Direct nanoscale observation of zeolite framework dynamics during bioethanol dehydration catalysis

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Resumo/Abstract

RESUMO - Zeólitas são materiais de destaque em processos de catálise heterogênea e separação, principalmente devido às suas estruturas microporosas bem definidas. Contudo, apesar dos avanços significativos, aspectos fundamentais relacionados à adsorção e difusão molecular sob confinamento nanoporoso ainda permanecem pouco compreendidos. A flexibilidade estrutural intrínseca dessas redes tem sido reconhecida como um fator chave que modula suas propriedades de adsorção, difusão e atividade catalítica. Neste trabalho, utilizamos imageamento por difração coerente de raios X de Bragg, em condições *in situ* e com resolução temporal, para visualizar diretamente as dinâmicas de rede cristalina de zeólitas sob ambiente reacional. Acompanhamos a evolução das deformações estruturais durante a reação de desidratação do etanol, com o objetivo de revelar como as estruturas respondem ao confinamento molecular e às condições catalíticas. Compreender esses comportamentos dinâmicos em nível nanoscópico é essencial para impulsionar o desenvolvimento de zeólitas com propriedades otimizadas de adsorção e seletividade.

Palavras-chave: Zeólitas, Dinâmica de rede, Imageamento in situ

ABSTRACT - Zeolites are key materials in heterogeneous catalysis and separation processes due to their well-defined microporous structures. However, despite extensive studies, fundamental questions remain regarding molecular adsorption and diffusion within their nanoporous frameworks. Notably, the intrinsic framework flexibility of zeolites is increasingly recognized as a critical factor influencing their adsorption, diffusion, and catalytic behavior. In this work, we employ *in situ* time-resolved Bragg coherent X-ray diffraction imaging to directly visualize the nanoscale lattice dynamics of zeolite crystals under catalytic conditions. By monitoring the evolution of crystal lattice deformations during ethanol dehydration reaction, we aim to uncover how zeolite frameworks respond to molecular confinement and reaction environments. Gaining insights into these dynamic structural responses is crucial to advancing the rational design of zeolites with enhanced adsorption capacities and catalytic selectivities.

Keywords: Zeolites, Lattice dynamics, In situ imaging

Introduction

Environmental concerns are driving the development of alternative routes for producing chemicals currently sourced from petroleum. Catalytic bioethanol dehydration represents a sustainable approach to obtain diethyl ether (DEE) and ethylene, key chemicals for fuel additives, solvents, and polyethylene production. Zeolites stand out as efficient catalysts for this process, offering higher activity and selectivity at lower temperatures due to their nanoporous frameworks and tailored acidity.

However, the catalytic performance of zeolites is intimately linked to the intracrystalline diffusion of molecules, a complex phenomenon affected by framework deformations — commonly referred to as zeolite flexibility. This flexibility, triggered by factors such as temperature, cation migration, and molecular adsorption, can alter pore dimensions, connectivity, and diffusion pathways, ultimately impacting catalytic selectivity. Notably, ITQ-55 zeolite demonstrates that minor pore aperture expansions can drastically improve separation performance (1), while some structures can undergo unit cell volume changes of up to 20 % (2).

Our previous studies using *in situ* Bragg coherent diffraction imaging (BCDI) revealed significant and anisotropic flexibility in FAU zeolite during ethanol dehydration (3), but were limited by time resolutions on the order of hours.

In this work, we aim to evaluate how ethanol dehydration influences zeolite flexibility — specifically through lattice

expansion, contraction, and displacement — and how these dynamics correlate with catalytic activity. These insights are expected to deepen the understanding of zeolite behavior under reaction conditions and may be extended to other relevant transformations within the zeolite catalysis realm.

Experimental

Nano ZSM-5 Synthesis

The ZSM-5 sample with controlled crystallite size was synthesized using a procedure described elsewhere (4). The preparation of the acidic H-ZSM-5 sample followed a straightforward ion-exchange procedure using a NH_4NO_3 aqueous solution at 60 °C overnight followed by a 550 °C calcination.

Characterization and catalytic evaluation

Powder X-ray diffractograms (XRD) were obtained in a Bruker D8 Advance Eco diffractometer. The (200) peak was chosen for the BCDI investigation.

Scanning electron microscopy (SEM) images were captured using a FEI Inspect F50 microscope at the LNNano/CNPEM laboratory.

The gas-phase ethanol upgrading reaction was carried out in a plug-flow tubular reactor equipped with a quartz tube. During the reaction, ethanol was introduced into the reactor using a saturation flask and He serving as the carrier gas. A temperature-programmed reaction was performed to evaluate the catalytic activity different temperatures. The gas-phase products were analyzed in real time using a mass spectrometer.

In situ BCDI

In situ time-resolved BCDI experiments were performed at the ID01 beamline of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. Measurements were acquired using a Maxipix pixel detector (516 × 516 pixels², 55 × 55 μm²) with an incident X-ray energy of 8.9 keV, focused to a 1 × 1 μm² beam. Three-dimensional diffraction data were collected via rocking curve scans with 0.75° angular steps and 150 frames per scan (1 s exposure per frame). A single H-ZSM-5 particle was monitored throughout the experiment, initially under He and subsequently under reactive conditions simulating the ethanol dehydration reaction.

Results and Discussion

Nano-sized ZSM-5 zeolite crystals were synthesized by adjusting the water content in the synthesis gel, a well-established approach to limit crystal growth and obtain nanometric particles (4). The prepared sample exhibited an XRD pattern consistent with the theoretical MFI framework (5), confirming its phase and crystallinity (data not shown).

The SEM analysis displayed in Figure 1 revealed well-defined coffin-shaped crystals with a narrow size distribution around 400 nm, indicative of a controlled and reproducible synthesis process.

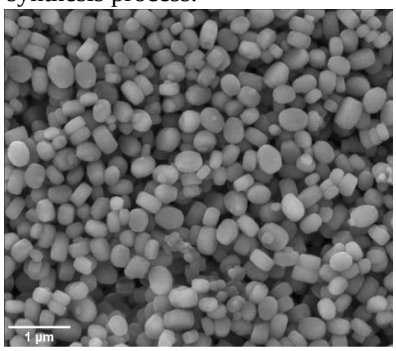

Figure 1. SEM image of the synthesized Na-ZSM-5 zeolite.

The *in situ* BCDI analysis provided nanoscale insights into the lattice strain distribution of a single ZSM-5 crystal under reaction-relevant conditions. The upper part of Figure 2 shows the 3D reconstruction of the crystal at room temperature (RT) under inert He atmosphere. The visualization allows clear identification of the crystal morphology and the attribution of the main exposed facets, including {010}, {100}, {001}, {101}, and {011}. This model serves as a structural reference for the subsequent analysis of lattice dynamics, confirming the typical coffin-shaped morphology associated with the MFI framework.

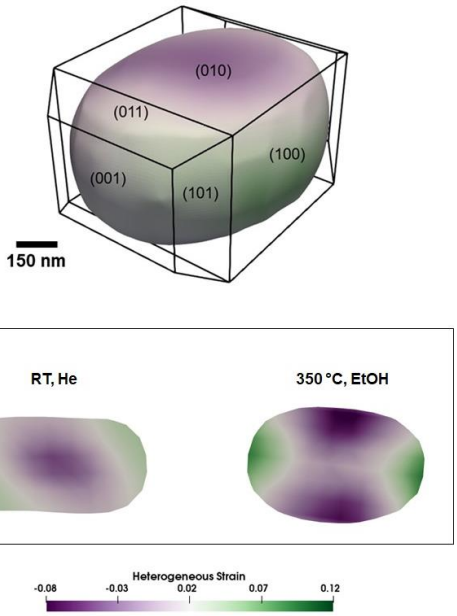

Figure 2. *In situ* visualization of lattice strain distribution in a single ZSM-5 nanocrystal during ethanol dehydration by BCDI. (Upper) 3D reconstruction of the ZSM-5 crystal at RT under He. (Lower) Comparison of heterogeneous strain distribution across the (100) plane at RT under He (left) and at 350 °C under ethanol dehydration conditions (right).

The lower part of Figure 2 presents a direct comparison of the heterogeneous strain distribution across the (100) plane at RT under He (left) and at 350 °C under ethanol dehydration conditions (right). Under inert conditions at RT, the crystal shows a relatively homogeneous strain distribution with only slight heterogeneity concentrated at the outer regions, likely associated with surface relaxation effects. Upon exposure to ethanol dehydration conditions at 350 °C, a pronounced increase in lattice heterogeneity is observed, characterized by intensified compressive and tensile strain zones. This evolution highlights the strong anisotropic framework flexibility of ZSM-5 under reaction environments, driven by the interplay of molecular adsorption, diffusion, and dehydration reaction within the micropores.

These lattice distortions correlate with the catalytic behavior observed for ethanol upgrading, where complete ethanol conversion was achieved at 350 °C, favoring ethylene and water production (6). The emergence of localized strain during reaction suggests that framework distortions are induced by confined molecular interactions and the formation of reaction intermediates, potentially contributing to dynamic changes in catalytic activity and selectivity. This evidence reinforces the concept that zeolite flexibility is not only inherent to the material but is also dynamically modulated by reaction conditions, with direct implications for zeolite-catalyzed processes.

Conclusions

The *in situ* BCDI analysis revealed that ethanol dehydration at 350 °C induces significant and anisotropic lattice distortions in ZSM-5 crystals, which should be correlated with the catalytic activity and product selectivity observed under these conditions. These findings demonstrate that zeolite flexibility is dynamically modulated by the reaction environment, influencing molecular diffusion and catalytic pathways. Ongoing investigations aim to explore a broader range of reaction temperatures to further elucidate the relationship between crystal lattice dynamics and catalytic performance.

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