Supporting Information for
Monolayer Assembly of Oriented Zeolite Crystals on α-Al₂O₃ Supported Polymer Thin Films

By Baoquan Zhang*, Ming Zhou, and Xiufeng Liu

School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China
*To whom correspondence should be addressed. E-mail address: bqzhang@tju.edu.cn

1. Monolayer assembly of zeolite crystals on the α-Al₂O₃ supported PVA or chitosan film using the stacking and sonication method

Scheme S1. The procedure for assembling zeolite crystals onto the α-Al₂O₃ supported PVA film via surface-tethered CP groups.

Scheme S2. The procedure for assembling zeolite crystals onto the α-Al₂O₃ supported chitosan film via surface-tethered CP and TMS groups.
2. Assembly of silicalite-1 crystals on the $\alpha$-Al$_2$O$_3$ supported PVA film using the reflux and stirring method

3. Manual assembly of zeolite crystals on the $\alpha$-Al$_2$O$_3$ supported PEO film

There are abundant ether linkages in PEO molecules which are ready to be associated with hydroxyl groups on the surface of zeolite crystals or $\alpha$-Al$_2$O$_3$ substrates to form hydrogen bonds (Figure S3A). Therefore, zeolite crystals can be manually assembled onto the $\alpha$-Al$_2$O$_3$ supported PEO thin film via hydrogen bonding as shown in Figure S3B.
4. Adhesion strength between silicalite-1 crystals and the substrate surface after calcination in N₂

The silicalite-1 monolayer on the α-Al₂O₃ supported PVA film was first calcined in a temperature-programmed furnace under the atmosphere of nitrogen or air. After calcination, the PVA film was removed in air or partly carbonized in nitrogen. As shown in Figure S4A, the microstructure of the silicalite-1 monolayer (including orientation, degree of coverage and degree of close packing) kept the same after calcination in nitrogen, which could be further confirmed by the corresponding XRD pattern of the calcined silicalite-1 monolayer shown in Figure S4B. However, the morphology of the calcined silicalite-1 monolayer was significantly deformed after sonication in toluene for 15 min. Although the orientation was preferentially in b-axis, some crystal grains were moved from their original positions besides some voids left for detached crystals due to the weight loss underneath the silicalite-1 monolayer during sonication (Figure S4C). The relative intensity of (020) to the characteristic peak of α-Al₂O₃ at 25.54° was dramatically decreased after sonication (Figure S4B and D). By accounting the number of detached crystal grains in ten different locations of the silicalite-1 monolayer via SEM images, the percentage of detached crystal grains from the substrate surface thus calculated was less than 10%.

5. Adhesion strength between silicalite-1 crystals and the substrate surface after calcination in air

The silicalite-1 monolayer on the α-Al₂O₃ supported PEO film was also calcined under the atmosphere of nitrogen or air as above. After calcination, the PEO film was removed in air or
partly carbonized in nitrogen. As shown in Figure S5A, the microstructure of the silicalite-1 monolayer (including orientation, degree of coverage and degree of close packing) was slightly changed after calcination in air. This could be confirmed by the corresponding XRD pattern of the calcined silicalite-1 monolayer shown in Figure S5B. Furthermore, the silicalite-1 monolayer could withstand the sonication in toluene for 15 min with almost no morphology change except that 7% of the attached zeolite crystals were detached from the substrate surface (Figure S5C). This could be further verified by comparing the XRD patterns of the silicalite-1 monolayer before and after sonication.

*Figure S5.* A, B) The typical SEM image and the corresponding XRD pattern of the zeolite monolayer on $\alpha$-Al$_2$O$_3$ substrate after calcination in air. C, D) The SEM image and the corresponding XRD pattern of the calcined zeolite monolayer on $\alpha$-Al$_2$O$_3$ after sonication in toluene for 15 min. The asterisk marks the peak originating from the $\alpha$-Al$_2$O$_3$ substrate.