

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



Journal Name

ARTICLE

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

DOI: 10.1039/x0xx00000x

Yu-Ri Lee,^a Sung-Min Cho,^a Sung-Hyeon Baeck,^a Wha-Seung Ahn*^a and Won-Seung Cho^b

www.rsc.org/

A Ti-MIL125-NH₂ membrane with a high surface coverage of uniform crystals was prepared on a TiO₂ disc using a unique combination of microwave-assisted nucleation followed by ultrasonic irradiation, which produced a highly stable catalytic film for a liquid phase Knoevenagel condensation reaction.

Metal-organic frameworks (MOFs) are a new class of porous crystalline materials that are constructed of metal ions or clusters bridged via rigid organic linker groups.¹ Owing to their high surface area in well-ordered porous structures and diverse post-synthetic functionalization,² these materials have been considered for gas storage,³ adsorption/separation,⁴ catalysis,⁵ and other applications.⁶ Recently, MOF films or membranes supported on a different substrates⁷ have attracted increasing interest for gas separation⁸ and catalysis.⁹

It is difficult to produce a dense and continuous membrane,¹⁰ by direct in-situ solvothermal preparation,¹¹ in which all nucleation, growth and intergrowth of crystals on a substrate take place during the synthesis step. Therefore, it is usually necessary to introduce a suitable functional group on the support a priori, which can interact either with the metal ions or organic linkers¹² to promote nucleation and adhesion on the support.¹³ On the other hand, it is still a challenge to form strong chemical bonding between the support surface and MOF organic linkers¹⁴ to prepare a mechanically robust MOF membrane.^{7,15} Consequently, improved techniques, such as rubbing,¹⁶ dip-coating,¹⁷ spin coating,¹⁸ wiping,¹⁹ microwave-assisted seeding,²⁰ thermal seeding,²¹ reactive seeding,²² and repeated growth,²³ have been proposed to improve the interaction between the seed layer and support. More significantly, a support material made of the same metallic species as the MOF structures was demonstrated to be desirable,

because the metal source on the substrate can provide the crystallization nuclei and enhance the adhesion between the MOF layers and substrates, such as in MIL-53(Al) membrane²² on an alumina support and HKUST-1 membrane over a copper net.⁷

This communication reports for the first time the fabrication of a continuous and defect-free amino-functionalized Ti-MIL125-NH₂ membrane on a TiO₂ support. TiO₂ is a good catalyst support due to the strong metal support interaction, chemical stability, and acid-base property. Heterogeneous TiO₂ supported catalysts show a high potential in photocatalyst-related applications^{24,25}. The Ti-MIL125-NH₂ is isostructural to the Ti-MIL125, which is comprised of cyclic octamers constructed from corner- or edge-sharing titanium octahedral units connected to 12 other cyclic octamers through organic linkers,²⁶ except that the benzene dicarboxylate (BDC) ligand is replaced with 2-amino benzene dicarboxylate (BDC-NH₂) in the framework. In Ti-MIL125-NH₂, the amino groups are free without coordination, and octahedral and tetrahedral cages with free diameters of 10.7 Å and 4.7 Å, respectively, are accessible through triangular 5-7 Å windows (Scheme S1, ESI†). Ti-MIL125-NH₂ was recently tested for photocatalytic oxidation of amines.²⁷ Herein, a strong adhesive and uniform seeding layer on the TiO₂ support was prepared and subsequently grown into a continuous highly inter-grown Ti-MIL125-NH₂ membrane after being subjected to combination of microwave (MW) and ultrasonic (US) irradiation. The physicochemical properties of the prepared membranes were evaluated and compared with those samples prepared by MW or US alone. Finally, the catalytic activity of the Ti-MIL125-NH₂ membrane was tested for the Knoevenagel condensation reaction between benzaldehyde and ethyl cyanoacetate to confirm the membrane stability.

Fig. 1 presents the synthesis steps employed to prepare a continuous and defect-free Ti-MIL125-NH₂ membrane supported on a porous TiO₂ disc using the two-step combined MW and US irradiation. Although MOFs have usually been prepared via hydrothermal/solvothermal methods,²⁸ there are reports of alternative syntheses, such as MW²⁹ or US³⁰ methods, in which high/intense MW and US waves led to homogeneous

^a Department of Chemistry and Chemical Engineering, Inha University, Incheon 402-751, Republic of Korea. E-mail: whasahn@inha.ac.kr; Fax: +82 32 8720959; Tel: +82 32 8607466

^b School of Materials Science and Engineering, Inha University, Incheon 402-751, Republic of Korea.

† Electronic Supplementary Information (ESI) available: [Materials, experimental details, characterizations, catalytic reaction, schematic structure of Ti-MIL-125-NH₂, SEM, XRD, N₂ adsorption-desorption isotherm, SEM-EDX, and recycling test]

nucleation, rapid crystallization, and accelerated synthetic chemical reactions³¹ during MOFs synthesis. These desirable features can be of equal importance for the preparation of MOFs in film form.¹⁴ The experimental details for the preparation/synthesis of the Ti-MIL125-NH₂ membrane and in powder form are given in ESI†.

As illustrated in the figure, the TiO₂ support was chemically modified by reacting with the NH₂-BDC ligand, which can improve heterogeneous nucleation by inducing covalent bonding between the linker and the support. Subsequently, the pre-treated support was soaked with a precursor solution of Ti-MIL125-NH₂ and then to-step secondary crystal growth process was conducted by MW flowed by a US treatment under different synthesis condition. Hereafter, the membrane samples obtained were designated depending on the synthesis method and its treatment duration (M; microwave, U; ultrasonic, and number; duration in min). For example, Ti-MIL125-NH₂ (M60/U60) represents a sample prepared by MW followed by a US treatment for 60 min each.

Initially, an attempt was made to prepare directly a Ti-MIL125-NH₂ membrane supported on a bare TiO₂ support using either MW or US alone. Unfortunately, no Ti-MIL125-NH₂ crystals formed on the support despite the extended synthesis for 4 h at the maximum power level of 500 W (Fig. S1). Only after the seed layer was formed on the support with the aid of the NH₂-BDC ligand, were crystals of Ti-MIL125-NH₂ detected after MW heating for 60 min (As the MW irradiation time was increased from 30 to 120 min, the characteristic Ti-MIL125-NH₂ peaks emerged steadily). A similar US treatment, however, was ineffective in crystallization. Therefore, a seeding step was necessary to fabricate the MOF membrane, which provided the heterogeneous nucleation sites for the initial MOF layer formation. MW irradiation was, in addition, more effective in initiating nucleation than US under the same power level. Haque et al.³² reported that the activation energy for MOF crystal nucleation decreased more sharply with MW than with a US treatment.

Fig. S1 presents SEM images of Ti-MIL125-NH₂ membrane growth at different stages. As shown in Fig. S1(b), the seed layer was formed evenly over the surface of the porous TiO₂ substrate while no Ti-MIL125-NH₂ peaks were detected. After the MW treatment at 250 W for 60 min, disk-shaped Ti-MIL125-NH₂ crystals, approximately 4 μm size, formed but the crystal density at the surface of the Ti-MIL125-NH₂ (M60) membrane was rather poor (Fig. S1(e)). A further increase in synthesis time from 60 to 120 min resulted in higher number density of the MOF crystals in the Ti-MIL125-NH₂ (M120) membrane (Fig. S1(f)), but this was not sufficient to provide complete surface coverage. These results suggest that the construction of a continuous membrane densely populated with Ti-MIL125-NH₂ crystals was not possible with MW only in this case. As shown in Fig. S2, the intensity of the XRD peaks of Ti-MIL125-NH₂ (M120) was considerably lower than that of the simulated or powder form of Ti-MIL125-NH₂.

US irradiation was then tested to make the Ti-MIL125-NH₂ (M60) membrane denser in the crystal population, since the

crystallization rates are also known to be accelerated strongly under US conditions both in the nucleation and crystal growth steps compared with the standard solvothermal processes.³³ In addition, when crystals already exist on the surface, they can act as templates for the formation of new crystal nuclei or fragment to produce more nucleation sites.³⁴ Therefore, the pre-formed crystals on the surface of the Ti-MIL125-NH₂ (M60) can provide “secondary nucleation” sites for subsequent membrane growth, which can increase the crystal density on the surface when subjected to additional US irradiation. The growth of pre-existing crystals on the membrane eliminate the gaps between the particles, and the recrystallization and growth of the crystals with the incorporation of multiple MOF layers occurred by secondary seeded growth.³⁵

After introducing US irradiation to the Ti-MIL125-NH₂ (M60) at 400 W for 30 min, approximately 90% of the surface of the obtained Ti-MIL125-NH₂ (M60/U30) membrane was covered with crystals, ca. 4 μm and 1.23 μm in length and width, respectively (Fig. S1(g) and (g-1)). However, impurities, unreacted precursors, are also present on the surface. Upon further increases in the US irradiation time to 60 min, a homogeneously yellow-coloured Ti-MIL125-NH₂ (M60/U60), of which the surface was covered densely and uniformly with highly inter-grown disk-shaped Ti-MIL125-NH₂ crystals, ca. 2.5 μm and 1.24 μm in length and width, respectively, were obtained without pinholes or cracks on the support (Fig. 2(b) and S1(h-1)). The surface crystal morphology of the membrane was similar to that of Ti-MIL125-NH₂ powder (Fig. 2(a)), but the Ti-MIL125-NH₂ crystals were grown mostly orientated toward c-axis. Fig. 2 (c) shows cross sections of the membrane layer, which was bonded uniformly and tightly to the support with a thickness of approximately 23.5 μm. Unlike those of the Ti-MIL125-NH₂ (M60/U30), Ti-MIL125-NH₂ (M60/U60) consisted of more dense and uniform crystals without impurities. XRD of the Ti-MIL125-NH₂ (M60/U60) membrane (Fig. 3A (d)) revealed the characteristic peaks of both the TiO₂ support and Ti-MIL125-NH₂ particles (Fig. 3A; (a) and (c)), which confirmed that phase-pure crystals formed on the TiO₂ support in the absence of other impure phases. Fig S3 shows the N₂ adsorption–desorption isotherms of the Ti-MIL-125-NH₂ particles. The sample exhibited type I isotherms at 77 K with no hysteresis and a BET surface area of 1458 m²/g with a pore volume of 0.64 cm³/g. As shown in Fig. S4, EDS showed that there was a soft transition between the Ti-MIL125-NH₂ layer (N signal) and TiO₂ support (Ti signal), suggesting that the support was covered fully and evenly with the Ti-MIL125-NH₂ crystals.

Following the successful fabrication of the densely-packed Ti-MIL125-NH₂ (M60/U60) membrane, its heterogeneous catalytic activity for the Knoevenagel condensation reaction between benzaldehyde and ethyl cyanoacetate was investigated (the detailed experimental procedure is given in ESI†). Although the bulk of the MOF membranes have been applied for separation,³⁶ MOF-based film/membrane can also function as a recyclable heterogeneous catalyst with easy catalyst separation compared to the micron-sized low density MOF particles that require rigorous centrifuging for catalyst

separation after the chemical reactions.⁹ The MOF membrane also enables reactions in a continuous mode with a low pressure drop³⁷. As shown in Fig. 4, the benzaldehyde conversion increased steadily from 41 to 60 % as the reaction time was increased from 0.5 to 4 h. After removing the membrane catalyst in a hot filtration experiment, no further reaction took place in the mother liquor, which confirmed the heterogeneous nature of the catalytic reaction. For a further evaluation of the stability of the catalytic membrane in the liquid phase reaction, the reactions were repeated for up to 5 cycles under the same reaction conditions (see Fig. 4 (b)). At the end of each reaction cycle, the catalyst membrane was removed from the solution mixture and the catalyst was reused after washing with the solvent.

As shown in Fig. 4(b), the catalytic activity of Ti-MIL125-NH₂ (M60/U60) was maintained at 60 % conversion after the 5th recycle run in the reaction, suggesting that no structural deterioration or detachment of the membrane layer from the TiO₂ disc occurred after the catalytic reaction. XRD showed no obvious decrease in the intensity of the Ti-MIL125-NH₂ characteristic peaks (see Fig. 3B). On the other hand, the conversion of the IRMOF-3 membrane prepared previously decreased from 87 % to 77 % after repeated runs due to loss of some weakly bond IRMOF-3 particles to the support.^{38,39}

In conclusion, a densely packed Ti-MIL125-NH₂ membrane was prepared on a TiO₂ support with a uniform and high surface coverage using MW/US combined heating technique. The key step in this method was to utilize 'secondary nucleation' site of the porous support by changing the synthesis method from MW to US, resulting in the rapid heterogeneous nucleation and crystal growth of Ti-MIL125-NH₂ crystals. Subsequent multi-secondary growth of the seeded layer produced highly inter-grown Ti-MIL125-NH₂ membrane upon US irradiation. The product obtained was applied as a heterogeneous catalyst for the Knoevenagel condensation reaction, and exhibited stable and recyclable catalysis that enables easy catalyst separation.

This study was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (Grant number: NRF-2015R1A4A1042434).

Notes and references

- H. Li, M. Eddaoudi, M. O'Keeffe and O. M. Yaghi, *Nature*, 1999, **402**, 276; D. J. Tranchemontagne, J. L. Mendoza-Cortés, M. O'Keeffe and O. M. Yaghi, *Chem. Soc. Rev.*, 2009, **38**, 1257.
- L. J. Murray, M. Dinča and J. R. Long, *Chem. Soc. Rev.*, 2009, **38**, 1294; U. Muller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Armdt and J. Pastré, *J. Mater. Chem.*, 2006, **16**, 626; A. Corma, H. Garcia and F.X. L. Xamena, *Chem. Rev.*, 2010, **110**, 4606.
- J. L. C. Rowsell, E. C. Spencer, J. Eckert, J. A. K. Howard and O. M. Yaghi, *Science*, 2005, **309**, 1350.
- S. H. Jung, J. H. Lee, J. W. Yoon, C. Serre, G. Férey and J. S. Chang, *Adv. Mater.*, 2007, **19**, 121.
- S. Bhattacharjee, D. A. Yang and W. S. Ahn, *Chem. Commun.*, 2011, **47**, 3637.
- S. Achmann, G. Hagen, J. Kita, I. M. Malkowsky, C. Kiener and R. Moos, *Sensors*, 2009, **9**, 1574; S. M. Humphrey and P. T. Wood, *J. Am. Chem. Soc.*, 2004, **126**, 13236; P. Horcajada, T. Chalati, C. Serre, B. Gillet, C. Sebrie, T. Baati, J. F. Eubank, D. Heurtaux, P. Clayette, C. Kreuz, J. S. Chang, Y. K. Hwang, V. Marsaud, P. Bories, L. Cynober, S. Gil, G. Férey, P. Couvreur and R. Gref, *Nat. Mater.*, 2010, **9**, 172.
- H. Bux, A. Feldhoff, J. Cravillon, M. Wiebcke, Y. S. Li, and J. Caro, *Chem. Mater.*, 2011, **23**, 2262; L. Fan, M. Xue, Z. Kang, H. Li and S. Qiu, *J. Mater. Chem.*, 2012, **22**, 25272; H. Bux, C. Chmelik, R. Krishna and J. Caro, *J. Membr. Sci.*, 2011, **369**, 284; K. Huang, S. Liu, Q. Li and W. Jin, *Sep. Purif. Technol.*, 2013, **119**, 94; H. Guo, G. Zhu, I. J. Hewitt and S. Qiu, *J. Am. Chem. Soc.*, 2009, **131**, 1646.
- Y. Liu, Z. Ng, E. A. Khan, H. K. Jeong, C. Ching and Z. Lai, *Micropor. Mesopor. Mater.*, 2009, **118**, 296; L. Diestel, H. Bux, D. Wachsmuth and J. Caro, *Micropor. Mesopor. Mater.*, 2012, **164**, 288; S. Zhou, X. Zou, F. Sun, H. Ren, J. Liu, F. Zhang, N. Zhao and G. Zhu, *Int. J. Hydrogen Energy*, 2013, **38**, 5338; J. A. Bohrman and M. A. Carreon, *Chem. Commun.*, 2012, **48**, 5130.
- S. Aguado, J. Canivet and D. Farrusseng, *J. Mater. Chem.*, 2011, **21**, 7582; R. Jin, Z. Bian, J. Li, M. Ding and L. Gao, *Dalton Trans.*, 2013, **42**, 3936; S. Aguado, J. Canivet and D. Farrusseng, *Chem. Commun.*, 2010, **46**, 7999; E. V. Ramos-Fernandez, M. Garcia-Domingos, J. Juan-Alcañiz, J. Gascon and F. Kapteijn, *Appl. Cat. A Gen.*, 2011, **391**, 261; Y. Mao, J. Li, W. Cao, Y. Ying, P. Hu1, Y. Liu, L. Sun, H. Wang, C. Jin and X. Peng, *Nat. Commun.*, 2014, **5**, 5532.
- Y. P. Yampolskii, I. Pinnau and B. D. Freeman, *Materials Science of Membranes for Gas and Vapor Separation.*; John Wiley & Sons, Ltd., New York, 2006.
- M. Shah, M. C. McCarthy, S. Sachdeva, A. K. Lee and H. K. Jeong, *Ind. Eng. Chem. Res.*, 2012, **51**, 2179.
- R. Semino, N. A. Ramsahye, A. Ghoufi and Guillaume Maurin, *ACS Appl. Mater. Interfaces*, 2016, **8**, 809.
- F. Schreiber, *Prog. Surf. Sci.*, 2000, **65**, 151; J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo and G. M. Whitesides, *Chem. Rev.*, 2005, **105**, 1103; A. Huang, W. Dou and J. Caro, *J. Am. Chem. Soc.*, 2010, **132**, 15562; E. Biemmi, C. Scherb, and T. Bein, *J. Am. Chem. Soc.*, 2007, **129**, 8054.
- Y. Yoo and H. K. Jeong, *Chem. Commun.*, 2008, 2441.
- J. Gascon and F. Kaptejin, *Angew. Chem., Int. Ed.*, 2010, **49**, 1530.
- R. Ranjan and M. Tsapatsis, *Chem. Mater.*, 2009, **21**, 4920; K. Tao, C. Kong and L. Chen, *Chem. Eng. J.*, 2013, **220**, 1.
- Z. Zhao, X. Ma, Z. Li and Y. S. Lin, *J. Mem. Sci.*, 2011, **382**, 82.
- J. Hu, H. Cai, H. Ren, Y. Wei, Z. Xu H. Liu and Y. Hu, *Ind. Eng. Chem. Res.*, 2010, **49**, 12605.
- Y. C. Pan, B. Wang and Z.P. Lai, *J. Membr. Sci.*, 2012, **292**, 421.
- H. T. Kwon and H. K. Jeong, *Chem. Commun.*, 2013, **49**, 3854.
- V. V. Guerrero, Y. Yoo, M. C. McCarthy and H. K. Jeong, *J. Mater. Chem.*, 2010, **20**, 3938.
- Y. Hu, X. Dong, J. Nan, W. Jin, X. Ren, N. Xu and Y.M. Lee, *Chem. Commun.*, 2011, **47**, 737.
- M. C. McCarthy, V. Varela-Guerrero, G. V. Barnett and H. K. Jeong, *Langmuir*, 2010, **26**, 14636.
- Y. Liu, J. Li, B. Zhou, H. Chen, Z. Wang and W. Cai, *Chem. Commun.*, 2011, **47**, 10314.
- Y. Liu, J. Li, B. Zhou, S. Lv, X. Li, H. Chen, Q. Chen and W. Cai, *Appl. Catal. B: Environ.*, **485**, (2012) 111.
- M. A. Moreira, J. C. Santos, A. F. P. Ferreira, J. M. Loureiro, F. Ragon, P. Horcajada, P. G. Yot, C. Serre and A. E. Rodrigues, *Langmuir*, 2012, **28**, 3494.

- 27 D. Sun, L. Ye and Z. Li, *Appl. Catal. B: Environ.*, **164**, (2015) 428.
- 28 G. Férey, *Chem. Soc. Rev.*, 2008, **37**, 191.
- 29 S. H. Jung, J. H. Lee, J. W. Yoon, C. Serre, G. Férey and J. S. Chang, *Adv. Mater.*, 2007, **19**, 121; H. Y. Cho, D. A. Yang, J. Kim, S. Y. Jeong and W. S. Ahn, *Catalysis Today*, 2012, **185**, 35.
- 30 J. Kim, S. T. Yang, S. B. Choi, J. Sim, J. Kim and W. S. Ahn, *J. Mater. Chem.*, 2011, **21**, 3070; H. Y. Cho, J. Kim, S. N. Kim and W. S. Ahn, *Micropor. Mesopor. Mater.*, 2013, **169**, 180.
- 31 K. Suslick, *Science*, 1990, **247**, 1439; K. H. Kim and K. B. Kim, *Ultrason. Sonochem.*, 2008, **15**, 1019.
- 32 E. Haque, N. A. Khan, J. H. Park and S. H. Jung, *Chem. Eur. J.*, 2010, **16**, 1046.
- 33 N. A. Khan and S. H. Jung, *Coord. Chem. Rev.*, 2015, **285**, 11.
- 34 M. D. Luque de Castro and F. P. Capote, *Ultrasonic. Sonochem.*, 2007, **14**, 717.
- 35 J. A. Bohrman and M. A. Carreon, *Chem. Commun.*, 2012, **48**, 5130.
- 36 S. Qiu, M. Xue and G. Zhu, *Chem. Soc. Rev.*, 2014, **43**, 6116; S. R. Venna and M. A. Carreon, *Chem. Eng. Sci.*, 2015, **124**, 3.
- 37 A. E. W. Beers, T. A. Nijhuis, N. Aalders, F. Kapteijn and J. A. Moulijn, *Appl. Catal. A Gen.*, 2003, **243**, 237.
- 38 Y. R. Lee, S. M. Cho, W. S. Ahn, C. H. Lee, K. H. Lee and W. S. Cho, *Micropor. Mesopor. Mater.*, 2015, **213**, 161.
- 39 The amount of the catalytic NH₂ species attached to IRMOF-3 particles is *ca.* 1.4 times higher than that of Ti-MIL-125-NH₂ particles for equal weight of the sample used due to different chemical structures.

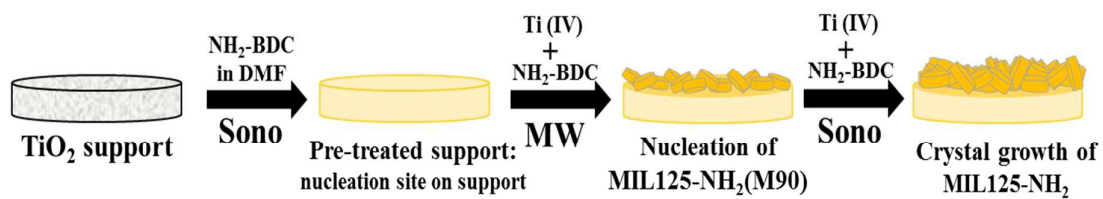


Fig. 1 Schematic diagram of the fabrication steps for the Ti-MIL125-NH₂ membrane on a TiO₂ support via combined ultrasonic/microwave heating methods.

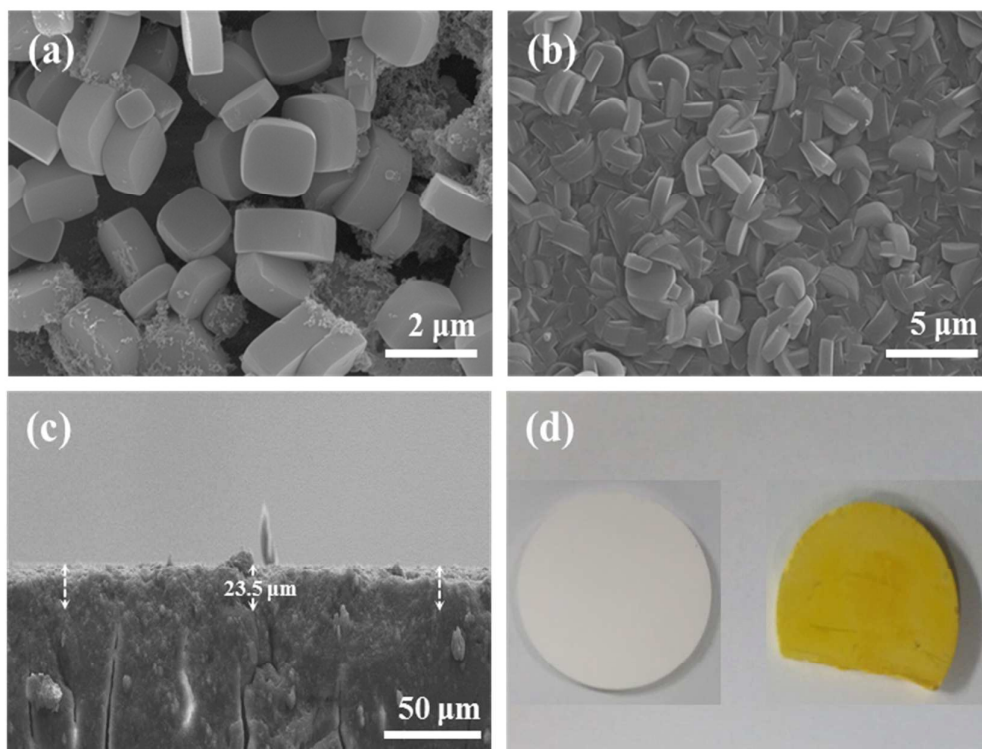


Fig. 2 SEM images of (a) MIL-125-NH₂ powder, (b) top- and (c) cross-section view of Ti-MIL-125-NH₂ (M60/U60) membrane, and (d) photographic images of original TiO₂ support (left) and MIL-125-NH₂ (M60/U60) membrane (right).

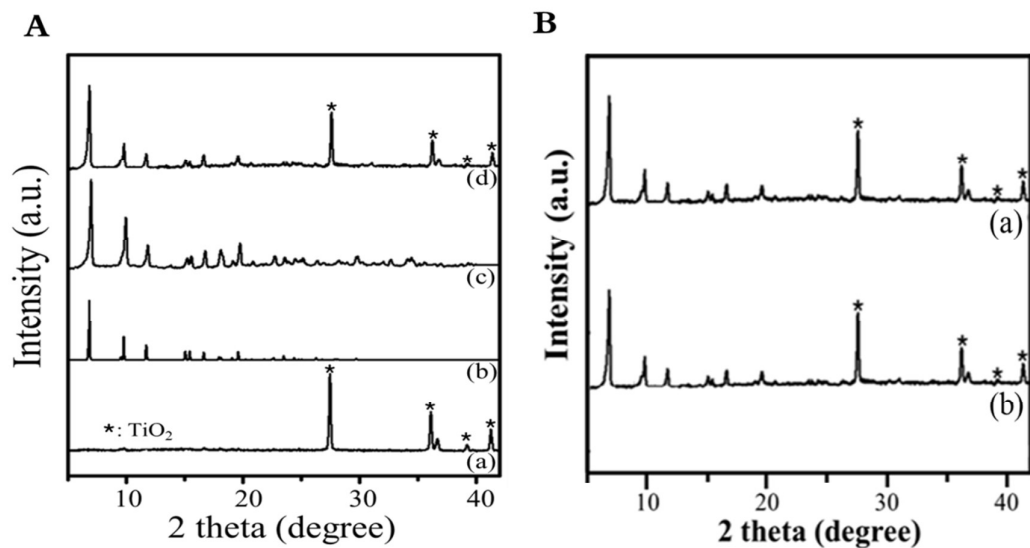


Fig. 3 XRD patterns of A: (a) porous TiO₂ support, (b) simulated Ti-MIL125-NH₂, (c) Ti-MIL125-NH₂ powder and (d) Ti-MIL125-NH₂ (M60/U60) membrane and B: Ti-MIL125-NH₂ (M60/U60) membrane (a) before and (b) after the recycling tests in Knoevenagel condensation reaction. The asterisk (*) in the inset corresponds to the TiO₂ support.

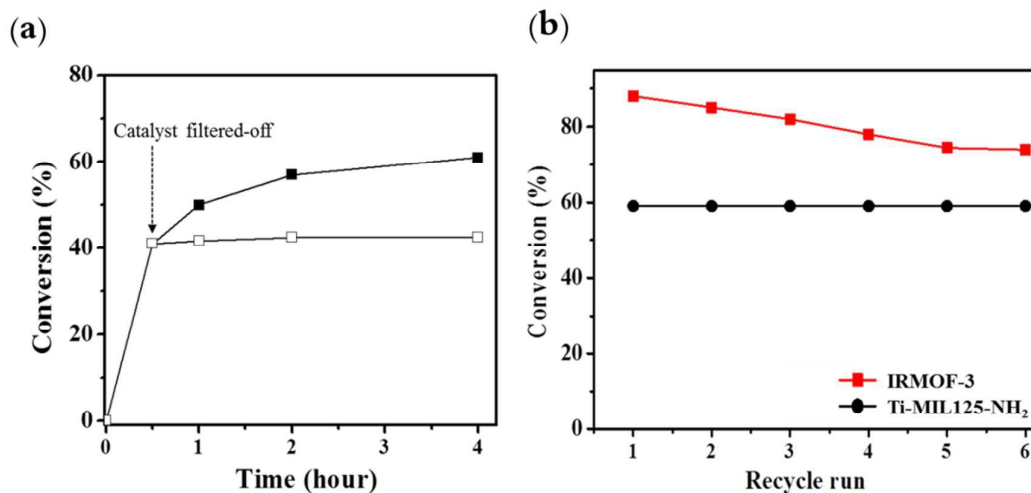


Fig. 4 (a) Progress of the Knoevenagel condensation reaction over the Ti-MIL-125-NH₂ (M60/U60) membrane (■: Reaction with catalyst, □: reaction after catalyst removal) and (b) comparison of the recycling tests of the IRMOF-3 (red) and Ti-MIL125-NH₂ (M60/U60) (black) membranes in a Knoevenagel condensation reaction. The IRMOF-3 membrane was prepared on an alumina disc at 400 W for 1 h [38]. (Amount of the catalysts: ca. 9 mg of Ti-MIL-125-NH₂ and ca. 6.2 mg of IRMOF-3 crystals on the TiO₂ and Al₂O₃ support, relatively).

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

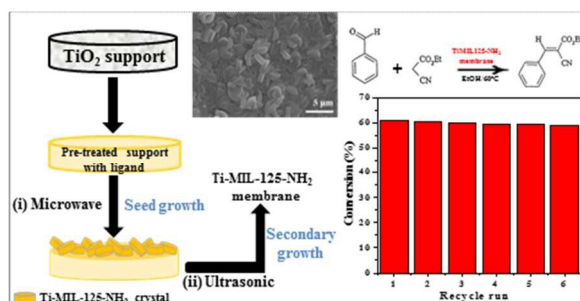
Yu-Ri Lee,^a Sung-Min Cho,^a Sung-Hyeon Baek,^a Wha-Seung Ahn*^a and Won-Seung Cho^b

^aDepartment of Chemistry and Chemical Engineering, Inha University, Incheon 402-751, Korea

^bSchool of Materials Science and Engineering, Inha University, Incheon, 402-751, Korea

Graphical abstract

Ti-MIL125-NH₂ membrane with uniform crystals was prepared on TiO₂ disc using microwave/ultrasonic irradiation, which exhibited as reusable catalyst for Knoevenagel reaction.



Corresponding author: W.S. Ahn

Tel : +82-32-860-7466, Fax : +82-32-872-0959, E-mail : whasahn@inha.ac.kr