**Supplementary Material**

**An Sn-Lignosulfonate Catalyst for the Dehydration of Xylose into Furfural in Biphasic System**

Xueqin Liu1, Qingchong Xu1, Yao Liu1, Junli Ren1,\*, Lihong Zhao1, Ruonan Zhu1, Xingjie Wang1 and Wei Qi2

1State Key Laboratory of Advanced Papermaking and Paper-Based Materials, South China University of Technology, Guangzhou, 510640, China

2Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, CAS Key Laboratory of Renewable Energy, Guangdong Provincial Key Laboratory of New and Renewable Energy Research and Development, Guangzhou, 510640, China

\*Corresponding Author: Junli Ren. Email: renjunli@scut.edu.cn

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**Figure S1:** XRD pattern of SnO2.



**Figure** **S2:** XPS survey scans of SnO2, LS and Sn(20)@LS.

**Table S1:** Acid properties of SnO2, LS and Sn(20)@LS.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Catalysts | Temperature (°C) | Brónsted Acid | Lewis Acid | B/L ratio | Total acid quantity |
| Content (mmol/g)a | Content (mmol/g)a | Content (mmol/g)b |
| Sn(20)@LS | 110 | 0.036 | 0.111 | 0.324 | 1.439 |
| 250 | 0.026 | 0.039 | 0.667 |
| SnO2 | 110 | 0.010 | 0.025 | 0.400 | 0.042 |
| 250 | 0.006 | 0.011 | 0.545 |
| LS | 110 | 0.040 | 0.075 | 0.533 | - |
| 250 | 0.027 | 0.030 | 0.900 |
|  |  |  |  |  |  |

a The Lewis and Brønsted acidic sites of the catalysts were tested by pyridine-adsorbed FT-IR spectra under vacuum conditions at two desorption temperatures, 110 and 250°C. b Acidity of the catalysts was determined with NH3-TPD with a programmed temperature: heating from 50 to 250ºC at a rate of 10 ºC/min and then kept at 250ºC for 60 min gas desorption.

**Table S2:** The elemental analysis results of various catalysts.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Catalysts | Content（wt.%） | | | | |
| Metal iona | Cb | Hb | Nb | Sb |
| LS | - | 30.26 | 3.61 | - | 6.61 |
| Zr(20)@LS | 23.39 | 19.21 | 2.93 | 0.02 | 3.89 |
| Al(20)@LS | 2.03 | 53.83 | 7.25 | 0.24 | 1.37 |
| Cr(20)@LS | 3.78 | 46.26 | 2.59 | 0.32 | 2.59 |
| Sn(10)@LS | 14.35 | 14.79 | 2.14 | - | 0.98 |
| Sn(15)@LS | 21.90 | 15.71 | 1.31 | - | 1.19 |
| Sn(20)@LS | 24.13 | 16.96 | 1.63 | - | 1.13 |
| Sn(25)@LS | 28.01 | 13.10 | 1.32 | - | 1.03 |
| Sn(30)@LS | 29.04 | 13.41 | 1.72 | - | 0.84 |

a Determined by ICP-OES. b Determined by elemental analysis.

**Molecular Dynamics Simulation**

Initially, a 5×5×5 nm cubic box was created and filled with organic solvent molecules. The system underwent energy minimization, followed by a 2 ns NVT equilibration and a 20 ns NPT equilibration. Subsequently, the box was elongated in the Z direction, and four xylose molecules and four furfural molecules were randomly added. The remaining volume was filled with water molecules to form a biphasic system. Periodic boundary conditions (PBC) were applied in all three dimensions. Xylose, furfural and organic solvent molecules were described with the OPLS/AA force field [1–3], and water molecules with the TIP4P force field [4]. Energy minimization, 2 ns NVT equilibrium and 2 ns NPT equilibrium were performed after the construction of the system was completed, until the energy and structure of the system reached a steady state, with the density of the system and the dimensions of the box remaining unchanged. After that the NVT ensemble is selected for simulation for 20 ns. Table S3 shows the composition and dimensions of the system after simulation. Temperature control (298 K) was performed using a V-rescale thermostat [5]. Pressure coupling was performed using the Parrinello-Rahman method [6]. A Langevin kinetic integrator was used with a time step of 2 fs. All bond lengths involving hydrogen atoms were constrained by the LINCS algorithm [7] and the neighbor list was updated using the Verlet algorithm [8]. The cut-off radius for both electrostatic and van der Waals forces was set to 1.2 nm. The electrostatic interactions are performed by the PME (Particle Mesh Ewald) method [9], and long-range dispersion corrections for energy and pressure are considered. The GROMACS 2022.6 package was used to perform all the MD simulations and visualized using VMD 1.9.3 [10].

**Table S3:** Composition and dimensions of the system after MD simulation

|  |  |  |  |
| --- | --- | --- | --- |
| System | Number of water  molecules | Number of  organic solvent molecules | Cell size after MD (nm\*nm\*nm) |
| CTC | 600 | 3555 | 4.64623\*4.64623\*9.29246 |
| CPME | 419 | 2820 | 4.35701\*4.35701\*8.71402 |
| DMC | 600 | 2717 | 4.32605\*4.32605\*8.65209 |
| IPA | 660 | 2824 | 4.33380\*4.33380\*8.66760 |
| MIBK | 411 | 2886 | 4.42321\*4.42321\*8.84642 |
| MIPK | 498 | 3107 | 4.48165\*4.48165\*8.96330 |
| MTHF | 500 | 2892 | 4.40020\*4.40020\*8.80040 |
| PHME | 498 | 3108 | 4.49366\*4.49366\*8.98732 |

Molecular dynamics simulations of eight two-phase systems containing furfural and xylose were performed. Snapshots of the simulated systems are shown in Fig. S3. First, furfural molecules were transferred to the organic phase after simulation and xylose stayed in the aqueous phase, except for the IPA-H2O, DMC-H2O and CPME-H2O systems; and second, most of the water molecules were extruded out of the organic phase, whereas there were almost no water molecules in the CTC and PhMe phases, except for the systems of IPA-H2O, MIPK-H2O and DMC-H2O. water molecules were present. The CTC-H2O system still had obvious phase separation after simulation, indicating that the CTC phase could effectively extract furfural throughout the reaction to avoid its side reaction, which might be one of the reasons for its higher furfural.

From the 20 ns simulations, the average number of solvent-solute hydrogen bonds was calculated using geometrical hydrogen bond criteria: the donor-acceptor distance <3.5 Å and hydrogen-donor–acceptor angle <30°. Table S4 showed the average number of hydrogen bonds between xylose or furfural and the solvent in the two-phase system. There were more hydrogen bonds between xylose and water, mainly between the 4 hydroxyl groups of the xylose molecule and the oxygen atoms of water. Hydrogen bonds could be formed between the 4 hydroxyl groups of the xylose molecule and organic solvents. Among them, the number of hydrogen bonds between xylose and IPA, DMC and PhMe was high (7.2, 5.0, 1.6), indicating a strong affinity between xylose and IPA, DMC and PhMe, which was consistent with the results of RDF and SDF. No hydrogen bond was formed between xylose and CTC. The oxygen atom of furfural could form hydrogen bonds with water molecules. Hydrogen bonding between furfural and water was more in CTC, MIPK, IPA, DMC and CPME systems (6.4, 5.6, 4.6, 4.6, 7.6). There was no hydrogen bond formation between furfural and most organic solvents because neither had a hydrogen bond donor, whereas IPA could form hydrogen bonds with furfural. Hydrogen bonding between furfural and organic solvents may lead to degradation of furfural.

The radial distribution function curves (Fig. S4) showed the distribution density of solvents around xylose and furfural. Firstly, comparing the RDF of xylose in organic solvents and water (blue and purple lines), it could be seen that in the systems of CTC-H2O, MIBK-H2O, MIPK-H2O, CPME-H2O and MTHF-H2O, the RDF curves of xylose in water were much more upwardly shifted than that in organic solvents, which indicated that the density of water molecules around the xylose is higher and the molecular density of organic solvents is lower in these systems. In IPA-H2O, DMC-H2O and PhMe-H2O, the shift between these two curves was not significant, indicating that the density of the organic solvent molecules around xylose increases and the difference between the density of the organic solvent molecules and the density of the water molecules decreases in these two systems, and it also indicated that IPA, DMC and PhMe had a stronger affinity for xylose than the first five organic solvents, in agreement with the hydrogen bonding data.

Comparing the RDFs of furfural in organic solvents and water (red and green lines), the RDF curves of furfural in organic solvents were much more shifted upward than that in water in all systems, which indicated that furfural was surrounded by high molecular densities of organic solvents and very low densities of water, and meanwhile, the shifts between these two curves were smaller in CTC-H2O, IPA-H2O, and DMC-H2O systems, which indicated that the CTC-H2O, IPA-H2O, and DMC-H2O systems had a weak affinity for furfural.

Figure S5 showed the spatial density distribution of organic solvent (blue) and water (orange) around xylose or furfural. It could be seen that water molecules (orange) dominated around xylose and organic solvent (blue) around furfural. The solvent distribution map around furfural was enlarged, and it was found that the distribution points of water molecules around furfural were different in different systems, and the water molecules were distributed around the two oxygen atoms of furfural in the systems of CTC-H2O and DMC-H2O, and the H2O were distributed around the hydrogen atoms of furfural in the systems of other organic solvents. The distribution of different organic solvents around furfural was also different, MIBK, IPA, DMC, CPME, and MTHF were distributed in the front and back of the plane of five-membered ring of furfural, and CTC, MIPK, PhMe were distributed in the same plane of the five-membered ring of furfural.

The simulation results showed that in the eight solvent systems, water molecules were mainly aggregated around xylose and organic solvent molecules were mainly aggregated around furfural, and also because of the different affinities between xylose, furfural, water, and organic solvents, which leaded to the different distributions of water and organic solvents around xylose and furfural. In particular, IPA, DMC, and PhMe possessed a stronger affinity for xylose, resulting in more organic solvents entering the aqueous phase. This might affect the xylose conversion, leading to lower xylose conversion. In the CTC-H2O, MIPK-H2O, IPA-H2O, DMC-H2O, and CPME-H2O systems, furfural possessed a stronger affinity between furfural and water, resulting in more of the aqueous phase entering the organic phase and affecting furfural extraction.

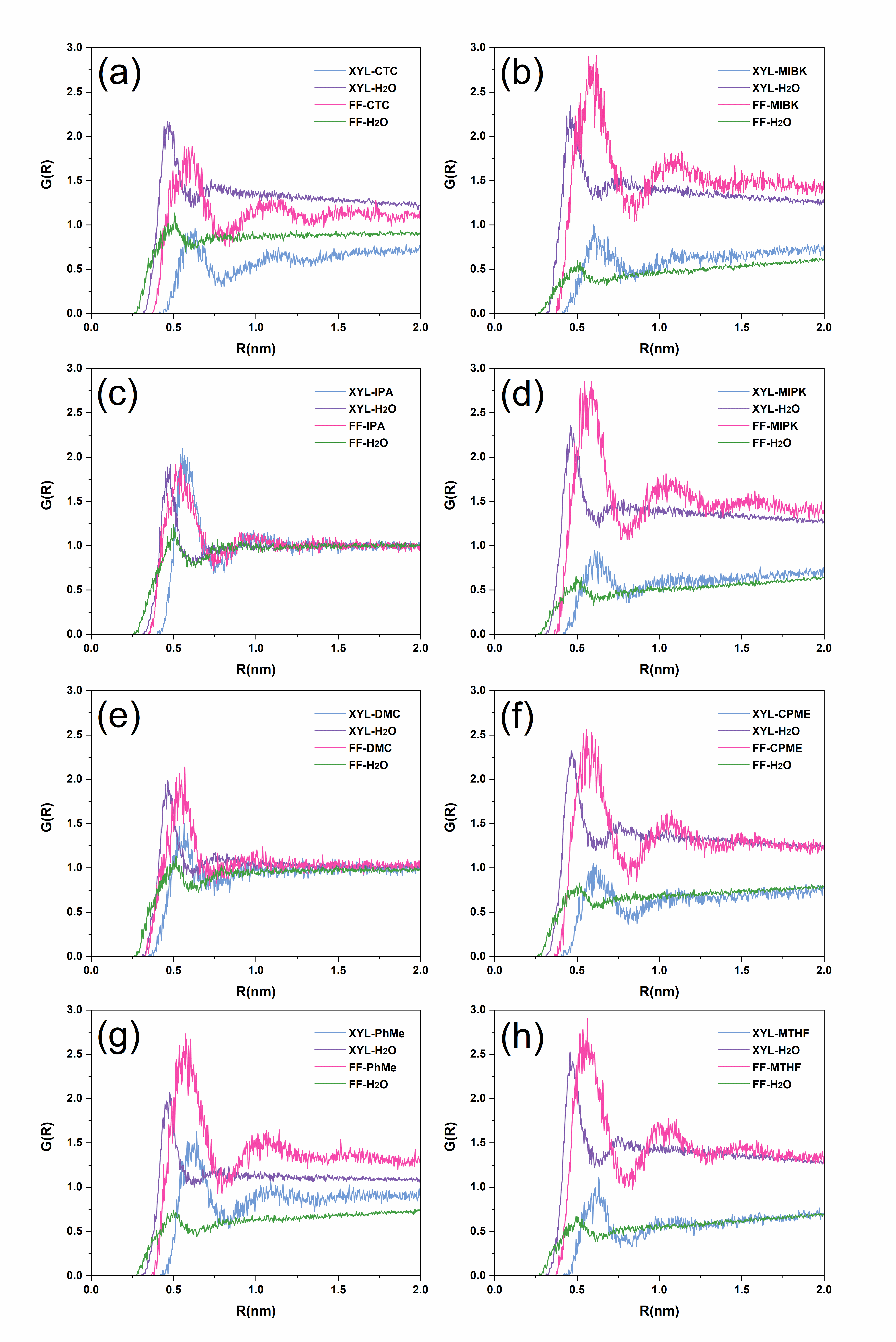
Molecular dynamics simulations showed that xylose and furfural were well confined in the aqueous and organic phases in the CTC-H2O and PhMe-H2O systems, respectively, whereas in the IPA-H2O, MIPK-H2O and DMC-H2O system, xylose and furfural had chaotic trajectories due to the stronger mutual solubility of IPA, MIPK and DMC with water. Of the eight systems simulated, only IPA had a hydrogen bonding association with furfural, which may cause furfural to react with it and reduced the yield of furfural. The lack of hydrogen bonding between the other organic solvents and furfural kept the furfural molecule in a relatively stable state and provided a protective shell for furfural. In addition, there is no hydrogen bonding produced between xylose and organic solvents in the CTC-H2O system, which may reduce the unwanted consumption of xylose.

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**Figure S3:** Snapshots of biphasic systems after molecular dynamics simulation. Blue: water; red: organic solvent; green: xylose; yellow: furfural. (a) CTC-H2O, (b) MIBK-H2O, (c) IPA-H2O, (d) MIPK-H2O, (e) DMC-H2O, (f) CPME-H2O, (g) PhMe-H2O and (h) MTHF-H2O systems.

**Table S4:** The average number of H-bonds between xylose or furfural and solvent.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Phase system | Xylose-organic solvent | Xylose-H2O | Furfural-H2O | Furfural-organic solvent |
| CTC-H2O | - | 69.6 | 6.4 | - |
| MIBK-H2O | 0.2 | 71.8 | 2.4 | - |
| IPA-H2O | 7.2 | 47.2 | 4.6 | 1.0 |
| MIPK-H2O | 1.0 | 56.4 | 5.6 | - |
| DMC-H2O | 5.0 | 49.5 | 4.6 | - |
| CPME-H2O | 0.8 | 49.8 | 7.6 | - |
| PhMe-H2O | 1.6 | 62.0 | 3.0 | - |
| MTHF-H2O | 0.8 | 67.8 | 2.5 | - |



**Figure S4:** Centre of mass radial distribution functions (RDF) of solvent molecules with respect to xylose or furfural.



**Figure S5:** The isosurfaces of the time averaged distribution of the organic solvent (blue) and water (orange) around xylose or furfural.

**Table S5:** Effect of NaCl on the conversion of xylose to furfural**a**.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Entry. | Organic solvent | NaCl | Conversion(%) | FF yield (%)**b** | | Total yield(%) |
|  |  |  |  | Organic | Aqueous |  |
| 1 | CTC | + | 99.9 | 63.6 | 16.7 | 80.3 |
| 2 | CTC | - | 99.4 | 51.3 | 27.2 | 78.5 |

**a**Reaction condition: xylose (0.1 g), catalyst (0.02 g), solvent (15 m), reaction temperature (180℃) and time (60 min). **b**The yield of FF was calculated as the mol FF per mol xylose.



**Figure S6:** Analyses of recovered and fresh Sn(20)@LS catalysts after five cycles: (a, b) SEM images, (c) XRD patterns, (d) FT-IR spectra, (e) TG curves, (f) DTG curves.

**Table S6:** The elemental analysis results of recovered and fresh Sn(20)@LS catalysts.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Catalysts | Content（wt.%） | | | | |
| Sna | Cb | Hb | Nb | Sb |
| Fresh-Sn(20)@LS | 24.13 | 16.96 | 1.63 | - | 1.13 |
| Recycled-Sn(20)@LS | 18.86 | 21.79 | 1.73 | - | 1.01 |

a Determined by ICP-OES. b Determined by elemental analysis.

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