Zeolite membranes hold great potential in gas/liquid separation. In particular, the preparation of dominantly $b$-oriented MFI (siliceous ZSM-5, [Si$_{96}$O$_{192}$]) molecular sieve membranes is highly significant in isomer separation (such as $i$-/n-butane or $p$-/o-xylene) [1,2]. Compared with in-situ growth, secondary (seeded) growth method exerts more effective control over the membrane formation process by decoupling the nucleation and growth steps [3]. Nevertheless, it is still very challenging to effectively suppress undesired twin growth of the seed layer, which often arises during secondary growth and severely degrades the performance of the final MFI films.

It was generally accepted that the adherence of newly formed MFI nuclei in the bulk solution to the $(0 k 0)$ faces of the original MFI seeds was the main cause of twin growth during seeded growth. In this report, we firstly prepared compact and highly $b$-oriented MFI seed layer by air-liquid interface assisted seeding technique developed in our group [4,5]. Consequently, relying on the nucleation-related bottleneck effect of microwave irradiation, twin-free and dominantly $b$-oriented MFI membrane was successfully fabricated by microwave heating. Moreover, compared with conventional hydrothermal growth, MFI grains composing the membrane were more orderly arranged on substrate, which may be beneficial in improving the lattice matching and reducing potential inter-crystalline defects. Finally, defect-free MFI membranes with diverse microstructure were successfully fabricated on Pt electrodes. Methanol electrochemical oxidation results illustrated that suppression of twins in MFI membrane was effective in decreasing mass transfer resistance of guest molecules in MFI nano-channels.

Considering the optimized microstructure of prepared MFI membranes, it is promising that attractive gas separation results can be obtained with this membrane, which is currently under investigation. Meanwhile, the nucleation-related suppressive effect of microwave irradiation may be also illustrative for suppressing twins in other inorganic membranes.

Fig. 1. The X-ray rocking curve patterns of MFI films obtained through a) direct microwave-assisted heating at 150 °C for 30 min, and b) conventional hydrothermal growth at 150 °C for 5 h. The 2 theta value was set between 8.6 and 9.1 degree. Inset: XRD patterns of (0 2 0) diffraction peak obtained with conventional XRD technique. Inset (bottom): FWHM values of MFI films obtained by fixing 2-theta angle and doing a theta scan. SEM images of MFI films c) prepared by direct microwave-assisted synthesis at 150 °C for 30 min, and d) under conventional hydrothermal conditions at 150 °C for 5 h.

References


Keywords: MFI membrane, microwave irradiation, twin suppression, orientation