

Electronic Supplementary Information for
**Nanoparticulate and microporous solid acid catalysts bearing aliphatic sulfonic acids
for biomass conversion**

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Experimental Sections

SEM and TEM images were obtained using a JSM6700F and a JEOL 2100F, respectively. EDS mapping images and ED patterns were obtained using a JEOL 2100F. Surface areas and the porosity of materials were analyzed through the analysis of N₂ adsorption-desorption isotherm curves (77K) which were obtained using a Micromeritics ASAP2020 and a BELSORP II-mini analyzer. Pore size distribution diagrams were obtained by the DFT method. IR absorption spectra were obtained using a Bruker VERTEX 70 FT-IR spectrometer. Solid state CP/TOSS ¹³C NMR spectra were obtained using a 500 MHz Bruker ADVANCE II NMR spectrometer at the National Center for Inter-University Research Facilities of Seoul National University. A 4 mm magic angle spinning probe was used at the spinning rate of 5 kHz. PXRD patterns were obtained using a SmartLAB (Rigaku, Japan) 3kW (Cu target) D/teX Ultra250 (filtered Cu-Kα radiation). TGA curves were obtained using a Seiko Exstar 7300 analyzer. The contents of sulfonic acids in the materials were analyzed by the acid-base titration using a 0.01 M NaOH solution. Solution state ¹H NMR spectra were obtained using 400 MHz and 500 MHz Varian spectrometers. Biphenyl was used as an internal standard.

Synthesis of N-MON-AS and MON-AS

1,3,5,7-Tetra(4-ethynylphenyl)adamantane was prepared by the synthetic procedures reported in the literature.¹ 1,4-Bis(trimethylsilylethynyl)-2,5-dibromobenzene was prepared by the synthetic procedures reported in the literature.² For the preparation of N-MON particles, poly(vinylpyrrolidone) (PVP, Mw: 40,000, Aldrich Co., 1.24 g), (PPh₃)₂PdCl₂ (42 mg, 60 μmol), and CuI (7.0 mg, 37 μmol) were added to a flame-dried 100 mL Schlenk flask. After ethanol (40 mL) and triethylamine (20 mL) were added, the mixture was sonicated for 20 min at room temperature. After 1,3,5,7-tetra(4-ethynylphenyl)adamantane (0.19 g, 0.36 mmol) and 1,4-bis(trimethylsilylethynyl)-2,5-dibromobenzene (0.31 g, 0.72 mmol) were added, the reaction mixture was heated with stirring at 80°C for 2 days. After being cooled to room temperature, the solid was separated by centrifugation, washed with methanol (40 mL), acetone (40 mL), methylene chloride (40 mL) three times each, and dried under vacuum. The MON nanoparticles were added to a mixture of water (15 mL), methanol (10 mL), and HF solution (45% aqueous solution, 5 mL) in a 50 mL Falcon tube. *Caution: The HF solution is extremely toxic and should be handled with special gloves in a hood.* The reaction mixture was stirred for 2 h at room

temperature. The powder (N-MON) was separated by centrifugation, washed with a mixture of water (30 mL) and methanol (10 mL) three times and methanol (40 mL) two times, and dried under vacuum.

For the preparation of N-MON-AS, the N-MON nanoparticles (0.25 g) was added to a flame dried 100 mL Schlenk flask. After AIBN (1.6 g, 9.9 mmol) and sodium 2-mercaptoethanesulfonate (1.6 g, 9.9 mmol), and DMF (80 mL) were added, the mixture was sonicated for 5 min at room temperature. Then, the reaction mixture was heated at 90°C with stirring for 1 day. After being cooled to room temperature, the solid was separated by centrifugation, washed with methanol (40 mL) three times, acetone (40 mL) three times, and methylene chloride (40 mL) three times, and dried under vacuum. The solid was added to a mixture of water (30 mL), sulfuric acid (5 mL), and methanol (10 mL) in a Falcon tube. *Caution: The sulfuric acid was added very slowly.* The reaction mixture was stirred at room temperature for 2 h. The solid (N-MON-AS) was separated by centrifugation, washed with a mixture of water (30 mL) and methanol (10 mL) until the pH of solution became 7. After the solid was further washed with methanol (40 mL) two times and dried under vacuum.

For the preparation of micron-sized MON materials,³ (PPh₃)₂PdCl₂ (42 mg, 60 μmol), and CuI (7.0 mg, 37 μmol) were added to a flame-dried 100 mL Schlenk flask. After triethylamine (60 mL) was added, the mixture was sonicated for 20 min at room temperature. After 1,3,5,7-tetra(4-ethynylphenyl)adamantane (0.19 g, 0.36 mmol) and 1,4-bis(trimethylsilylethynyl)-2,5-dibromobenzene (0.31 g, 0.72 mmol) were added, the reaction mixture was heated with stirring at 80°C for 2 days. After being cooled to room temperature, the solid was separated by centrifugation, washed with methanol (40 mL), acetone (40 mL), methylene chloride (40 mL) three times each, and dried under vacuum. The MON nanoparticles were added to a mixture of water (15 mL), methanol (10 mL), and HF solution (45% aqueous solution, 5 mL) in a 50 mL Falcon tube. *Caution: The HF solution is extremely toxic and should be handled with special gloves in a hood.* The reaction mixture was stirred for 2 h at room temperature. The powder (N-MON) was separated by centrifugation, washed with a mixture of water (30 mL) and methanol (10 mL) three times and methanol (40 mL) two times, and dried under vacuum. The synthetic procedures of MON-AS were the same as those of N-MON-AS except for using MON materials instead of N-MON nanoparticles.

Procedures of catalytic reactions

D-fructose (0.304 g, 1.69 mmol), biphenyl (internal standard, 0.130 g, 0.844 mmol), and N-MON-AS (0.731 mmol SO₃H/g based on acid-base titration, 46 mg, 2 mol% SO₃H for fructose), biphenyl (internal standard, 0.130 g, 0.844 mmol), and distilled DMSO (5 mL) were added to a 20 mL vial. In the case of MON-AS (0.284 mmol SO₃H/g based on acid-base titration), the amount of 119 mg corresponds to 2 mol% SO₃H for fructose. *Caution: The by-products that can be formed through the decomposition of fructose are hardly detected in the ¹H NMR analysis. Thus, the HMF yield should be checked by the internal standard.* The reaction mixture was heated at 60, 80, 120, and 140°C for 0.5 ~20 h. The yields of HMF were analysed by ¹H NMR based on the internal standard method based on the ¹H peak of HMF at 5.55 ppm and ¹H peak of internal standard at 7.38 ppm. ¹H NMR of HMF (DMSO-d₆, 500 MHz): δ = 4.51 (d, J = 5.5 Hz, 2H), 5.55 (t, J = 5.9 Hz, 1H), 6.61 (d, J = 3.5 Hz, 1H), 7.50 (d, J =

3.6 Hz, 1H), 9.56 (s, 1H) ppm. ¹H NMR of biphenyl (DMSO-d₆, 500 MHz): δ = 7.38 (t, J = 7.4 Hz, 2H), 7.48 (t, J = 7.8 Hz, 4H), 7.67 (d, J = 7.2 Hz, 4H) ppm. In the recyclability testes, D-fructose (0.304 g, 1.69 mmol), biphenyl (internal standard, 0.130 g, 0.844 mmol), and N-MON-AS (0.731 mmol SO₃H/g based on acid-base titration, 2.0 mol% SO₃H to fructose, 46 mg), and distilled DMSO (5 mL) were added to a 20 mL vial. The reaction mixture was stirred at 100°C for 5 h. After being cooled to room temperature, the catalyst was retrieved by centrifugation, washed with methanol (40 mL) three times, acetone (40 mL) three times, dichloromethane (40 mL) three times, and hexane (40 mL) three times, dried under vacuum, and used for the next run. TON values were calculated by the following equation; TON = (HMF yield)/(mol% of SO₃H to fructose).

References

1. H. Lee, H. Kim, T. J. Choi, H. W. Park and J. Y. Chang, *Chem. Commun.* 2015, **51**, 9805-9808.
2. K. Takimiya, Y. Knoda, H. Ebata, N. Niihara and T. Otsubo, *J. Org. Chem.* 2015, **70**, 10569-10571.
3. K. Cho, J. Yoo, H. -W. Noh, S. M. Lee, H. J. Kim, Y. -J. Ko, H. -Y. Jang and S. U. Son, *J. Mater. Chem. A* 2017, **5**, 8922-8926.

Fig. S1 Size distribution diagrams of N-MON-AS and MON-AS.

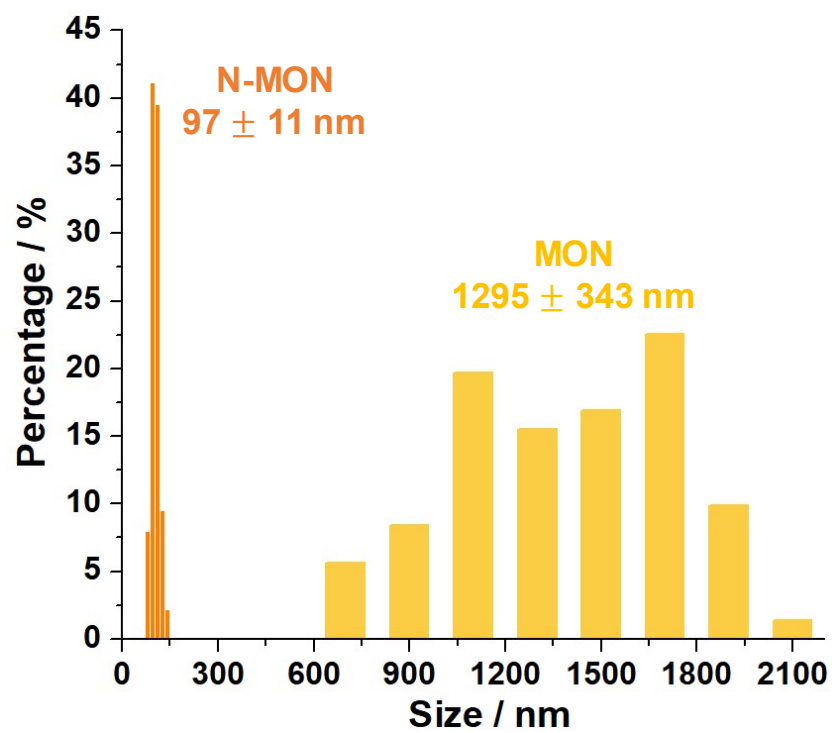


Fig. S2 SEM images of MON materials obtained depending on the amount of PVP with fixed amounts of tetra(4-ethynyl phenyl)adamantane (0.36 mmol) and 1,4-dibromo-2,5-bis(2-trimethylsilylethynyl)benzene (0.72 mmol).

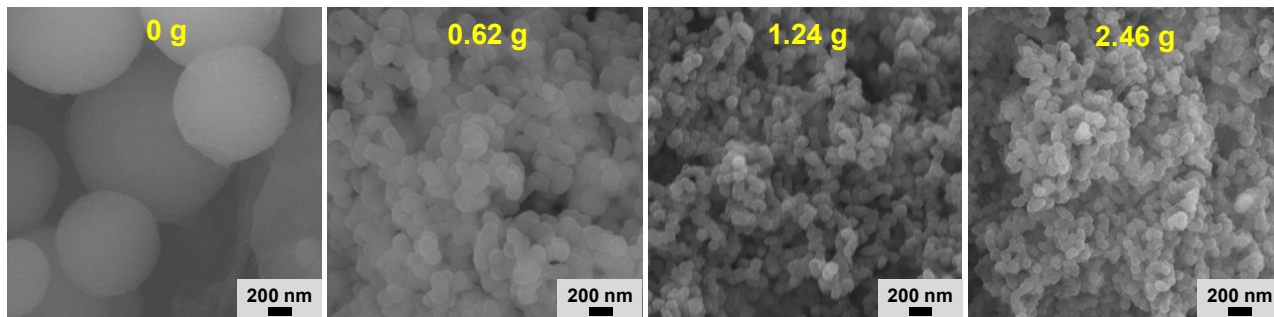


Fig. S3 PXRD and ED patterns of MON, MON-AS, N-MON, and N-MON-AS.

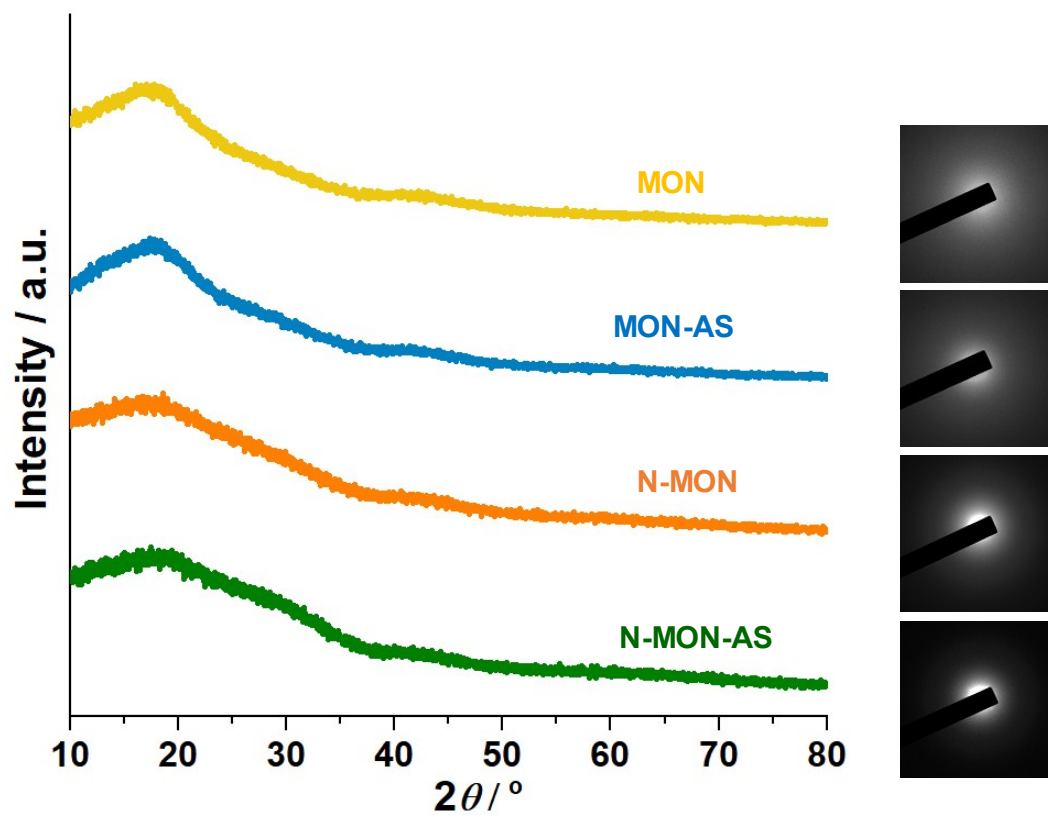


Fig. S4 TGA curves of N-MON-AS and MON-AS.

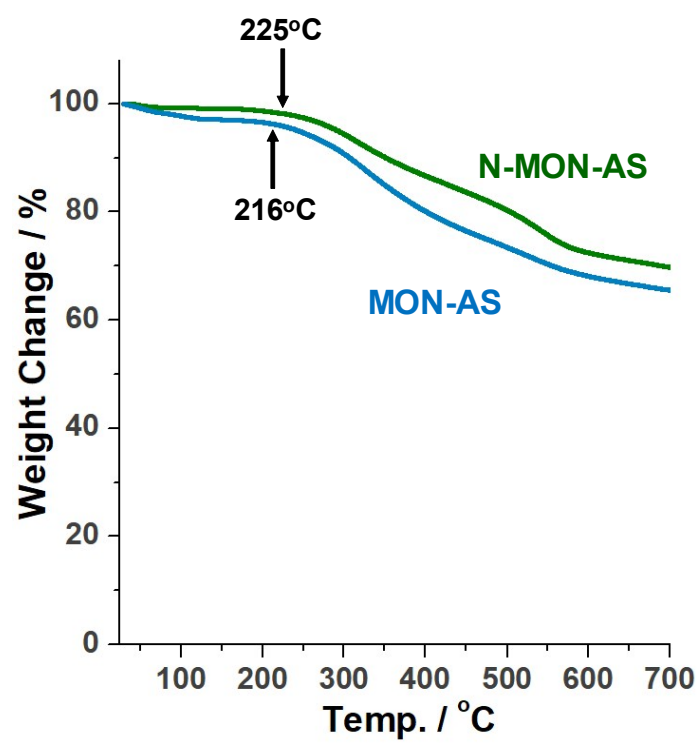


Fig. S5 ^1H and ^{13}C NMR and IR spectra of HMF.

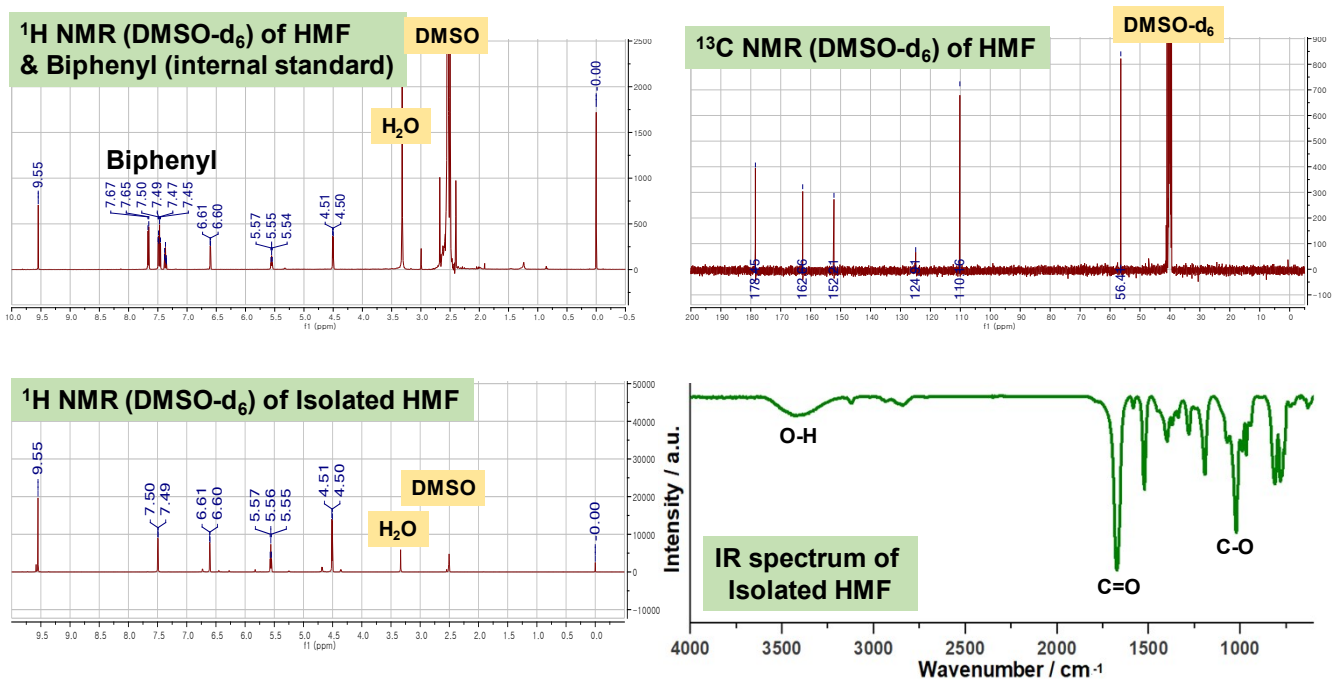


Fig. S6 (a) SEM images and (b) N₂ adsorption-desorption isotherm curves and pore size distribution diagrams of

N-MON-AS materials before and after catalytic reaction.

