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Direct Demonstration of Enhanced Diffusion in Mesoporous ZSM-5 Zeolite Obtained via Controlled Desilication

Johan C. Groen,*[†] Weidong Zhu,[†] Sander Brouwer,[†] Steven J. Huynink,[†]
Freek Kapteijn,[†] Jacob A. Moulijn,[†] and Javier Pérez-Ramírez[‡,§]

Contribution from the DelftChemTech, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands, Institute of Chemical Research of Catalonia (ICIQ), Avenida Països Catalans 16, 43007 Tarragona, Spain, and Catalan Institution for Research and Advanced Studies (ICREA), Passeig Lluís Company 23, 08010 Barcelona, Spain

Received August 8, 2006; E-mail: j.c.groen@tudelft.nl

Abstract: A 2 orders of magnitude gas transport improvement in a medium pore ZSM-5 zeolite has been achieved upon introduction of intracrystalline mesoporosity in gradient-free crystals by desilication post-treatment in alkaline medium.

Introduction

Zeolites represent an important class of materials exhibiting a well-defined hydrothermally stable framework with pores of molecular dimensions 0.3−1.5 nm.[1] One of the main drawbacks arising in catalytic applications concerns the limited molecular transport in these micropores, and it has been demonstrated ad infinitum that mass transfer limitations restrict the extent of catalytic conversions over zeolites.[2] To circumvent this, since 1992, ordered mesoporous materials have widely attracted the attention of scientists in view of improved transport in the pores covering the lower nanometer-size range. The overall relatively poor (hydro)thermal stability, lack of (strong) acidity, and absence of confinement effects have, however, resulted in limited practical applications. Given this situation, materials exhibiting a hierarchical architecture of porosity are gaining increased interest. The larger pores facilitate physical transport, whereas each micropore acts as a nanoreactor providing active sites and shape selectivity. The importance and implication of these structures have been comprehensively reviewed by Hartmann,[3] van Donk et al.,[4] and recently by Tao and co-workers.[5] Hydrothermal treatment and/or acid leaching are classical post-synthesis approaches in research labs and industry to induce mesoporosity in acidic zeolites. Small zeolite domains immobilized in mesoporous matrices,[6,7] delaminated zeolites,[8] and mesoporous zeolite crystals prepared via carbon templating[9] are other recent examples of materials that have the potential for improved transport properties in zeolite catalysis.

An innovative methodology is desilication, a post-synthesis modification treatment in which, contrarily to the well-known dealumination treatment, silicon is selectively extracted from the zeolite framework.[10−13] Tuneable extraction of silicon can be realized by the presence of optimal amounts of framework aluminum in the zeolite.[14] Particularly, ZSM-5 with framework Si/Al ratios in the range of 25−50 has shown so far to be an eligible structure for the introduction of mesoporosity via this approach. Impressive increases in mesopore surface areas (from 40 m^2 g^{-1} in the original zeolites up to 250 m^2 g^{-1} in the alkaline-treated zeolites) have been reported, coupled to a retained structural integrity of the crystals.[12]

Despite the many efforts in the synthesis, characterization, and catalytic evaluation of these hierarchical porous structures, reports on diffusion characteristics that directly assess the improved transport in the combined micro- and mesoporous crystals are scarce. This is associated with the meticulous requirements regarding the selection of specimen, technique, and probe molecule. Frequently, improved catalytic performance of hierarchical porous zeolite structures has been tentatively attributed to enhanced diffusion, while no direct evidence of the diffusion characteristics was attained.[15−17] Kortunov and co-

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[†] Delft University of Technology.

[‡] Institute of Chemical Research of Catalonia.

[§] Catalan Institution for Research and Advanced Studies.

(1) Baerlocher, C.; Meier, W. M.; Olson, D. H. *Atlas of Zeolite Framework Types*, 5th ed.; Elsevier: Amsterdam, 2001.

(2) Kärger, J.; Ruthven, D. M. *Diffusion in Zeolites and Other Microporous Solids*; Wiley and Sons: New York, 1992.

(3) Hartmann, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 5880−5882.

(4) van Donk, S.; Janssen, A. H.; Bitter, J. H.; de Jong, K. P. *Catal. Rev.* **2003**, *45*, 297−319.

(5) Tao, Y.; Kanoh, H.; Abrams, L.; Kaneko, K. *Chem. Rev.* **2006**, *106*, 896−910.

(6) Prokesova, P.; Mintova, S.; Èejka, J.; Bein, T. *Microporous Mesoporous Mater.* **2003**, *64*, 165−174.

(7) Wang, S.; Dou, T.; Zhang, Y.; Li, X.; Yan, Z. *Catal. Commun.* **2005**, *6*, 97−91.

(8) Corma, A.; Díaz-Cabañas, M. J.; Martinez-Triguero, J.; Rey, F.; Rius, J. *Nature* **2002**, *418*, 514−517.

(9) Christensen, C. H.; Johannsen, K.; Schmidt, I.; Christensen, C. H. *J. Am. Chem. Soc.* **2003**, *125*, 13370−13371.

(10) Ogura, M.; Shinomiya, S.; Tateno, J.; Nara, Y.; Kikuchi, E.; Matsukata, M. *Chem. Lett.* **2000**, 882−883.

(11) Ogura, M.; Shinomiya, S.; Tateno, J.; Nara, Y.; Nomura, M.; Kikuchi, E.; Matsukata, M. *Appl. Catal. A* **2001**, *219*, 33−43.

(12) Groen, J. C.; Peffer, L. A. A.; Moulijn, J. A.; Pérez-Ramírez, J. *Chem. Eur. J.* **2005**, *11*, 4983−4995.

(13) Groen, J. C.; Moulijn, J. A.; Pérez-Ramírez, J. *J. Mater. Chem.* **2006**, *16*, 2121−2131.

(14) Groen, J. C.; Jansen, J. C.; Moulijn, J. A.; Pérez-Ramírez, J. *J. Phys. Chem. B* **2004**, *108*, 13062−13065.

(15) Zhou, Q.; Wang, Y. Z.; Tang, C.; Zhang, Y. H. *Polym. Degrad. Stab.* **2003**, *80*, 23−30.

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workers recently communicated on the diffusion of *n*-octane and 1.3.5-triisopropylbenzene in steam-dealuminated USY zeolite.[18] Contrary to what is generally presumed, their work literally concluded that the mesopores introduced via steam treatment only moderately impacted the intracrystalline diffusion. This is due to the isolated nature of the created porosity (i.e., the mesopores do not constitute an interconnected accessible network). This latter statement is in agreement with the work reported by Janssen et al.[19] The authors demonstrated, based on 3-D TEM investigations, that, predominantly, cavities were obtained by hydrothermal treatment of zeolite Y and explicitly questioned the significant contribution of these pores to the overall diffusivity.

Here, we provide experimental evidence for the remarkably improved diffusion in mesoporous ZSM-5 zeolites obtained via controlled desilication. To achieve this aim, the synthesis of a suitable zeolite sample was essential. First, relatively large and uniformly sized crystals are required to obtain relatively large characteristic diffusion times and thus reliable uptake curves.[2] Besides, in the case of ZSM-5 type zeolites, it is well-documented that the synthesis of large crystals employing the typically used TPAOH as a template results in Al-zoned crystals.[20,21] The crystal interior is poor in aluminum, while the outer rim shows a relatively high concentration of aluminum. Subsequent alkaline treatment of these Al-zoned crystals has previously shown to result in a preferential dissolution of the aluminum-poor center and the formation of hollow crystals with a relatively preserved outer surface.[21] Similar to the conclusion drawn by Kortunov and co-workers,[18] this anisotropic distribution of mesoporosity would limitedly contribute to the overall diffusion properties of the resulting crystals. As a consequence, a modified synthesis procedure was required to acquire micrometer-sized crystals with a uniform size and aluminum distribution, to optimally tune the introduction of the mesoporosity by desilication. Subsequently, an accurate assessment of the diffusion characteristics was made by means of the tapered element oscillating microbalance (TEOM) technique, a high-resolution microbalance that enables real-time measurement of mass changes during gas−solid interactions.[22,23]

Experimental Procedures

Hydrothermal synthesis of the ZSM-5 crystals was carried out using 1,6-hexanediol as a template, adapted from the synthetic protocol as previously reported by Althoff et al.[24] The chemical composition of the reaction mixture was 170 SiO_2 2 Al_2O_3/140 $C_6H_{12}(OH)_2$/32 H_2SO_4/15 000 H_2O. Sodium waterglass (27.5% SiO_2 and 8.3% NaOH) was stirred at 1000 rpm in a Teflon beaker with half the amount of water. In a separate beaker, the remaining water and H_2SO_4 were used to dissolve $AlCl_3$. After complete dissolution, the aluminum-containing solution was added to the silica solution and stirred for 5 min at 1000 rpm. Subsequently, the reaction gel was transferred to a Teflon-lined autoclave and kept at 453 K for 60 h. Afterward, the crystals were filtered, washed with demineralized water, dried at 353 K, ion-exchanged with a 0.1 M NH_4NO_3 solution (3 times), and finally calcined in static air at 823 K for 7 h (heating rate of 1 K min^{-1}).

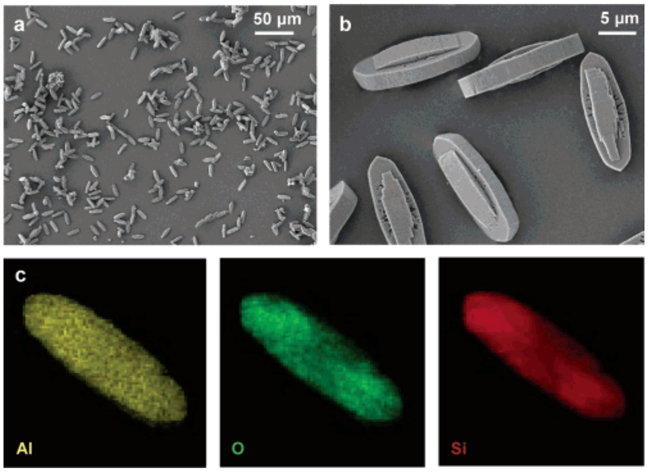

Figure 1. (a) Low and (b) medium magnification SEM and (c) SEM-EDX images of calcined monosized 17 μm gradient-free ZSM-5 crystals.

Alkaline treatment of the crystals was performed in 0.2 M NaOH solution at 338 K for 120 min. The resulting crystals were washed with demineralized water and dried at 353 K. Prior to further characterization, the alkaline-treated sample was ion-exchanged and calcined following similar procedures as for the as-synthesized sample.

Crystal size and morphology of the non-treated and treated zeolites were investigated using SEM on a JEOL JSM-6700F electron microscope. The spatial distribution of the elemental composition in the zeolite crystals including detailed point analysis of aluminum, silicon, and oxygen was measured over polished crystals using SEM-EDX in a JEOL JSM 5600 microscope.

N_2 adsorption at 77 K was performed in a Quantachrome Autosorb-6B gas sorption analyzer to study the micro- and mesoporosity in the zeolite crystals. The contribution from both micro- and mesoporosity was derived from the *t*-plot method according to Lippens and de Boer.[25] The mesopore size distribution was calculated using the Barret−Joyner−Halenda[26] (BJH) pore size model applied to the adsorption branch of the isotherm. High-resolution low-pressure Ar adsorption experiments at 87 K were conducted on a Micromeritics ASAP 2010 to analyze the uptake at low pressures to determine the micropore size distribution by the Saito−Foley (SF) pore size model.[27] Hg porosimetry experiments were carried out in a Thermo Electron Pascal 140/440 system, thereby covering the pore size range of 120 μm to 4 nm, which also provides information on the accessibility and interconnectivity of the porosity. Prior to the characterization of the previously mentioned techniques, the samples were evacuated at 573 K for 12 h.

X-ray diffraction patterns were recorded in a Bruker-AXS D5005 diffractometer with Bragg−Brentano geometry, using Cu Kα radiation and a diffracted beam graphite monochromator.

A Rupprecht and Patashnick TEOM 1500 mass analyzer was used to measure the uptakes of neopentane in the calcined and alkaline-treated ZSM-5 crystals. A thin layer of the sample was used for the uptake experiments, and the amount of the zeolite crystals loaded in the TEOM microreactor was 14.6 mg. A detailed description of the

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(16) Su, L.; Liu, L.; Zhuang, J.; Wang, H.; Li, Y.; Shen, W.; Xu, Y.; Bao, X. *Catal. Lett.* **2003**, *91*, 155−167.

(17) Xiao, F.-S.; Wang, L.; Yin, C.; Lin, K.; Di, Y.; Li, J.; Xu, R.; Su, D.; Schlögl, R.; Yokoi, T.; Tatsumi, T. *Angew. Chem., Int. Ed.* **2006**, *45*, 3090−3093.

(18) Kortunov, P.; Vasenkov, S.; Kärger, J.; Valiullin, R.; Gottschalk, P.; Fé Elía, M.; Perez, M.; Stöcker, M.; Drescher, B.; McKeever, L. D.; Berger, C.; Gläser, R.; Weitkamp, J. *J. Am. Chem. Soc.* **2005**, *127*, 13055−13059.

(19) Janssen, A. H.; Koster, A. J.; de Jong, K. P. *Angew. Chem., Int. Ed.* **2001**, *40*, 1102−1104.

(20) von Ballmoos, R.; Meier, W. M. *Nature* **1981**, *289*, 782−783.

(21) Groen, J. C.; Bach, T.; Ziese, U.; Paulaime-van Donk, A. M.; de Jong, K. P.; Moulijn, J. A.; Pérez-Ramírez, J. *J. Am. Chem. Soc.* **2005**, *127*, 10792−17093.

(22) Zhu, W.; van de Graaf, J. M.; van den Broeke, L. J. P.; Kapteijn, F.; Moulijn, J. A. *Ind. Eng. Chem. Res.* **1998**, *37*, 1934−1942.

(23) Zhu, W.; Kapteijn, F.; Moulijn, J. A. *Microporous Mesoporous Mater.* **2001**, *47*, 157−171.

(24) Althoff, R.; Schulz-Dobrick, B.; Schüth, F.; Unger, K. K. *Microporous Mater.* **1993**, *1*, 207−218.

(25) Lippens, B. C.; de Boer, J. H. *J. Catal.* **1968**, *4*, 319−323.

(26) Barret, E. P.; Joyner, L. G.; Halenda, P. H. *J. Am. Chem. Soc.* **1951**, *73*, 373−380.

(27) Saito, A.; Foley, H. C. *Microporous Mesoporous Mater.* **1995**, *3*, 531−542.

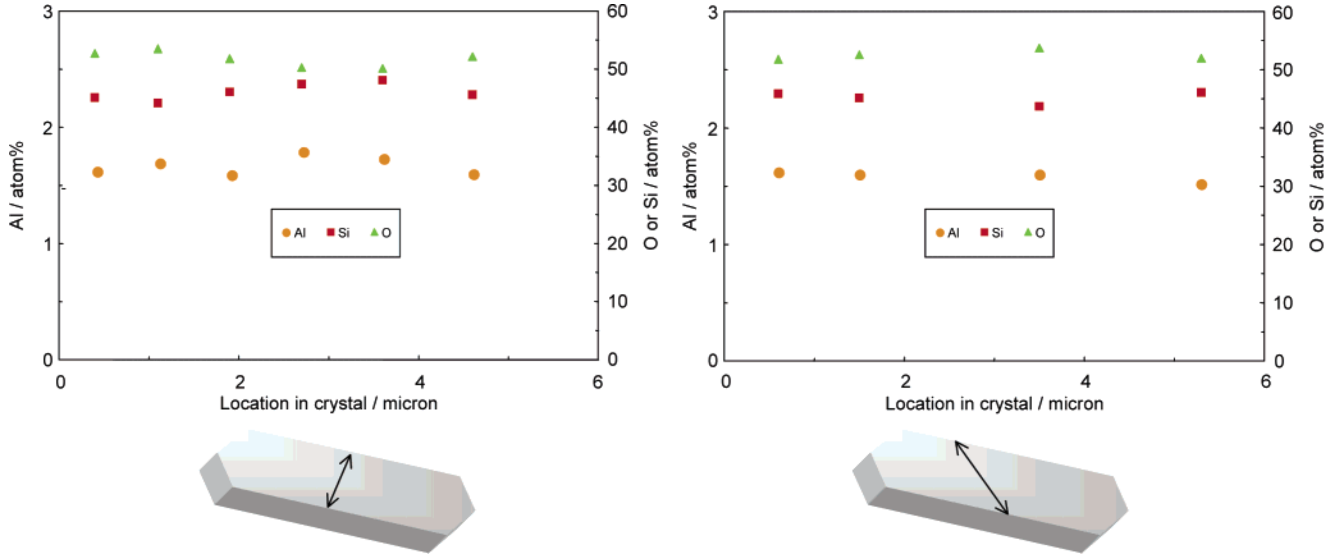

Figure 2. Concentration profiles in two different calcined ZSM-5 crystals by SEM-EDX point analysis, confirming the uniform distribution of the various elements throughout the crystal volume.

Table 1. Textural Properties and Chemical Composition of Calcined and Alkaline-Treated (Mesoporous) ZSM-5 Crystals

sample	molar Si/Al[a]	S_{BET}[b] ($\mathrm{m^2\,g^{-1}}$)	S_{meso}[c] ($\mathrm{m^2\,g^{-1}}$)	V_{micro}[c] ($\mathrm{cm^3\,g^{-1}}$)	$V_{\mathrm{meso,N2}}$[d] ($\mathrm{cm^3\,g^{-1}}$)	$V_{\mathrm{meso,Hg}}$[e] ($\mathrm{cm^3\,g^{-1}}$)
calcined	30	350	5	0.14	0.01	0.00
alkaline	24	415	120	0.12	0.16	0.13

[a] ICP-OES. [b] BET method. [c] *t*-plot. [d] Pore volume in the range of 4−100 nm derived from N_2 adsorption. [e] Pore volume in the range of 4−100 nm derived from Hg intrusion curve.

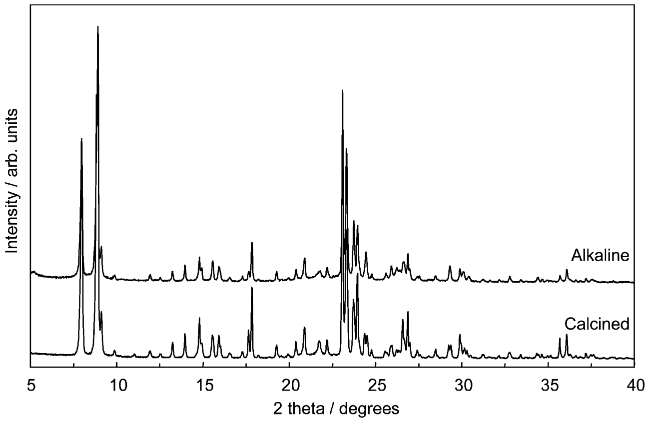

Figure 3. XRD patterns of the calcined and alkaline-treated crystals.

TEOM operating principles and transient measurements is given elsewhere.[22,23] Prior to the uptake experiments, the ZSM-5 crystals were outgassed in the following way. After a temperature rise with a rate of 10 K min^{-1} in a He flow of 200 cm^3 (NTP) min^{-1} (NTP: 298 K and 101.3 kPa), the sample was heated at 473 K overnight. The uptake of neopentane with a partial pressure of 0.476 kPa in flowing He (total flow rate of 200 cm^3 (NTP) min^{-1} and a total pressure of 127 kPa) was subsequently measured at 393 K.

Results and Discussion

Our synthesis procedure, adapted from previous work by Althoff et al.,[24] resulted in ca. 17 μm elongated crystals displaying a uniform concentration of aluminum throughout the crystal volume, as was evidenced by SEM-EDX analysis (Figure 1). Detailed point analysis of the aluminum, silicon, and oxygen concentrations in the calcined crystals is shown in Figure 2, confirming the minor local differences in concentration of the various elements. The textural properties and chemical composition are summarized in Table 1. It can be observed that the mesopore surface area in the calcined crystals, as derived from N_2 adsorption, is only 5 m^2 g^{-1}. This should be attributed to the purely microporous nature of the crystals coupled to a relatively large crystal size and a low surface roughness (Figure 1).

Upon alkaline treatment, the overall size and morphology of the outer surface of the zeolite crystals is not significantly affected as was evidenced by SEM, while XRD measurements have confirmed the intact crystalline structure (Figure 3). Despite the apparent preservation of the pristine crystal structure, N_2 adsorption has revealed a marked mesoporosity development. Contrary to the calcined sample, the nitrogen isotherm of the alkaline-treated zeolite crystals exhibits an enhanced uptake at higher pressures and a distinct hysteresis loop (Figure 4). The mesopore size distribution evidences newly created pores centered around 10 nm, leading to a mesopore surface area of 120 m^2 g^{-1}, whereas the micropore volume only decreases by 15% (Table 1). In addition, the isotherms obtained by high-resolution low-pressure argon adsorption indicate analogous adsorption properties at low relative pressures, suggesting preservation of the original micropore size, whereas the enhanced uptake of the alkaline-treated sample at higher relative pressures is in accordance with the mesoporosity as evidenced with N_2 adsorption (Figure 5a). The micropore size distributions derived from the argon adsorption isotherms using the Saito−Foley pore size model indeed confirm that the original micropore size is not affected by the alkaline treatment (Figure 5b), in agreement with previous observations over nanosized commercial ZSM-5 zeolites.[28,29] Moreover, the micropore volumes of 0.14 and 0.12 cm^3 g^{-1} obtained from the micropore size distributions of the calcined and alkaline-treated crystals,

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(28) Groen, J. C.; Peffer, L. A. A.; Moulijn, J. A.; Pérez-Ramírez, J. *Colloid Surf., A* **2004**, *241*, 53−58.
(29) Groen, J. C.; Moulijn, J. A.; Pérez-Ramírez, J. *Microporous Mesoporous Mater.* **2005**, *87*, 153−161.

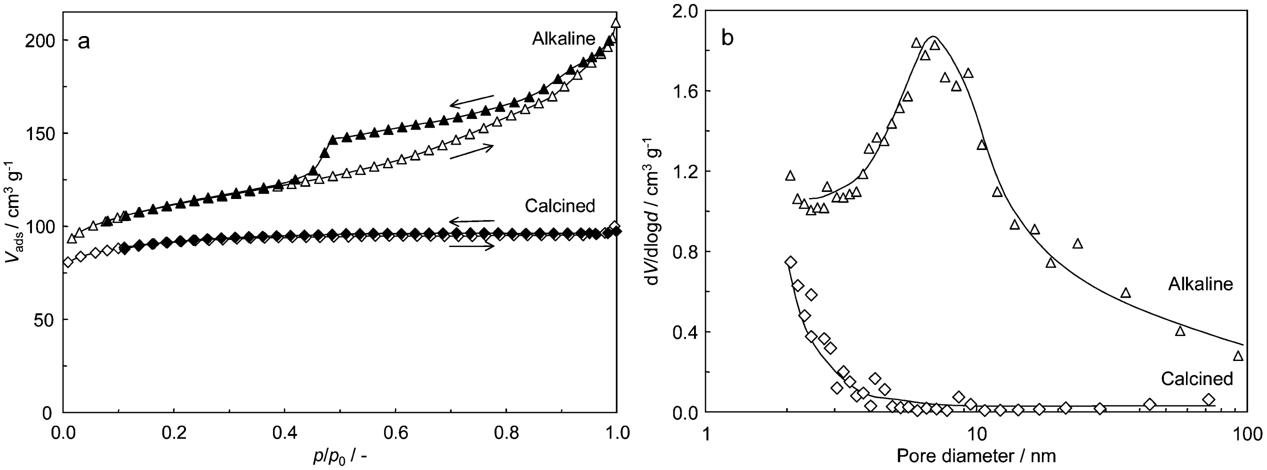

Figure 4. (a) N_2 adsorption−desorption isotherms at 77 K and (b) derived BJH mesopore size distributions (adsorption branch).

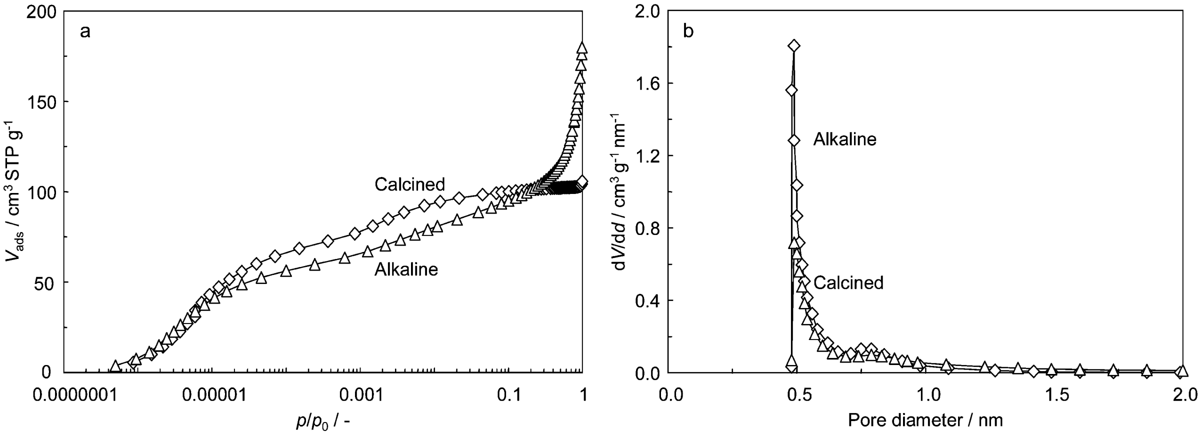

Figure 5. (a) High-resolution low-pressure Ar adsorption isotherms at 87 K and (b) SF micropore size distribution.

respectively, are in excellent agreement with those acquired by N_2 adsorption in Table 1.

Hg intrusion experiments on the calcined and alkaline-treated crystals reaffirmed our previous conclusions. Hardly any mercury can penetrate in the calcined zeolite crystals at higher pressures, indicating no significant porosity in the mesopore size range of 4 nm and larger, while in the alkaline-treated crystals a distinct, fully reversible intrusion occurs in the pressure range of 10−400 MPa, correlating with pores in the range of 4−200 nm (Figure 6). Moreover, the intruded volume of 0.13 cm^3 g^{-1} is in reasonable agreement with the mesopore volume of 0.16 cm^3 g^{-1} derived from N_2 adsorption (Table 1).

The observations that (i) the pore size and volume of both techniques are in good agreement and (ii) the Hg intrusion and extrusion curves exhibit full reversibility provide manifest evidence that the mesoporosity in the alkaline-treated zeolite is entirely accessible from the outer surface, supporting the presence of a connected network of mesopores. This is a crucial requisite when improved diffusion is desired. The presence of solely isolated mesopores or cavities would typically lead to a negligible intrusion of mercury,[30] whereas a low degree of interconnectivity would lead to irreversible intrusion curves due to mercury entrapment.[31]

Diffusion studies in zeolites are frequently carried out using hydrocarbons as probe molecules.[32,33] One of the drawbacks in the use of hydrocarbons over acidic zeolites can be cracking processes resulting in coke formation even at typically applied low temperatures. Particularly, the latter phenomenon is detrimental when explicit assessment of the diffusion properties is attempted. To verify the improved transport properties of the alkaline-treated ZSM-5 crystals, we selected neopentane as a probe to make a comparative study on the uptakes in the calcined and alkaline-treated samples. First, the relatively large molecular size of neopentane, which is similar to the channel openings of ZSM-5, allows an accurate assessment of the uptake rates. In addition, the low predisposition of neopentane to cracking over acidic zeolites as compared to other hydrocarbons avoids eventual coke formation.[34]

As expected, the uptake of neopentane in the calcined ZSM-5 crystals as measured in the TEOM is extremely slow (Figure 7a). Approximately 120 min are required to reach 50% of the maximum uptake. Contrary, the uptake rate of neopentane in the alkaline-treated ZSM-5 crystals is greatly enhanced, especially in the initial stage where the uptake is sharply increased and a similar uptake of 50% is achieved only after 2 min. At

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(30) Janssen, A. H.; Koster, A. J.; de Jong, K. P. *J. Phys. Chem. B* **2002**, *106*, 11905−11909.

(31) Wardlaw, N. C.; McKellar, M. *Powder Technol.* **1981**, *29*, 127−143.

(32) van Donk, S.; Bitter, J. H.; Verberckmoes, A.; Versluijs-Helder, M.; Broersma, A.; de Jong, K. P. *Angew. Chem., Int. Ed.* **2005**, *44*, 1360−1363.

(33) Bonardet, J.-L.; Domeniconi, T.; N'Gokoli-Kékélé, P.; Springuel-Huet, M.-A.; Fraissard, J. *Langmuir* **1999**, *15*, 5836−5840.

(34) Ono, Y.; Osako, K.; Yamawaki, M.; Nakashiro, K. *Stud. Surf. Sci. Catal.* **1994**, *83*, 303−312.

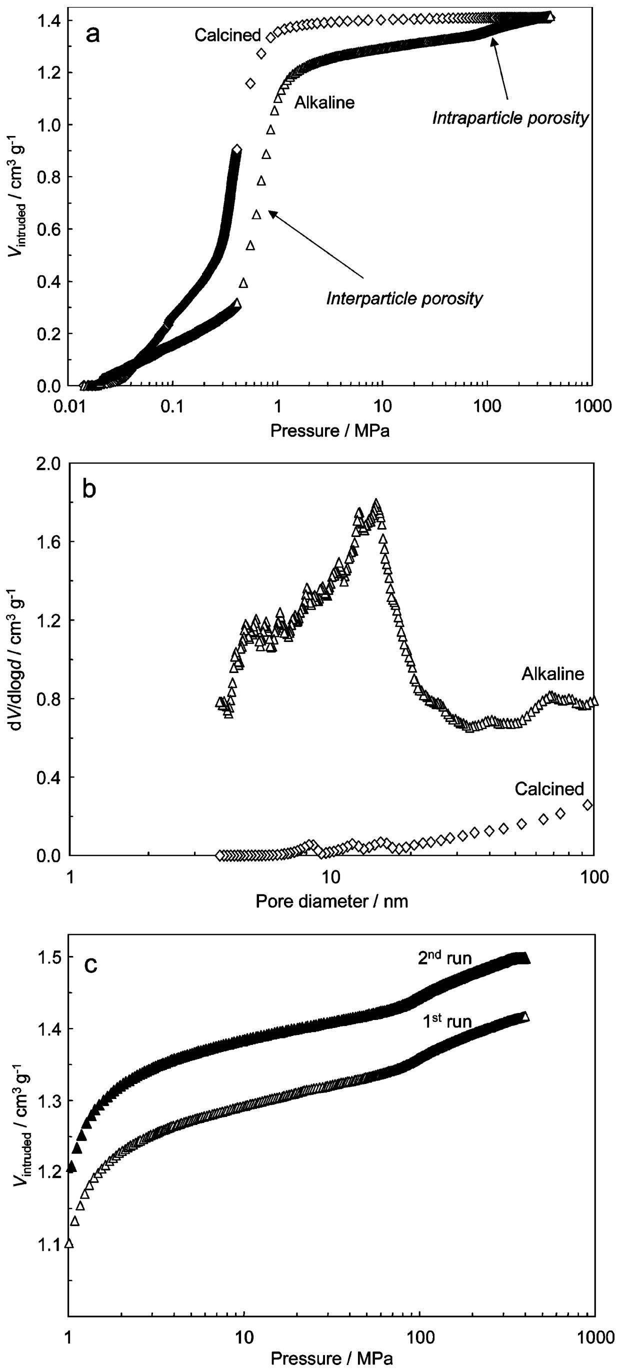

Figure 6. (a) Hg intrusion curves and (b) derived mesopore size distributions. (c) Reversibility of the intrusion curves of the mesoporous crystals at high pressure. For the sake of clarity, the re-intrusion curve (second run) is shifted 0.1 cm^3 g^{-1} upward.

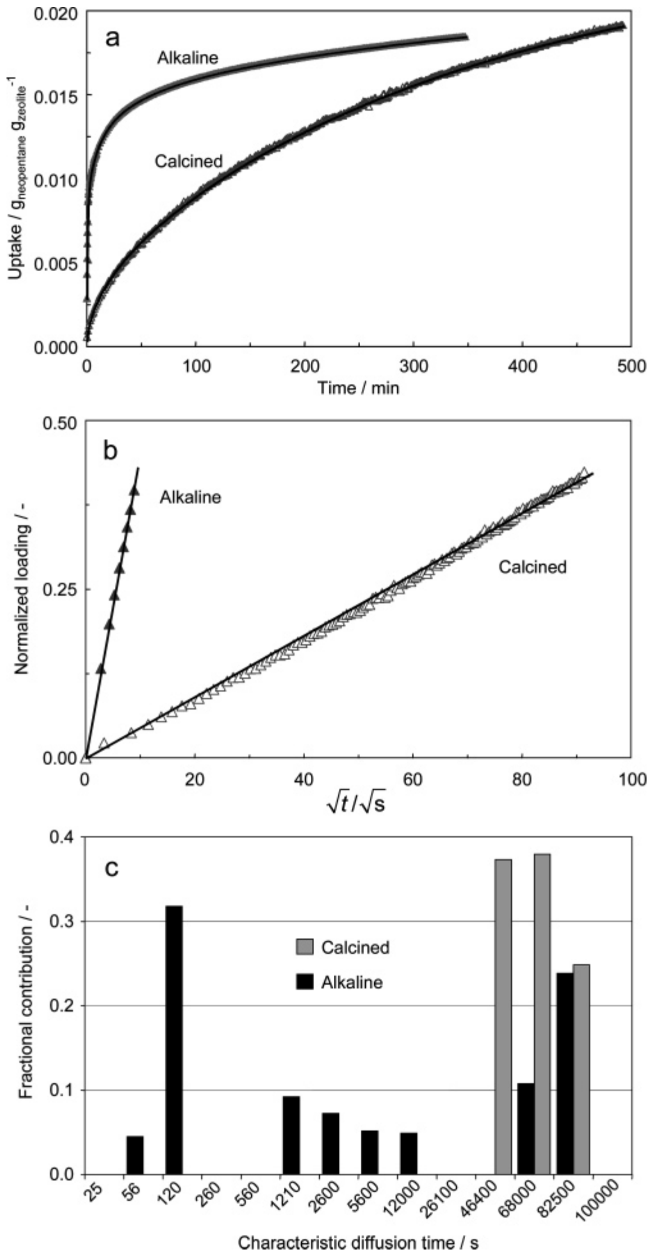

Figure 7. (a) Neopentane uptake curves of the calcined and alkaline-treated ZSM-5 crystals measured in the TEOM at 393 K. Lines are obtained by fitting using eq 1. (b) Normalized uptake profiles in a short time domain. Straight lines correspond to fitting by eq 2. (c) Distribution of diffusion lengths in the calcined and alkaline-treated crystals derived from the fitted lines in panel a.

the conditions applied, the amount of neopentane adsorbed in the alkaline-treated crystals after achieving equilibrium was ca. 15% lower than in the calcined counterparts, which can be ascribed to the lower micropore volume of the former, as was derived from N_2 adsorption data (Table 1). The uptake curves in Figure 7a were reproduced several times over the same sample, confirming that the reaction accompanied by coke formation indeed can be discarded, and thus, the observed differences should be entirely ascribed to altered diffusion properties. The absence of coke in the neopentane-contacted zeolites after TEOM experiments was furthermore confirmed by thermogravimetric analyses.

From a fundamental point of view, the alkaline treatment does not change the micropore properties of ZSM-5 in terms of adsorption and diffusion, which indicates that the intrinsic diffusivity of neopentane in the micropores should be the same in the two samples. Therefore, the enhanced uptake rate of neopentane in the alkaline-treated ZSM-5 crystals must be attributed to an improved accessibility to and a shorter diffusion path length in the micropores resulting from an accessible network of mesopores obtained by selective framework silicon extraction.

Further quantification of the diffusion properties in the different zeolite crystals was attained using Fick's second law, which describes the change of the concentration of molecules inside the zeolite crystals as a function of time

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2}\right) \tag{1}$$

During the initial stage of uptake in a slab-like crystal, the following appropriate solution applies:

$$\frac{q(t)}{q(\infty)} = \frac{2}{\sqrt{\pi}}\sqrt{\frac{D}{L^2}}\sqrt{t} \tag{2}$$

where $q(t)/q(\infty)$ is the normalized loading, D is the diffusivity, L is the characteristic diffusion length, and t is time.[2] The characteristic diffusion length L of the crystals in the calcined zeolite was derived from high-resolution SEM and estimated at 0.8 μm ($L = V_p/S_p$ for slab-like particles, where V_p and S_p are the volume and external surface area of the particle, respectively). Plotting the normalized loading versus the square root of time for the calcined crystals leads to a straight line, as shown in Figure 7b. This fitting adequately describes the experimental data covering the uptake curve up to $q(t)/q(\infty) \sim 0.8$ and leads to a characteristic diffusion time of $L^2/D = 6.3 \times 10^4$ s. Combined with $L = 0.8$ μm, a diffusivity D of approximately 1×10^{-17} m^2 s^{-1} is obtained. Since the diffusivity in both zeolite systems is the same, the neopentane uptake curve over the alkaline-treated crystals can then be used to estimate the characteristic diffusion length in the modified zeolite. The characteristic diffusion time has been determined during the initial uptake up to $q(t)/q(\infty) = 0.5$, where a straight line has been obtained (Figure 7b). This provides an average characteristic diffusion time of 5.8×10^2 s, which is more than 2 orders of magnitude shorter than in the calcined crystals. The resulting characteristic diffusion length is ca. 0.08 μm and accounts for ca. 50% of the total uptake. The extraction of framework silicon upon alkaline treatment obviously will induce some heterogeneity in the various regions of the desilicated crystals. Accordingly, the uptake curve of neopentane over the alkaline-treated crystals is the result of a distribution of diffusion lengths. Fitting the entire uptake curves in Figure 7a by means of eq 1 leads to a distribution of diffusion lengths showing that in the alkaline-treated sample more than 60% of the original micropore network was effectively shortened upon controlled desilication, while the remaining fraction remained intact (Figure 7c). This can be correlated with the straight part of the curve in Figure 7b that accounts for ca. 50% of the total uptake and further confirms that the action of the alkaline treatment in the zeolite crystal is macroscopic rather than having a localized character.

In summary, we have shown that desilication in alkaline medium of large ZSM-5 crystals, presenting a homogeneous distribution of framework aluminum, originates in an accessible interconnected network of intracrystalline mesopores and preserved crystallinity. As a result, the characteristic diffusion path length in the mesoporous crystals is dramatically shortened, resulting in an approximately 2 orders of magnitude faster diffusion of neopentane in the majority of the micropores, whereas ca. one-third of the crystal volume is not affected by the treatment. The substantial mesoporosity and in particular its high degree of accessibility makes desilication an advantageous approach to manufacture hierarchically structured micro- and mesoporous ZSM-5 zeolites for improved gas transport properties as compared to the classical dealumination post-treatments. This enables a more efficient utilization of the zeolite in industrially relevant processes that are affected by diffusional limitations. Besides, in view of its simplicity and reproducibility,[13] desilication is a preferable modification method over the more laborious novel approaches such as the carbon templating route or the preparation of composites by incorporation of zeolite nanocrystals in mesoporous supports.

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