4. Jakovlev, V. S., *Ukrain. Khim. Zh.* **30**, 289 (1964).
5. Mikhailova, E. A., *Acta Physicochim. URSS* **10**, 653 (1939).
6. Johnson, C. L., *Anal. Chem.* **24**, 1572 (1952).
7. Krause, A., *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* **8**, 331 (1960).

M. Markvart
Vl. Pour

Institute of Inorganic Chemistry
Czechoslovak Academy of Sciences
Prague, Czechoslovakia
Received September 28, 1966

Application of the Halsey Form Correlation to Nitrogen Adsorption on Metal and Supported Metal Substrates

It has been shown (*1*) that porous structure can significantly affect the apparent relationship between adsorbed multilayer thickness and relative pressure in the nitrogen isotherm technique for determining volume–area distributions. Studies based on adsorption–desorption isotherms for nitrogen on a number of alumina samples with widely differing pore shapes, sizes, and specific surface areas (*2*) have demonstrated that structural effects on multilayer adsorption are very well correlated by an expression of the form:

$$\ln (N) = (1/n) \ln [\ln (X_M)/\ln (X)] + \ln (a') \qquad (1)$$

in which N is the number of adsorbed monolayers, X the relative pressure, X_M the relative pressure at monolayer coverage, and n and a' constants which can be related to properties characteristic of a given porous structure. Equation (1) derives from a form originally proposed by Halsey (*3*).

Since there is obvious application to a large range of supported catalysts and materials other than alumina, it is the purpose of this note to examine application of the proposed correlation to such materials. In Table 1 are listed properties of four representative samples selected for the wide range in surface area, porosity, and composition involved. Sample I is a high surface area, gelatinous boehmite reported by de Boer and Lippens under the designation of A-120. Sample II is an alumina-supported Co-Mo catalyst of moderate surface area; the composition of this material (approximately 10% Mo, 5% Co) is such that the adsorbent surface is only partially covered by these metals. Sample III is an alumina-supported chromium catalyst of low surface area, 15% by weight Cr. In this sample proportionately more of the surface is covered by the metal than in II; however, complete coverage is unlikely since the catalyst is composed of a mechanical mixture of Cr_2O_3 and gamma alumina. Sample IV is a pure copper catalyst of low surface area. The pore structures of these samples also differ considerably, as indicated by the $\bar{r}, S_{BET}$ data of Table 1, and by the shapes of the nitrogen isotherms reported or measured for the degassed materials in a flow system at liquid nitrogen temperature (Samples II–IV), as shown in Fig. 1.

These data establish the diversity of structure and surface composition of the test materials. The adsorbed layer thickness correlation is evaluated on the basis of the consistency of results of volume–area distribution computations and comparison with those obtained employing alternative (*4, 5, 6*) correlations. A major part of this comparison and consistency test follows from the observation that for extremes of porous structure types the surface area computed from nitrogen *desorption* isotherm data cannot be smaller than S_{BET}, but may be larger. An additional important con-

TABLE 1
PROPERTIES OF SAMPLES AND COMPARISON OF DISTRIBUTION COMPUTATIONS

Multilayer correlation, ref.	(1)	(4)	(5)	(6)
Sample I, boehmite (A-120); S_{BET} = 609 m²/g, $\bar{r}$ = 65 Å				
Area (m²/g)	719	745	701	679
r for total desorption (Å)[a]	18.6	21.7	24.8	9.5
Volume assigned (% total)[b]	0	0	0	3
Sample II, Co–Mo on Al_2O_3; S_{BET} = 217 m²/g, $\bar{r}$ = 9.3 Å				
Area (m²/g)	240	225	198	243
r for total desorption (Å)	9.5	9.5	14.9	9.5
Volume assigned (% total)	12	7	0	24
Sample III, Cr_2O_3–Al_2O_3; S_{BET} = 45 m²/g, $\bar{r}$ = 64.5 Å				
Area (m²/g)	72	62	57	77
r for total desorption (Å)	9.5	12.3	20.8	9.5
Volume assigned (% total)	4	0	0	13
Sample IV, Cu; S_{BET} = 22 m²/g, $\bar{r}$ = 18.4 Å				
Area (m²/g)	20	17	15	25
r for total desorption (Å)	9.5	9.5	12.5	9.5
Volume assigned (% total)	20	10	0	32

[a] All volume in capillaries of $r < 12$ Å assigned to capillaries of average $r = 9.5$ Å.
[b] Volume, according to distribution computation, in pores of $r < 12$ Å.

sideration is minimization of the volume assignment for small capillaries, i.e., the difference between calculated cumulative pore volume and the actual volume of material desorbed. Computations based on some correlations result in unreasonably large volumes of adsorbate implied to be contained in very small ($r < 10$ Å) capillaries where, indeed, the validity of the capillary condensation theory involved in the calculation is doubtful at best. It should be noted that for structures which contain a large proportion of total volume of voids in the small capillary region this consistency test cannot be used due to the large uncertainty in cumulative area corresponding to the required volume assignment. The isotherm data of Fig. 1 for the four test materials indicate that the majority of volume is contained in larger pores (higher relative pressure), so this restriction is not violated.

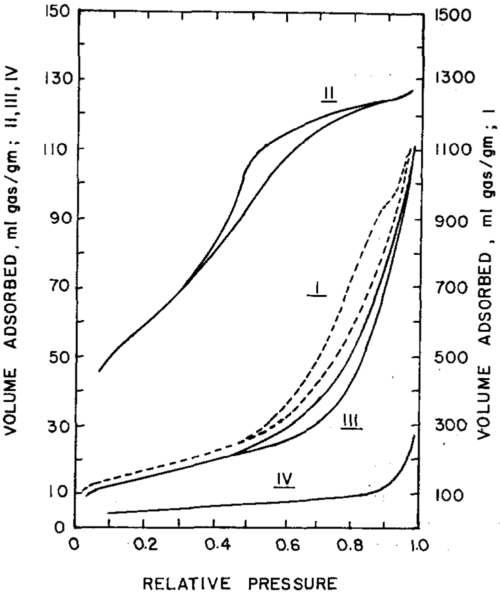

FIG. 1. Nitrogen isotherms for test samples.

A comparison of the results of volume–area distribution calculations using the Barrett-Joyner-Halenda method (7) with four different multilayer thickness correlations for nitrogen is given in Table 1 for the four samples. The correlations of Shull and Wheeler result in violation of the surface area criterion for some of the structures measured (II and IV, and IV, respectively), similar to previous experiences with all-alumina samples (*1*). The two correlations (*1, 6*) based on the form of Eq. (1) yield the same general results here, although rather large volume assignments are required for samples II and IV, particularly for the Mingle and Smith correlation. It has also been shown that this correlation is not consistent for certain types of porous structures (*1*).

The present results, thus, affirm the applicability of the correlation reported by Butt to various types of porous structures and demonstrate that this correlation is valid for adsorption on substrates other than the aluminas employed for the original study.

The assistance of Mr. D. D. Whiteley in the experimentation is gratefully acknowledged.

REFERENCES

1. BUTT, J. B., *J. Catalysis* **4**, 685 (1965).
2. DEBOER, J. H., AND LIPPENS, B. C., *J. Catalysis* **3**, 38 (1964).
3. HALSEY, G., *J. Chem. Phys.* **16**, 931 (1948).
4. SHULL, C. G., *J. Am. Chem. Soc.* **70**, 1405 (1948).
5. WHEELER, A., *Catalysis* **2**, 116. (Reinhold, New York, 1955.)
6. MINGLE, J. O., AND SMITH, J. M., *Chem. Eng. Sci.* **16**, 31 (1960).
7. BARRETT, E. P., JOYNER, L. G., AND HALENDA, P. P., *J. Am. Chem. Soc.* **73**, 373 (1951).

JOHN B. BUTT

Department of Engineering and Applied Science
Yale University, New Haven, Connecticut
Received October 3, 1966;
revised January 3, 1967

Effect of Solid-State Properties on Catalytic Selectivity

Decomposition of Isopropyl Iodide on a Cuprous Iodide Catalyst*

We wish to report briefly some evidence that the selectivity of a catalyst can be controlled by suitable adjustment of its solid-state properties. We have investigated the decomposition of isopropyl iodide on a cuprous iodide catalyst because it appeared feasible to modify the electronic properties of the catalyst by electrochemical means. By applying a voltage between an anode embedded close under the surface and a cathode in the interior of the solid catalyst, we changed the stoichiometric composition (Cu/I ratio), and thereby the electronic properties of the CuI, and observed the resulting changes in the distribution of reaction products, i.e., in the selectivity of the catalyst. A model mechanism for the catalytic reaction has been developed to explain the role of solid-state properties.

EXPERIMENTAL

The solid catalyst consisted of cuprous iodide made from hydrogen-reduced 99.99% copper and resublimed iodine according to Wagner's procedure (*1*). A ¾-inch diameter pellet was made by compression (vacuum, 4400 psi) around a central copper cathode and a cage-shaped platinum anode embedded just under the pellet surface; its geometric surface area was 11 cm^2. The reaction was carried out in a continuous stream of helium carrier gas. The partial pressure of the reactant isopropyl iodide (iso-PrI) was controlled by bubbling the carrier gas through a reservoir of iso-PrI kept at constant temperature. At intervals, samples of the gaseous reactor effluent were withdrawn, and analyzed for the decomposition products, C_3H_6 and

---

* This work was done in Stanford Research Institute's Solid State Catalysis Laboratory and supported in part by a group of industrial companies.