Simultaneous improvement of accessibility and hydrophobicity in zeolites: water-tolerant nanosized crystals

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Resumo/Abstract

RESUMO - Zeólitas apresentam limitações difusionais devido à presença exclusiva de microporos. A redução do tamanho dos cristais aumenta a acessibilidade, mas resulta em maior densidade de silanóis, prejudicando a estabilidade hidrotérmica. Neste trabalho, foram sintetizadas zeólitas do tipo MFI com tamanhos variando de 1200 a 70 nm para investigar a relação entre tamanho de cristal e estabilidade hidrotérmica.
Palavras-chave: cristais nanométricos, silicalita-1, estabilidade hidrotérmica.

ABSTRACT - Zeolites suffer from diffusion limitations due to their purely microporous structure. Reducing crystal size enhances accessibility but increases silanol density, compromising hydrothermal stability. In this study, MFI-type zeolites ranging from 1200 to 70 nm were synthesized to investigate the relation between crystal size and hydrothermal stability.
Keywords: nanosized crystals, silicalite-1, hydrothermal stability.

Introduction

Zeolites, also known as molecular sieves, are microporous crystalline aluminosilicates with relevant applications in ion exchange, adsorption, and catalysis. Their micropores (0.3-2 nm) form a regular network of channels and cages with distinct sizes and shapes (1).

However, zeolite-catalysed reactions may face severe limitations related to the diffusion of bulky molecules within the micropores. A straightforward strategy to overcome this challenge relies on reducing the zeolite particles to nanometric scale, thus improving pore accessibility (1,2). This approach, however, leads to a significant increase of silanol defects, which compromises the hydrothermal stability of the zeolite (2,3).

The central focus of this work is to obtain hidrothermally stable nanosized MFI type zeolites (with particle sizes smaller than 100 nm) through the development of silanol defect-healing strategies.

Experimental

MFI Zeolites Synthesis

The pure silica silicalite-1 (MFI type) synthesis was performed based on a hydrothermal method described previously by Medeiros-Costa (4). The hydrothermal conditions and the molar composition of the precursor solution for each synthesis are summarized in Table 1. In a usual synthesis protocol, TPAOH (tetrapropylammonium hydroxide solution, 1.0 mol/L in H_2O, Aldrich), deionized water and TEOS (tetraethyl orthosilicate, 98%, Aldrich) were stirred for 18 h. Then, the precursor solution was hydrothermally treated in a Teflon-lined stainless-steel autoclave. The zeolite was purified, dried overnight and calcined at 550 ºC/5 h to remove the organic template. This resulted in calcined MFI-x samples, where x indicates crystal size.

Table 1. Synthesis conditions for obtaining silicalite-1.

Sample	Precursor solution	Temperature (ºC)	Time (h)
MFI-70	1 SiO_2:0,28 TPAOH:12 H_2O	80	28
MFI-100	1 SiO_2:0,28 TPAOH:12 H_2O	90	28
MFI-170	1 SiO_2:0,28 TPAOH:40 H_2O	90	28
MFI-330	1 SiO_2:0,28 TPAOH:40 H_2O	140	360
MFI-1200	1 SiO_2:0,14 TPAOH:40 H_2O	170	360

Stability Test of MFI Zeolites

The tests assessing the zeolites' hydrothermal stability were conducted based on the procedure described by Resasco and coworkers (3). In each run, 0.5 g of calcined zeolite and 25 mL of deionized water were loaded into a Teflon-lined stainless steel autoclave. The stability tests were carried out at 190°C for 7 days. Then, the sample was recovered by centrifugation and dried overnight.

Results and Discussion

Synthesis of silicalite-1 samples

Fig. 1 shows the X-ray diffractograms of the calcined silicalite-1 samples. A decrease in particle size leads to a noticeable reduction in peak intensity and a broadening of the diffraction peaks.

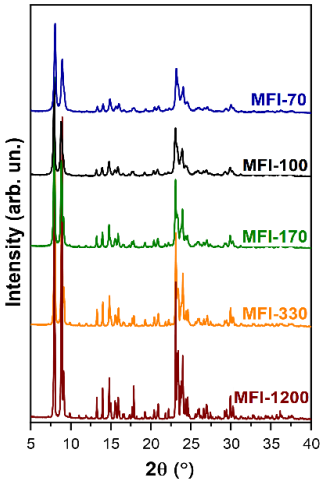

Figure 1. XRD patterns of calcined silicalite-1.

$^{29}Si\{^{1}H\}$ CP-MAS NMR spectra (cross-polarized with hydrogen) are shown in Fig. 2, where the signal is intensified by hydrogen from SiOH groups. Highly crystalline zeolites show dominant Q^4 peaks, related to $Si(OSi)_4$ species, in a narrower region at -110 to -120 ppm, as observed for MFI-1200. For the other samples, a broadening of the Q^4 signal is observed with the decrease in crystal size. The region from -90 to -105 ppm refers to Q^2 and Q^3 regions, related to $Si(OSi)_2(OH)_2$ and $Si(OSi)_3(OH)_1$ respectively, associated with silanol defects.

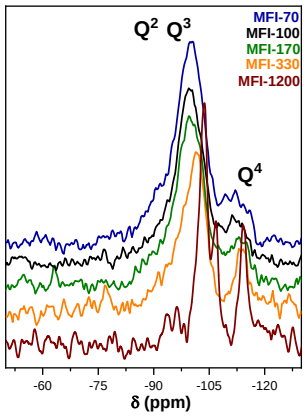

Figure 2. $^{29}Si\{^{1}H\}$ CP-MAS NMR spectra of calcined silicalite-1 samples.

Stability Test of MFI Zeolites

As shown in Fig. 3, the MFI-1200 sample preserved its crystallinity after hydrothermal treatment at 190 °C for 7 days, while the MFI-70 sample exhibited significant loss of crystallinity. This instability is associated with the higher concentration of surface silanol defects in the nanosized sample. As reported by Resasco *et al.* (3), defective sites are a key factor influencing the stability of zeolites in hot liquid water. To address this issue, post-synthesis strategies aimed at healing silanol defects will be explored to enhance the hydrothermal stability of nanosized MFI zeolites.

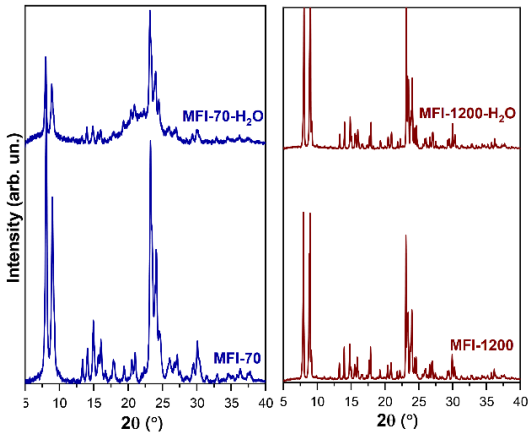

Figure 3. X-ray diffraction patterns comparing the stability in hot water at 190 ºC for 7 days of MFI-1200 and MFI-70.

Conclusions

Silicalite-1 samples with crystal sizes ranging from 1200 to 70 nm were synthesized via hydrothermal treatment and evaluated for hydrothermal stability in hot liquid water. The MFI-1200 remained stable, whereas the 70 nm sample showed significant crystallinity loss, attributed to a higher concentration of surface silanol defects. Post-synthesis defect-healing strategies will be investigated to enhance the hydrothermal stability of nanosized MFI zeolites.

Acknowledgments

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