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Crack formation in α-alumina supported MFI zeolite membranes studied by *in situ* high temperature synchrotron powder diffraction

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Abstract

Cracks are frequently formed in α-alumina supported MFI membranes during calcination. To better understand crack formation, *in situ* powder diffraction data were collected during calcination of a type of MFI membrane (ca. 1800 nm thick) which is known to crack reproducibly. In addition, data for MFI powder and a blank support were also collected. Both a synchrotron radiation facility and an in-house instrument were used. The unit cell parameters were determined with the Rietveld method, and the strain in the direction perpendicular to the film surface was calculated for the film as well as for the support. The microstrain in the support was also estimated. Based on the results obtained here, a model for crack formation in this type of MFI membrane was proposed. The lack of cracks in other types of MFI membranes (ca. 500 nm) prepared in our laboratory is also explained by the model. In thicker MFI films, the crystals are well intergrown. During heating, the MFI crystals contract and the α-alumina support expands. Consequently, a thermal stress develops in the composite which eventually leads to formation of cracks in the film and structural defects in the support. In thinner films, the crystals are less well intergrown and the thermal expansion mismatch leads to opening of grain boundaries rather than cracks.

Keywords: MFI zeolite membrane; *In situ* study; Synchrotron powder diffraction; Crack formation; Rietveld method

1. Introduction

The potential industrial applications of polycrystalline zeolite membranes are not fully explored. This explains the increasing number of papers and patents on this specific topic. To this aim, MFI is a particularly interesting zeolite structure topology due to the pores with a size close to the kinetic diameter of many industrially important molecules. MFI zeolites with a high Si/Al ratio generally require the addition of organic template molecules for the synthesis. Frequently used organic templates are quaternary ammonium cations such as TPA^+ (tetrapropylammonium). The template molecules are trapped in the zeolite channels and are usually removed by calcination to activate the membrane.

For good separation performance, no alternative pathways in the form of defects such as open grain boundaries, pinholes and cracks should exist in the film [1–4]. Cracks are possibly the most troublesome type of defect and may form during calcination [1].

In an early work, crack formation during template removal of MFI single crystals (cube-shaped silicalite, fluoride-synthesized silicalite and vanadium-containing silicalite) was investigated [5]. In large crystals (>300 μm average crystal size) some straight cracks along the *c*-axis developed at 260 °C. The occurrence of straight cracks seems to be related to the dehydration of the framework during the initial Hofmann elimination reaction of TPA^+. Random cracking was observed in cube-shaped crystals larger than 150 μm (more severe in larger crystals). These observations match the temperature interval in which degradation of tripropylamine via β-elimination reactions occurs. It was postulated that the development of random cracks was related to the formation of carbonaceous species within

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the zeolite framework. Pachtová et al. [6] studied the TPA removal in large silicalite-1 crystals of three different sizes. No cracks were observed in the smallest crystal ($L_c = 130\ \mu m$) after calcination in air. In larger crystals, cracks developed in both air and nitrogen atmosphere. In the medium-sized crystals ($L_c = 190\ \mu m$), cracks were found after complete template removal, whereas in the largest crystals ($L_c = 230\ \mu m$) they already appeared after partial calcination. Hence, in concert with the results of Geus and van Bekkum [5], the formation of cracks was apparently dependent on the crystal size.

It is well known that a thermal expansion mismatch between bonded materials may result in stress and consequently cracks in a composite. In fact, Geus and van Bekkum suggested that cracks in supported MFI membranes were due to thermal stress during calcination [5]. The MFI structure experiences a strong contraction during template removal, which occurs in the approximate temperature range 300–500 °C [5,7–9]. Instead, the α-alumina supports used for MFI films expand during heating [8–10]. Furthermore, the unit cell of the calcined framework is smaller than the as-synthesized one [5,7,9,11]. The difference is due to the contraction of the *b*- and *c*-axes which is only partly compensated by an expansion of the *a*-axis in the calcined form [7,9,11]. den Exter et al. [12] studied *b*-oriented silicalite-1 films on dense silicon wafers. Derived from crystallographic data for as-synthesized and calcined silicalite-1, the authors reported that the change (%) in the unit cell dimensions after calcination (*ex situ* data) was −0.71, +1.05 and −0.105 for the *a*-, *b*- and *c*-axis, respectively. Based on these results and a quantitative estimation of the *a*- and *b*-oriented crystallites in the film, the calcined crystal layer would show an expansion with respect to the as-synthesized film. In fact, a buckling of the calcined crystal layer was evident. The cracks observed in the film were attributed to compressive stress in the calcined layer.

To better understand the crack formation process in MFI membranes, the thermal behavior of the porous support as well as that of the zeolite film must be investigated. An appropriate technique is high temperature X-ray powder diffraction (HT-XRPD) which allows to follow the *d*-spacings of the crystal planes as a function of temperature. Consequently, the strain in the sample can be followed as a function of temperature by comparing the *d*-spacings in the film with those in a non-stressed sample.

Dong et al. [8] performed a HT-XRPD study of silicalite-1 films on porous yttria-doped zirconia (YZ) supports as well as ZSM-5 films on porous α-alumina supports. The films were composed of randomly oriented crystals. The MFI crystals formed in the bulk of the synthesis solution were also investigated. The films were defective after calcination. Open grain boundaries were present in the calcined ZSM-5 films whereas cracks were detected in the films of silicalite-1. Thermal expansion curves of the composites were determined during heating of the as-synthesized samples. It was shown that the MFI unit cell experiences a large contraction during template removal, while the support expands. During cooling, after template removal, the zeolite expands while the support contracts. In addition, the thermal expansion of the various samples was shown to be different. However, the strain in the films during the temperature ramp was not reported, possibly because the different Si/Al ratios in the samples masked the difference in unit cell dimension caused by strain in the film.

Crack-resistant MFI membranes were recently studied by Jeong et al. [10]. The authors performed a HT-XRPD study (using synchrotron radiation (SR)) of an oriented MFI film with a thickness of about 10 μm. The film was prepared on a thin mesoporous silica layer deposited on a porous α-alumina support. They found that the crystals in the film experienced an in-plane compressive strain (i.e. in the direction parallel to the film surface) during the entire calcination procedure. It was speculated that this behavior possibly could explain the lack of cracks in this system.

No HT-XRPD study of α-alumina supported MFI films which crack during calcination had been reported. This recently prompted a preliminary HT-XRPD investigation of such a film [9]. In addition, MFI powder was also investigated. The Rietveld method was used to determine the unit cell parameters in the MFI film and the α-alumina support as well as MFI powder *in situ* during the entire calcination procedure (i.e. both heating and cooling) [9]. The different thermal behavior of the film and the powder was attributed to tensile stress in the film during heating. The results of the preliminary investigation were however not sufficient to formulate a conclusive model for the crack formation process observed in the α-alumina supported MFI films prepared in our laboratory [1,9]. The present work is a natural follow-up of the preliminary study. For the first time, the Rietveld method and high resolution HT-SRPD data were used to investigate a type of MFI membrane (ca. 1800 nm thick) which reproducibly crack during calcination. The unit cell parameters of the MFI film as well as the TPA^+ occupancy were determined as a function of temperature during the entire calcination procedure. In addition, the microstructure of the α-alumina support was followed in temperature by pattern decomposition and Williamson–Hall plots. HT-XRPD data collected with an in-house instrument were used to determine unit cell parameters as a function of temperature for a blank α-alumina support and MFI powder, which where used as references to calculate the strain in the membrane. The information obtained in this study will be used to formulate a model for crack formation. The model also explains the lack of cracks in thinner MFI membranes (ca. 500 nm) synthesized in our laboratory. The model will be compared to those existing in the literature.

2. Experimental

Zeolite films were prepared on graded α-alumina filters (Inocermic GmbH, Germany). The top layer is 30 μm thick with 100 nm pores and the bottom layer is 3 mm thick with 3 μm pores. The zeolite film investigated by synchrotron radiation was grown on a slice (20 mm × 3 mm × 1 mm) cut from the as-purchased α-alumina filters using a diamond saw (Discotomo cutter). A full-size filter (diameter of 25 mm) was used for the preparation of the membrane investigated by an in-house HT-XRPD instrument.

All supports were carefully washed with acetone, ethanol and a dilute (0.1 M) ammonia solution. Silicalite-1 seed crystals