

ISSUES IN THE ASSESSMENT OF TEXTURAL PROPERTIES OF MICRO/MESOPOROUS ZEOLITIC MATERIALS USING LOW TEMPERATURE NITROGEN ADSORPTION

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ABSTRACT

In this work, problems in the application of low temperature nitrogen adsorption for the estimation of textural properties of micro/mesoporous materials are discussed. Materials obtained via two different approaches were studied: alkaline treated ZSM-5 zeolites and synthesized MCM-41/ZSM-5 structures. Appropriate ranges of p/p^0 for BET method and t values for t -plot were considered.

Keywords: nitrogen adsorption, BET method, t -test, hierarchical zeolites.

INTRODUCTION

Low temperature nitrogen adsorption is the most commonly used method for assessment of textural properties of solid materials. Although the method is routinely performed, obtained results can lead to erroneous conclusions if raw data are not investigated with caution. This paper addresses these issues illustrated on two sets of hierarchical materials, one with predominantly microporous structure and the other containing mostly mesopores.

EXPERIMENTAL

Hierarchical porosity in ZSM-5 zeolite (Zeolyst, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 23, 50$ and 80) was induced via alkaline treatment^[1]. Treatment parameters: concentration of NaOH (0.05 M, 0.2 M, 0.5 M), temperature (30°C, 60°C, 90°C) and duration (10 min, 30 min, 60 min) were varied. As a separate set of samples, hierarchical materials were prepared as follows: an amorphous precursor (gel) with molar composition $12.5\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 60\text{SiO}_2 \cdot 8\text{TPABr} \cdot 4000\text{H}_2\text{O}$ ^[2] was used. For samples MZ1 and MZ2 a template for mesopores (CTAB) was added immediately, while for sample MZ3 the amorphous precursor was aged for 3 hours at 80°C, cooled to RT, before CTAB was added. CTAB/ SiO_2 ratio for samples MZ1 and MZ3 was 0.1, and 0.2 for sample MZ2. The reaction mixtures were aged for 24 hours at 60°C, and subsequently synthesized during 48 hours at 150°C. Solid samples were separated from the liquid phase, washed with demineralized water, dried at 60°C (24 h) and calcined for 4 hours at 550°C. N_2 adsorption at 77 K was performed on a Micromeritics 2010 apparatus, after pretreatment in vacuum at 400°C for 4 hours. The t -plot method was used for discrimination between micropores from mesopores; Harkins-Jura equation was used^[3]. XRD patterns were recorded on a Bruker D5005 (Cu $K\alpha$, 2° to 80° (2 θ), 0.02° s⁻¹). SAXS analysis was performed at the synchrotron facilities of Elettra-Sincrotrone Trieste, on the Austrian SAXS Beamline, with beamline energy of 8 keV and 2D Pilatus 1M detector system. TEM was carried out using a

JEOL JEM-1400 Plus microscope operated at 120 kV. Particle size distributions were performed using Mastersizer 2000 from Malvern.

RESULTS AND DISCUSSION

Alkaline treatment of ZSM-5 zeolites resulted in mesopore formation, which occurs on the crystallite surface. The newly formed pores are not created in a homogeneous manner, especially in the case of severe treatment conditions where macropores also develop (Fig. 1c). A detailed textural analysis for selected samples is presented elsewhere^[1].

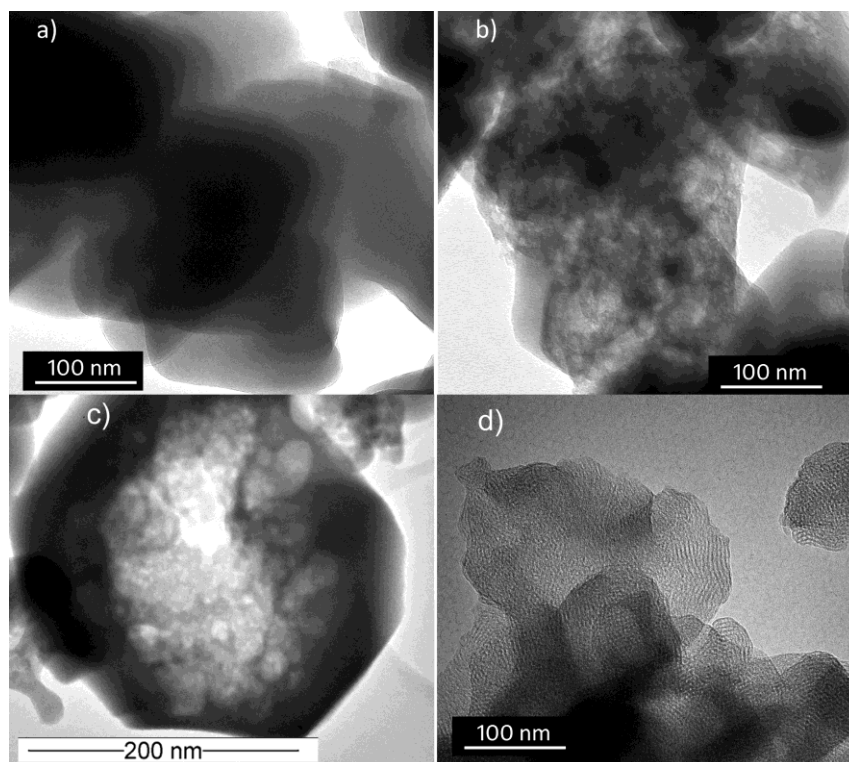


Figure 1. TEM micrographs of a) parent; alkaline treated ZSM-5: b) 60°C, 30 min; c) 90°C, 60 min; and d) MZ3.

N₂ isotherms (Fig. 2a) of the hierarchical samples are type IIb, with H3 hysteresis and they exhibit well defined linear parts which makes t-test easily applicable for calculation of external surface (S_{ext}) and microporous volume (V_{mic}). Indeed, our results showed that the region of t values with best linearity of t-curves was 0.3-0.6, i.e. the same region recommended for purely microporous zeolites^[4]. Also, mesopore presence was related to the measured increase of S_{ext} : particle size analysis confirmed that no changes in particle sizes occurred during treatment. However, microporous surface (S_{mic}) is calculated as $S_{\text{mic}} = S_{\text{BET}} - S_{\text{ext}}$ and its determination suffers from all known problems associated with BET theory application to microporous solids like zeolites^[3,5]. Nevertheless, BET method is still the most used procedure for zeolite characterization. It has been proposed^[5] that the p/p^0 region selection is crucial to BET model applicability in the presence of micropores: only those p/p^0 values for which $n(p^0-p) = f(p/p^0)$ is a continually increasing function can be used. This criterion is illustrated in Figure 2b for a hierarchical ZSM-5 sample obtained using 0.2 M NaOH at 60°C during 30 min. Applying the

stated rule, only points below $p/p^0 < 0.1$ are allowed. This yielded $S_{\text{BET}} = 505 \text{ m}^2/\text{g}$ and a positive C value^[5], as opposed to $S_{\text{BET}} = 470 \text{ m}^2/\text{g}$ and a negative C value which were calculated using the regular BET region $0.05 < p/p^0 < 0.3$. This underestimation of S_{BET} consequently impacts the evaluation of S_{mic} .

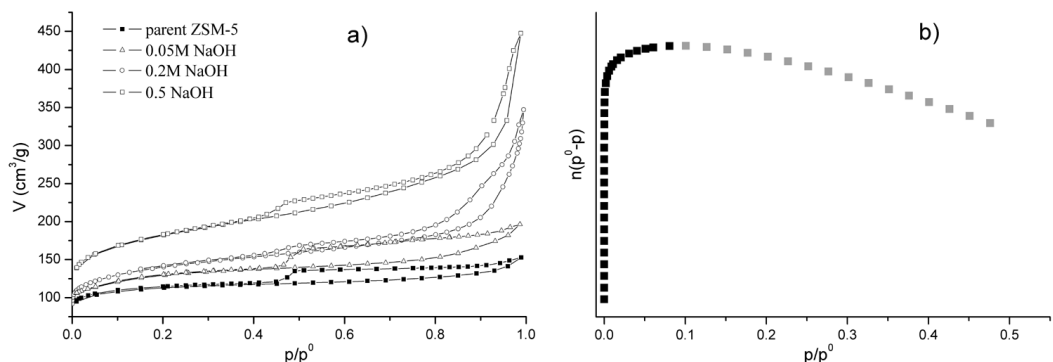


Figure 2. a) Nitrogen isotherms of ZSM-5 treated with NaOH of different concentrations; b) function $n(p^0-p) = f(p/p^0)$ as a criterion for selecting p/p^0 region for S_{BET}

In the case of hierarchical materials synthesized in this work, N_2 isotherms exhibit shapes commonly observed for mesoporous MCM-41. The existence of MCM-41-like structure in the samples as well as ZSM-5 was confirmed by SAXS and XRD. In this case, t-test applied to linear part of the t-curve at $t = 0.3-0.6$ yields $S_{\text{meso+ext}}$ and V_{micro} , while when applied to the linear part at high p/p^0 , S_{ext} and V_{total} are obtained (Fig.3b)^[4]. Results in Table 1 show that the extent of microporous surface is rather small compared to the mesoporous. Also, S_{mic} decrease with increasing concentration of CTAB, as expected, and is favoured in the sample MZ3, where the precursor mixture was aged before CTAB addition. It is important to note that, unlike for alkaline treated samples, mesoporosity is not detected as external surface.

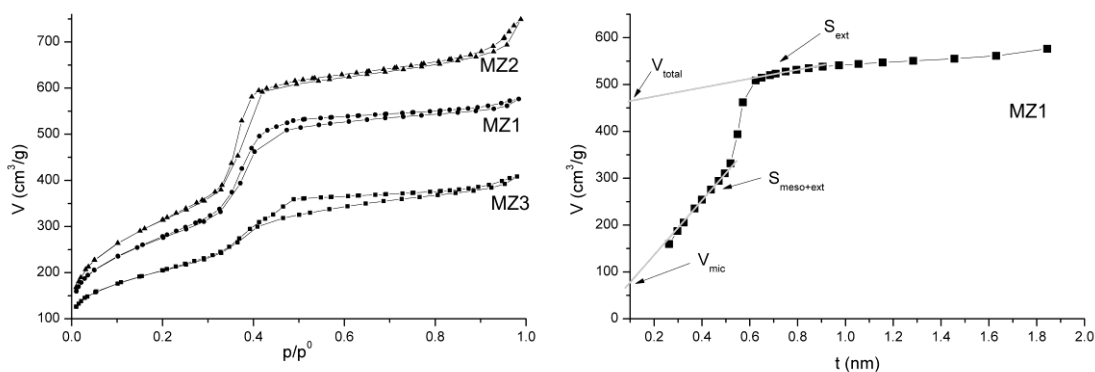


Figure 3. a) Nitrogen isotherms for synthesized hierarchical samples; b) t-curve for sample MZ1.

Table 1. Textural parameters of synthesized hierarchical samples.

	S_{BET} (m ² /g)	S_{ext} (m ² /g)	$S_{\text{meso+ext}}$ (m ² /g)	S_{mic} (m ² /g)	S_{meso} (m ² /g)
MZ1	985	137	935	50	798
MZ2	1133	173	1106	27	933
MZ3	722	156	634	88	478

However, calculating microporous volumes and surfaces in micro/mesoporous materials using t-test has been questioned by some authors. It has been shown^[6] that V_{mic} obtained for simple mechanical mixtures of FAU and MCM-41 were significantly underestimated. If so, this fact may be a large problem, since not only S_{mic} and V_{mic} would be affected, but also values of S_{meso} and V_{meso} . However, these remarks still have to be proven in further investigations, preferably by applying different complementary methods. Furthermore, if the material possesses a significant microporous content, previously mentioned S_{BET} calculation problems could also be a source of error.

CONCLUSION

Presented results show that, in the case of alkaline treated zeolites with predominantly microporous structure, BET surface determination must be made in accordance with recommended criteria for p/p^0 region selection or at least p/p^0 region must be cited, for comparison reasons. For MCM-41/ZSM-5 hierarchical materials t-test applicability for the estimation of microporous surface and volume is considered ambiguous and should be verified by complementary methods.

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