

Estimating the Surface Area of Micro-Meso-porous Catalytic Materials

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Introduction

Multi-porous materials are being developed as catalysts wherein the mesopores allow access of larger molecules throughout the particles where microporosity affords shape selectivity. While characterization of mixed porosity systems depends primarily on physical ad-desorption measurements, these calculations are problematic. The BET method of surface area calculation does not apply to microporous materials; further, surface areas are employed in many common methods of calculating pore size distributions (e.g., BJH).

The presence of the microporosity in a solid sample partly obfuscates the calculation of the BET surface areas of micro-mesoporous materials such as SBA-15, thus preventing one from correctly estimating the surface areas of the materials. Therefore, how can we separate the micropore contribution to the calculated BET surface areas? In this work, we seek to answer this question by utilizing two methods: 1. A "filled pore method" to estimate the external surface areas of zeolite materials. *n*-nonane was used as a preadsorbate to block the micropores. 2. Analyses of the high resolution region of the isotherm ($P/P_0 < 10^{-4}$) separate from the pore filling region ($10^{-2} < P/P_0 < 10^0$). These analyses are compared and their relative merits are analyzed.

We applied these techniques to SBA-15, a bimodal porous system as well as several zeolite materials. Comparing the nitrogen or argon adsorption before and after *n*-nonane preadsorption on selected microporous and micro-mesoporous samples revealed that a substantial amount of the calculated BET surface area was inherently due to the presence of micropores within the samples. For microporous samples, the BET surface areas are 5 to 25 times exaggerated and for micro-mesoporous samples, by a factor of 1.5. The sequential adsorption method could be further applied to membrane systems to better estimate the surface area excluding the micropores.

Materials and Methods

The microporous materials consisted of, a VET framework zeolite sample provided by Stacey Zones (Chevron-Texaco), and MFI structured silicalite-1 samples i) obtained from Union Carbide ii) synthesized with microwave heating are used.

Micro-mesoporous SBA-15 materials were synthesized according to the procedure by You.[1]

Adsorption experiments were performed using nitrogen at 77 K or argon at 87 K on the prepared samples using an AUTOSORB®-1-C (Quantachrome Instruments, Boynton Beach, FL) adsorption instrument. For the sequential adsorption experiment, we followed the procedure introduced by Kaliaguine *et al.*[2]

Results and Discussion

Figure 1 show the argon isotherm of SBA-15 before an after preadsorption with *n*-nonane. It can be seen that the *n*-nonane significantly decreases the micropore volume ($< 10^{-1} P/P_0$) but does not affect the mesopore region ($> 0.2 P/P_0$). The BET surface areas and constants are

shown in Table 1 for microporous zeolites and SBA-15 materials before and after *n*-nonane preadsorption. *n*-nonane blocks the microporosity of the zeolites reducing the surface area to the external surface area. Furthermore, BET constants are within the accepted range (20-200) indicating this theory is valid for the isotherms after preadsorption.

A second method was developed in which the micropore volume was subtracted from the isotherm at various pressures ($P/P_0 = 10^{-5} - 10^{-3}$) in order to obtain appropriate fit of the BET theory. It was found that subtraction of the micropore volume at $P/P_0 = 10^{-4}$ gave BET constants in the valid range. The preadsorption and micropore volume subtraction methods allow for the valid calculation of the BET surface area of new micro-mesoporous catalyst materials.

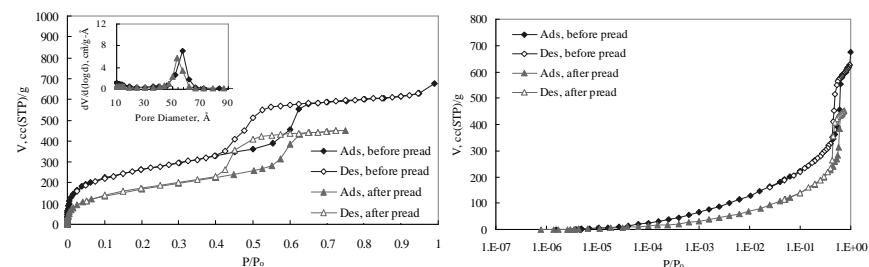


Figure 1. Argon adsorption on SBA-15, at 87 K before and after *n*-nonane preadsorption: normal scale (left) and logarithmic scale (right).

Table 1 BET surface area, micropore volume, and BJH mesopore size calculation based on the adsorption isotherms obtained before and after *n*-nonane preadsorption.

Sample	S _{BET} (m ² /g) / C _{BET}		V _μ (cc/g)		D _{BJH} (Å)	
	Before	After	Before	After	Before	After
cMFI (N ₂ /77 K)	471.1 / -98.0	19.1 / 98.6	0.159	-0.014		
mwMFI (N ₂ /77 K)	497.3 / -83.9	28.3 / 17.5	0.103	-0.018		
VET (Ar/87 K)	548.4 / -76.7	96.0 / 38.8	0.172	0.001		
SBA-15(a) (Ar/87 K)	814.9 / 130.0	556.1 / 53.3	0.122	0.024	57.3	53.6
SBA-15(b) (Ar/87 K)	879.8 / 74.6	550.2 / 48.1	0.122	0.040	78.2	78.7

S_{BET}: surface area estimated by BET method; C_{BET}: corresponding BET C constant;

V_μ: micropore volume estimated from α_c-method; D_{BJH}: mesopore diameter by BJH calculation

Significance

This work describes new methodology to determine the accurate surface area of new microporous-mesoporous catalysts.

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References

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