

Strain of MFI crystals in membranes: An in situ synchrotron X-ray study

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Abstract

Temperature-resolved in situ synchrotron X-ray diffraction is used for the first time to study the microstructure evolution of a preferentially oriented zeolite membrane (siliceous ZSM-5) during calcination of the organic structure directing agent (tetrapropyl ammonium, TPA). Use of transmission sample geometry allowed us to discriminate in-plane from out-of-plane reflections and to calculate strain imposed on the zeolite layer along the in-plane (parallel to the support) as well as the out-of-plane (perpendicular to the support) direction over the entire calcination process. The results strongly suggest that the zeolite crystals of the membrane are under compressive in-plane stress and that their thermal behavior is quite different from free standing powder.

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1. Introduction

Zeolite films have drawn considerable research interest with potential uses as selective membranes, membrane reactors, chemical sensors, optical devices as well as in other new applications [1–3]. In particular, zeolite films as selective membranes for gas and liquid separation have been extensively studied for their outstanding potential to recognize molecules at the subnanometer level and their ability to operate at high temperature [4,5].

Zeolite membrane thickness, preferred orientation, and grain size may play important role in determining

overall membrane performance and more specifically in the tendency for crack formation during calcinations [6]. Some understanding of the causes leading to crack formation and propagation can be obtained by measuring the zeolite unit cell expansion/contraction during the calcination process. Here, we use temperature-resolved in situ synchrotron X-ray diffraction to examine the evolution of microstructure in a preferentially oriented siliceous ZSM-5 film (from now on called MFI) during the calcination process for the removal of the structure directing agent tetrapropylammonium cation (from now on called TPA).

So far few studies have been undertaken to investigate mechanical stability in zeolite films upon removal of templates. Geus and Bekkum addressed this issue indirectly in an early study of TPA-MFI single crystals and found an overall contraction (0.5–0.9% in volume) of the MFI framework upon removal of TPA [7]. Considering this behavior along with the thermal expansion coefficient of alumina supports they suggested the

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development of thermal stresses leading to crack formation. den Exter et al. examined the thermal stability of *a*- and *b*-oriented MFI films grown on dense silicon wafers [8]. The unit cell of MFI framework by removal of TPA was found to expand along the *b*-axis and contract along *a*- and *c*-axis. Thus, the crystal-orientation dependant thermal behavior gives rise to different stress (thus different stability) in oriented zeolite films, i.e., tensile stress in the *b*-oriented films and compressive stress in *a*-oriented ones. Lin and co-workers [9] first studied the microstructure development of MFI crystals on porous substrates by in situ high temperature XRD and gas permeation. They have found that compressive stress develops in the MFI films during the cooling process when the MFI crystals are chemically bound to the support after template removal and suggested that this stress is inducing cracks in the membrane. However, the reflection sample geometry adopted for their X-ray diffraction measurements allowed them to measure only the out-of-plane reflections (i.e., reflections from crystallographic planes oriented parallel to the support), which provides only an indirect measure of the in-plane stress responsible for the crack formation.

In this study, temperature-resolved in situ synchrotron XRD with transmission sample geometry is employed to study the effect of the membrane microstructure on the framework structure of preferentially oriented MFI crystals on a porous substrate upon template removal by measuring strain. The evolution of the strain of MFI zeolite crystals imposed by the porous substrate during the calcination process is calculated by comparing the framework structure of the MFI crystals of the membranes with that of MFI powder.

2. Experimental

MFI powder was prepared following the previously reported procedure [4]. The crystallinity and morphology of the MFI crystals were confirmed using powder XRD patterns and SEM images. An MFI membrane with preferred orientation was also prepared using the secondary growth technique on a mesoporous silica coated porous α -alumina support (see Ref. [4] for details). SEM images and XRD pattern confirmed that the membrane has *c*-(*h0h*)-out-of-plane orientation (see Fig. 1).

Temperature-resolved (or time-resolved) in situ synchrotron X-ray diffraction data were collected on beam line X7B of the National Synchrotron Light Source (NSLS). For the MFI powder sample, the crystals were loaded into an open sapphire capillary that was attached to a flow-reaction cell similar to those described in Ref. [10]. The sample was heated using a small resistance hea-

ter wrapped around the capillary. For the membrane sample, a thin slice (width of about 2 mm) cut from the membrane was loaded into the center of a ceramic heater as presented in Fig. 2a. Diffraction patterns were collected at temperatures in the range of 25–550 °C with the temperature program shown in Fig. 2b. For the powder sample, 5% O₂/95% He gas mixture was purged at the flow rate of about 20 sccm. A MAR345 image-plate detector was used to record the in situ XRD data. The typical time required for collecting an individual diffraction pattern was about 2.5 min. For the powder samples, the 2D rings ($\lambda = 0.9225 \text{ \AA}$) were cylindrically averaged using the FIT2D code [11] to produce 1D patterns. The d-spacings of the (200)/(020) and (002) reflections were obtained from the 1D XRD patterns by Gaussian fit of the peaks with over the entire temperature range. The (200) and (020) reflections could not be resolved due to the insufficient resolution of the detector. Consequently, the average d-spacing of the (200) and (020) planes, both of which are in the plane of the zeolite layer, was obtained. A slight correction to the MFI d-spacing was derived from the offset between observed and reference d-spacings of the alumina lines.

Typical 2D XRD patterns of the randomly oriented MFI powder and the preferentially oriented MFI membrane are given in Fig. 3a and c, respectively. The rings with uniform intensities in the powder patterns (like the one shown in Fig. 3a) collected at various temperatures are integrated, giving rise to the 1D patterns in Fig. 3b. For easy comparison the 2-theta angles listed in Fig. 3b (as well as Fig. 3d and e) are the corresponding angles for Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$).

Unlike the powder patterns, the 2D diffraction pattern of oriented membrane displays streaking (rings of non-uniform intensity), clearly indicating the presence of preferentially orientated MFI crystals with respect to the support. Consistent with the *c*-(*h0h*)-out-of-plane preferential orientation, the (200)/(020) ring, for example, is more intense in the in-plane (parallel to the support) direction and the (002) ring is more intense in the out-of-plane (perpendicular to the support) direction. Fig. 4 provides a schematic illustration of the relationship between preferential orientation and non-uniformities in the intensity of the diffraction rings. In order to analyze separately in-plane and out-of-plane reflections, the 2D patterns were masked such that integration could be performed only along the in-plane and out-of-plane directions resulting in the 1D patterns of Fig. 3d (in-plane) and e (out-of-plane). Red and green rectangles in Fig. 3c are the areas over which integration was performed to give the in-plane and the out-of-plane 1D patterns, respectively. Subsequently the d-spacings of in-plane (200)/(020) and out-of-plane (002) reflections were obtained over the entire temperature range and are shown in Fig. 5.

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