C) and argon (— 196 °C). The activated entry effects give rise to increase in adsorption with increase in temperature of adsorption measurement and are due to the presence of narrow constrictions in otherwise larger pores (pores of variable cross--section). Such effects are observed in the use of many molecular sieve active carbons and coals. For example, for a sample of coal (80% carbon content), Gregg and Pope[15] obtained the following values of apparent surface areas by adsorption of N_2 (— 196 °C), O_2 (— 183 °C) and butane (0 °C); 107, 147 and 215 m²/g, respectively. Finally, the specificity in adsorption does not seem to influence the adsorption in the micropores. However, once chromia is hydroxylated its water uptake does decrease[16]; evidence can be obtained by measuring a second adsorption isotherm after prolonged outgassing of the sample used for the measurement of the first isotherm.

On the other hand, referring to results obtained with methanol and iso-propanol, Table I, a comparison of surface areas obtained with argon and water may suggest some molecular screening. On the average, the alcohols gave about 20% less apparent surface area which can be expected on the basis of their comparatively larger molecular sizes, 0.41 and 0.5 nm diameter, respectively. However, a word of caution must be expressed. A larger molecular probe will be more influenced by the curvature of very narrow pores, and hence, its effective cross-sectional area can be greater than, for example, that on the surface of larger pores or on a plane surface.

With regard to evaluation of microporosity, unfortunately the specifity in adsorption of the vapors employed does not permit the isotherms to be used as standard isotherms; so comparison plot methods (i. e., α_s, t, n-plot, etc.) cannot be used. However, since the B-point monolayer capacity includes the contributions due to micropores and the external surface, we can calculate the micropore volumes by subtracting the adsorbed amounts due to external surface. An analysis of the α_s-plot of argon gave the external area of the microporous chromia to be 24.3 m²/g (see below). If we assume the constancy of external area, then the monolayer adsorption of these vapors on the external surface would be: 6.92, 7.18, and 6.92 mg/g, for water, methanol, and iso-propanol, respectively. The subtraction of the foregoing adsorbed amounts from the B-point monolayer capacity given in Table I and the division of the balance by the respective liquid densities of the respective vapors yield the following micropore volumes; 65.2, 60.5, and 55.5×10^{-3} cc/g, for water, methanol and isopropanol, respectively. The micropore volume determined from the α_s-plot of argon is found to be 61.9×10^{-3} cc/g (see below), which is not very far from the estimated values for water and the alcohols. The equality of the micropore volumes indicates very little if any molecular screening by the pores. However, confirmation requires the examination of results obtained with hydrocarbons of varying sizes and configurations; these are discussed below. The appropriate physical properties, especially molecular configuration and critical sizes[17-19] of these probes have been well documented and will not be presented here.

B. *Sorption of Straight and Branched Hydrocarbons.* — First, it is appropriate to consider the adsorption isotherms of hydrocarbons on hydrous chromia, because these isotherms will be used as »standard isotherms« for the evalutation of microporosity of microporous chromia by α_s-method[14]. These adsorption isotherms are shown in Figure 1. Note the similarities in adsorption of the branched versus straight chain hydrocarbons in the monolayer region. The results derived from the BET analysis are presented in Table II. It must be pointed out that the isotherms shown in Figure 1. were reproducible and the isotherms shown represent the best of three determinations.

TABLE II

Sorption Characteristics of Hydrocarbons on Hydrous Chromia B3[1]

Adsorbate	BET		Surface Area, Based on Liquid Density (L. D.) m²/g	Area per Molecule		
	$V_m \times 10^3$ cc²(liq)/g	C		L. D.	ADS[3]	ADS[4]
Argon	3.86	52	11.8 (14.4)[3]	0.138	0.168	—
Butane	4.51	22	9.4	0.323	0.497	0.48
Isobutane	3.47	19	7.0	0.323	0.662	0.500
Neopentane	4.65	22	8.6	0.382	0.641	0.570
Heptane	7.17	22	12.7	0.418	0.474	0.582

[1] Hydrous chromia, activated at room temperature for 48—72 hours. Argon adsorption at liq. N_2 temperatures; organics at 0 °C.

[2] Monolayer capacities are expressed as liquid volumes: Liquid densities at temperature of adsorption, 1.4652, 0.6181, 0.6020, 0.5784, 0.7006 g/cm³, for argon, butane, isobutane, neopentane, and heptane, respectively.

[3] Based on 0.168 nm² per argon molecule, see Figure 1.

[4] Data from literature (McClellan & Harnsberger[25]) for adsorption on aluminas.
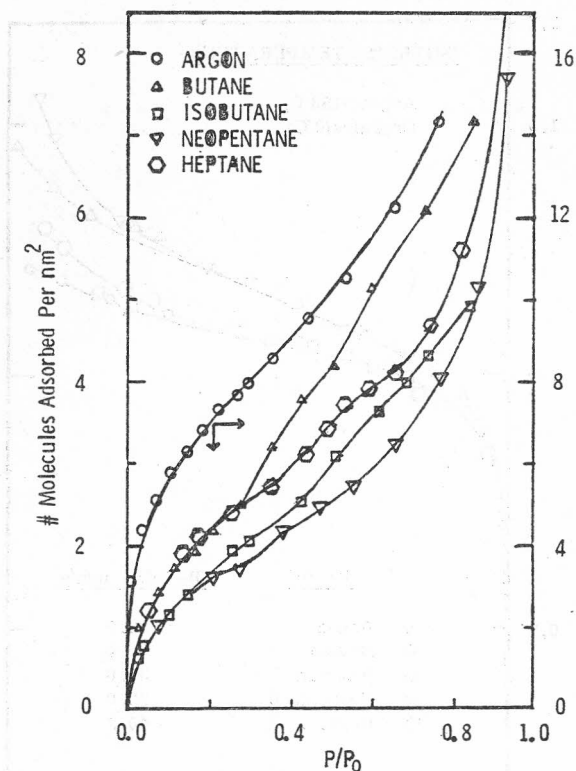
Figure 1. Adsorption Isotherms of Argon (—196 ⁰C) and Four Selected Hydrocarbons (0 ⁰C), for Hydrous Chromia B₃ (Activated in Vacuum at Room Temperature for 60 h.). The Isotherms Are Normalized With Argon Surface Area of the Hydrous Oxide, 14.4 m²/g (cross-sectional area of argon: 0.168 nm²/molecule).

The adsorption isotherms of argon and of the four hydrocarbons measured with microporous chromia are shown in Figure 2. The isotherms though predominantly Type I, also have a pronounced Type II character. Apparently, the activation of hydrous chromia in argon, contrary to that in vacuum[4], gives rise to a small amount of mesoporosity. Furthermore, while the adsorption isotherms of argon were completely reversible, the hydrocarbons gave wider (neopentane and heptane) and narrower (butane and isobutane) hysteresis loops upon desorption. Though desorption branches are not shown in the figure for clarity reasons, it is apparent that neopentane and heptane comparatively show more sensitivity in the detection of mesoporosity. This result can be explained by the Kelvin Equation; the $\gamma \, V_m/RT$ factors for argon, butane, isobutane, neopentane, and heptane are found to be 0.65, 0.61, 0.5⁵ 0.78 and 1.33 nm, respectively. Therefore, neopentane and heptane detected (due to greater depression of vapor pressure for a given pore size) the mesoporosity better than other probes. However, it will be shown later that the mesoporosity contributes very little, if any, to the estimated micropore volumes.
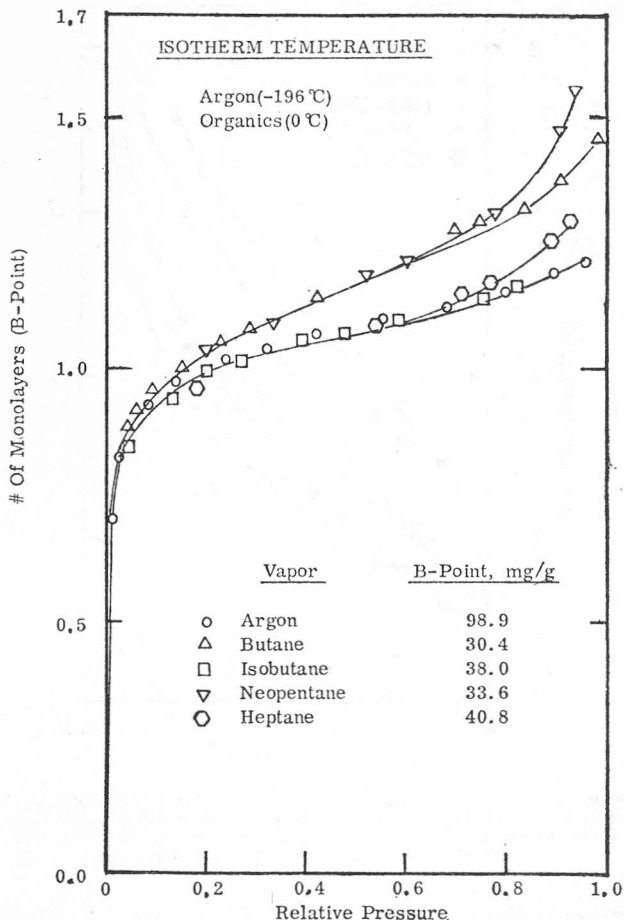
Figure 2. Sorption Isotherms of Argon and Four Selected Hydrocarbons on Microporous B₃ Obtained by Activation of Hydrous Chromia at 450 ⁰C in 100 Torr Argon.

The α_s-plots of the isotherms of Figure 2., using isotherms of hydrous chromia given in Figure 1 as the standard, are shown in Figure 3. As can be seen, all the α_s-plots show the expected downward deviation in the low relative pressure region (α_s, < 1.0) due to microporosity. On the other hand, with the exception of neopentane and heptane, all other probes give a reasonable straight line in the high relative pressure region. In the case of neopentane and heptane, the region of α_s-plot which showed most linearity in the high relative pressure region is selected for the evaluation of microporosity.

Another noteworthy feature of the α_s-plots of the isotherms of Figure 3., is that, contrary to the argon case, the low relative pressure points of the α_s-plots of all of the hydrocarbons are shifted towards the ordinate or smaller values of α_s. This shift can be attributed to the rather sparse packing or localized adsorption (on hydrous oxide). Hence, these was less uptake of
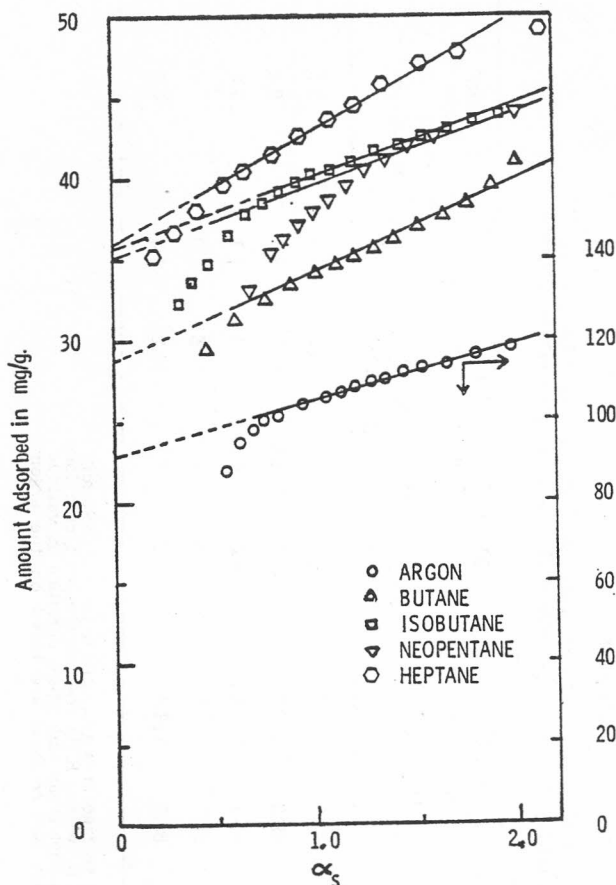
Figure 3. α_s-Plots of the Sorption Isotherms Shown in Figure 2. Isotherms Shown in Figure 1. are used as Standard Isotherms.

hydrocarbons in the monolayer region, which in turn yielded smaller values of α_s. Since this shift of low relative pressure region cannot influence the shape of an α_s-plot in the high relative pressure region, the estimated slopes and intercepts remain unaffected. It must be pointed out that the intercepts of α_s-plots yield micropore volumes whereas the slopes yield external surface areas. The results of the α_s-plot analysis along with the results derived from BET and B-point analysis of respective isotherms (Figure 2.) are summarized in Table III. A comparison of the external area obtained with argon (24.3 m²/g) with the total argon area of the hydrous oxide (14.4 m²/g, Table II) does indeed suggest that the microporous chromia also has some mesoporosity.

Before we discuss micro and meso porosity, it is desirable to comment on the consistency of various results presented in Table III. A summation of V_{mic} and V_{ext} shows that this sum agrees very well with the B-point monolayer capacity; a maximum divergence of ca 4% is found for all but the neopentane. For neopentane, the forementioned sum is ca 16% larger than the B-point

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TABLE III

Sorption Characteristics of Various Hydrocarbons on Microporous Chromia B3 (Activated in Argon); B-Point, BET, and αs-Method Analysis of Adsorption Results

Adsorbate	C_{BET}	»Monolayer« capacity, $V_m \times 10^3$ cc/g (1) Equivalent and Surface Area, m²/g (2)				Microporosity by α_s-Method			Molecules per nm² on External Surface	
		BET		B-point		$V_{mic} \times 10^3$ cc/g	$V_{ext}^* \times 10^3$ cc/g	Σ_{ext} m²/g	α_s	B-point**
		1	2	1	2					
Argon	224	60.5	225.3	67.5	250.4	61.9	6.3	24.3	6.0	5.3
Butane	183	44.1	140.4	49.2	156.7	46.3	5.0	15.9	1.4	0.8
Isobutane	467	47.4	196.4	63.1	264.9	58.0	4.2	17.4	1.1	1.6
Neopentane	183	47.1	145.5	58.1	180.2	62.6	4.7	14.6	1.0	—
Heptane	280	51.0	102.3	58.2	116.4	51.2	7.1	14.2	1.3	0.9

* V_{ext} is the monolayer equivalent of the external surface area (Σ_{ext} given in next column).
** B-point external area $\Sigma_B - \Sigma_{m(c)}$ or $(V_B - V_{m(c)}) \times K$, where K is the conversion factor for surface area. See Tables II and III for cross-sectional areas and liquid densities of various adsorbates. Adsorption concentration given in last two columns are based on the argon external area (24.3 m²/g).

monolayer capacity. Nevertheless, the results obtained here strongly suggest that the B-point monolayer capacity, deduced from the Type I isotherms of a microporous adsorbent, gives a reasonable estimate of the micropore volume plus the monolayer equivalent of the external surface. In the case of highly microporous adsorbents with negligible external surface, e. g., zeolites, certain active carbons or silica gels, etc., the B-point monolayer capacity may indeed represent the micropore volume. Therefore, it appears that if the external surface area is known, either from the geometry and size distribution of the particles as in the case of the chromia under study, or from the α_s-plot analysis of an isotherm of a single and commonly used adsorbate, e. g., Ar or N_2, the micropore volume available to other adsorbates can be easily deduced from the B-point even without reference to a comparison plot of these adsorbates. The comparison plots become important only when an adsorbent contains small degrees of porosity or mixed porosity. However, the versatility of comparison plots in the detection of porosity in general can not be contested.

In view of the limited linearity associated with some of the α_s-plots of hydrocarbons as well as the partial Type II character of the isotherms themselves, another approach was utilized to test the consistency of the results presented in Table III. The multilayer portion of the isotherms shown in Figure 2. were analyzed for mesoporosity by the application of Brunauer's corrected modelless method[20]. The t-values for the correction of adsorption on pore walls were obtained from the standard isotherms used for the α_s-plot (Figure 1.), and area and volume of mesopores were counted up to a cylinderical pore diameter of 2.0 nm. The results are summarized in Table IV. The micropore volumes were estimated by subtraction of mesopore volumes (column 2) and monolayer adsorption on the non-porous (hydrous oxide) surface (column 3) from the total sorption capacity, V_s, which was taken equal to adsorption at a relative pressure of 0.98. Similarly, the total external surface area was obtained from the summation of the mesopore area plus non-porous area of the hydrous

TABLE IV

*Micropore Volumes and External Surface Areas Estimated From the Analysis of Multilayer Portion of the Adsorption Isotherms of Microporous Chromia B3 (Figure 2.) For Mesoporosity**

Adsorbate	Volume adsorbed $\times 10^3$, cc/g				Surface Area,m²/g	
	V_s $p/p_o = 0.98$	V_{meso}	V_{np}	V_{mic}	Mesopores	Total External
	1	2	3	4	5	6
Argon	82.4	15.3	3.9	63.2	6.3	20.7
Butane	71.3	20.3	4.5	46.5	8.6	23.0
Isobutane	78.2	13.2	3.5	61.5	6.4	20.8
Neopentane	98.7	39.2	4.7	54.8	12.0	26.4
Heptane	80.9	23.3	7.2	50.4	4.6	19.0

* Mesaporosity is analysed by the application of Brunauer's corrected modelless method; mesopore volume and area are counted up to a cylindrical pore diameter of 2.0 nm.
V_{np} of column 3 is obtained from Table II, and total external surface area (column 6) is calculated by adding the area of hydrous oxide (14.4 m²/g) to the area which can be attributed due to mesopores (column 5). V_{np} represents the monolayer adsorption on non-porous surface.

oxide. The reader may question the foregoing summation, but it must be emphasized that the mesopore area estimated from Brunauer's method equals the total surface area of a mesoporous adsorbent only when the nonporous or geometrical surface area is negligible.

A comparison of micropore volumes given in column 4 of Table IV with the micropore volumes given in Table III shows that the above procedure and α_s-plot analysis yielded almost the same results. The foregoing has to be true because the α_s-plot only separates the adsorption contributions due to micropores and external surface. However, the value of the above method, especially when slight mesoporosity is also present, need not be emphasized; the method becomes less subjective of the peculiarity of the α_s-plot shapes.

Referring to Tables III and IV, it can be seen that, if taken as a group, the straight chain hydrocarbons, butane and heptane, yield smaller micropore values (ca 20%) than the branched hydrocarbons, isobutane and neopentane. Apparently, the nearly spherical configuration and larger effective sizes (larger than the widths of the straight chain hydrocarbons) of the branched molecules were more responsible to the effect of pore narrowing. That is, these branched molecules experience greater interaction energy and hence show enhanced micropore filling. It is also interesting to note that the enhanced micropore filling of branched molecules even compensated for their large sizes as they yield micropore volumes which can be compared with the volume given by smaller probes like argon, water and methanol.

Furthermore, it can be concluded from the above that the pores can not be smaller than the molecular size of the largest probes employed (neopentane 0.59 nm, heptane 0.62 nm; both sizes based on liquid density). It should be noted that straight hydrocarbons, butane and heptane filled the micropores by virtue of their smaller width (0.46 nm) even though their linear sizes differ by a factor of 2, 0.73 vs 1.38 nm, respectively.

Uniformity of Micropores. — The fact that eight different molecular probes give micropore volumes within 20% of each ather suggests that the pores must be larger than the critical sizes of the molecular probes employed. In addition, if the differences in micropore volumes given by each probe can be attributed to their sizes, configuration and packing, the equality of micropore volumes also indicates the uniformity of pore geometry as well as their sizes. If the pores would have non-uniform cross-sections, like cylinders of variable cross-section or ink-bottle shape or cone shape, we would observe significant molecular screening. Moreover, since the results presented here are obtained by activating new samples of chromia for each set of adsorption measurements, at least two determinations with most of the probes, the reproducibility of the pore structure was also evident. Such excellent reproducibility was never demonstrated in previous studies with chromia produced by other methods.

Moreover, if the micropores are indeed larger than the critical sizes of the above molecular probes, then the distribution in pore sizes might still be expected. Taking 2 nm as the upper limit of micropore size[14] and in view of above results, pore sizes must fall between 0.6 and 2.0 nm. Now, the calculation of distribution of pore sizes within these limits is not a straight forward easy task. The difficulty lies in the fact that, especially in the case of adsorption of vapors (as studied here), the surface coverage and the volume filling become indistinguishable. However, in the case of adsorption of gases at very low

pressures, Henry's low region, the pore filling effect becomes negligible, and the method of Everett and Powl[21] can be used to estimate the average pore sizes.

On the other hand, in the case of vapor adsorption, two methods of micropore size distribution analysis are available. One, the method of Spitzer, Biba and Kadlec[22], say method I, which is based on the theory of volume filling of Dubininin[23] and the DeBoer-Custers[24] relation giving the potential of the adsorption forces as a function of adsorbent-adsorbate interaction distance in a cylinderical pore. Second, the aforementioned MP method of Brunauer and his co-workers[12-13], Method II, is based on the analysis of a V_1-t plot. Method I requires the determination of the constants of the potential energy function, and hence has been applied only to extensively studied activated carbons for which detailed calculations exist.

Therefore, we have utilized the MP method to calculate the distribution in sizes of micropores; the details of the calculation procedure can be found in the cited reference.

The implementation of the MP method with an argon isotherm of micro-porous chromia is illustrated in Figure 4.; the results derived therefrom are summarized in Table V. A standard pore volume distribution curve can be obtained by differentiating the r_h (hydraulic radius; volume to surface ratio) versus V_1 plot. As can be seen in Table V, there is no significant distribution of pore sizes in this case; about 90% of the micropore volume can be attributed to pores with a hydraulic radius of ~ 0.3 nm.

In addition, with regard to pore size and geometry, the r_h value of ~ 0.3 nm would correspond to a pore width of ~ 0.6 nm if the pores are considered

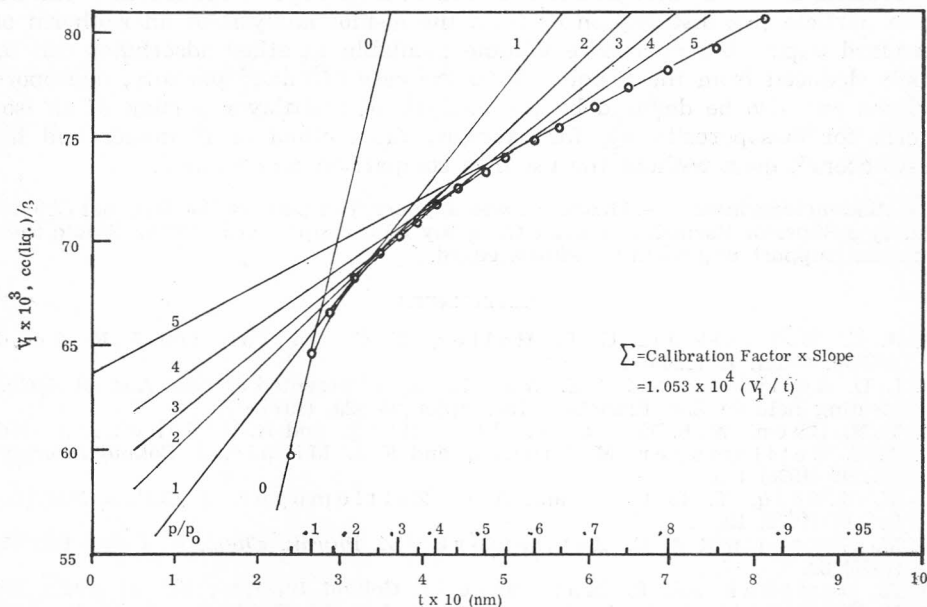Figure 4. V_1 Versus t Plot of An Argon Isotherm of Microporous Chromia B_3 (Figure 2.); Micropore Volume Distribution Analysis of MP Method[12,13].

TABLE V

The Volume Distribution of Micropores of Chromia B3 Calculated According to MP Method (Figure 4)

Pore Group	S_{i+1} m²/g	$S_i - S_{i+1}$ m²/g	Mean r_h nm	V_i/cm³ g⁻¹
1	45.3	200.9	0.30	0.0603
2	40.3	5.0	0.35	0.0017
3	33.8	6.5	0.40	0.0026
4	28.3	5.5	0.45	0.0025
Total		217.9		0.0671

parallel plates. In view of the results obtained with hydrocarbons, this width is too small. Therefore, the micropores of chromia are likely to be cylinderical with a diameter of about 1.2 nm ($4 \times r_h$). Similar computations with the results obtained with other molecular probes, Tables I and III gave an average micropore diameter of about 1.5 nm, a value close to the above estimate.

In summary, we conclude that the micropores in the chromia produced by 450 °C activation in 100 torr argon posseses quite a narrow distribution of pore sizes in this 1.2—1.5 range. Produced from the Matijević hydrous oxide of narrow particle size distribution, the micropores appear to be cylinderical and without narrow recesses or ink-bottle throttles.

On the methods of microporosity evaluation by vapor adsorption methods, we can say that 1) the use of molecular probes of various sizes and configuration is the most direct method of size and in favorable cases geometry evaluation, 2) if the external surface area of a micropores adsorbent is known from particle size distribution or from the α_s-plot analysis of an isotherm of standard vapor, the micropore volume available to other adsorbates can be easily deduced from the B-point, 3) in the case of mixed porosity, micropore volume can also be deduced by the analysis of multilayer portion of an isotherm for mesoporosity by, for example, the method of Brunauer and his co-workers[20], even without the use of a comparison plot method.

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SAŽETAK

Sorpcija vodene pare i polarnih ili nepolarnih organskih para na mikroporoznom Cr_2O_3

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Proučavana je adsorpcija vode, alkohola i nižih parafinskih ugljikovodika na mikroporoznim uzorcima Cr_2O_3. Pokazano je da su molekule različite veličine osobito prikladne kao direktne sonde za određivanje geometrije i veličine pora. Iz podataka o vanjskoj specifičnoj površini uzorka mikroporoznog adsorbensa koja je izračunana iz analize veličina čestica, ili pak iz Sing-ovih α_s-krivulja za standardne adsorbate, može se jednostavnim mjerenjem B-točke na BET-izotermi izračunati volumen mikropora za proizvoljni adsorbat. Za materijal heterogene poroznosti volumen mikropora može se izračunati iz dijela izoterme koji odgovara višeslojnoj adsorpciji po metodi Brunauera i suradnika bez primjene usporedbene izoterme.