

Zeolites Surface Area Calculation from Nitrogen Adsorption Data

INTRODUCTION

The BET equation of two parameters (I) is used as a routine method for the calculation of the specific areas of solids which are not porous or contain transitional pores or macropores. The interpretation of gas adsorption in microporous solids is very complex and there is not a general agreement on how to estimate the specific areas of these solids from the experimental adsorption isotherms. In the case of zeolites, crystalline aluminosilicates with microporous structure, the BET equation of two parameters is sometimes used (2, 3), while other times the Langmuir equation is employed (2, 4). The hypothesis in which these two equations are based does not totally represent the situation present in these solids. Brunauer (5) states that in many cases the application of the BET equation to the adsorption of nitrogen allows the measurement of the areas of microporous solids as well as that of solids with macropores, while others, like Gregg and Sing (6), doubt the validity of the BET equation in microporous solids.

In this work, a continuation of previous work (7), the BET equation of three parameters is used, in the way given by Joyner *et al.* (8). Although some simpler equations (9, 10) exist that are derived from this one, in the low relative pressures region they do not introduce any significant difference in the experimental data fit. The BET equation of three parameters was rarely used, although now it is very easy to handle with any small desktop computer. It contains, as extreme cases, Langmuir and BET equations of two parameters. The specific areas of many Y-type zeolites, partially exchanged and/or impregnated, were calcu-

lated using the equation whose n , average number of adsorbed layer, had the best adjustment of the experimental isotherm data.

EXPERIMENTAL METHODS AND RESULTS

A type-Y sodium zeolite, NaY, Linde SK-40, was used. From it, zeolites containing ammonium ions, cobalt, or palladium were prepared by ionic exchange and others containing molybdenum by impregnation with a solution of ammonium molybdate. The data which correspond to the preparation of zeolites is shown in Table 1. In the case of the H-NaY, the percentage of sodium ions exchanged with ammonium ions is indicated in parentheses. In the zeolites containing palladium, the percentage in weight of metallic palladium is indicated, and in those zeolites containing cobalt and/or molybdenum the percentage in weight of cobalt and of MoO₃ is also indicated, respectively. The order in which these exchanges and/or impregnations were done is also indicated in Table 1.

The prepared zeolites were activated using different procedures depending on the exchanged or impregnated species. In this way, those containing NH₄⁺ were activated in N₂ for 8 hr at 480°C, and this treatment was followed by a reduction in H₂ at 520°C if in addition to NH₄⁺ they contained Pd²⁺. The zeolites with cobalt and/or molybdenum were activated in air at 550°C for 4 hr. It was determined, through X-ray diffraction, if the prepared and activated zeolites kept their crystallinity, and for this reason the powder method was used, and the lines of diffraction corresponding to the (331), (533), and (751) planes, characteristics of the NaY Faujasite (11), were considered.

The adsorption methods of N₂ on activated and degasificated samples were per-

TABLE I
Preparation of Zeolites

Preparation Method	Solid denomination	Crystallinity	
I.E.	67% NH_4^+	H(67)-NaY	Yes
I.E.	74% NH_4^+	H(74)-NaY	Yes
I.E.	86% NH_4^+	H(86)-NaY	Yes
I.E.	74% NH_4^+ , 2% Pd	Pd(2)H(74)-NaY	Yes
I.E.	86% NH_4^+ , 2% Pd	Pd(2)H(86)-NaY	Yes
I.E.	4% Co^{2+}	Co(4)-NaY	Yes
I.E., I.	4% Co^{2+} , 12% MoO_3	Mo(12)Co(4)-NaY	Yes
I.	12% MoO_3	Mo(12)-NaY	No
I., I.E.	12% MoO_3 , 4% Co^{2+}	Co(4)Mo(12)-NaY	No

Note. I.E. = Ionic exchange; I. = impregnation. Temperature = 25°C, pH exchange solution or impregnation = 6.0.

formed in volumetric BET conventional equipment at -195.6°C . The value $16.0 (\text{\AA})^2$ was used as the effective adsorption section of N_2 molecule. The mass of the dry sample was about 0.3 g in all the measurements.

The adsorption N_2 measurement data, on every one of the zeolites shown in Table 1, showed isotherms like that presented in Fig. 1 corresponding to the type I of the B.D.D.T. classification (12).

These experimental values fitted very well to Langmuir and BET equations of two parameters, although the specific calculated areas are notably different.

Using the BET equation with three parameters the value of n , average number of adsorbed layers, which gives the best fit for the experimental data was determined. The statistical criteria of the correlation coefficient,

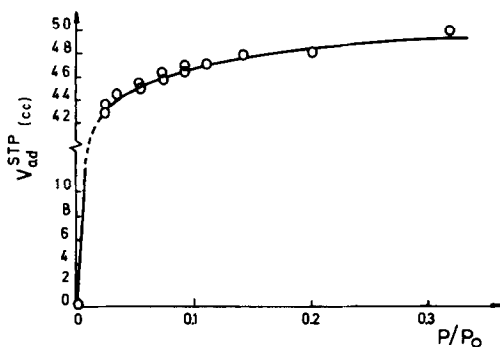


FIG. 1. N_2 adsorption isotherm on Pd(2)H(74)-NaY.

Fisher F function, and Exner Φ function were used, for values of n increased in 0.1 starting with $n = 1.0$. In all cases it was found that, for the zeolites, the best fit corresponded neither to $n = 1$ nor to $n = \infty$, but to values around 1.4. The best adjusted values ($n_{b.a.}$) and the specific areas calculated with this value of $n_{b.a.}$, and for $n = 1$ and $n = 10$, are given in Table 2. The area corresponding to $n = 10$ is equal to the specific area for $n = \infty$, because for values of n equal or greater than 7 the calculated area remained constant.

DISCUSSION

Previously, it was found (7) for a zeolite H(86)-NaY that the best adjustment of BET equation of three parameters was obtained with $n = 1.5$. In Table 2 it is shown that the value of $n_{b.a.}$ in all the zeolites that remained crystalline after the exchange and/or impregnation and activation procedures is approximately 1.4. In the zeolites in which ammonium molybdate was first impregnated and the crystallinity was lost, the $n_{b.a.}$ value increased notably. A Girdler T-126 $\gamma\text{-Al}_2\text{O}_3$ whose best adjustment corresponds to BET equation of two parameters is included in Table 2. Also, we must mention that the constant value c for $n_{b.a.}$ is over 1000 for the zeolites that remained crystalline, different from that of $\gamma\text{-Al}_2\text{O}_3$, whose c

TABLE 2
Specific Areas

Solid	$n_{b.a.}$	S (m ² /g)		
		$n = 1$	$n = n_{b.a.}$	$n = 10$
NaY	1.4	914	814	633
H(67)-NaY	1.4	785	705	568
H(74)-NaY	1.4	759	661	423
H(86)-NaY	1.4	679	607	460
Pd(2)H(74)-NaY	1.3	746	685	532
Pd(2)H(86)-NaY	1.3	732	673	532
Co(4)-NaY	1.4	564	507	404
Mo(12)Co(4)-NaY	1.3	512	475	394
Mo(12)-NaY	2.0	366	321	311
Co(4)Mo(12)-NaY	3.9	185	115	111
γ -Al ₂ O ₃	10	322	174	174

= 40, and for the zeolites which lost their crystallinity, whose c is approximately 50; these values are in reasonable agreement in relation to the isotherm forms (13).

If we observe the specific areas given in Table 2 we can see a big difference between the values calculated with $n = 1$, $n = 10$, and $n = n_{b.a.}$ for the zeolites. If we accept the value of the calculated area with $n_{b.a.}$ to be the most reasonable one for these solids, we can infer that for zeolites the calculated area with Langmuir equation will have an excess of approximately 10%, whereas BET area ($n = \infty$) will be less by about 20%. This would agree with Yates (14), and with Brunauer, who stated that, for microporous solids, the use of two-parameter BET equations will give a value of v_m that is 20% lower than the one obtained from the three-parameter equation, for $n = 1.4$ (15).

We can conclude that in order to estimate specific areas of zeolites, in comparative studies, from the adsorption data of N₂, the BET equation of three parameters with $n = 1.4$ will give the most reasonable area values.

ACKNOWLEDGMENTS

This work was supported by Dirección de Investigación, Universidad de Concepción, Chile.

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RUBY CID¹
RENAN ARRIAGADA
FRESIA ORELLANA

Chemistry Department
Faculty of Sciences, P.O. Box 3-C
University of Concepción
Concepción, Chile

Received July 16, 1982; revised October 15, 1982

¹ To whom correspondence should be addressed.