Formation of Uniform Mesopores in ZSM-5 Zeolite upon Alkaline Post-treatment?

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Alkaline post-treatment (0.2 M NaOH at 353 K) of ZSM-5 leads to substantial formation of mesoporosity. The created mesopores do not have a uniform size of 4 nm,[1] but show a broad distribution around 10 nm. The sharp peak at 4 nm in the pore size distribution derived from the N_2 desorption isotherm should be attributed to the Tensile Strength Effect of the adsorbate instead.

ZSM-5 zeolite shows a wide range of applications in catalytic and separation processes due to the unique three-dimensional intersecting of sinusoidal and straight channels of molecular dimensions.[2] However, the purely microporous character of this material often leads to diffusion limitations and limited accessibility, which can be prejudicial in the various applications. Tailoring micro- and mesoporous materials by development of bimodal pore size distributions is thus currently being subject of many publications.[3–5] The presence of regular micropores (<2 nm) and larger mesopores (2–50 nm) in the same material offers an enhanced accessibility to the active sites and shape selectivity properties.

Development of extra-porosity is normally achieved by application of different post-treatments on the synthesized zeolitic material, including steaming at relatively high temperature, acid leaching, or alkaline treatments. The last method removes mainly Si from the zeolite framework,[1,5] while the former ones lead to dealumination.[6] Ogura *et al.*[1] recently reported interesting changes in the porous structure of ZSM-5 upon alkaline treatment. The message from that communication was the creation of uniform mesopores of *ca.* 4 nm having a similar narrow distribution as in M41S-type materials. This conclusion was based on the pore size distribution (PSD) derived from N_2 adsorption at 77 K. The explanation given by the authors for the mesopore formation was the dissolution of Si at the boundaries of twinning/neighbouring crystals, resulting in intercrystallite voids.[7] In this contribution we would like to comment on the interpretation of the results obtained in Ogura's study and give some guidelines to interpret PSDs derived from N_2 adsorption measurements.

In our laboratory we have treated a similar commercial NH_4-type ZSM-5 sample (CBV 8020, Zeolyst, Si/Al = 37.5) according to the procedure described by Ogura *et al.*[1] The as-received ZSM-5 zeolite was stirred in a 0.2 M NaOH aqueous solution at 353 K for 5 h. The resulting slurry was filtered, dried at 383 K, and finally rinsed at 353 K with distilled water. XRD measurements of the as-received and alkali-treated samples (not shown here) confirmed that the crystal structure of the zeolite was not altered by the alkaline treatment, as anticipated by Ogura *et al.*[1] The N_2 adsorption isotherm of the alkali-treated sample shows a dramatic increase in uptake compared to the as-received sample (Figure 1). The increased uptake is due to newly created mesoporosity and gives rise to a hysteresis loop. As a consequence the external surface area, as calculated from the *t*-plot, increases from $40\,m^2{\cdot}g^{-1}$ in the as-received sample to $130\,m^2{\cdot}g^{-1}$ in the alkaline-treated sample at the expense of microporosity (V_{micro} decreases from 0.17 to $0.13\,cm^3{\cdot}g^{-1}$, see also Table 1). However, the mesopore size is not so well defined as proposed in the work by Ogura *et al.*[1] Both the adsorption and the desorption branch show a similar trend at $p/p_0 > 0.5$, but a quite different behaviour is observed around $p/p_0 = 0.45$. In the case of a narrow distribution of physical mesopores, both the adsorption and desorption branch of the isotherm show a well defined step as observed in *e.g.* MCM-41.[7,8] However, the adsorption branch shows a progressive increase in volume adsorbed, while the desorption branch shows a pronounced step around $p/p_0 = 0.45$ resulting in the closure of the hysteresis loop. This last step is characteristic for the adsorptive used (N_2 at 77 K) rather than being dependent on the porous properties of the sample under investigation, and therefore always appears at the same position, even for different adsorbents. This phenomenon, often referred to as the so-called Tensile Strength Effect (TSE),[9,10] causes the artefact at ~4 nm pore diameter (according to Barrett-Joyner-Halenda and Dollimore-

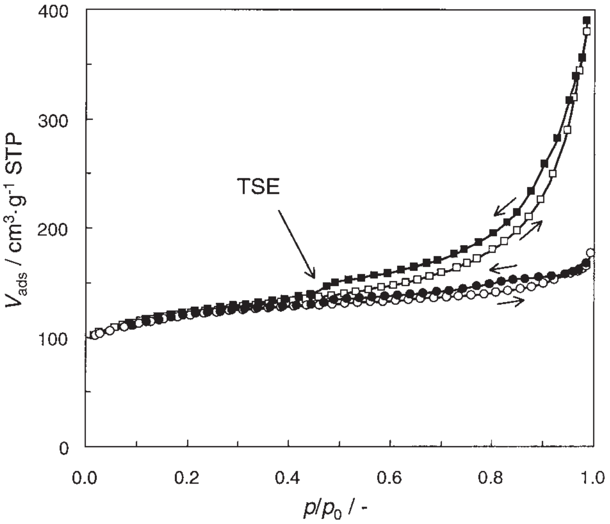

Figure 1. N_2 adsorption isotherms at 77 K for as-received (○, ●) and alkaline-treated (□, ■) NH_4ZSM-5. Open symbols: adsorption isotherm, solid symbols: desorption isotherm.

Table 1. Porous properties of as-received and alkaline-treated NH_4ZSM-5 obtained from N_2 adsorption measurements

	S_{BET}[a] $m^2{\cdot}g^{-1}$	S_{ext}[b] $m^2{\cdot}g^{-1}$	V_{total} $cm^3{\cdot}g^{-1}$	V_{micro}[b] $cm^3{\cdot}g^{-1}$
As-received	440	40	0.26	0.17
Alkaline-treated	450	130	0.59	0.13

[a]BET method. [b]*t*-plot method.

Heal models).

The TSE can be physically explained by the presence of an unstable meniscus in small mesopores upon desorption. Along the desorption branch, in the presence of mesopores, a hemispherical meniscus is being developed separating the vapor and the capillary condensed adsorbate in the pores. At a certain relative pressure ($p/p_0 = 0.45$ for N_2 at 77 K), the tensile strength in this capillary condensed adsorbate becomes thermodynamically unstable, leading to complete evaporation of the condensed phase and closure of the hysteresis loop. The fact that at this pressure a condensed phase is still present indicates the presence of smaller pores than those corresponding to the emptying pressure (exactly 3.9 nm according to BJH model). Application of this model to the desorption branch of the isotherm will, in these cases, give a completely different result compared to that obtained from the adsorption branch, where the TSE phenomenon is absent.

It can be reasonably inferred that the uniform PSD in the alkaline-treated ZSM-5 sample reported by Ogura *et al.*[1] is based on the TSE phenomenon. The PSD derived from the desorption branch clearly shows the intense peak at the characteristic 4 nm position, which is absent in the adsorption PSD (Figure 2). This clear difference supports the non-physical nature of this peak, which in the case of extraction of Si from the boundaries of the zeolite crystallites would more likely result in voids of variable dimensions, especially when the crystallites have a different size and shape. Comparison of the PSD of the as-received and alkaline-treated material derived from the adsorption branch shows an increase in the contribution from pores centered around ~10 nm (Figure 3). The distribution is relatively broad as can be expected from the proposed mechanism of mesopore formation.[7] This shows that the applied alkaline treatment indeed produced mesopores but a more random distribution is obtained. Although the shape of the hysteresis loop is different from the one observed in Ogura's study,[1] a more similar loop is obtained in a recent publication by the same authors.[11] Experimental variables like number of points measured, equilibration time and operation mode (continuous or discontinuous) of the instrument may affect the shape and closing point of the hysteresis loop, explaining the differences observed.

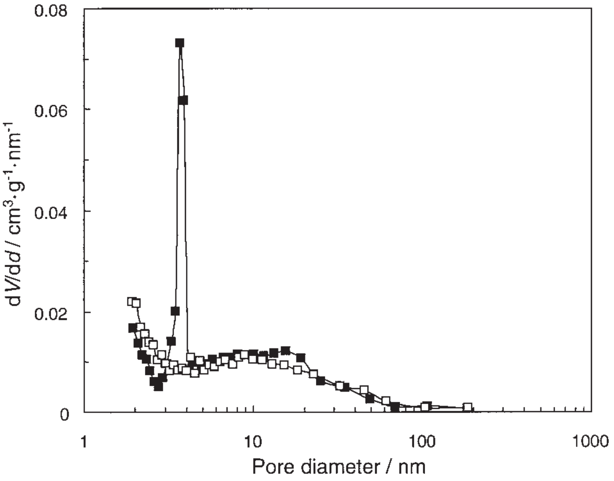

Figure 2. BJH adsorption (□) and desorption (■) pore size distribution for alkaline-treated NH_4ZSM-5.

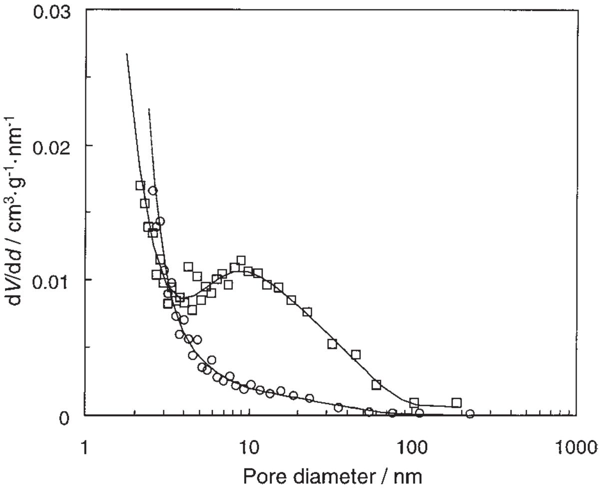

Figure 3. BJH adsorption pore size distribution for as-received (○) and alkaline-treated (□) NH_4ZSM-5.

The attribution of the peak at 4 nm to physical pores is not limited to the case of the alkaline treated ZSM-5 materials. The formation of a bimodal distribution in MCM-41 materials showing pores at 2.5 and 4 nm and a sharp 4 nm mesopore size distribution in ZrO_2 prepared via the sol-gel method are other recent examples of misinterpreted PSDs by the TSE phenomenon.[12,13] Comparison of the adsorption and desorption PSD can simply be used as a diagnostic tool to evaluate the non-physical nature of this peak.

References

1 M. Ogura, S. Shinomiya, J. Tateno, Y. Nara, E. Kikuchi, and M. Matsukata, *Chem. Lett.*, **2000**, 882.
2 Ch. Baerlocher, W. M. Meier, and D. H. Olson, "Atlas of Zeolite Framework Types," 5th ed., Elsevier Science, Amsterdam (2001).
3 A. H. Janssen, A. J. Koster, and K. P. de Jong, *Angew. Chem. Int. Ed.*, **40**, 1102 (2001).
4 C. Pak and G. L. Haller, *Micropor. Mesopor. Mater.*, **44-45**, 321 (2001).
5 T. Suzuki and T. Okuhara, *Micropor. Mesopor. Mater.*, **43**, 83 (2001).
6 J. Scherzer, *ACS Symp. Ser.*, **248**, 157 (1984).
7 M. Ogura, E. Kikuchi, and M. Matsukata, *Stud. Surf. Sci. Catal.*, **135**, 11-P-30 (2001).
8 J. C. Groen, M. C. Doorn, and L. A. A. Peffer, in "Adsorption Science and Technology," ed. by D. D. Do, World Scientific, Singapore (2000), p 229.
9 S. J. Gregg and K. S. W. Sing, "Adsorption Surface Area and Porosity," 2nd ed., Academic Press, London (1982), p 154.
10 O. Kadlec and M. M. Dubinin, *J. Colloid Interf. Sci.*, **31**, 479 (1969).
11 M. Ogura, S. Shinomiya, J. Tateno, Y. Nara, M. Nomura, E. Kikuchi, and M. Matsukata, *Appl. Catal. A*, **219**, 33 (2001).
12 Z. Y. Yuan, J. Z. Wang, Z. L. Zhang, T. H. Chen, and H. X. Li, *Micropor. Mesopor. Mater.*, **43**, 227 (2001).
13 V. I. Pârvulescu, H. Bonneman, V. Pârvulescu, U. Endruschat, A. Rufinska, Ch. W. Lehmann, B. Tescha, and G. Poncelet, *Appl. Catal. A.*, **214**, 273 (2001).