Electronic Supplementary Information for

AB$_2$ polymerization on hollow microporous organic polymer: Engineering of solid acid catalysts for the synthesis of soluble cellulose derivatives

Su Kyung Chae,[a‡] Kyoungil Cho,[a‡] Sang Moon Lee,[b] Hae Jin Kim,[b] Yoon-Joo Ko,[c] and Seung Uk Son[a*]

[a]*Department of Chemistry, Sungkyunkwan University, Suwon 16419, Korea*

[b]*Korea Basic Science Institute, Daejeon 34133, Korea*

[c]*Laboratory of Nuclear Magnetic Resonance, National Center for Inter-University Research Facilities(NCIRF), Seoul National University, Seoul 08826, Korea*

‡ *These authors contributed equally to this work*

Experimental Sections

Conventional ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were obtained using 400 MHz and 500 MHz Varian spectrometers. Solid state ^{13}C NMR spectra were obtained at CP/TOSS mode using a 500 MHz Bruker ADVANCE II NMR spectrometer at the National Center for Inter-University Research Facilities of Seoul National University. Scanning and transmission electron images were obtained using a FE-SEM (JSM6700F) and a JEOL 2100F, respectively. Infrared absorption spectra were obtained using a Bruker VERTEX 70 FT-IR spectrometer. N_2 adsorption-desorption isotherm curves were obtained at 77K using a Micromeritics ASAP2020. Surface areas were obtained through analysis based on the Brunauer-Emmett-Teller theory. Pore size distribution was analyzed by the density functional theory method. Thermogravimetric analysis was performed using a Seiko Exstar 7300 and a Discovery TGA machine. Elemental analysis was conducted using a CE EA1110 analyzer. Powder X-ray diffraction studies were conducted using a Rigaku MAX-2200 (filtered Cu-Kα radiation).

Synthesis of H-MOP-TA and H-MOP@AB$_2$-TA

Silica spheres with a diameter of ~220 nm were prepared by the Stöber method.[1] Ethanol (200 mL), ammonia solution (28~20%, 5 mL), and distilled water (8 mL) were added to a 250 mL round-bottomed flask and the mixture was stirred for 30 min at room temperature. After tetraethyl orthosilicate (TEOS, 14 mL, 62 mmol) was added, the reaction mixture was stirred for 18 h at room temperature. Silica spheres were separated by centrifugation and washed with methanol (30 mL) three times, dichloromethane (30 mL) three time, and acetone (30 mL) once. Then, silica spheres were dried under vacuum, heat-treated at 550^{o}C for 5 h under air, and cooled to room temperature. 1,4-Dibromo-2,5-diethynylbenzene was prepared by the synthetic procedures reported in the literature.[2] H-MOP-TA was prepared by the modified synthetic procedures reported in the literature.[3] For the synthesis of SiO_2@MOP-TA, after silica spheres (0.30 g), $(PPh_3)_2PdCl_2$ (8.4 mg, 12 μmol), CuI (2.3 mg, 12 μmol), distilled triethylamine (20 mL), and distilled DMF (10 mL) were added to a flame-dried 100 mL Schlenk flask, the mixture was sonicated for 1 h at room temperature. After 1,4-dibromo-2,5-diethynylbenzene (0.10 g, 0.36 mmol) was added, the reaction mixture was heated at 80^{o}C for 12 h. After being cooled to room temperature, the solid was separated by centrifugation, washed with methanol (30 mL) twice, methylene chloride (30 mL) twice, and acetone (30 mL) once, and dried under vacuum. For the synthesis of H-MOP-TA, the SiO_2@MOP-TA was added to a mixture of aqueous HF solution (48-51%, 7.5 mL), methanol (25 mL), and water (25 mL). After the mixture was stirred for 2 h at room temperature, the solid was separated by centrifugation, washed with methanol (30 mL) twice, methylene chloride (30 mL) twice, and acetone (30 mL) once, and dried under vacuum. *Caution: the HF solution is extremely toxic. It should be handled with specific gloves in a hood. Excess HF solution should be quenched completely using NaOH solution.*

The AB_2 monomer, 3,5-diethynylbenzyl azide is an unknown compound. It was synthesized as follows. For the synthesis of 3,5-diethynylbenzyl azide, 3,5-bis(trimethylsilylethynyl)benzyl bromide was prepared by the synthetic procedures reported in the literature.[5] For the synthesis of 3,5-bis(trimethylsilylethynyl)benzyl azide, 3,5-bis(trimethylsilylethynyl)benzyl bromide (0.77 g, 2.1 mmol) was dissolved in DMF (30 mL) in a 100 mL Schlenk flask. After sodium azide (0.69 g, 11 mmol) was added and the glassware was wrapped with an Al foil to block light, the mixture was stirred at room temperature for 1 h. The product was extracted using ethyl acetate and brine solution. After the ethyl acetate solution was dried using $MgSO_4$, the solvent was evaporated. The 3,5-bis(trimethylsilylethynyl)benzyl azide was separated by silica column chromatography. Characterization data of 3,5-bis(trimethylsilylethynyl)benzyl azide: isolated yield = 88%, ^1H NMR (500 MHz, $CDCl_3$) δ = 7.55 (s, 1H), 7.36 (s, 2H), 4.28 (s, 2H), 0.25 (s, 18H) ppm, ^{13}C NMR (125 MHz, $CDCl_3$) δ = 136.0, 135.3, 131.4, 124.2, 103.6, 95.8, 54.1, 0.0 ppm. HR-MS: Calc. $[C_{17}H_{13}N_3Si_2]^+$, 325.1431, Obs. 325.1432.

For the synthesis of 3,5-diethynylbenzyl azide, 3,5-bis(trimethylsilylethynyl)benzyl azide (0.62 g, 1.9 mmol) was dissolved in THF (20 mL) in a 50 mL Schlenk flask. After being cooled to 0^oC using an ice bath, tetrabutylammonium fluoride solution (1.0 M in THF, 11 mL, 11 mmol) was added. The reaction mixture was further stirred at room temperature for 24 h. After adding a small amount of water, THF in the reaction mixture was evaporated. The product was extracted using diethyl ether and distilled water. After diethyl ether solution was dried using $MgSO_4$, ether was evaporated. The 3,5-diethynylbenzyl azide was separated by silica column chromatography. Characterization data of 3,5-diethynylbenzyl azide: isolated yield = 72%, ^1H NMR (500 MHz, $CDCl_3$) δ = 7.58 (s, 1H), 7.42 (s, 2H), 4.33 (s, 2H), 3.12 (s, 2H) ppm, ^{13}C NMR (125 MHz, $CDCl_3$) δ = 141.3, 134.6, 130.2, 123.7, 104.0, 95.2, 64.5 ppm. Elemental Analysis for $C_{11}H_7N_3$, Calc. C: 72.92%, H: 3.89%, N: 23.19%, Obs. C: 72.91%, H: 3.85%, N: 23.27%.

For the synthesis of H-MOP@AB_2-TA-2, after H-MOP-TA (50 mg), sodium ascorbate (9.0 mg, 46 μmol), $CuSO_4 \cdot 5H_2O$ (11 mg, 46 μmol), DMF (4 mL), and water (2 mL) were added to a 100 mL Schlenk flask, the reaction mixture was sonicated for 1 h at room temperature. After 3,5-diethynylbenzyl azide (0.13 g, 0.72 mmol) was added, the reaction mixture was stirred for 30 min at room temperature. After THF (4 mL) was added, the reaction mixture was heated at 50 ^oC for 24 h. After being cooled to room temperature, the solid was separated by centrifugation, washed with methanol (30 mL) twice, methylene chloride (30 mL) twice, distilled water (30 mL) thrice, and acetone (30 mL) once, and dried under vacuum. For the synthesis of H-MOP@AB_2-TA-0.5, H-MOP@AB_2-TA-1, and H-MOP@AB_2-TA-4, synthetic procedures were the same as those for H-MOP@AB_2-TA-2 except that 0.18, 0.36, and 1.44 mmol of 3,5-diethynylbenzyl azide were used, respectively.

Synthesis of H-MOP@AB$_2$-AS and control H-MOP-AS

For the synthesis of H-MOP@AB$_2$-AS, H-MOP@AB$_2$-TA-2 (59 mg), azobisisobutyronitrile (AIBN, 0.94 g, 5.8 mmol), sodium 3-mercapto-1-propanesulfonate (1.0 g, 5.8 mmol), and DMF (30 mL) were added to a flame-dried 50 mL Schlenk flask. After the glassware was wrapped with an Al foil to block light, the mixture was heated at 90^{o}C for 72 h. After being cooled to room temperature, the solid was separated by centrifugation, washed with methanol (30 mL) twice, THF (30 mL) twice, distilled water (30 mL) thrice, and acetone (30 mL) once, and dried under vacuum.

As a control material, H-MOP-AS was prepared by the modified synthetic procedures reported in the literature.[3-4] For the synthesis of H-MOP-AS, H-MOP-TA (59 mg), AIBN (0.47 g, 2.9 mmol), sodium 3-mercapto-1-propanesulfonate (0.51 g, 2.9 mmol), and DMF (30 mL) were added to a flame-dried 50 mL Schlenk flask. After the glassware was wrapped with an Al foil to block light, the mixture was heated at 90^{o}C for 72 h. After being cooled to room temperature, the solid was separated by centrifugation, washed with methanol (30 mL) twice, THF (30 mL) twice, distilled water (30 mL) thrice, and acetone (30 mL) once, and dried under vacuum.

Experimental procedures for catalytic reactions

For the experiment displayed in Entry 22 in Table 1, after H-MOP@AB$_2$-AS (30 mg), cellulose (0.30 g), acetic acid (0.78 µL, 14 µmol), acetic anhydride (0.69 mL, 7.3 mmol), and methylene chloride (6 mL) were added to a flame-dried 25 mL pressure tube under nitrogen, the mixture was stirred at 45^{o}C (bath temperature) for 10 h. After being cooled to room temperature, the reaction mixture was moved to a Falcon tube using methylene chloride (10 mL). Precipitates were separated by centrifugation. After the supernatant solution was moved to a 20 mL vial, the solvent was removed by an evaporator. After the solid was dried at 50^{o}C under vacuum, a mixture of acetone (10 mL) and distilled water (10 mL) was added. The solid was separated by centrifugation and dried at 50^{o}C overnight.

For recovery tests, unreacted cellulose was removed by further treating the separated mixture of catalyst and cellulose with a mixture of excess acetic acid (1 mL), acetic anhydride (1 mL), and sulfuric acid (5 mL) with stirring at room temperature for 6 h. The catalyst was separated by centrifugation, washed with a 1:1 mixture (30 mL) of methanol and water seven times, dried under vacuum overnight, and then used for the next run. To calculate the isolated yield, theoretical amount of product was calculated by the following equation: theoretical amount of product (g) = [0.30×(162.14+DS×42.03)]/162.14; 162.14=M_w of cellulose, 42.03=M_w of C_2H_2O, DS=degree of substitution. The isolated yield was calculated based on this theoretical amount of product. The degree of substitution (DS) was obtained by ^{1}H NMR studies based on the following equation: DS = [the integral of acetyl peaks (1.56~2.27 ppm) × 7]/ [the integral of other ^{1}H peaks (3.45~5.26 ppm) × 3], which was reported in the literature.[6]

References

1. W. Stöber, A. Fink and E. Bohn, *J. Colloid Inter. Sci.* 1968, **26**, 62-69.
2. D. Wang and T. Michinobu, *J. Polym. Sci., Part A: Polym. Chem.* 2011, **49**, 72-81.
3. K. Cho, S. M. Lee, H. J. Kim, Y. -J. Ko and S. U. Son, *J. Mater. Chem. A* 2018, **6**, 15553-15557.
4. (a) X. Han, M. Xu, S. Yang, J. Qian and D. Hua*, J. Mater. Chem. A* 2017, **5**, 5123-5128; (b) H. Urakami, K. Zhang and F. Vilela, *Chem. Commun.* 2013, **49**, 2353-2355; (c) B. Kiskan and J. Weber, *ACS Macro Lett.* 2012, **1**, 37-40
5. R. Hourani, A. Sharma and A. Kakkar, *Tetrahedron Lett.* 2010, **51**, 3792-3795.
6. L. J. Konwar, P. Mäki-Arvela, A. J. Thakur, N. Kumar and J. -P. Mikkola, *RSC Adv*. 2016, **6**, 8829-8837.

Fig. S1 SEM and TEM images of H-MOP@AB$_2$-TA-4 (For the synthesis of H-MOP@AB$_2$-TA-4, synthetic procedures were the same as those for H-MOP@AB$_2$-TA-2 except that 1.44 mmol of 3,5-diethynylbenzyl azide were used, respectively.).

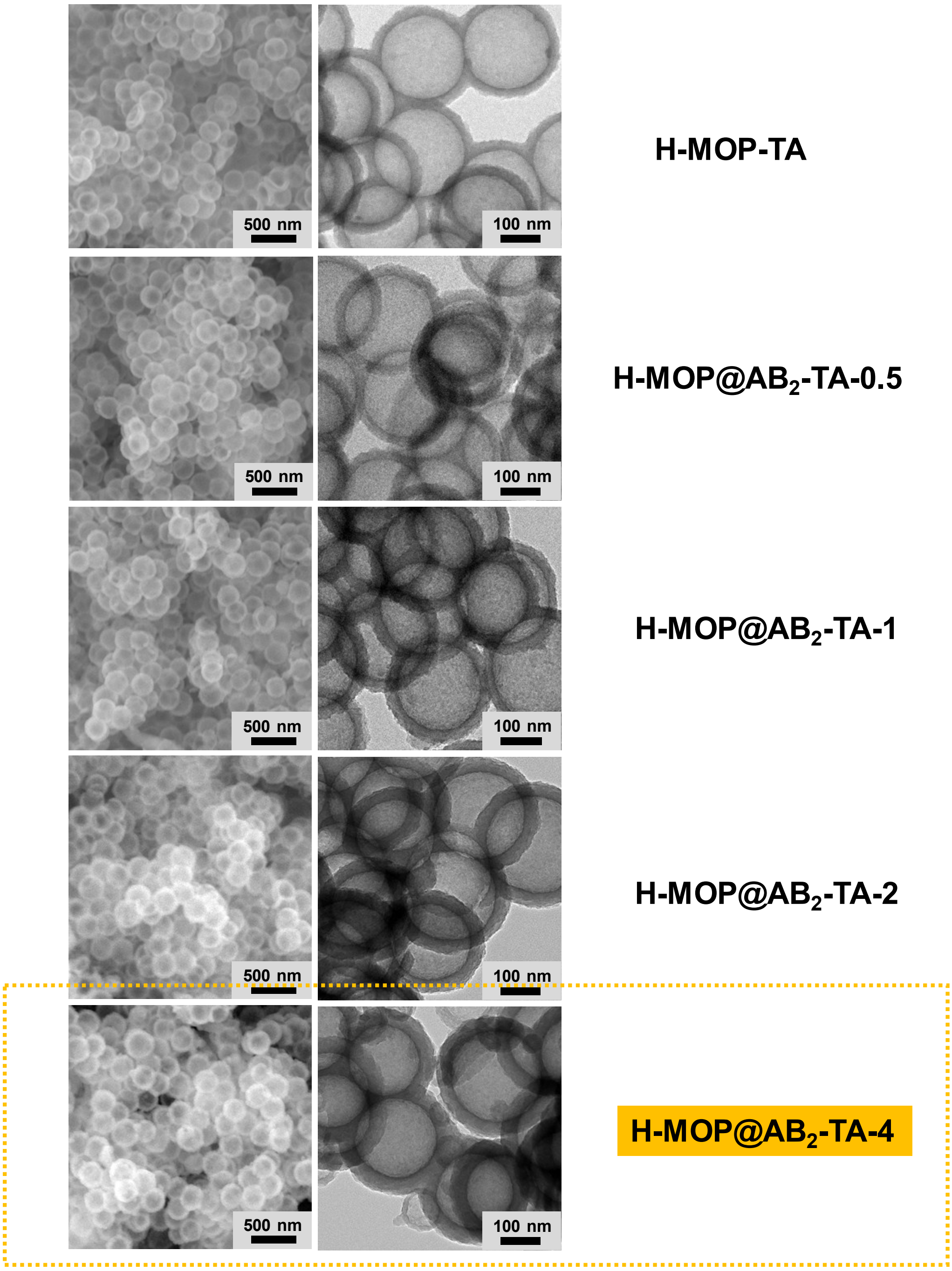

Fig. S2 PXRD patterns of H-MOP-TA, H-MOP@AB$_2$-TAs, H-MOP-AS, and H-MOP@AB$_2$-AS.

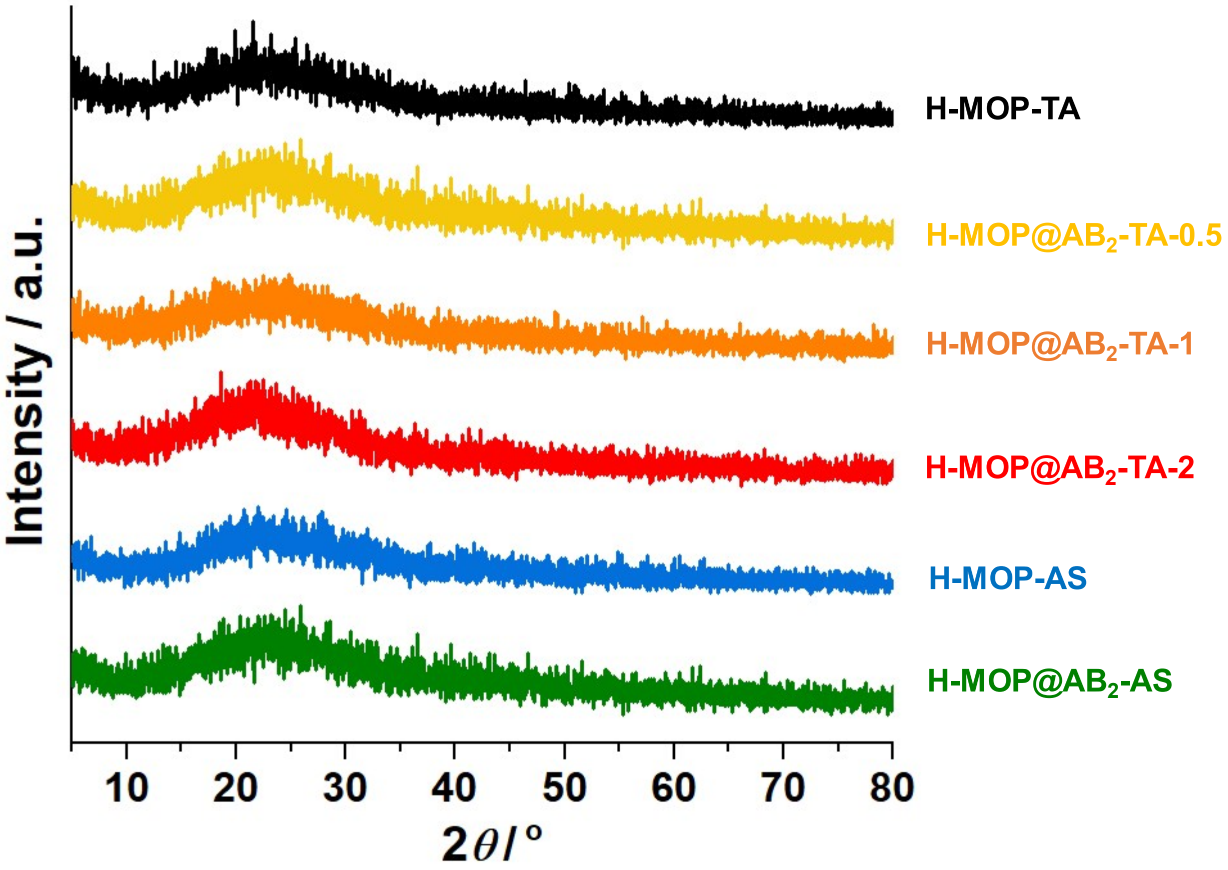

Fig. S3 TGA curves of H-MOP-AS and H-MOP@AB$_2$-AS.

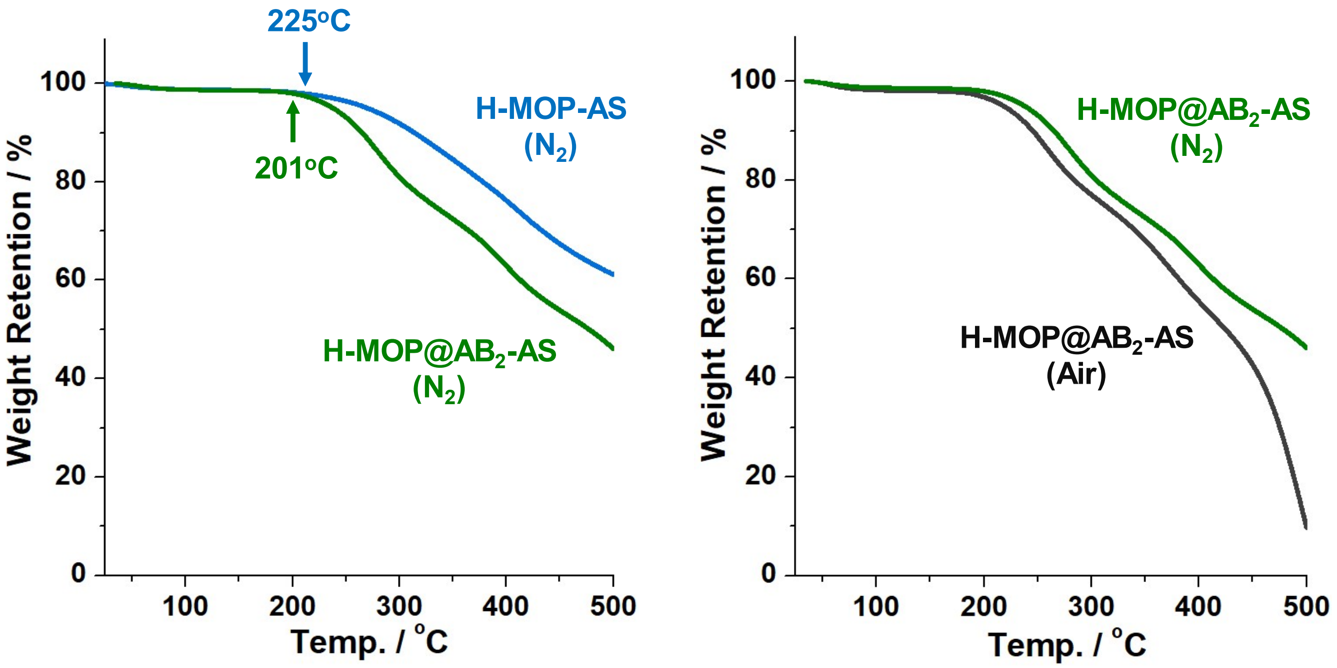

Fig. S4 ^{1}H (DMSO-d$_6$) and ^{13}C NMR (CDCl$_3$) spectra of isolated cellulose acetate.

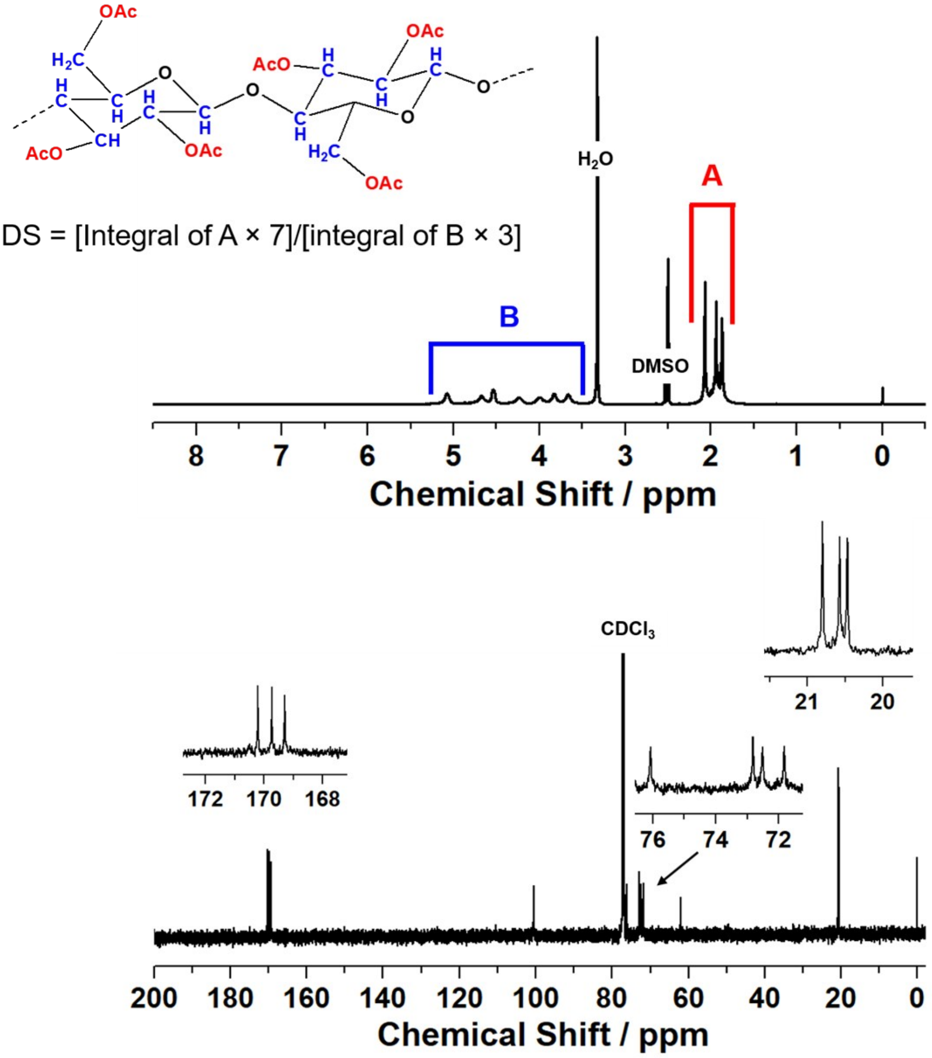

Fig. S5 (a) SEM images and (b) IR spectra of H-MOP@AB_2-AS before and after five successive catalytic reactions.