

Electronic Supporting Information (ESI):

Ti-MIL-125-NH₂ membrane grown on a TiO₂ disc by combined microwave/ ultrasonic heating: facile synthesis for catalytic application

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Materials

Titanium(IV) isopropoxide (99.8%, Aldrich), 2-aminoterephthalic acid (H₂BDC-NH₂, >98%, TCI), N,N-dimethylformamide (DMF, 99.9%, Aldrich), methanol (MeOH, >99.9%, Aldrich), ethylcyanoacetate (99%, Aldrich), benzaldehyde (>99.5%, Aldrich), dodecane (99+%, Aldrich), and ethyl alcohol (99.9%, DUKSAN) were used as received.

Experimental details

Preparation of TiO₂ discs

High purity TiO₂ (rutile, >99.99%, 2 μm, Kojundo chemical laboratory, Japan) was used as the starting powder. The powders were finely ball-milled with 0.5 wt. % polyvinyl butiral (PVB) for 24 h in ethanol using a plastic jar and PVB balls. The slurry was dried using a rotary evaporator. After drying and sieving, the powders were pressed uniaxially into disk green bodies at 100 MPa, and cold isostatic pressed (CIP) at 180 MPa. The obtained green compacts were sintered at 1000 °C for 2 h in air, and cooled to room temperature at a cooling rate of 20 °C/min. After grinding (400 grit diamond wheel) and polishing (1 μm diamond paste), disc samples with a mean pore size of *ca.* 110 nm, a porosity of 35 %, diameter of 24 mm and thickness of approximately 2 mm were obtained. Prior to the synthesis of a Ti-MIL125-NH₂ membrane, one side of the porous TiO₂ disc to be used as a support was polished using 1200-mesh SiC sandpaper, washed with acetone, and dried under vacuum at 90 °C for 6 h.

Preparation of Ti-MIL125-NH₂ powder

Ti-MIL125-NH₂ was synthesized using the procedure reported elsewhere [1]. Titanium(IV) isopropoxide (0.9 mmol) and H₂BDC-NH₂ (1.2 mmol) were dissolved in a 15 mL mixture of DMF and MeOH (1:1, (v/v)) and placed into a 35 mL glass tube, which was sealed with a rubber septum and placed in a microwave oven (Discover S-class, CEM, maximum power of 300 W). The substrate mixture was heated to 423 K, and microwaved for 90 minutes at 150 W. After the reaction, the yellow powder product was separated by centrifugation and washed three times with DMF, and placed in methanol, which was decanted and replenished three times in two days. Finally, the product was activated under vacuum at 423 K for 12 h.

Preparation of Ti-MIL125-NH₂ membrane

The sonicator used in this study was a VCX500 (SONICS, USA) model with an adjustable power output (maximum 500 W at 20 kHz). To prepare a Ti-MIL125-NH₂ membrane, a pretreated TiO₂ support was immersed in a ligand solution with 1.2 mmol of H₂BDC-NH₂ in a 15 mL mixture of DMF and MeOH (1:1 (v/v)), followed by sonication. The disc was then removed and dried at room temperature. Subsequently, the disc was transferred to a 35 mL glass tube containing 15 mL of the Ti-MIL125-NH₂ precursor solution of the substrates at the same molar ratio described above and heated by microwave at 423 K, held at 250 W for 30, 60, and 120 minutes to obtain a pale-yellow colored TiO₂ disc product, Ti-MIL125-NH₂ (M60) and (M120) membrane. The Ti-MIL125-NH₂ (M60) membrane was immersed into a 45 mL mixture of titanium(IV) isopropoxide (2.7 mmol) and H₂BDC-NH₂ (3.6 mmol) in DMF/MeOH (9:1, (v/v)), and transferred to a custom-made horn type 70 mL Pyrex reactor. The Pyrex reactor was fitted to a sonicator bar unit, and the reaction mixture containing the disc was subjected to an ultrasonic treatment at 400 W for 30 and 60 minutes. After treatment, the TiO₂ disc supported membrane was recovered, washed 2~3 times with DMF and MeOH, and dried at room temperature. The resulting yellow colored TiO₂ disc was designated Ti-MIL125-NH₂ (M60/U60).

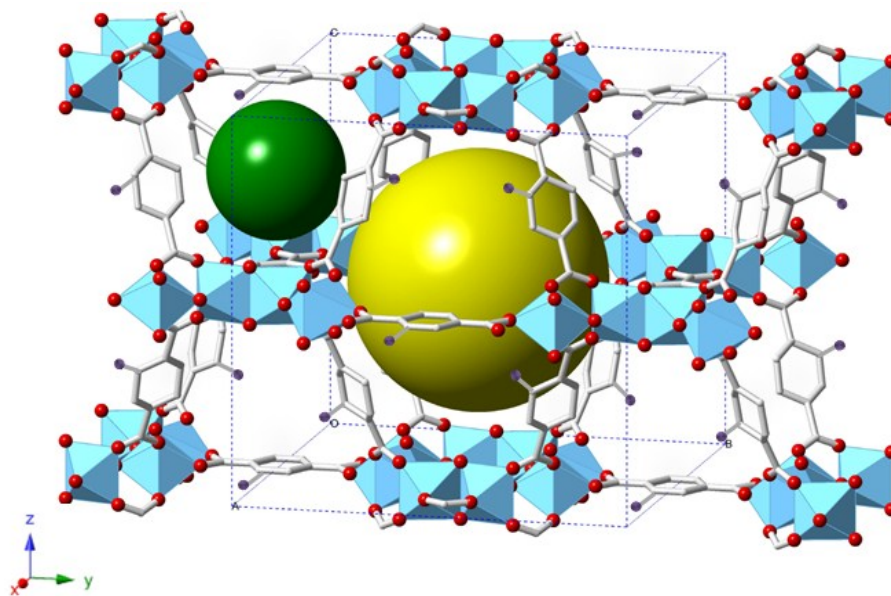
Characterizations

X-ray powder diffraction (XRD, Rigaku) was performed using $\text{CuK}\alpha$ ($\lambda = 1.54 \text{ \AA}$) radiation at $0.5^\circ / \text{min}$. The N_2 adsorption and desorption isotherms were measured in a BELsorp-Max (BEL, JAPAN) at liquid nitrogen temperature of 77 K. Before the adsorption measurements, the samples were activated at $150 \text{ }^\circ\text{C}$ for 12 h in a vacuum. The specific surface areas of the samples were calculated using the Brunauer, Emmett and Teller (BET) method. The surface morphology and cross-section of the membranes were examined by scanning electron microscopy (SEM, Hitachi S-4300).

Catalytic reaction

The Knoevenagel condensation reaction between benzaldehyde and ethyl cyanoacetate was carried out using the prepared Ti-MIL-125- NH_2 (M60/U60) membrane as a catalyst. The membrane contained *ca.* 9 mg of Ti-MIL-125- NH_2 crystals on the support, (estimated by the weight difference between the bare TiO_2 substrate and the membrane grown on the disc after synthesis). The membrane was placed inside the glass reactor of the chemistation unit (PPS-2510, Japan) containing 8 ml of an ethanolic solution with 1.06 mmol of benzaldehyde and 0.93 mmol of ethyl cyanoacetate, and the mixture was stirred magnetically at 333 K for 4 h.

After the reaction was complete, the membrane grown disc was removed and conversion was measured using a gas chromatograph (Agilent 7890) fitted with a flame ionization detector (FID) and a high performance HP-5 capillary column (30 m, 0.320 mm, 0.25 μm). A hot filtration experiment was carried out by separating the catalyst disc quickly from the reaction mixture after a 30 min reaction time, and the filtrate mixture was maintained at 333 K for an additional duration of up to 4 h.



Scheme S1 Schematic structure of Ti-MIL-125-NH₂. Hydrogen atoms were omitted. The green and yellow spheres describe the void regions inside tetrahedral and octahedral cages, respectively. (C white; Ti blue; O red; N purple).

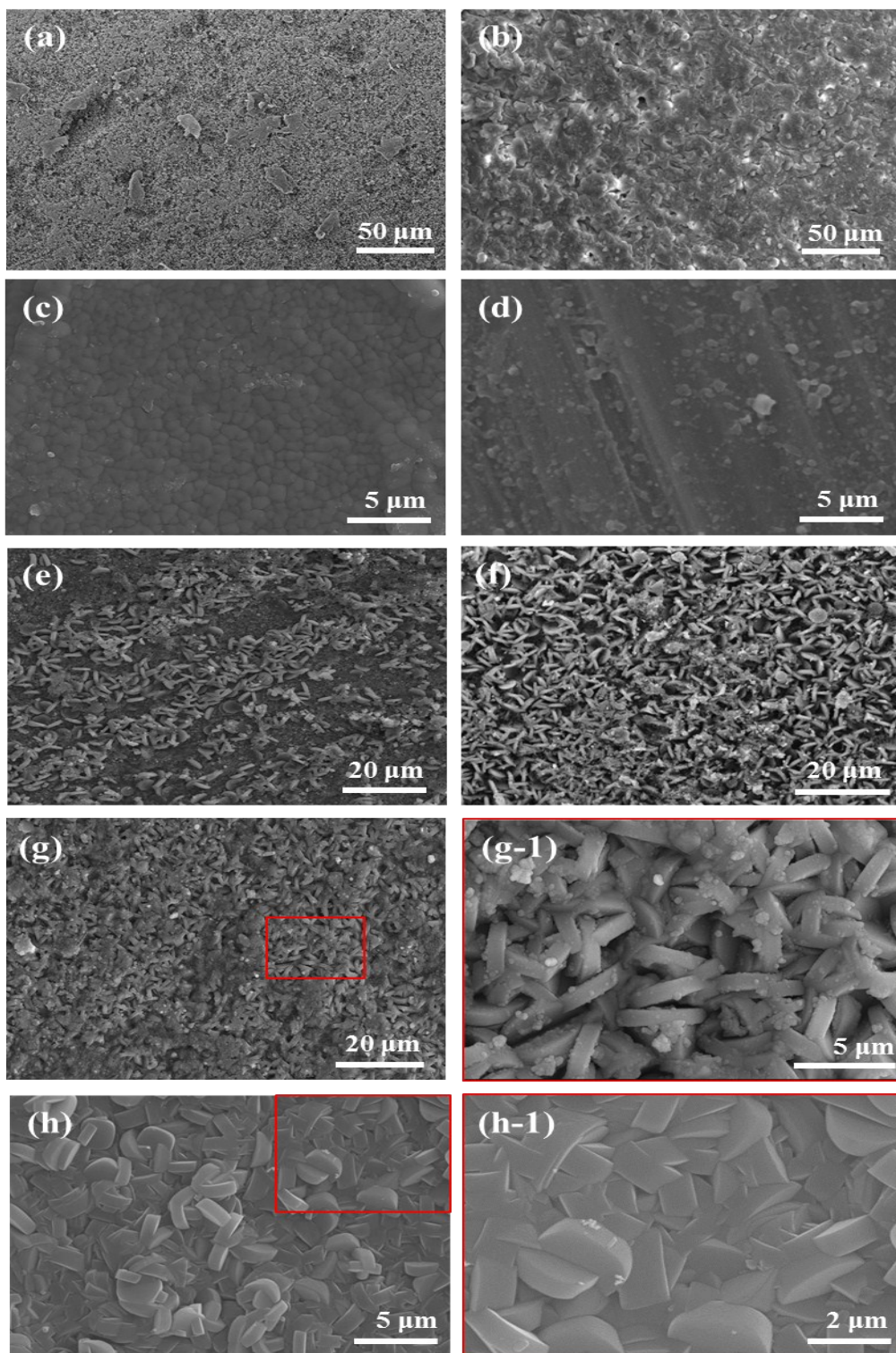


Fig. S1 SEM images at different stages of Ti-MIL-125-NH₂ membrane growth: (a) porous TiO₂ surface, (b) seed layer, and top-view of (c) Ti-MIL-125-NH₂ (U60), (d) Ti-MIL-125-NH₂ (M30), (e) Ti-MIL-125-NH₂ (M60), (f) Ti-MIL-125-NH₂ (M120), (g) Ti-MIL-125-NH₂ (M60/U30) [(g-1) enlarged image of the rectangular section in (g)], and (h) Ti-MIL-125-NH₂ (M60/U60) [(h-1) enlarged image of the rectangular section in (h)].

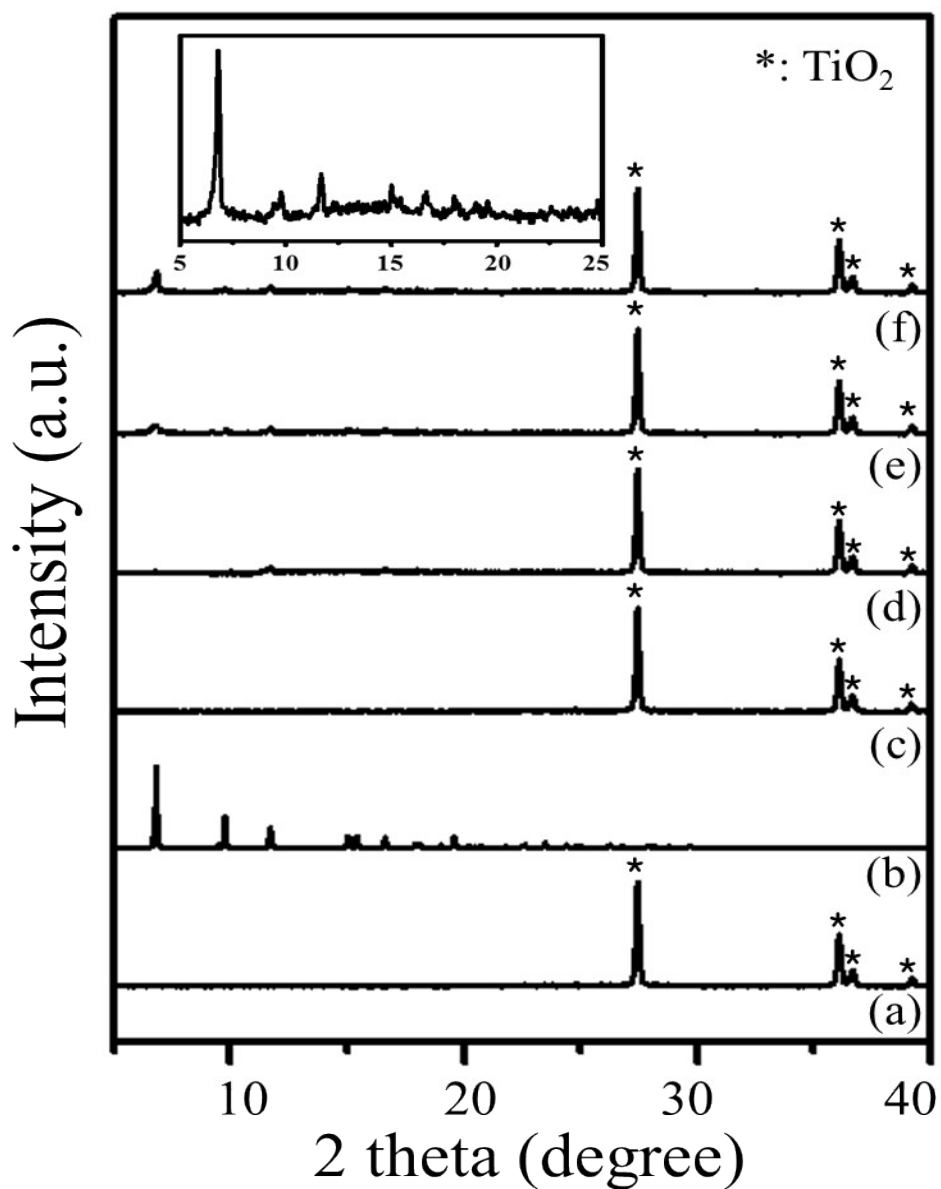


Fig. S2 XRD patterns of (a) porous TiO₂ support, (b) simulated Ti-MIL-125-NH₂, (c) seed layer, (d) Ti-MIL125-NH₂ (M30), (e) Ti-MIL125-NH₂ (M60), and (f) Ti-MiIL-125 (M120). The inset shows the magnified patterns in (f). The reflections marked by * correspond to the TiO₂ support.

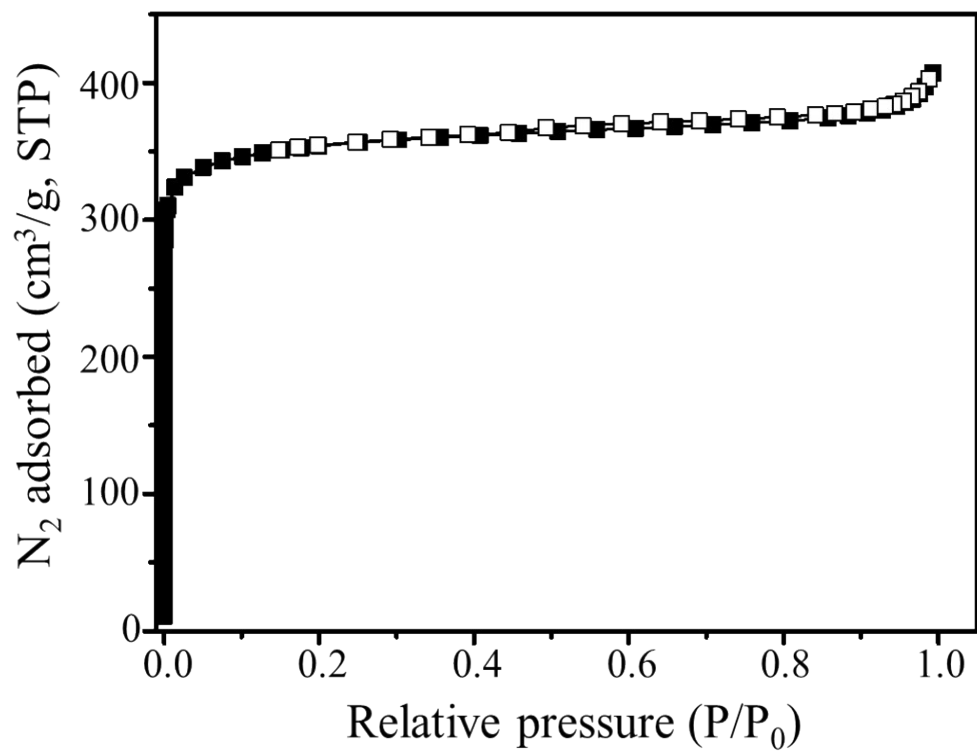


Fig. S3 N₂ adsorption-desorption isotherm of Ti-MIL-125-NH₂ particles at 77 K.

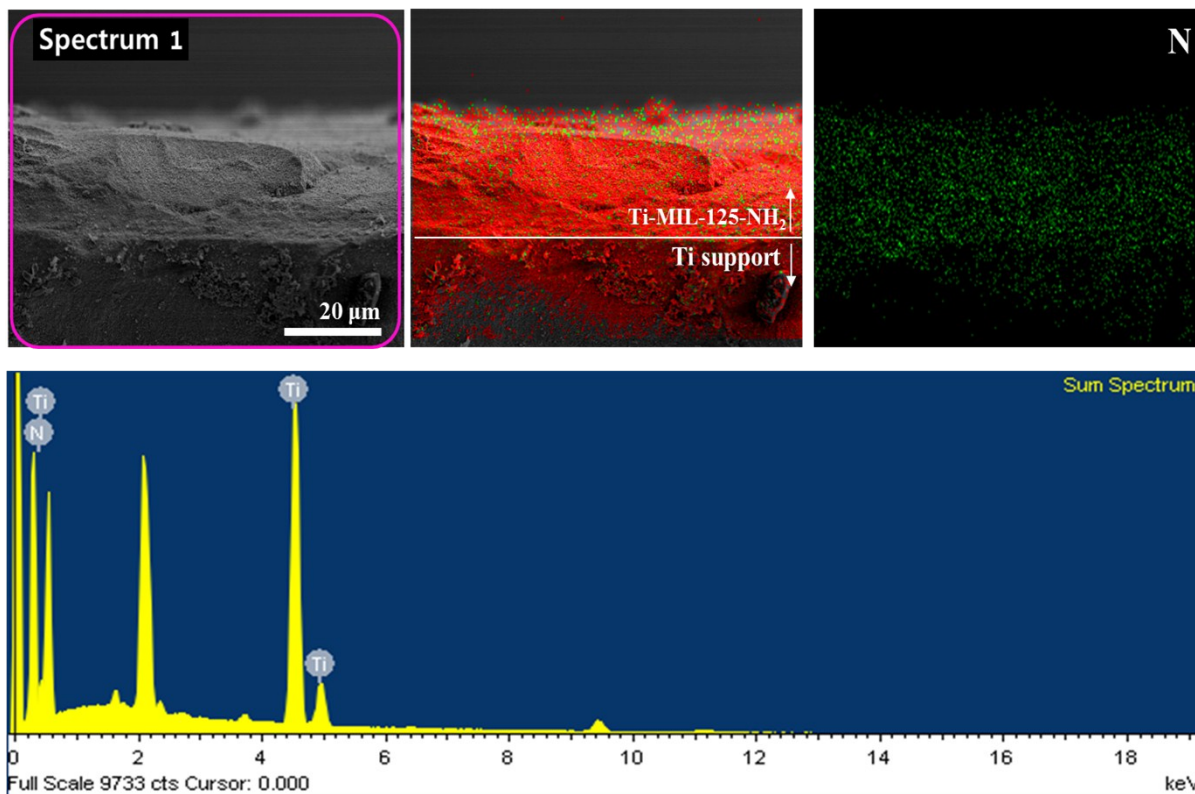


Fig. S4 SEM-EDS elemental mapping of Ti-MIL-125-NH₂ (M60/U60) membrane cross-section (red : Ti, green : N).

References

- [1] S. N. Kim, J. Kim, H. Y. Kim, H. Y. Cho and W.S. Ahn., *Catalysis Today*, 2013, **204**, 85.