Empirical Model for the Characterization of Microporous Catalysts

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Introduction

The porous structure of catalyst materials such as zeolites, is typically characterized using adsorption techniques. The gas adsorption of microporous materials gives rise to a steep increase in volume over a short pressure range in the isotherm region below P/Po < 10^{-2}. This steep increase or "step" in the isotherm corresponds to the micropore pore filling. The size of the micropores is most often estimated using either the Horvarth- Kawazoe (HK, slit-like pores, usually for carbon based materials), Saito-Foley (SF, spherical and cylindrical models for oxide materials), the Dubinan-Radushkevich (DR) method or density functional theory (DFT). These models are based on the interaction of gas molecules and the walls of the microporous materials. Often there is a large discrepancy between the calculated pore size from the models (HK, SF, DR and DFT) and the actual pore size determined from crystallographic techniques as shown by Maglara[1].

The "step" in the isotherm will shift in relative pressure depending on the pore size. An empirical model using the relative pressures at the "step" filling in the isotherm and the pore sizes from crystallography of a set of standard microporous materials, would give a correlation of size versus pressure directly from experimental data rather from theoretical models. Hence, a simplistic correlation may be able to be used instead of complicated models and give a more realistic pore size estimation of an unknown sample. An unknown sample is likely to consist of one of the new type of nanopoorus materials, including MCM and SBA type materials. For example, SBA-15 is known to contain both microporous and mesoporous pores depending on the synthesis conditions. New adsorption analysis techniques are required to give better estimation of the pore sizes from these new complex porous materials.

Materials and Methods

In Table 1 is listed the standard one dimensional zeolite samples used to calibrate the adsorption pressure of micropore af specific crystallographic sizes.

Table 1 Zeolite samples and dimensions for standard adsorption pressures.

Zeolite	Structure, space group	Ring size	Channel type	Pore shape	Pore dimensions from X-ray crystallography (Å)
ZSM-23 (MTT)	Orthorhombic, Pmmn	10 MR	1D	Ellipse	4.5 x 5.2[2]
SSZ-20 (TON)	Monoclinic, Cmcm	10MR	1D	Ellipse	4.6 x 5.7[2]
ZSM-12 (MTW)	Monoclinic, C2/m	12 MR	1D	Ellipse	5.6 x 6.0[2]
SSZ-41 (VET)	Monoclinic, P-4	12 MR	1D	Circular	6.0 [3]
SSZ-55 (ATS)	Monoclinic, $Cmc2_1$	12MR	1D	Ellipse	6.52 x 7.22 [4]

Argon adsorption at 87 K of the zeolite samples was run using an Autosorb-1C (Quantachrome Instruments). A sample of about 0.035 g was weighed for each of the zeolites and placed in a spherical sample tube. Each of the samples was out-gassed at a temperature of 300ºC, with a temperature ramp rate of 200°C/h. Surface area and micropore analysis was carried out using Autosorb ASWin ver 1.51 (Quantachrome) software. Micropore size to filling pressures from isotherms of the five zeolites and literature values were combined to develop the empirical models, of ID and 3D micropores, using Microsoft Excel™ spreadsheets.

Results and Discussion

Low-pressure isotherms of five 1D-channel type zeolites MTT, TON, MTW, ATS and VET, of varying pore size, were obtained using argon adsorbate at 87 K, between 10^{-7} and 0.2 P/Po. The isotherms were characterized using several standard analysis techniques, including BET surface area, Vt-plot, α-plot micropore volume. An empirical correlation between the crystallographic pore diameter and the relative pressure of the isotherm "step" was determined for 1D and 3D zeolite types combining also literature data. Figure 1 shows three different models fitted to experimental data for 1D type zeolites. It can be seen that all tree types, in particular the Halsey give a very good fit. Using these models we were able to apply it to determine the micropore distribution of complex meso-microporous materials; SBA-15.

Significance

Many new microporous catalyst materials such as SBA-15 type meso-microporous systems are being developed and employed in the catalytic and separation industry. The accurate estimation of the pore size of these materials is critical in order to fully utilize the structural properties of these systems. This model allows the quick and accurate determination of micropores from isotherm data.

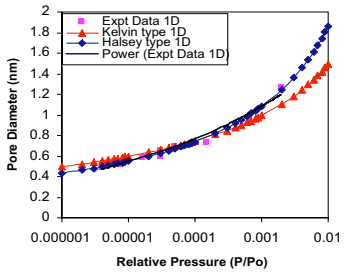

Figure 1. Correlation between pore diameter and relative pressure for 1D zeolites, with three types of mathematical equation fits, Kelvin, Halsey and power type.

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