Electronic Supplementary Material (ESI) for Green Chemistry.

A Hemicellulose-First Approach: One-Step Conversion of Sugarcane Bagasse to Xylooligosaccharides over Activated Carbon Modified with Tandem Plasma and Acid Treatments

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Surface area measurements

As can be seen from Fig. S1, the curves exhibit a combination of types I and IV isotherms according to the IUPAC classification [1].

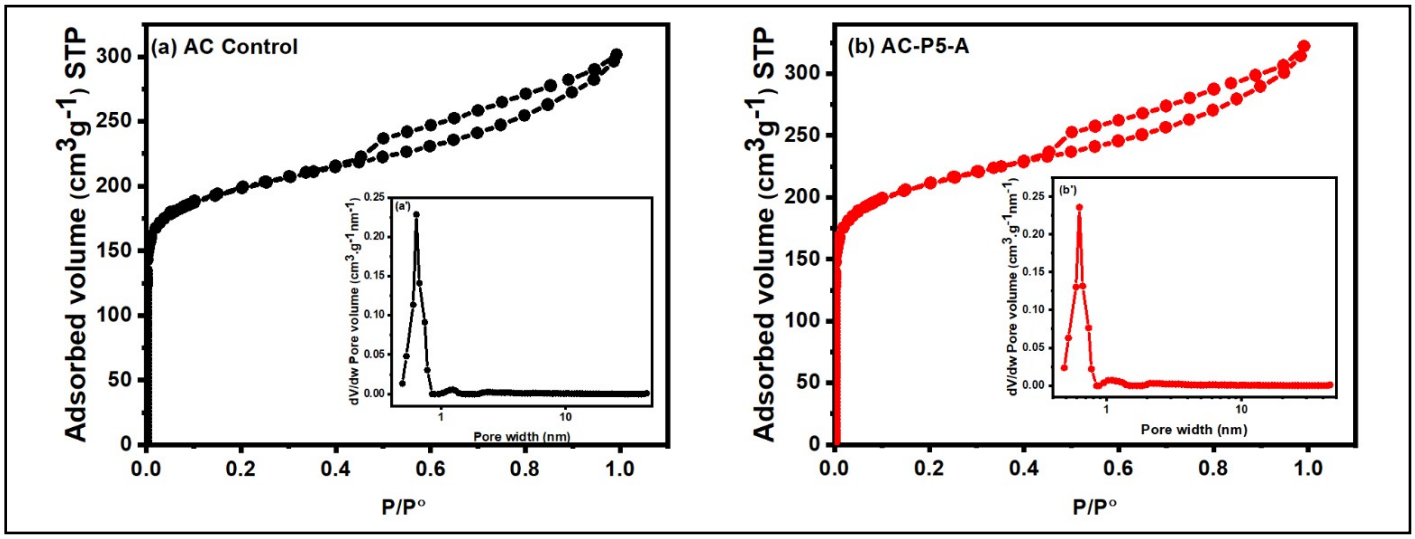

Fig. S1 N_2 adsorption isotherms of AC Control and AC-P5-A.

XPS analysis

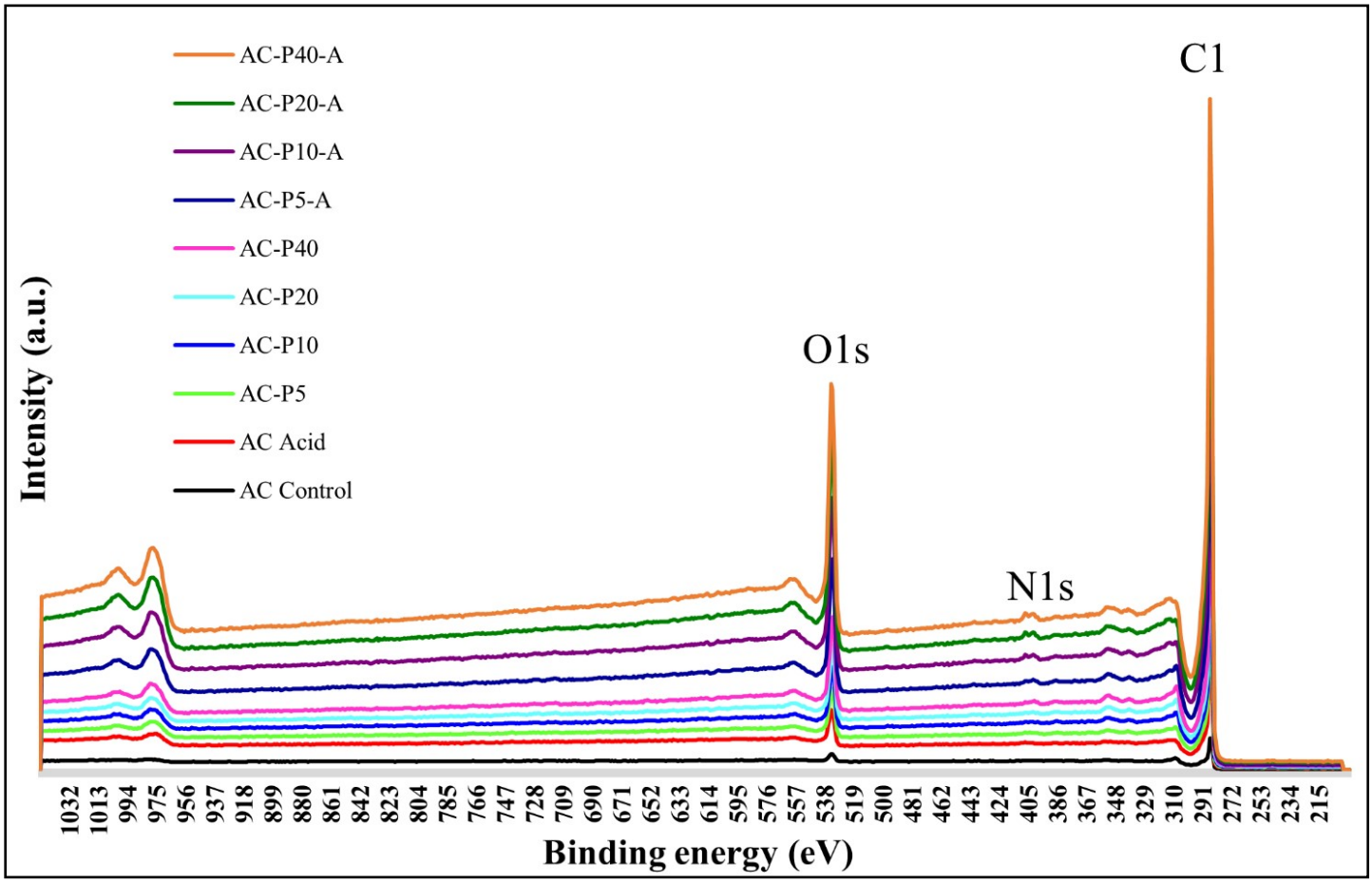

Fig. S2 showed that the main elements of each sorbent were carbon and oxygen at the peaks of ~285 eV (C1s) and ~533 eV (O1s), with having some samples with ~400 eV (N1s).

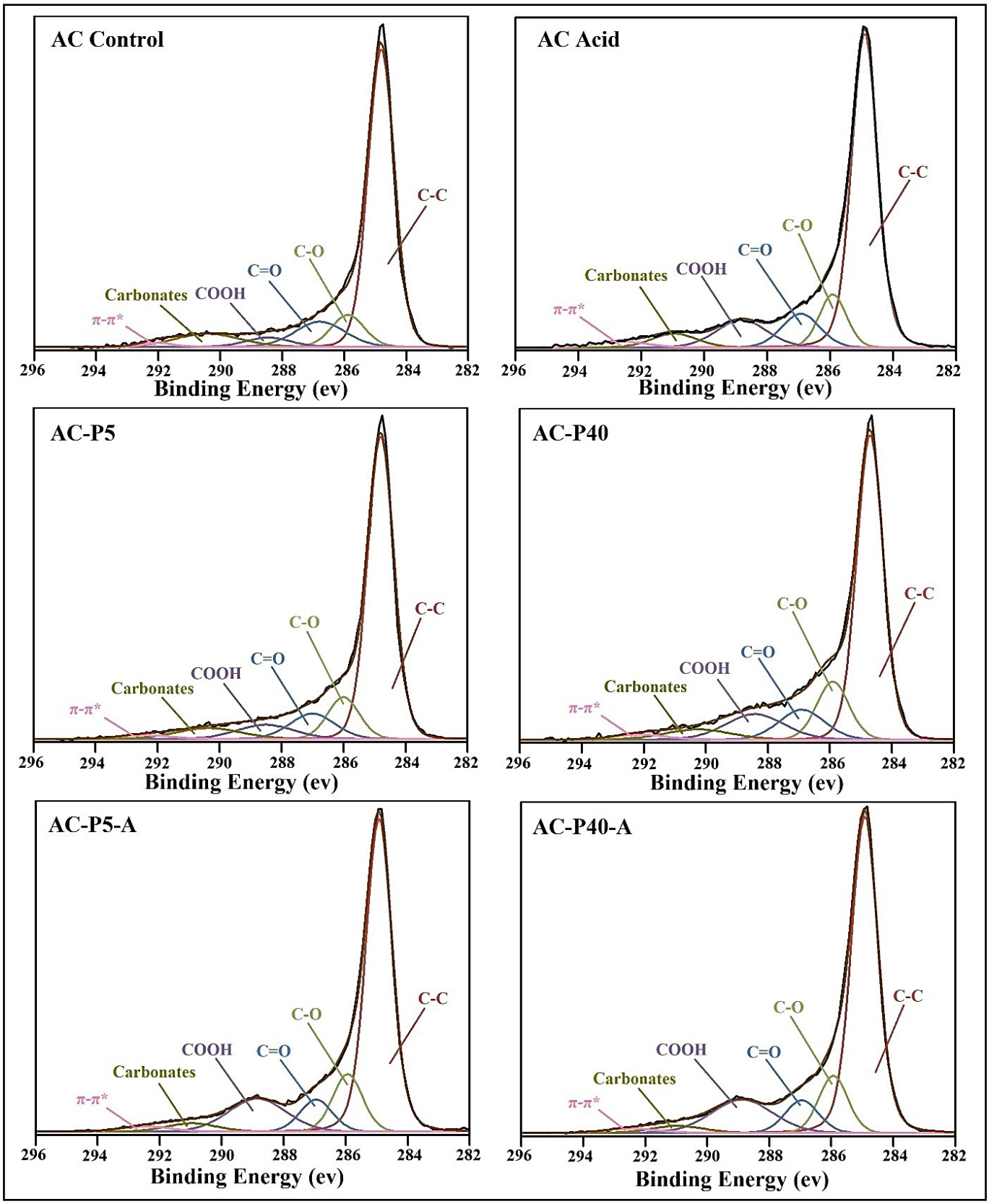

Fig. S3 XPS spectra of the high-resolution scan of C1s for different catalyst.

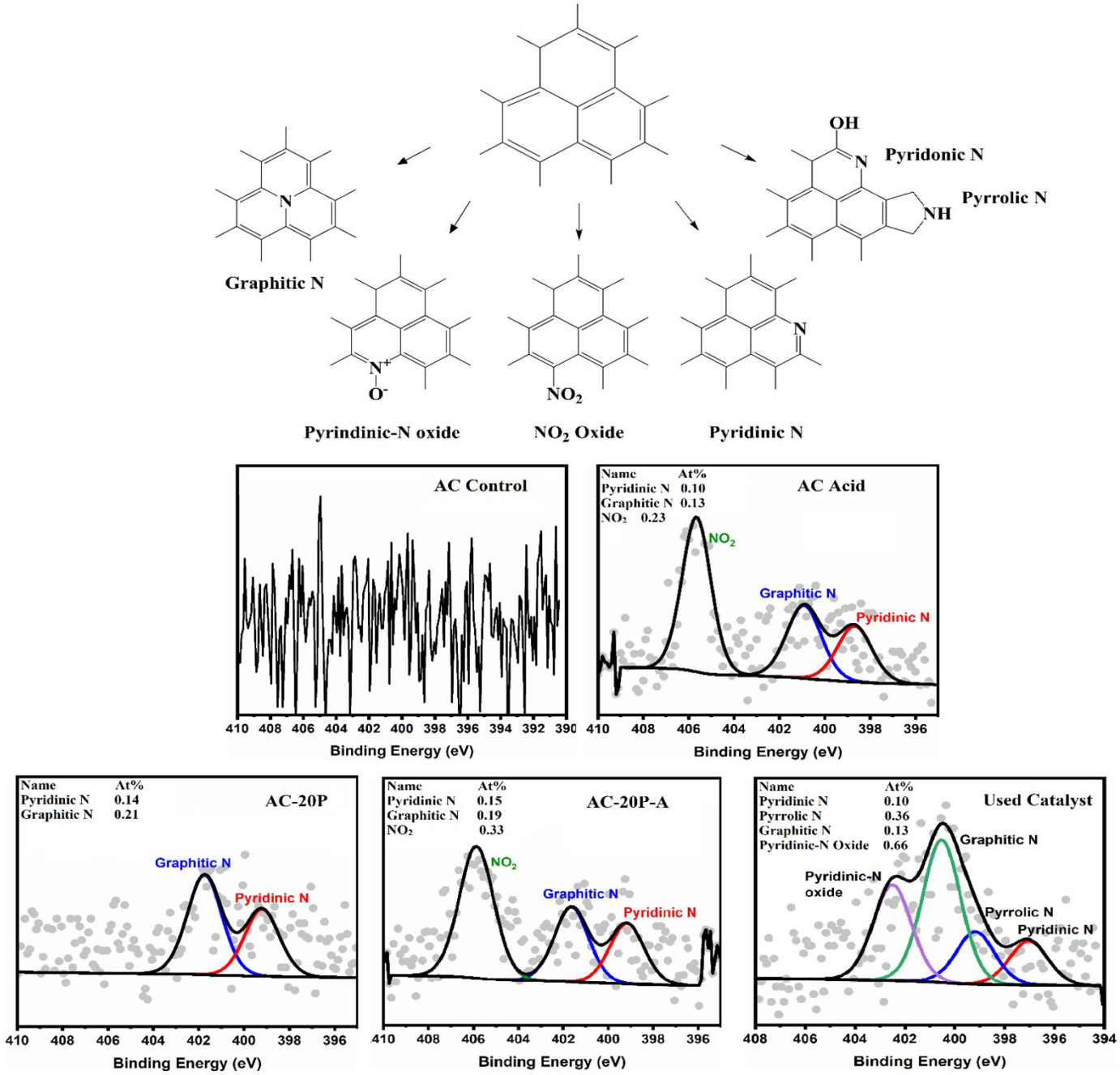

Fig. S4 XPS spectra of the high-resolution scan of N1s of different catalysts.

SEM analysis

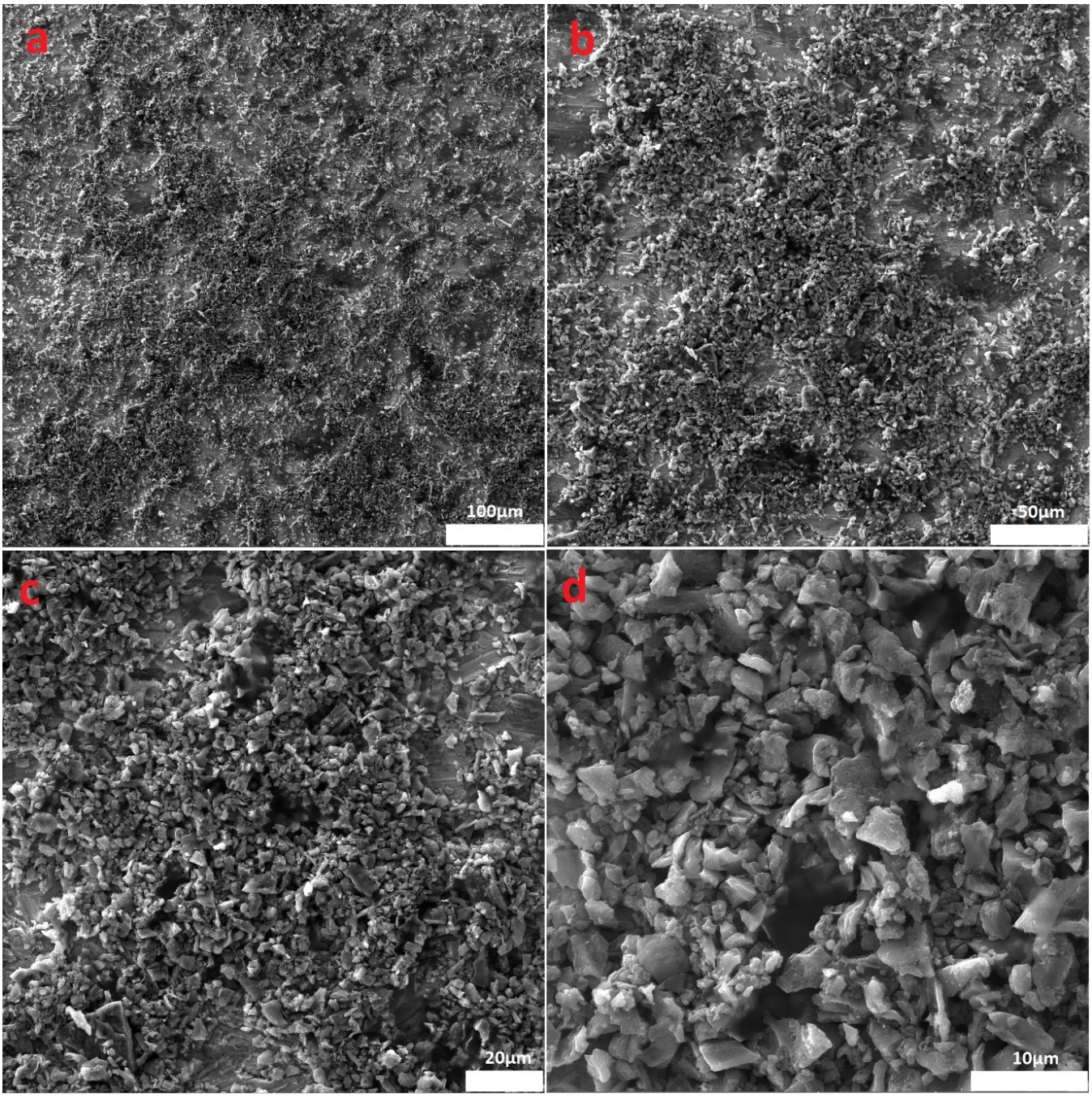

Fig. S5 SEM of submicrometer particles collected after acid treatment. (a) 100 µm, (b) 50 µm, (c) 20 µm, and (d) 10 µm,.

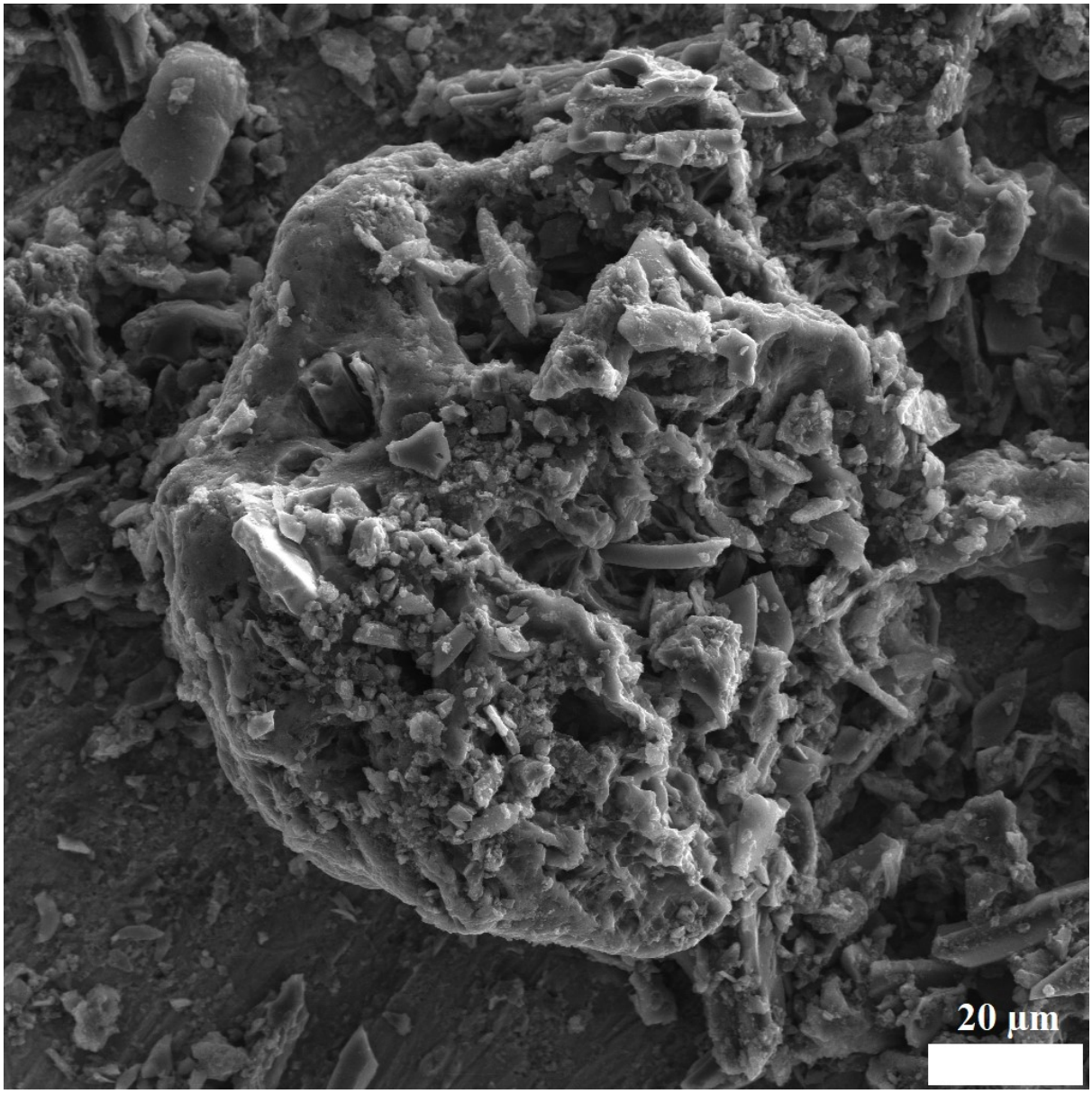

Fig. S6 The SEM of catalyst derived from acid treatment followed by plasma irradiation of AC - AC-A-5P.

Calibration Curve

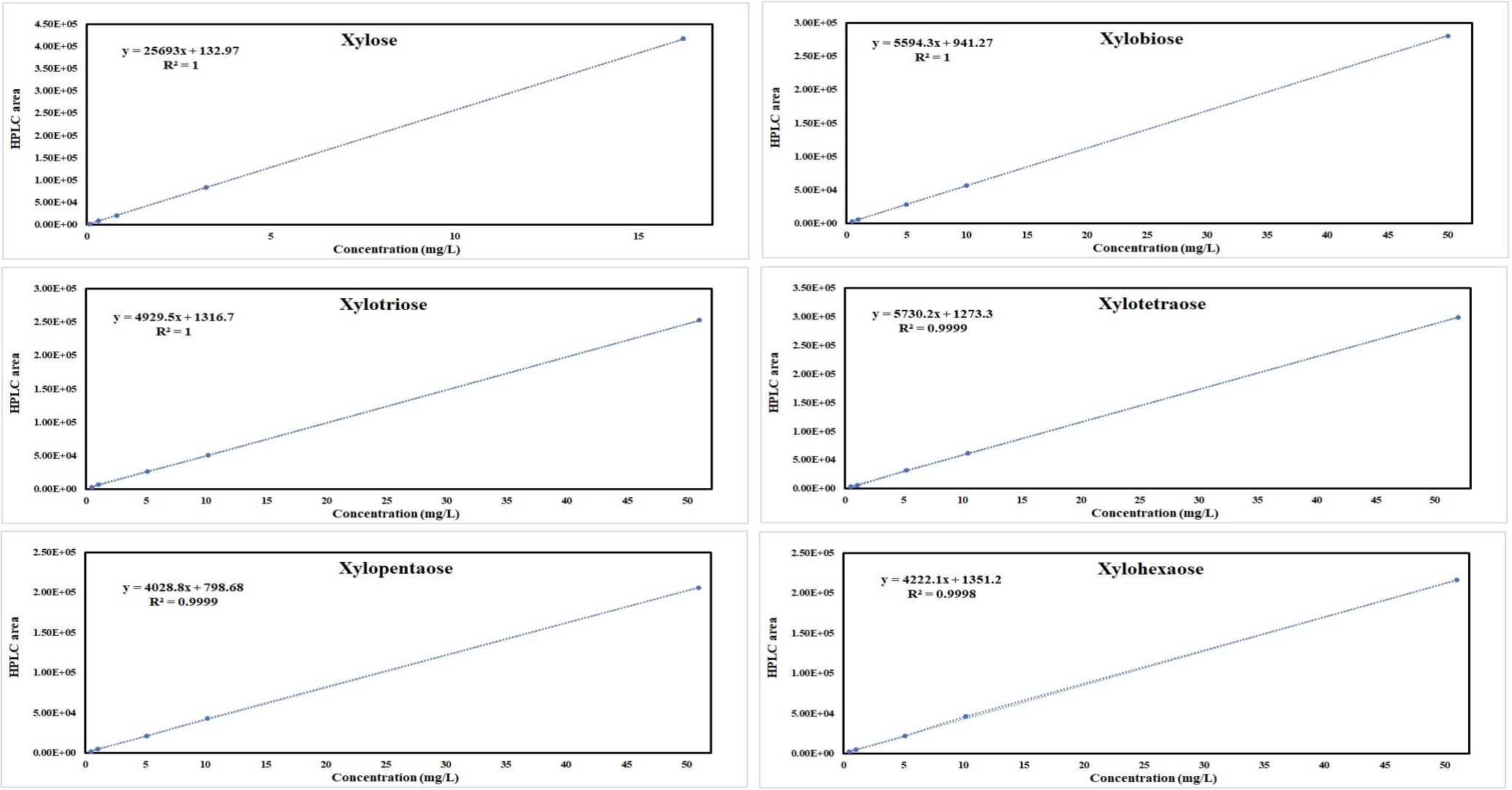

Fig. S7 HPLC calibration curve of X1, X2, X3, X4, X5, and X6 based on commercial standards.

Hydrolysis of Solka Floc

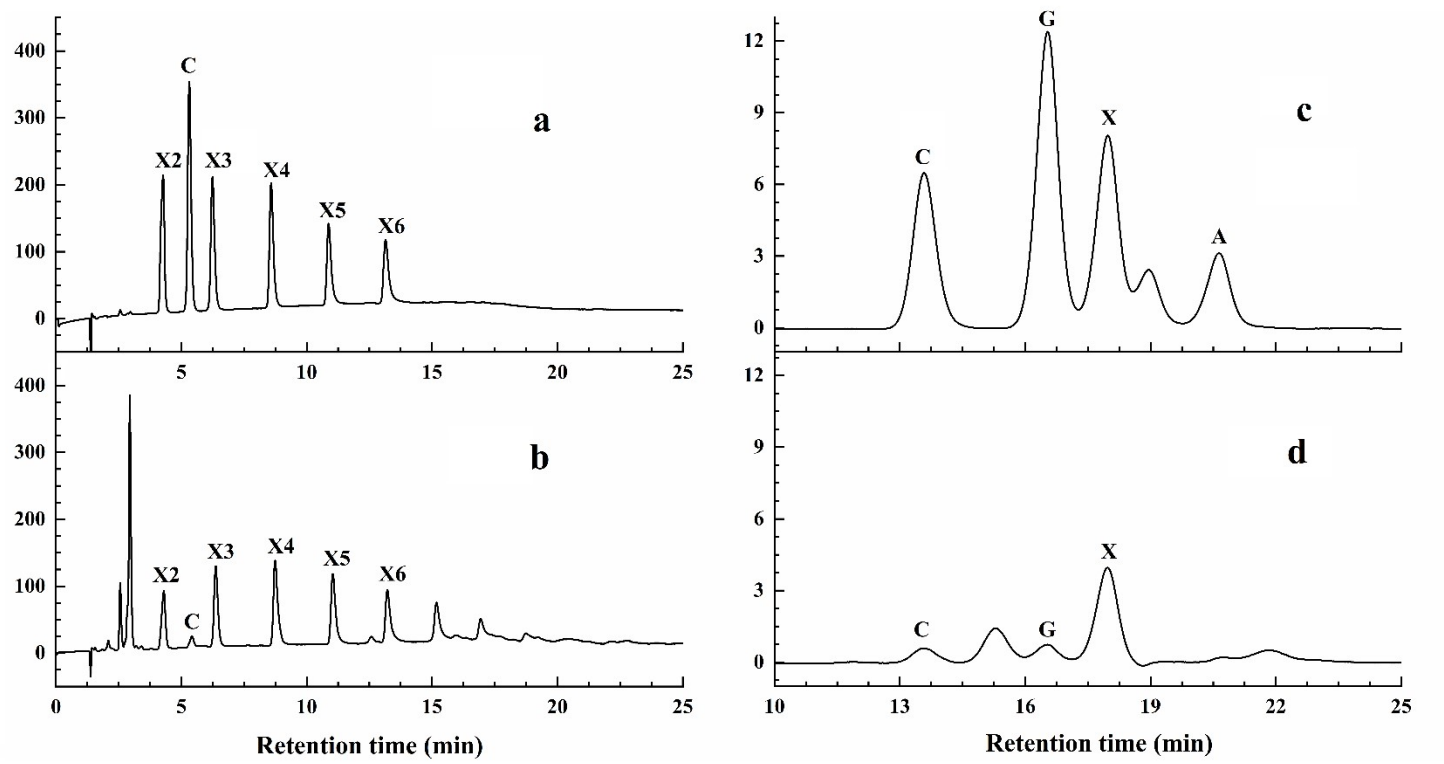

Fig. S8 Typical HPLC chromatograms of (a) XOS standard, (b) XOS from hydrolyzed Solka Floc (c) sugar monomer standards, (d) sugars from hydrolyzed Solka Floc The positions of xylose (X), glucose (G), arabinose (A); lower than detection limits), cellobiose (C), xylobiose (X2), xylotriose (X3), xylotetraose (X4), xylopentaose (X5), xylohexaose (X6), are shown.

Table S1 The yields of xylose and xylooligosaccharides in the hydrolysate of Solka Floc.

Catalyst	Weight of catalyst (mg)	The yields of xylose and XOS (%)							
		Xylose	Xylobiose	Xylotriose	Xylotetraose	Xylopentaose	Xylohexaose	Total XOS	Total conversion
AC Control	5	ND	ND	ND	ND	ND	ND	0.0	0.0
	15	ND	ND	ND	ND	ND	ND	0.0	0.0
	30	ND	ND	ND	ND	ND	ND	0.0	0.0
	50	ND	0.7	0.3	0.2	0.2	ND	1.4	1.4
	100	ND	ND	ND	ND	ND	ND	0.0	0.0
AC Acid	5	ND	1.9	2.4	2.3	2.5	2.0	11.2	11.2
	15	21.0	3.0	4.57	3.05	ND	2.6	13.2	34.2
	30	12.4	4.2	4.8	4.3	3.1	1.6	18.0	30.4
	50	11.3	8.2	8.5	5.2	2.2	0.5	24.5	35.8
	100	10.9	5.3	1.8	0.2	ND	ND	7.4	18.2
AC-P5	5	ND	ND	ND	0.1	0.2	ND	0.3	0.3
	15	ND	ND	ND	ND	ND	ND	0.0	0.0
	30	ND	ND	ND	ND	ND	ND	0.0	0.0
	50	ND	ND	ND	ND	ND	ND	0.0	0.0
	100	ND	ND	ND	ND	ND	ND	0.0	0.0
AC-P10	5	ND	ND	ND	0.1	0.2	ND	0.3	0.3
	15	ND	ND	ND	ND	ND	ND	0.0	0.0
	30	ND	ND	ND	ND	ND	ND	0.0	0.0
	50	ND	0.3	ND	ND	ND	ND	0.3	0.3
	100	ND	ND	ND	ND	ND	ND	0.0	0.0
AC-P20	5	ND	ND	ND	0.1	0.1	0.2	0.4	0.4
	15	ND	ND	ND	ND	ND	ND	0.0	0.0
	30	ND	ND	ND	ND	ND	ND	0.0	0.0
	50	ND	ND	ND	ND	ND	ND	0.0	0.0
	100	ND	ND	ND	ND	ND	ND	0.0	0.0
AC-P40	5	ND	ND	ND	0.1	0.1	0.1	0.3	0.3
	15	ND	ND	ND	ND	ND	ND	0.0	0.0
	30	ND	1.3	1.0	0.7	0.5	0.4	3.9	3.9
	50	ND	ND	ND	ND	ND	ND	0.0	0.0
	100	ND	ND	ND	ND	ND	ND	0.0	0.0
AC-P5-A	5	ND	3.6	4.8	4.5	5.0	1.3	19.2	19.2
	15	19.7	4.8	6.1	5.8	6.0	4.7	27.4	47.1
	30	14.7	12.9	10.4	6.0	2.2	4.6	36.1	50.8

	50	15.0	6.7	5.8	1.9	0.4	0.8	15.6	30.6
	100	15.3	3.9	1.3	0.4	ND	ND	5.6	20.9
AC-P10-A	5	ND	4.6	6.3	6.0	6.3	2.1	25.2	25.2
	15	10.1	9.8	10.2	8.6	5.3	4.2	38.1	48.3
	30	18.3	14.4	10.6	5.2	1.7	4.5	36.3	54.6
	50	21.7	15.4	8.2	3.5	0.3	0.4	27.7	49.4
	100	20.7	10.5	2.3	0.5	ND	ND	13.2	34.0
AC-P20-A	5	10.4	10.0	10.0	9.0	7.2	4.7	40.9	51.4
	15	21.4	18.2	14.9	9.2	3.3	8.5	54.0	75.7
	30	28.6	19.3	11.6	8.6	1.7	8.8	50.1	78.6
	50	28.3	16.0	6.9	4.2	0.1	3.2	30.4	58.7
	100	21.3	6.5	1.0	0.1	0.1	ND	7.2	28.5
AC-P40-A	5	ND	4.3	4.9	5.0	5.5	4.6	24.2	24.2
	15	12.1	9.6	9.1	7.5	5.2	2.1	33.4	45.5
	30	13.7	9.6	7.9	3.7	1.1	2.1	24.4	38.2
	50	14.9	9.0	4.0	0.8	0.2	1.0	15.1	29.9
	100	11.9	4.0	0.6	0.1	ND	ND	4.8	16.6
Only Water	0	ND	0.1	0.1	0.2	0.2	0.2	1.0	1.0

ND ≤ 0.1 %

arabinose was not detected.

100 mg of Solka Floc, 15 mg of catalysts—plasma treated, acid-treated, plasma-acid treated (AC-20P-A), untreated, and another batch without catalyst addition—10 mL of deionized water was loaded into a 100 mL glass tube reactor. The hydrolysis reactions were conducted at a temperature of 120 °C for 24 h.

Table S2 The yields of xylose and xylooligosaccharides in the hydrolysate of Bagasse in 6 cycles.

	The yields of xylose and XOS (%)							
Reusability	Xylose	Xylobiose	Xylotriose	Xylotetraose	Xylopentaose	Xylohexaose	Total XOS	Total conversion
Cycle 1	15.6 (1.3)	14.1 (0.7)	11.9 (0.2)	8.8 (0.3)	9.1(0.4)	6.0 (0.3)	50.0 (1.9)	65.6 (3.2)
Cycle 2	5.2 (0.5)	3.9 (0.1)	3.2 (0.1)	2.0 (0.1)	1.8 (0.1)	1.1 (0.0)	12.0 (0.5)	17.2 (0.2)
Cycle 3	0.0 (0.0)	1.2 (0.0)	1.0 (0.0)	0.5 (0.0)	0.5 (0.0)	0.3 (0.0)	3.5 (0.0)	3.5 (0.0)
Cycle 4	0.0 (0.0)	0.5 (0.0)	0.5 (0.0)	0.3 (0.0)	0.3 (0.0)	0.2 (0.0)	1.7 (0.0)	1.7 (0.0)
Cycle 5	0.0 (0.0)	0.4 (0.0)	0.3 (0.0)	0.2 (0.0)	0.2 (0.0)	0.1 (0.0)	1.3 (0.1)	1.3 (0.1)
Cycle 6	0.0 (0.0)	0.3 (0.0)	0.3 (0.0)	0.2 (0.0)	0.2 (0.0)	0.1 (0.0)	1.1 (0.2)	1.1 (0.2)
Total conversion (C1 to C6)							69.6 (2.7)	90.4 (3.7)

100 mg of bagasse (particle sizes of <0.125 mm), 15 mg of catalyst (AC-20P-A), and 10 mL of deionized water were loaded into a 100 mL glass tube reactor. The hydrolysis reactions were conducted at a temperature of 120 °C in 6 cycles (each cycle lasted 24 h).

FT-IR analysis

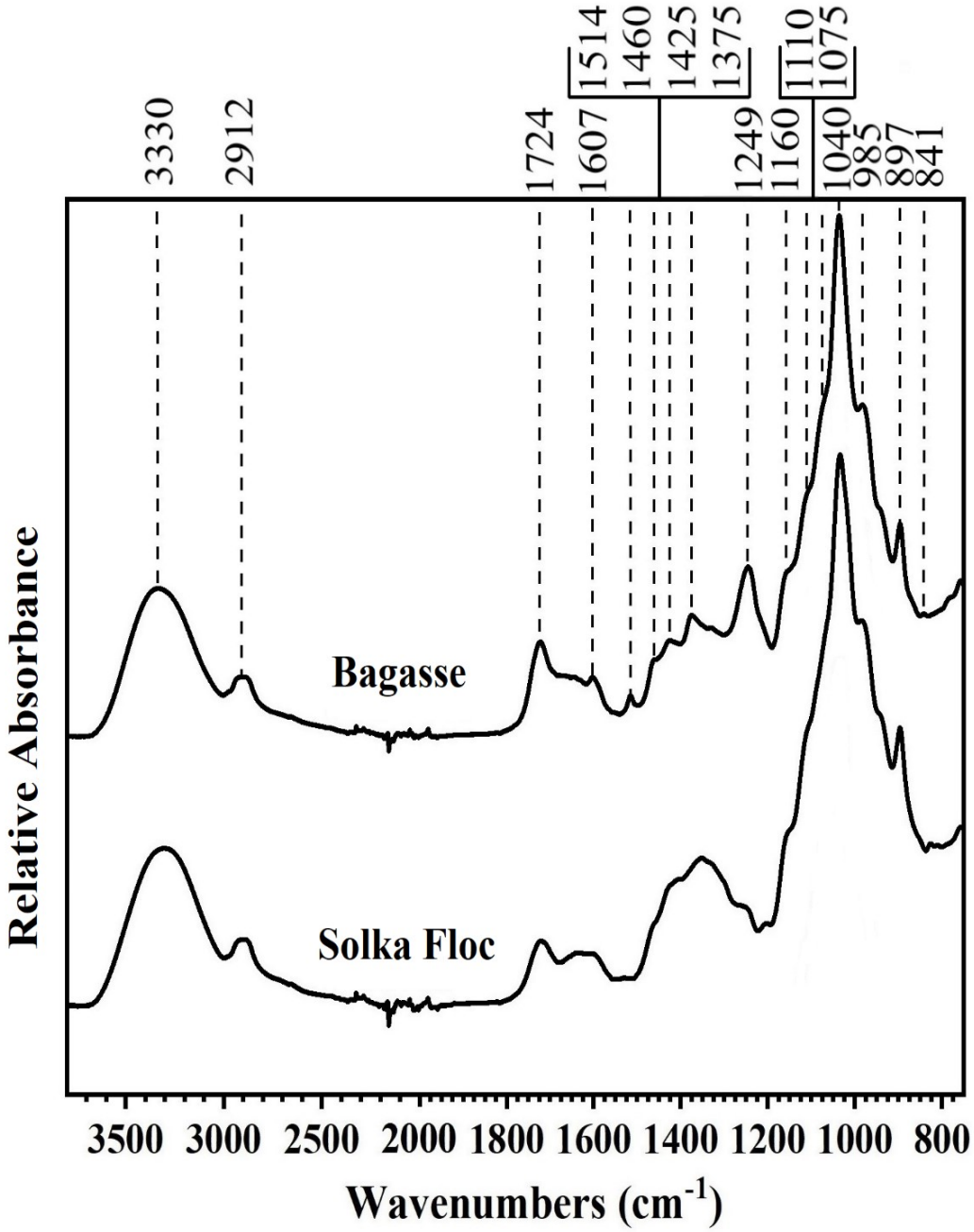

Fig. S9 FT-IR spectra of the hydrolyzed XOS using AC-20P-A catalysts for Solka Floc and sugarcane bagasse.

HSQC NMR analysis

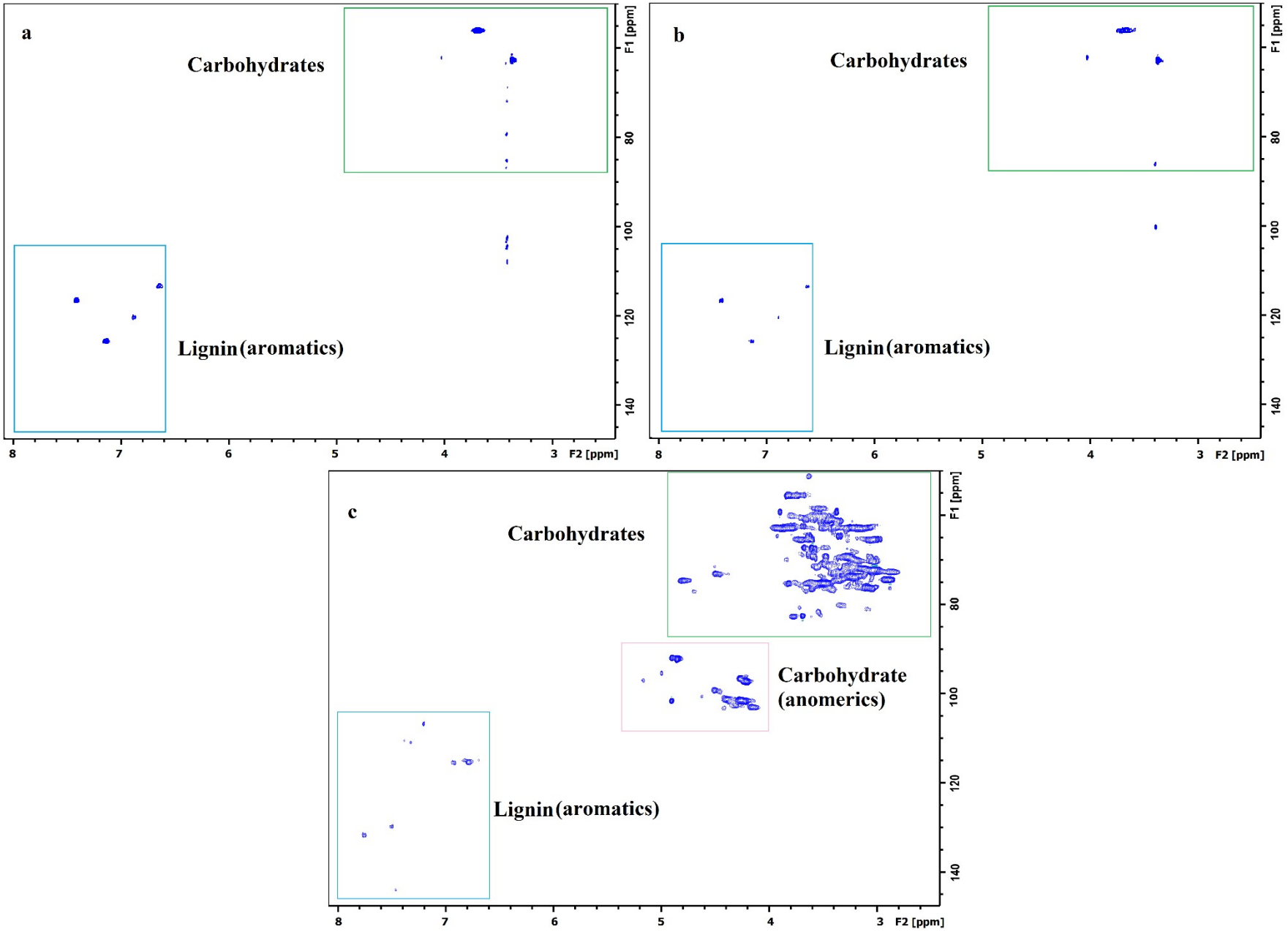

Fig. S10 The overlay 2D ^{1}H–^{13}C HSQC spectra of (a) bagasse and (b) its residue after the hydrolysis reaction, and (c) the hydrolysate from bagasse hydrolysis.

Table S3 Hydrolysis at different reaction times.

	The yields of xylose and XOS (%)							
Reaction time (h)	Xylose	Xylobiose	Xylotriose	Xylotetraose	Xylopentaose	Xylohexaose	Total XOS	Total conversion
1	0	0.3	0.4	0.5	0.7	0.6	2.6	2.6
3	0	1.0	1.3	1.5	2.2	1.8	7.7	7.7
6	0	1.7	2.2	2.4	3.2	2.6	12.2	12.2
12	0	4.4	5.4	4.1	4.0	1.8	19.7	19.7
18	16.0	9.8	10.1	7.0	4.6	1.5	33.2	49.2
24	21.7	18.2	14.9	9.2	3.3	8.5	54.0	75.7
30	25.9	16.2	15.5	8.8	4.4	1.3	46.2	72.1
36	30.6	17.5	14.2	6.1	2.7	0.9	41.5	71.9

100 mg of bagasse (particle sizes of <0.125 mm), 15 mg of catalyst (AC-20P-A), and 10 mL of deionized water were loaded into a 100 mL glass tube reactor. The hydrolysis reactions were conducted at a temperature of 120 °C for different reaction times (1–36 h).

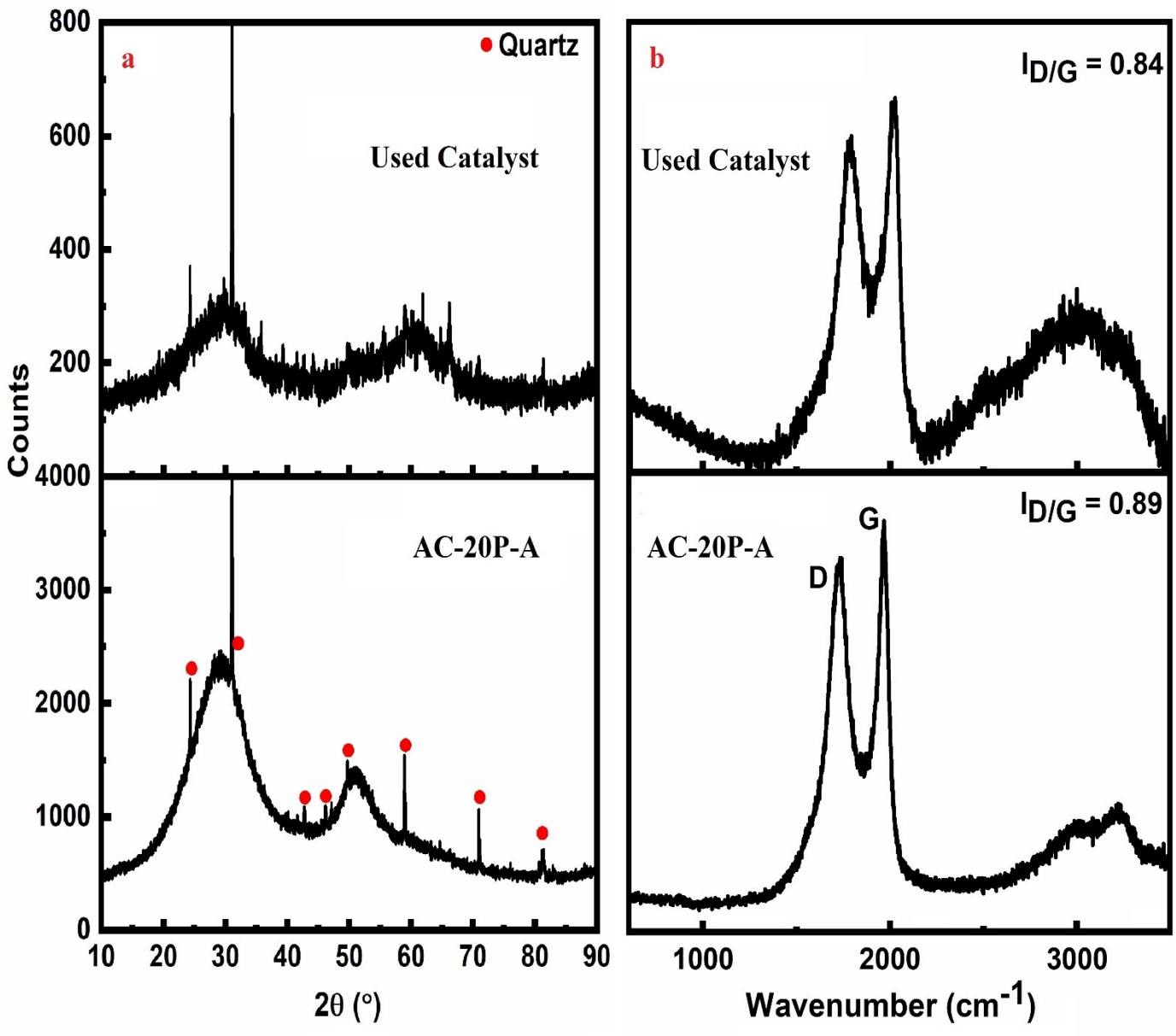

Fig. S11 (a) Catalyst XRD patterns, and (b) Raman spectroscopy spectra of used and fresh catalyst (AC-20P-A).

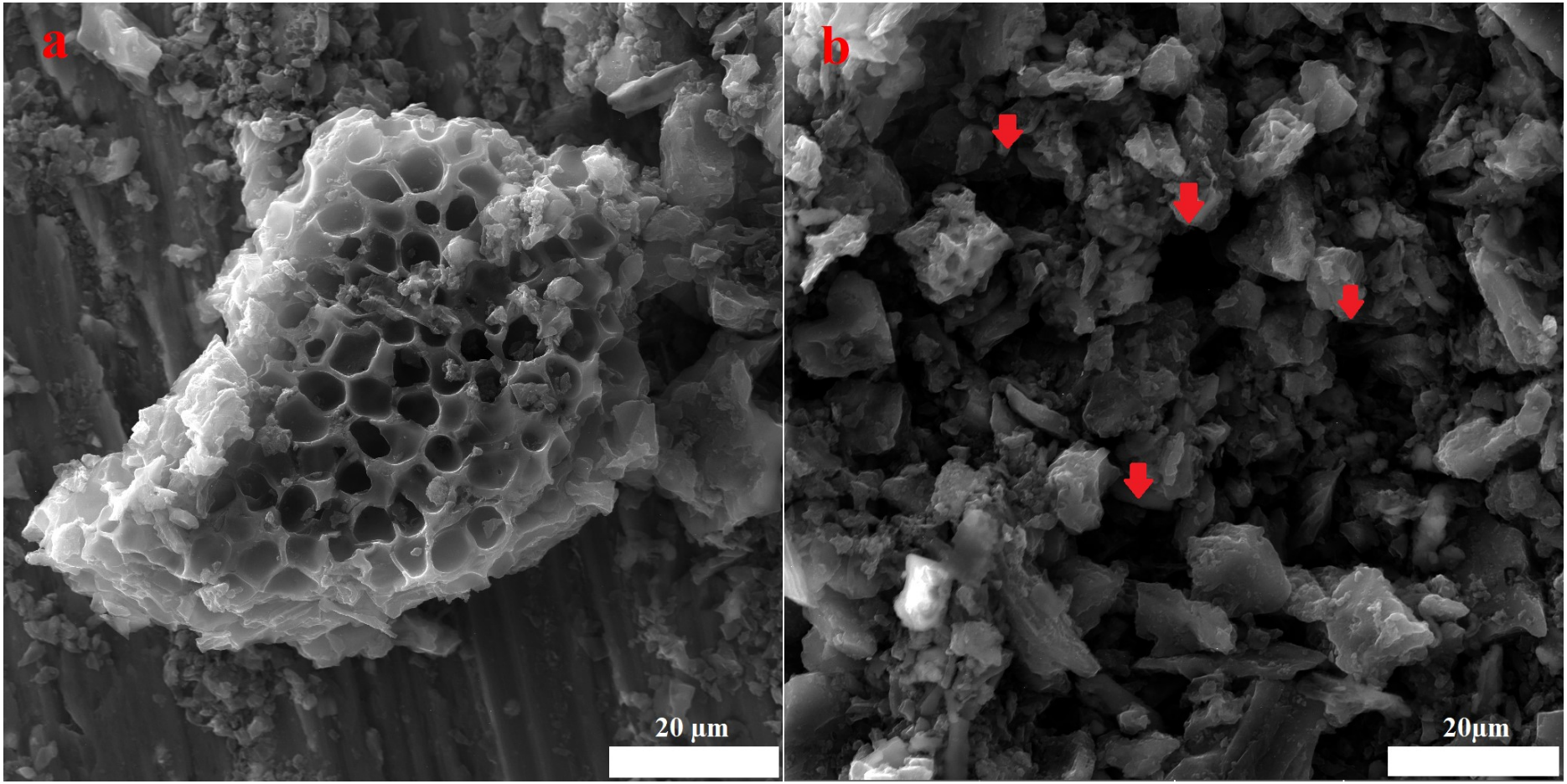

Fig. S12 The SEM of AC-20P-A (a) fresh, and (b) used catalyst.

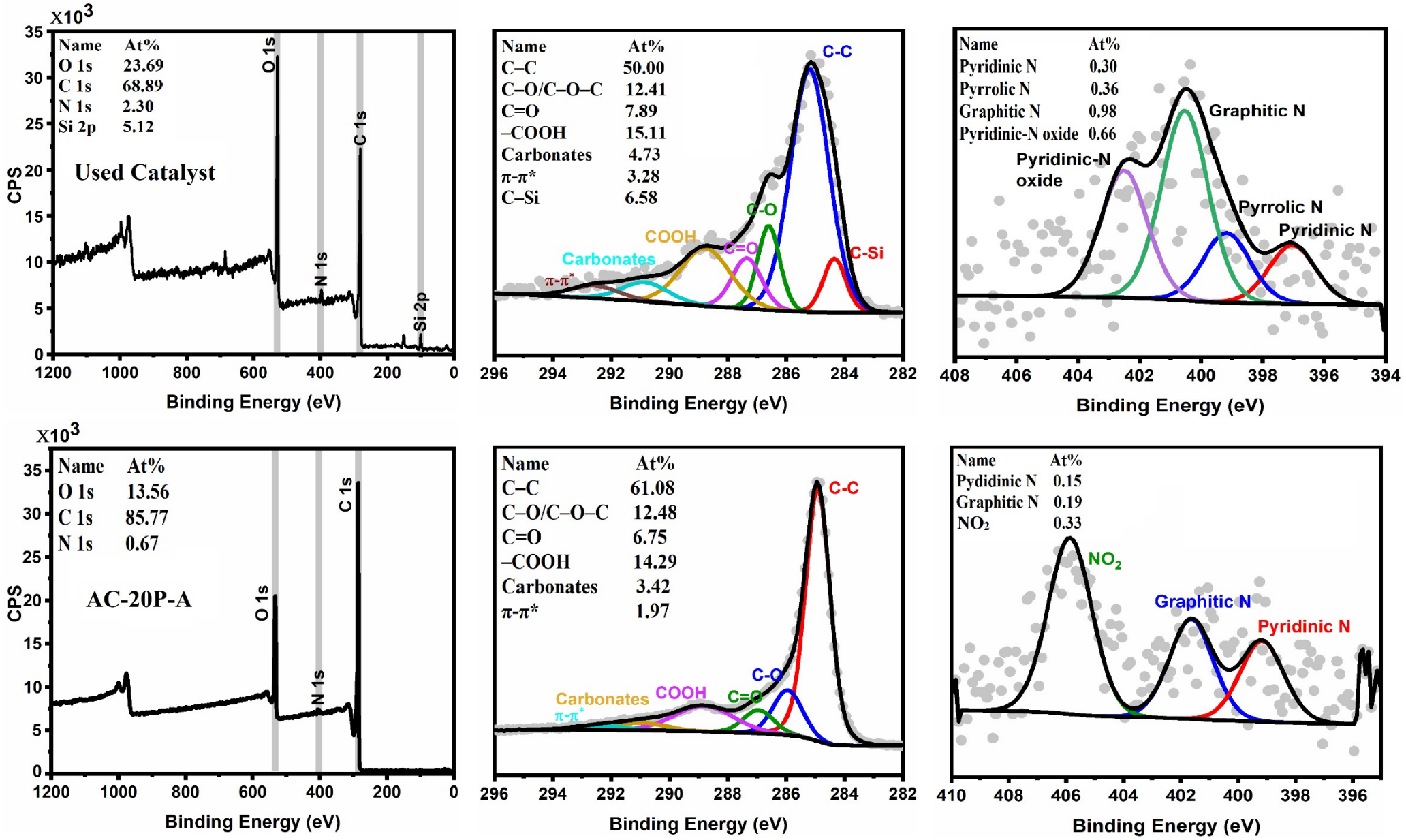

Fig. S13 The XPS of AC-20P-A (a) fresh, and (b) used catalyst.

Table S4 SEM-EDX, elemental analysis of used catalyst.

	C	H	N	O	Si
SEM-EDX	51.05	-	-	45.10	3.85
Elemental analysis	59.53	1.87	3.14	35.46	-

Error in duplicate (<0.1 %)

Boehm titration

The equation below was used to calculate the concentration of the surface functional groups:

$$n_{CSF} = [B] \times V_B - [HCL] \times V_{HCL} \times \frac{V_B}{V_a}$$

(1)

where [B] and V_B are the concentration and volume, respectively, of each aqueous solution (NaOH, Na_2CO_3, and $NaHCO_3$) mixed with the AC samples to give the number of moles of NaOH, Na_2CO_3, and $NaHCO_3$ that are required to react with the surface functionalities of the carbon surface. n_{CSF} refers to the total number of moles of the acid functional groups present on the carbon surface that reacted with NaOH, Na_2CO_3, and $NaHCO_3$ individually during the mixing phase. The amount of the aliquot taken from V_B is referred to as V_a. Terms [HCl] and V_{HCl} are the concentration and volume, respectively, of acid, added to the aliquot of the initial sample. This gives the moles of acid added into the aliquot, free for reaction with the remaining base. The types of acid groups were calculated on the basis that all surface groups (carboxylic, lactonic, and phenolic groups) were neutralized by NaOH; carboxylic and lactonic groups were neutralized by Na_2CO_3, and carboxylic groups were neutralized by $NaHCO_3$. The number of phenols on the surface is calculated by taking the difference between the measured n_{CSF} of NaOH and Na_2CO_3. Likewise, the number of lactonic groups is the difference between Na_2CO_3 and $NaHCO_3$ and the n_{CSF} measured from $NaHCO_3$ is the number of carboxylic acid groups.

Product analysis of the monomers, oligomers, and degradation products

A Waters High Performance Liquid Chromatography (HPLC) instrument with an electrochemical detector (Waters 2465), pump, and auto sampling system (Waters e2695, US), as well as a Dionex CarboPac™ PA-100 column (BioLC™ 4×250 mm, Thermo Scientific, US), were used to quantify xylose oligomers (xylobiose, xylotriose, xylotetraose, xylopentaose, and xylohexaose) in the reaction solution. A mixture of solvent A (150 mM NaOH) and solvent B (150 mM sodium acetate and 150 mM NaOH) were used as the mobile phases. The gradient method according to Curve 6 (detection waveform from Dionex Technical Note 21 (Thermo Scientific, US)) was applied to the column at 30 °C with a flow rate of 1 mL min^{-1}. The gradient method started (0–1 min) with 86.7 % solvent A and 13.3 % solvent B. Over 1–30 min, the A to B volume ratio was changed to 0 %: 100 %, then to 86.7 %: 13.3 % over 30–32 min, and then at this ratio over 32–40 min. A Waters HPLC with an RPM monosaccharide column (300 mm × 8.0 mm, Phenomenex, Australia), a pump (Waters 1515, US), a refractive index (RI) detector (Waters 410, US), and an autosampler (Waters 2707, US), were used to determine the monosaccharides in the reaction solution. The RPM column was heated to 85 °C, and the mobile phase was water, flowing at 0.5 mL min^{-1}. A Waters HPLC system with an Aminex HPX-87H column (300 mm × 8.0 mm, Bio-Rad, US), an integrated pump and auto sampling system (Waters e2695, US), an RI detector (Waters 410, US), and a dual-wavelength UV absorbance detector (Waters 2487, US), was used to measure sugar degradation products (*i.e.*, furfural, 5-hydroxymethylfurfural (HMF) and organic acids such as levulinic acid or formic acid) in the reaction solution. The mobile phase was 5 mM H_2SO_4 with a 0.5 mL min^{-1} flow rate and a column temperature of 65 °C.

The xylose, XOS yield was calculated according to the following equations.

$$\text{Xylose yield}\ (\%) = \frac{\text{xylose [g] in supernatants}}{\text{xylan [g] in raw material}} \times 100$$

(2)

$$\text{XOS yield } (\%) = \frac{\text{sum of all XOS in supernatants } (\text{DP } 2 - 6)[\text{g}]}{\text{xylan } [\text{g}] \text{ in raw material}} \times 100$$

(3)

$$\text{Individual XOS } (\text{X2 - X6}) \text{ yield } (\%) = \frac{\text{Individual XOS } (\text{X2 - X6})[\text{g}] \text{ in supernatants}}{\text{xylan } [\text{g}] \text{ in raw material}} \times 100$$

(4)

References

1. Sreńscek-Nazzal, J., et al., *Modification of Commercial Activated Carbons for CO 2 Adsorption.* J Acta Physica Polonica, A., 2016. **129**(3).