3D ptychography characterization of hierarchical ZSM-5 crystals: visualizing pore architecture at the single-crystal level

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Resumo/Abstract

RESUMO - Zeólitas hierárquicas apresentam desempenho catalítico aprimorado devido à maior acessibilidade e à redução das limitações difusionais. Neste trabalho, sintetizamos cristais de ZSM-5 com tamanho e morfologia controlados, visando sua aplicação em reações de valorização do etanol. A principal inovação consiste na aplicação da pticografia de raios X tridimensional para investigar a porosidade interna de cristais individuais de zeólita. As reconstruções pticográficas revelaram informações estruturais inéditas, como a conectividade e a heterogeneidade dos poros; aspectos não acessíveis por técnicas convencionais. As distribuições de densidade eletrônica permitiram segmentar os domínios porosos da matriz zeolítica, viabilizando um mapeamento quantitativo da porosidade. Esses resultados ressaltam o potencial do imageamento coerente para orientar o design de zeólitas com desempenho superior em processos de conversão de biomassa.
Palavras-chave: ZSM-5, zeólitas hierárquicas, pticografia, valorização do etanol, imageamento 3D

ABSTRACT - Hierarchical zeolites offer improved catalytic performance due to enhanced accessibility and reduced diffusion limitations. Here, we synthesized ZSM-5 particles with controlled size and morphology, aiming at their application in ethanol valorization reactions. The main novelty of this study is the use of 3D X-ray ptychography to investigate the internal porosity of individual zeolite crystals. Ptychographic reconstructions revealed unprecedented structural information, such as pore connectivity and heterogeneity within crystals, not accessible by conventional techniques. Electron density distributions enabled segmentation of the pore and zeolite domains, providing a quantitative porosity mapping. These results demonstrate the potential of coherent imaging techniques for guiding the design of zeolites with improved performance in biomass conversion reactions.
Keywords: ZSM-5, hierarchical zeolites, ptychography, ethanol upgrading, 3D imaging

Introduction

Zeolites are crystalline microporous materials widely used as solid catalysts in petroleum refining and biomass upgrading. In reactions such as ethanol dehydration, diffusion limitations often hinder the performance of conventional zeolites. Hierarchical zeolites, combining micro- and mesoporosity, overcome such limitations by improving mass transport and increasing active site accessibility (1-3). However, the structural complexity introduced by hierarchical architectures poses challenges to conventional characterization methods. Visualizing the internal pore network in three dimensions, at the single-crystal level, is essential for correlating structure and function in catalytic systems (4-6).

Coherent X-ray diffraction techniques, including ptychography, provide quantitative 3D imaging of electron density at the nanoscale, enabling the direct observation of intracrystalline porosity and heterogeneity. In this work, we report the synthesis of ZSM-5 zeolite with micrometric size and hierarchical structure (through desilication), and its crystals characterization by ptychographic X-ray computed tomography at the Cateretê beamline (LNLS/Sirius).

Experimental

Synthesis of hierarchical ZSM-5 crystals

ZSM-5 zeolite crystals were synthesised using a hydrothermal method, tuning the synthesis gel composition and crystallization parameters to achieve monodisperse crystals. The samples were washed, dried and calcined at 550 °C. Desilication was carried out using a straightforward alkaline leaching approach using NaOH.

Ptychographic measurements

3D ptychographic measurements were carried out at the Cateretê beamline using a coherent beam at 6 keV. The zeolite powder sample was placed in a quartz capillary and scanned with a 5 µm beam size. The sample was reconstructed using CDtools ptychography package (7) for position refinement and PtychoShelves (8) for the proper alignment, reconstruction of 2D scans and the final tomogram.

Results and Discussion

The ptychographic reconstructions unveiled detailed three-dimensional internal features of the ZSM-5 crystals with sub-micrometric resolution. As shown in the top panel of Figure 1, two adjacent crystals were successfully segmented based on electron density contrast. The green regions correspond to low-density domains, which are interpreted as intracrystalline pores. The bottom panel presents the histogram of electron density values, used to differentiate pore-rich from zeolite-rich domains and to define threshold criteria for segmentation.

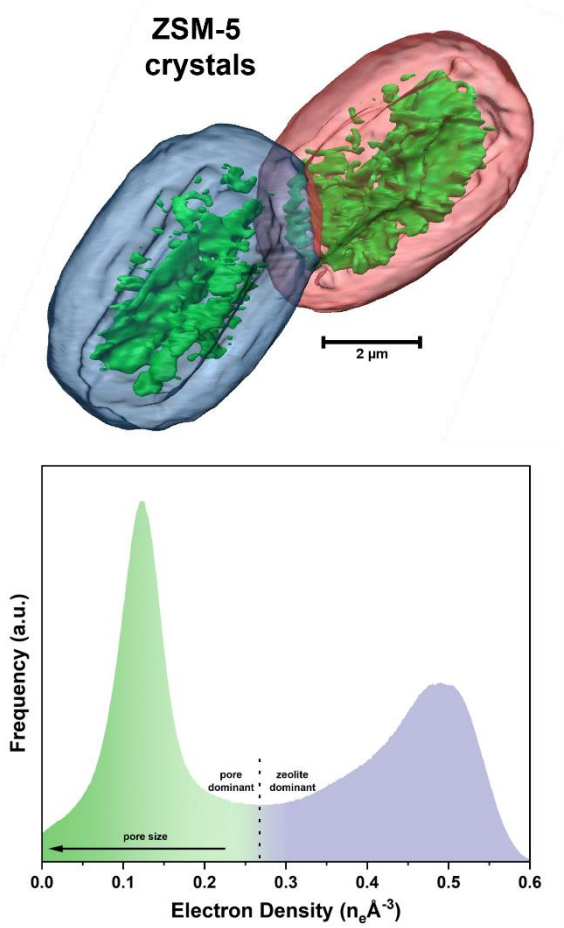

Figure 1. Top: 3D reconstruction of two ZSM-5 crystals highlighting internal porosity (green). Bottom: electron density histogram used for segmentation into pore-dominant and zeolite-dominant regions.

These reconstructions reveal that porosity is not uniformly distributed throughout the crystals. Certain particles exhibit core–shell-like morphologies, in which a denser central region is surrounded by a more porous outer shell, a feature often linked to synthesis kinetics or post-synthetic treatments. Moreover, quantitative analysis of the electron density distribution confirmed spatial heterogeneity in porosity across individual crystals, highlighting internal gradients that are often hidden in conventional bulk measurements.

Such structural variability among nominally similar particles underscores the relevance of single-crystal characterization. Ptychographic imaging proves to be a powerful tool in this context, allowing a direct and spatially resolved correlation between synthetic parameters and resulting hierarchical architectures. This level of insight is particularly valuable for the rational design of zeolites tailored for catalytic applications where diffusion and accessibility are critical.

Conclusions

This study demonstrates the potential of 3D X-ray ptychography to visualize and quantify the internal porosity of hierarchical ZSM-5 zeolites. The results provide essential structural information at the single-crystal level, revealing porosity gradients and heterogeneity that cannot be captured by conventional bulk techniques. These insights pave the way for correlating structural hierarchy with catalytic performance in ethanol valorization studies. Nevertheless, a comprehensive understanding of this relationship requires complementary ongoing characterization techniques. Catalytic testing under controlled conditions will be essential to confirm the impact of the observed structural hierarchy on activity and selectivity.

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