Electronic Supplementary Information (ESI)

Reactive Atmospheric Pressure Plasma for Highly Efficient Removal of Structure-Directing Agents from Zeolite Thin Films

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Experimental Sections

Materials

Tetraethyl orthosilicate (TEOS), tetrapropylammonium hydroxide (TPAOH), ethanol, triethoxy(octyl)silane, and TWEEN® 80 were purchased from Sigma-Aldrich. Toluene was purchased from Merck. All purchased chemicals were used without further purification. Water used for material synthesis was produced using the Thermo Scientific™ Barnstead™ NANOpure® DIamond™ analytical ultrapure water system. Silicon wafers (1 1 0) were purchased from Summit-Tech (Taiwan).

Synthesis of Casting Solutions for Preparation of Pure-Silica Zeolite MFI Films

Casting solutions for the fabrication of pure-silica zeolite MFI films were synthesized using a method similar to that proposed in previous studies\textsuperscript{1,2} with minor modifications.

A solution of molar composition 1 TEOS: 5.6 ethanol: 0.36 TPAOH: 12.2 water was prepared by mixing 12.1 g of TEOS, 14.9 g of ethanol, 16.9 g of TPAOH, and 12.7 g of water. This mixture was stirred in a poly(fluoroalkoxy) (PFA) bottle at 30°C. The solution was then transferred to a Teflon\textsuperscript{®} lined autoclave with maximum capacity of 203 mL, which was placed in an oven at 100 °C for 36 hours. The autoclave was showered with tap water until the temperature was reduced to room temperature. The synthesized solution was mixed with 4.7 g of ethanol and 0.53 g of TWEEN® 80 and
then stirred at 30°C for 3 hours. The resulting solution served as casting solution for the synthesis of pure-silica zeolite MFI films.

*Fabrication of Pure-Silica Zeolite MFI Films*

Silicon wafers (1 1 0) with a thin layer of thermal oxide were cut into squares (approximately 2cm × 2cm) for use as substrates in the casting of pure-silica zeolite MFI films. The above-mentioned casting solution was applied to the substrates in drops until the entire surface was covered by solution and then spun at 2600 rpm for 30s using a spin coater. The samples were the placed on a hot plate and baked at 150°C for 1 hour. The solid-state films formed on the substrates during baking are the as-synthesized thin films used in this paper. The removal of structure directing agent (TPAOH) from the as-synthesized thin films was achieved using either thermal calcination or atmospheric pressure plasma jet (APPJ) treatment. In the case of thermal calcination, the samples were placed in a furnace before bringing the temperature up to 450°C at an elevation rate of 1°C/minute and then held at that temperature for 5 hours. APPJ treatment used for the removal of structure directing agent is outlined in the following section.

*Treatment using Atmospheric Pressure Plasma Jet (APPJ)*

Fig. 2 in the manuscript illustrates the setup of the APPJ used for the treatment of as-
synthesized pure-silica zeolite MFI thin films, and details of which can be found in our previous reports.\textsuperscript{3,4} The diameter of the jet tube of our setup was 3cm. During treatment, nitrogen with a purity of 99.99\% was used as the gas source for the generation of plasma at a flow rate of 30 standard liter per min. The applied voltage was 275 volt with a 7/33 $\mu$s on/off duty cycle. The exit of the jet was surrounded by a glass tube to minimize the entrainment of ambient air to the jet downstream. The gap between the exit from the glass tube and the thin film samples was 1, 3, or 5mm. Treatment was applied for 20, 40, or 60 seconds. Thin film samples treated using APPJ with a jet-to-sample distance of 1mm for 20 seconds was denoted as 1mm-20s; the denotations of the rest of the samples can be deduced by analogy.

\textit{Surface Modification}

A number of the thin film samples were subjected to surface modification using triethoxy(octyl)silane as a reagent. A 105 mL of triethoxy(octyl)silane-toluene mixture in a molar ratio of 5:100 was prepared in a glass jar. Thin film samples were transferred into the jar, which was then sealed and placed in an oil bath at 90\textdegree C for 90 minutes. The thin film samples were then removed from the jar and rinsed with fresh toluene for the removal of non-immobilized triethoxy(octyl)silane.
Characterization Methods

FT-IR spectra of the thin film samples were recorded in attenuated total reflection (ATR) mode using a Jasco FT/IR-6700 spectrometer with a Ge coated KBr beam splitter. The ATR accessory was equipped with a ZnSe crystal. Each FT-IR spectrum was obtained from 100 scans at a resolution of 4 cm\(^{-1}\). Grazing-incidence X-ray diffraction (GIXRD) was performed on thin film samples using a PANalytical X’pert diffractometer operated with a Cu K\(\alpha\) source, scanning from 5 to 30° 2\(\theta\) with a step size of 0.02°. Top-view and side-view images of the thin films were obtained using a scanning electron microscope (FEI\textsuperscript{TM} Nova NanoSEM\textsuperscript{TM} 230). A thin layer of platinum was deposited on the samples prior to imaging. Energy dispersive X-ray spectroscopy (EDS) was performed using the same instrument when performing the top-view imaging of thin film samples. Measurements of water contact angle were obtained using a proprietary setup, comprising a CCD camera (M&T Optics Co.) for the recording of images and MATLAB\textsuperscript{®} for image processing and analysis.
Fig. S1. FT-IR spectra of various pure silica MFI thin films with (a) a narrower and (b) a wider spectral region taken near the center of the thin film samples. (c) FT-IR spectra of various pure silica MFI thin films taken near the edge of the samples.
Fig. S2. Raw EDS patterns for as-synthesized, calcined, and APPJ-treated thin films. The peak at approximately 2.2 keV is assigned to Pt deposited on the samples to enhance the quality of the SEM images.
Fig. S3. Top-view SEM images of as-synthesized, calcined, and APPJ-treated zeolite MFI thin films (treated for 60 seconds).
Fig. S4. Side-view SEM images of as-synthesized, calcined, and APPJ-treated zeolite MFI thin films (treated for 60 seconds).
Fig. S5. Raw images recorded during measurement of water contact angle on bare and modified as-synthesized, calcined, and APPJ-treated thin films (treated for 60 seconds).
Supplementary References


