

Optimal Aluminum-Assisted Mesoporosity Development in MFI Zeolites by Desilication

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Tetrahedrally coordinated aluminum in MFI zeolite frameworks controls the mechanism of intracrystalline mesopore formation by desilication in alkaline medium. The optimal molar Si/Al ratio in the range of 25–50 enables a controlled mesoporosity development with preserved crystalline and acidic properties, potentially leading to a more efficient zeolite utilization by improved diffusion characteristics.

Zeolites find widespread use in industry as heterogeneous catalysts due to a unique combination of properties such as high surface area, well-defined porosity, high thermal stability, intrinsic acidity, and the ability to confine active metal species. A more efficient use of zeolite-based catalysts can be foreseen if diffusional limitations in the microporous network could be minimized by mesopore formation in zeolite crystals. A relatively novel approach to induce mesoporosity is carbon templating, where porous carbon or carbon nanotubes are included in the synthesis of the zeolite, thereby leaving pores in the zeolite matrix after combustion of the carbon higher temperature.^{1–3} Although substantial mesoporosity can be obtained in this way, the crystallinity of the final product is often a major issue and this requires an adaptation and thorough optimization of the synthesis parameters. A different, well-established methodology to create mesoporosity in zeolites is by posttreatment of the parent zeolite. For instance, dealumination, which is generally achieved by steam treatment or, to a larger extent, by acid leaching, leads to selective removal of Al from the framework. Dislodgement of framework Al directly impacts on the (Brønsted) acidic properties of the dealuminated zeolite, often leading to formation of Lewis acid sites, which can be beneficial in specific catalytic applications. It is obvious that for mesoporosity development this method is primarily effective for zeolites with a relatively high Al content (low Si/Al ratios), such as zeolite Y and mordenite,⁴ but the acidic properties will unavoidably be altered. Recently, Si extraction by alkaline treatment (desilication) has been introduced as an effective approach to create significant extraporosity in various zeolites among which MFI zeolites appear to be the most suitable.^{5–11} The developed porosity is obtained by preferential extraction of framework Si due to hydrolysis in the presence of OH[−], basically preserving the Al environment and the related acidic properties. Due to its relative novelty, only a few studies have been reported on the optimization of this treatment. Previous investigations have shown the influence of time and temperature of the alkaline treatment on the kinetics of desilication for tuning mesoporosity formation.^{6,9} However, the influence of a more intrinsic parameter of the zeolite, the Si/Al ratio, has not been studied. Accordingly, this communication

highlights the role of aluminum on the desilication process and mechanism of pore formation in MFI zeolites. Framework Al highly determines the susceptibility of the zeolite toward Si extraction and acts as a mesopore-directing agent in the mechanism of pore formation during desilication in alkaline medium.

Table 1 shows the commercial ZSM-5 zeolites used in this study, which cover a broad range of nominal molar Si/Al ratios (15–1000). The alkaline treatment procedure has been described in detail elsewhere.⁹ Briefly, the zeolite was stirred in an aqueous NaOH solution at controlled temperature for a certain period of time. The remaining solid product was filtered, thoroughly washed, and dried at 373 K for 12 h. The alkaline-treated samples were converted into the H-form by ion exchange in 0.1 M NH₄NO₃ solution followed by calcination in air at 823 K for 5 h. The as-received materials were calcined under identical conditions, prior to the characterization and are hereafter denoted as nontreated.

N₂ adsorption and desorption isotherms at 77 K were measured on a Quantachrome Autosorb-6B gas sorption analyzer after a vacuum pretreatment at 573 K. Si and Al concentrations in the zeolites and filtrate obtained after alkaline treatment were determined by ICP-OES on a Perkin-Elmer Optima 3000DV. Fourier transform Infrared spectra were recorded in He at 473 K on a Nicolet Magna 860 Fourier transform spectrometer using a Spectratech diffuse reflectance (DRIFT) accessory, equipped with a high-temperature cell.

N₂ adsorption measurements on the nontreated ZSM-5 samples resulted in type I isotherms with a limited uptake of N₂ at higher relative pressures and no distinct hysteresis loop, typical for a microporous material without significant mesoporosity.¹² Application of the *t*-plot method¹³ confirms that the majority of the surface area (>90%) is obtained by microporosity (Table 1).

Alkaline treatment of the zeolites in NaOH leads to spectacular differences in mesopore formation. Development of mesoporosity in Z-35 was studied by us previously⁹ and has been shown to result in substantial mesoporosity (240 m² g^{−1}) in the final product upon treatment in 0.2 M NaOH at 338 K for 30 min. Ogura et al.⁶ applied similar treatment conditions to sample Z-20, and surprisingly, this hardly induced any mesopore formation (~15 m² g^{−1}). Only at a higher temperature (353 K) and preferably longer treatment times (>30 min), did

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TABLE 1: Chemical Composition and Textural Properties of the Nontreated Commercial MFI Zeolites

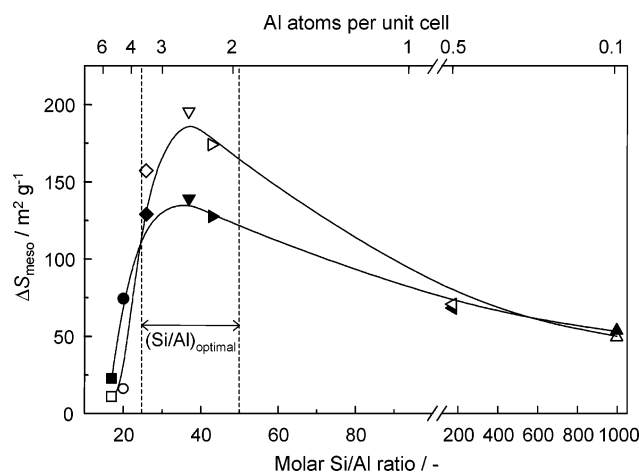
sample name	code and supplier	Si/Al ^a	S_{BET}^b (m ² g ⁻¹)	S_{meso}^c (m ² g ⁻¹)	V_{micro}^c (cm ³ g ⁻¹)	V_{meso}^d (cm ³ g ⁻¹)
Z-15	CBV 3024E, Zeolyst	17	415	40	0.15	0.10
Z-20	NTZS-4, TOSOH	19	400	10	0.16	0.03
Z-25	PZ 2/40, Chemie Uetikon	26	410	35	0.16	0.10
Z-35	CBV 8020, Zeolyst	37	430	40	0.17	0.09
Z-40	CBV 8014, Zeolyst	42	415	45	0.16	0.14
Z-200	PZ 2/400, Chemie Uetikon	176	405	30	0.17	0.06
Z-1000	T-960502, TOSOH	1038	390	15	0.16	0.03

^a Measured by ICP-OES. ^b BET method. ^c *t*-plot method. ^d $V_{\text{meso}} = V_{\text{ads},p/p_0=0.99} - V_{\text{micro}}$.

TABLE 2: Chemical Composition and Textural Properties of the Alkaline-Treated (at) MFI Zeolites in 0.2 M NaOH for 30 min at Different Temperatures

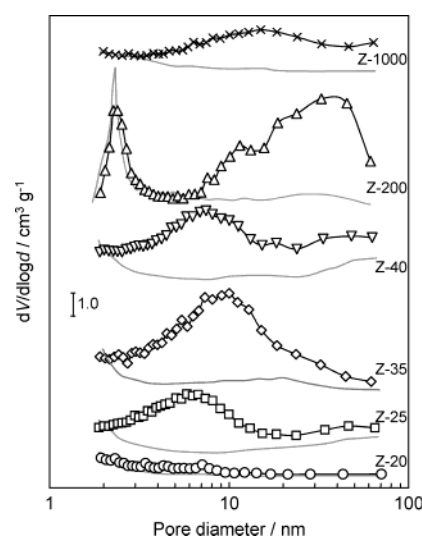
sample name	Si/Al ^a	$T = 338 \text{ K}$				$T = 358 \text{ K}$			
		S_{BET}^b (m ² g ⁻¹)	S_{meso}^c (m ² g ⁻¹)	V_{micro}^c (cm ³ g ⁻¹)	V_{meso}^d (cm ³ g ⁻¹)	S_{BET}^b (m ² g ⁻¹)	S_{meso}^c (m ² g ⁻¹)	V_{micro}^c (cm ³ g ⁻¹)	V_{meso}^d (cm ³ g ⁻¹)
Z-15-at	15	390	50	0.14	0.16	14	410	65	0.14
Z-20-at	18	385	25	0.14	0.04	16	425	80	0.14
Z-25-at	18	505	195	0.13	0.31	17	470	165	0.14
Z-35-at	24	510	235	0.13	0.48	23	505	180	0.13
Z-40-at	29	540	225	0.13	0.61	28	490	180	0.13
Z-200-at	133	425	105	0.16	0.33	11	445	100	0.16
Z-1000-at	560	475	75	0.16	0.20	460	440	80	0.15

^a Measured by ICP-OES. ^b BET method. ^c *t*-plot method. ^d $V_{\text{meso}} = V_{\text{ads},p/p_0=0.99} - V_{\text{micro}}$.

**Figure 1.** Evolution of the mesopore surface area vs the molar Si/Al ratio of the investigated MFI zeolites upon 30 min of alkaline treatment in 0.2 M NaOH at 338 K (open symbols) and 358 K (solid symbols).

some significant mesoporosity ($>60 \text{ m}^2/\text{g}$) develop, which is confirmed by our results (Table 2).

This difference in mesopore development strongly points to the crucial role of the framework Si/Al ratio of the zeolite in the mesoporosity formation process. To further investigate the impact of the Si/Al ratio, the zeolites in Table 1 were alkaline treated in 0.2 M NaOH for 30 min at temperatures of 338 and 358 K (Table 2). This leads to a remarkable volcano-type dependency of the mesopore surface area on the Si/Al ratio (Figure 1). ΔS_{meso} represents the increase in mesopore area as a consequence of the alkaline treatment, i.e., corrected for the mesopore surface area of the nontreated materials given in Table 1. The Si/Al range of 25–50 appears to be optimal for mesopore formation upon desilication leading to increased mesopore surface areas up to $\sim 200 \text{ m}^2 \text{ g}^{-1}$ and mesopores centered around 9 nm, as determined from the BJH¹⁴ pore size model, applied to the adsorption branch of the N_2 isotherm (Figure 2). The pore size distributions (PSDs) of the nontreated zeolites are also shown in the figure (gray line) for comparative purpose. At Si/Al < 25 and a treatment temperature of 338 K hardly any

**Figure 2.** BJH¹⁴ adsorption pore size distribution of the various nontreated (gray lines) and alkaline-treated (symbols) MFI zeolites. Conditions of alkaline treatment: 0.2 M NaOH at 338 K for 30 min.

increase in mesopore surface area is observed, in agreement with a relatively low Si extraction, as determined by ICP analysis of the filtrate (Figure 3). In contrast to this, a much higher degree of Si dissolution was found for zeolites with a high Si/Al ratio, and pores are being created in a very wide range of preferentially larger pore sizes and consequently the mesopore volume is rather high compared to the newly created mesopore surface area. Use of a higher treatment temperature (358 K) in particular impacts on the materials with a lower Si/Al ratio and leads to an enhancement of extracted Si and mesopore formation, whereas the zeolites containing less aluminum suffer from uncontrolled Si extraction resulting in a further enlargement of the mesopores and a decrease in specific surface area.⁹ The BJH pore size distribution in Figure 2 might suggest a well-defined distribution of pores around 2 nm in alkaline-treated Z-200. However, this contribution does not represent real pores and is a result of a fluid-to-crystalline like phase transition of the adsorbed phase,

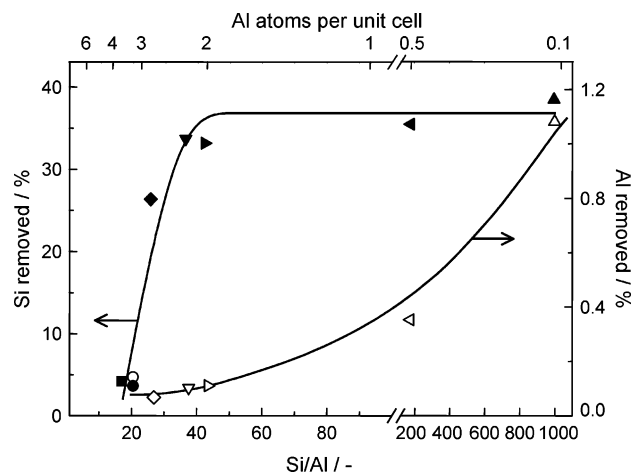


Figure 3. Percentage of removed Al (open symbols) and Si (solid symbols) from the various zeolites as measured in the filtrate upon alkaline treatment in 0.2 M NaOH at 338 K for 30 min.

which is typical for ZSM-5 zeolites and depends on the framework Si/Al ratio and synthesis procedure.^{15,16}

The remarkable behavior in Figures 1 and 2 is a consequence of the zeolite framework Si/Al ratio, which influences the kinetics of Si extraction and mechanism of porosity development, as is schematically represented in Scheme 1. As a result of the negatively charged AlO_4^- tetrahedra, hydrolysis of the Si–O–Al bond in the presence of OH^- is hindered compared to the relatively easy cleavage of the Si–O–Si bond in the absence of neighboring Al tetrahedra.¹⁷ Materials with a relatively high density of framework Al sites (low Si/Al ratio) are relatively inert to Si extraction and require the use of a higher temperature to obtain some degree of mesopore formation, whereas a relatively low Al content (high Si/Al ratio) induces the opposite effect. An intermediate framework Al content (optimal molar Si/Al ratio in the range 25–50) appropriately regulates the extent of Si extraction, leading to controlled porosity development. As the desilication process is initiated at the more susceptible silanol groups at the outer surface of the crystals, it is expected that the crystal size will impact on

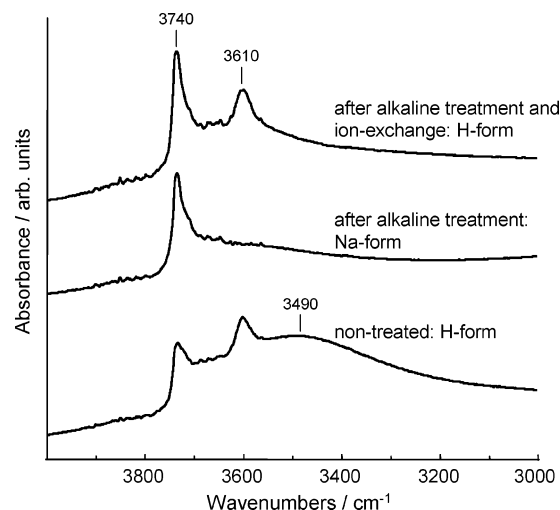


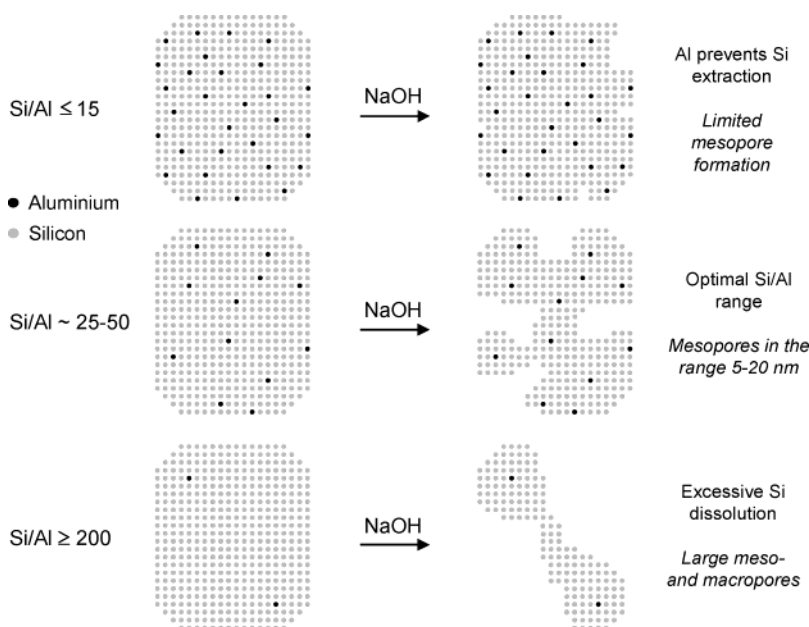
Figure 4. FT-IR spectra in He at 473 K of nontreated and alkaline-treated Z-35 in the OH stretching region.

the kinetics of Si extraction during alkaline treatment. This phenomenon is currently being investigated.

Formation of mesopores in the nm-size range (Figure 2) requires the dissolution of a significant volume of the zeolite crystals and consequently should be accompanied by the removal of both framework Si and Al. However, only a small fraction of the expected Al is measured in the filtrate after alkaline treatment (Figure 3). This leads us to believe that not all Al removed from the framework upon mesopore formation remains in the liquid phase but is reinserted in the treated zeolite (realumination), because the crystallinity and acidity are mostly preserved.^{9,10} The creation of mesopores, whose size clearly depends on the framework Al content, and the fact that the filtrate only contains a fraction of the expected Al, strongly suggest the coexistence of various Al sites,¹⁸ which are more or less susceptible to hydrolysis in NaOH solution.

FT-IR measurements over Z-35 in Figure 4 confirm that an optimal alkaline treatment in general preserves the zeolite acidity, supporting previously reported NH_3 -TPD results.¹⁰ The absorption band at 3610 cm^{-1} , which is typical of Brønsted acid

SCHEME 1: Simplified Schematic Representation of the Influence of the Al Content on the Desilication Treatment of MFI Zeolites in NaOH Solution and the Associated Mechanism of Pore Formation



sites, disappears after alkaline treatment but is fully regained upon ion exchange in 0.1 M NH_4NO_3 and subsequent calcination of the alkaline-treated zeolite. This acidity preservation is applicable to the various studied zeolites. Interestingly, no signs of extraframework Al species (3660 cm^{-1}) can be observed in the alkaline-treated sample, which has been confirmed by ^{27}Al MAS NMR measurements (not shown). In the alkaline-treated Z-35, the band at 3740 cm^{-1} becomes more intense whereas the broad band at 3590 cm^{-1} vanishes, indicating the development of isolated silanol groups and the removal of hydroxyl nests, respectively. These observations corroborate the hypothesis that mesoporosity formation is initiated preferentially at boundaries or defect sites of the zeolite crystals,¹¹ leading to a decrease of the respective absorption bands. The mesoporosity development, however, is accompanied by the creation of new isolated silanol groups at the higher “external” surface of these mesopores, inducing a more intense contribution at 3740 cm^{-1} . Moreover, realumination during the treatment would lead to “healing” of the hydroxyl nests, as was previously observed by various authors when treating zeolite β with Al-isopropoxide¹⁸ or Na-aluminate¹⁹ and dealuminated USY zeolite in alkaline medium,^{20,21} and results in a further decrease of the corresponding infrared band.

In summary, we have identified that the presence of framework Al plays a key role in the mechanism of mesopore formation in MFI zeolites in alkaline medium. The presence of high Al concentrations in the MFI zeolite framework ($\text{Si}/\text{Al} < 20$) prevents Si from being extracted, and thus limited pore formation is obtained, whereas highly siliceous zeolites ($\text{Si}/\text{Al} \gg 50$) show excessive and unselective Si dissolution, leading to creation of relatively large pores. A framework Si/Al ratio of 25–50 is optimal for a substantial intracrystalline mesoporosity combined with generally preserved Al centers. The knowledge on the regulating role of framework Al enables well-controlled desilication of MFI zeolites, which offers great potential in diffusion-limited applications, especially those in which acidic sites are favorable, due to a more efficient

utilization of the zeolite crystal by an improved intracrystalline diffusion to and from the active sites.

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