tert-Butanol intervention enables chemoselective conversion of xylose to furfuryl alcohol over heteropolyacids

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SUPPLEMENTARY INFORMATION

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Table S1. The current state-of-the-art processes for direct conversion of xylose to FA.

Entry	Solvent	Catalyst	Reaction condition	Xylose conversion, %	FA yield, %	FA selectivity, %	Ref.
1	*iso*-Propanol + H_2O	ZrO_2-SO_4 + Pt-SiO_2	130 °C, 6 h, 30 bar H_2	65	33.2	51	9
2	*iso*-Propanol + H_2O	Pt-ZrO_2-SO_4	130 °C, 6 h, 30 bar H_2	32	8.6	27	10a
3	*iso*-Propanol + H_2O	Pt-SBA-15-SO_3H	130 °C, 6 h, 30 bar H_2	56	48.7	87	10b
4	*n*-Butanol + H_2O	Cu/SBA-15-SO_3H	140 °C, 6 h, 40 bar H_2	93.7	62.6	66.8	11
5	γ-Butyrolactone + H_2O	Hβ zeolite + Cu/ZnO/Al_2O_3	150 °C, 10 h, 1 bar H_2 feed of 25 mL/min, fixed-bed reactor	99.9	87.2	87.3	12
6	*iso*-Propanol + H_2O	Zeolite beta	130 °C, 1 h, no external H_2	12.5	9.4	75	13a
7	*iso*-Propanol + H_2O	[Al]-SBA-15	130 °C, 4 h, no external H_2	~13	~12	90-95	13b
8	*tert*-Butanol + Formic acid	$H_4SiW_{12}O_{40}$	130 °C, 3 h, no external H_2	99.1	90.1	90.9	This work

Table S2. Comparison for the direct conversion of xylan and xylose to FA in *tert*-butanol/formic acid over HSiW[a].

Entry	Raw material	Reaction time, h	FA yield, %
1	Xylan[b], 0.15 g	2	78.6
2	Xylan, 0.15 g	3	85.0
3	Xylose, 1 mmol	2	84.2
4	Xylose, 1 mmol	3	90.1

[a] Reaction conditions: 0.1 mmol HSiW, 27 mL *tert*-butanol, 3 mL formic acid, 130 °C.

[b] Xylan is derived from corncob and supplied by Aladdin Reagent (Shanghai, China).

Table S3. Carbon balance for xylose processing in *tert*-butanol/formic acid over HSiW[a].

Ingredient	Proportion, %
Xylose conversion rate	100
Xylose convert into FF	6.1
Xylose convert into FA	90.1
Xylose convert into BFE[b]	0.5
Xylose convert into solid polymers	1.9
Unknown products	1.4

[a] Reaction conditions: 1 mmol xylose, 0.1 mmol HSiW, 27 mL *tert*-butanol, 3 mL formic acid, 130 °C, 3 h.

[b] BFE = *tert*-butyl furfuryl ether

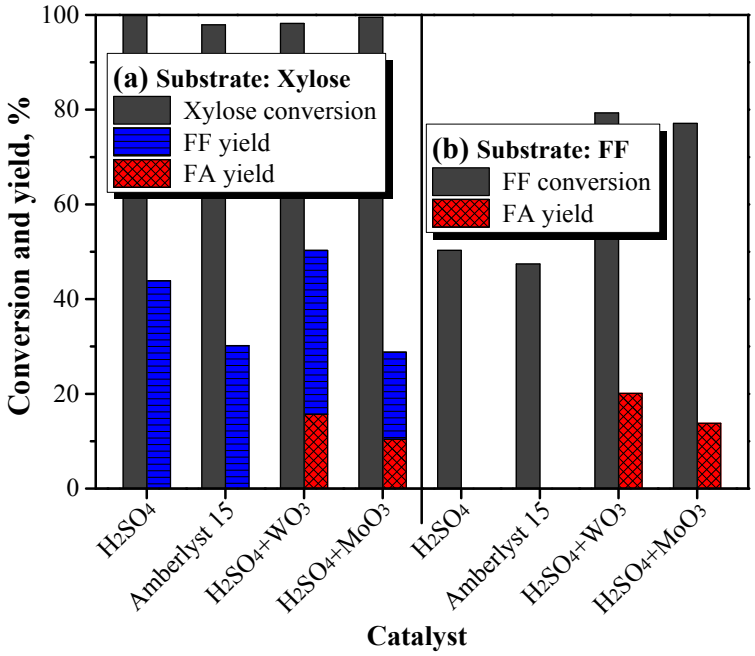

Fig. S1. Conversion of xylose (a) and FF (b) in *tert*-butanol over metal-free acid catalysts. Reaction conditions: 1 mmol xylose or FF, 0.05 g catalyst, 30 mL *tert*-butanol, 130 °C, 2 h.

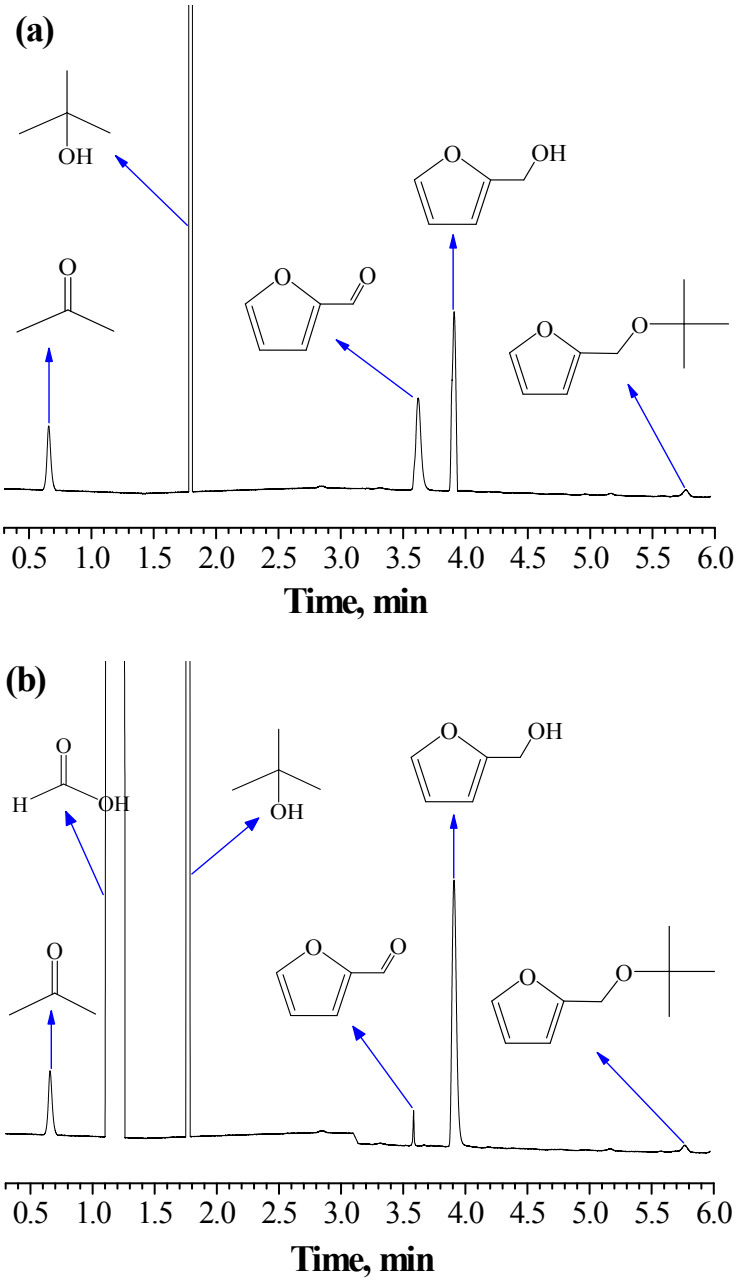

Fig. S2. GC spectra of the typical samples from the conversion of xylose catalyzed by HSiW in *tert*-butanol medium (a) and *tert*-butanol/formic acid medium (b).

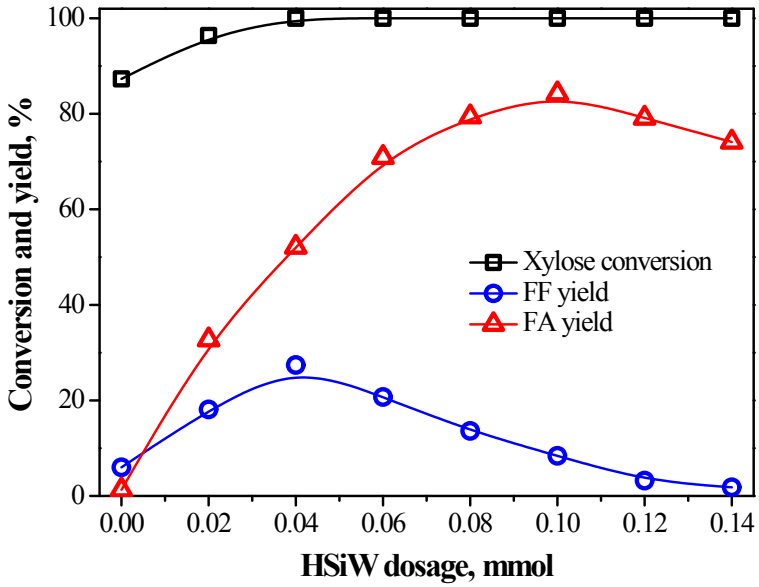

Fig. S3. Effect of HSiW dosage on the conversion of xylose to FA. Reaction conditions: 1 mmol xylose, 27 mL *tert*-butanol, 3 mL formic acid, 130 °C, 2 h.

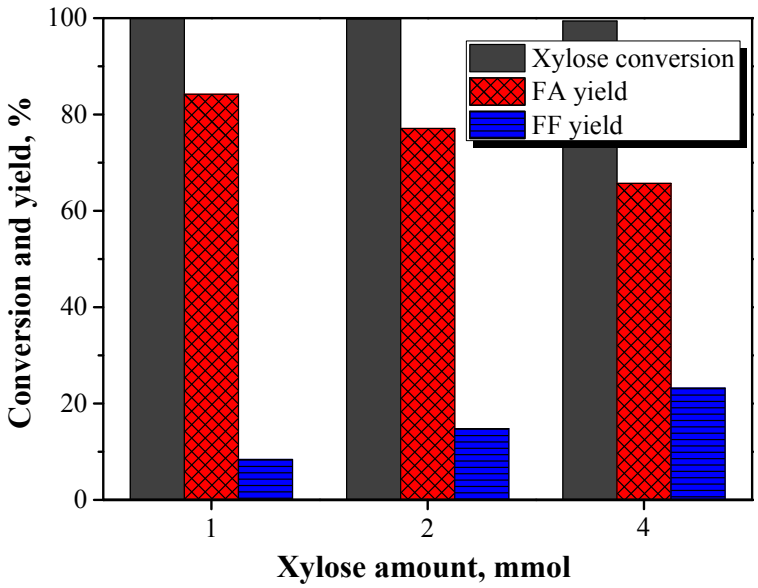

Fig. S4. Effect of substrate concentration on the conversion of xylose to FA. Reaction conditions: 0.1 mmol HSiW, 27 mL *tert*-butanol, 3 mL formic acid, 130 °C, 2 h.

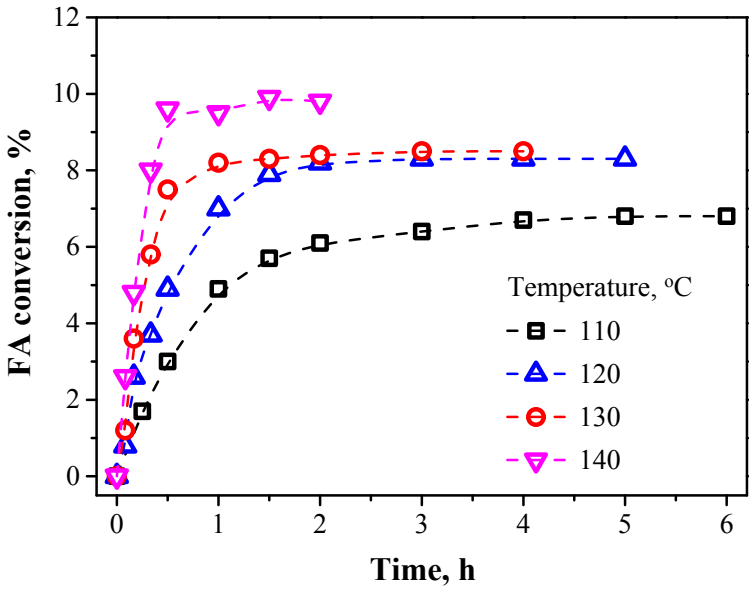

Fig. S5. Effect of reaction temperature as a function of time on FA conversion. Reaction conditions: 1 mmol FA, 0.1 mmol HSiW, 27 mL *tert*-butanol, 3 mL formic acid.

When FA was used as the starting substrate, the decomposition of FA as a function of reaction time can be represented by the following equation:

$$\frac{dC_{FA}}{dt} = -k_5 C_{FA} \qquad \text{(S1)}$$

Where k_5 is the reaction rate constant of FA decomposition, and C_{FA} is the FA concentration. The experimental data in Fig. S5 were fitted by Equation (S1) to obtain k_5.

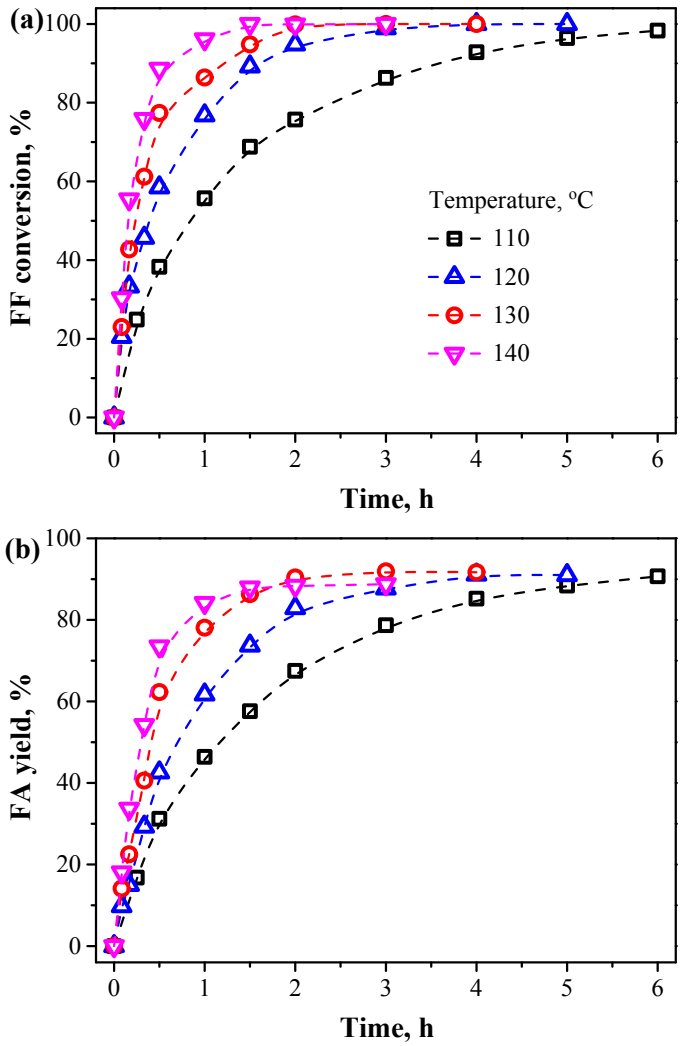

Fig. S6. Effect of reaction temperature as a function of time on FF conversion (a) and FA yield (b). Reaction conditions: 1 mmol FF, 0.1 mmol HSiW, 27 mL *tert*-butanol, 3 mL formic acid.

When FF was used as the starting substrate, the conversion of FF as a function of reaction time can be expressed by the following equations:

$$\frac{dC_{FF}}{dt} = -(k_3 + k_4)C_{FF} \quad \text{(S2)}$$

$$\frac{dC_{FA}}{dt} = k_3 C_{FF} - k_5 C_{FA} \quad \text{(S3)}$$

Where k_3 and k_4 are the reaction rate constants of FF conversion to FA and by-products, respectively. C_{FF} is the FF concentration. Based on the determined k_5, the experimental data in

Fig. S6 were fitted by Equations (S2) and (S3) to obtain k_3 and k_4.

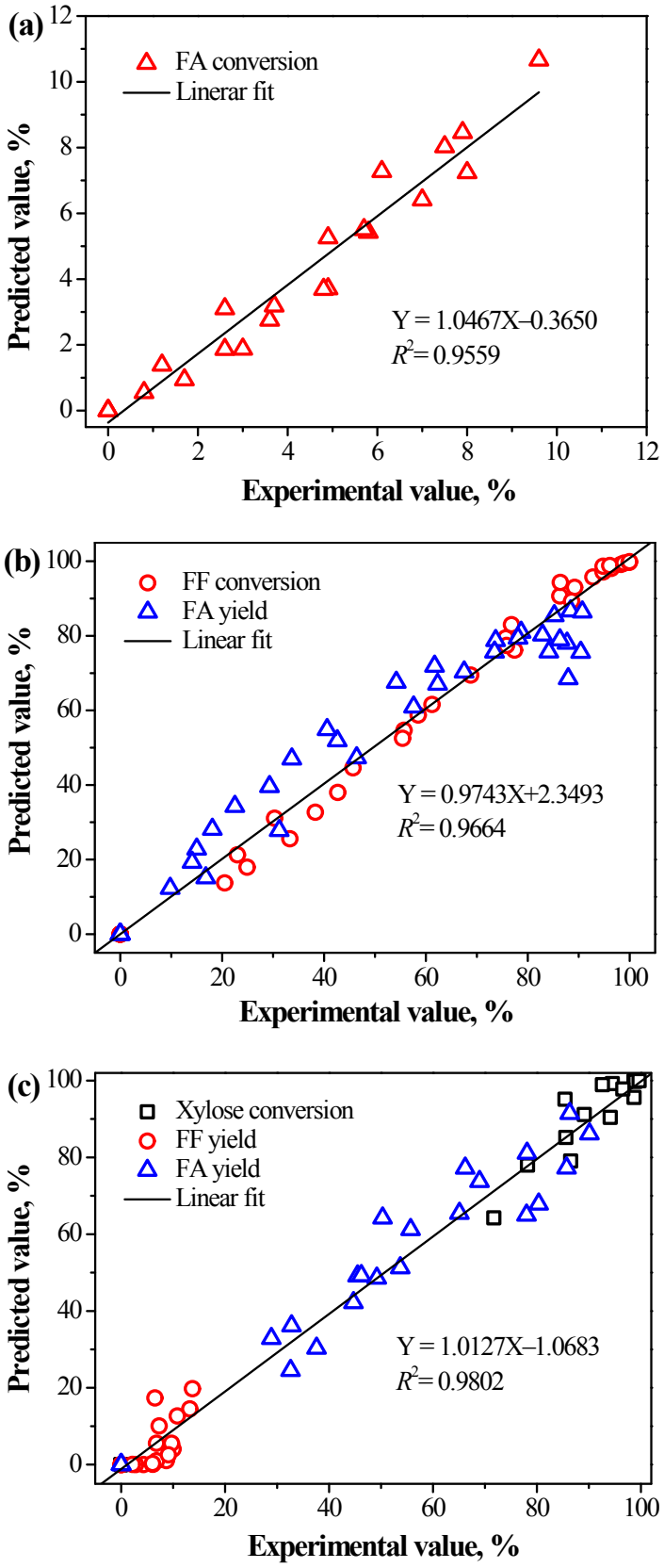

Fig. S7. The correlation between all experiment and predicted values for the conversion of FA

(a), FF (b), and xylose (c).

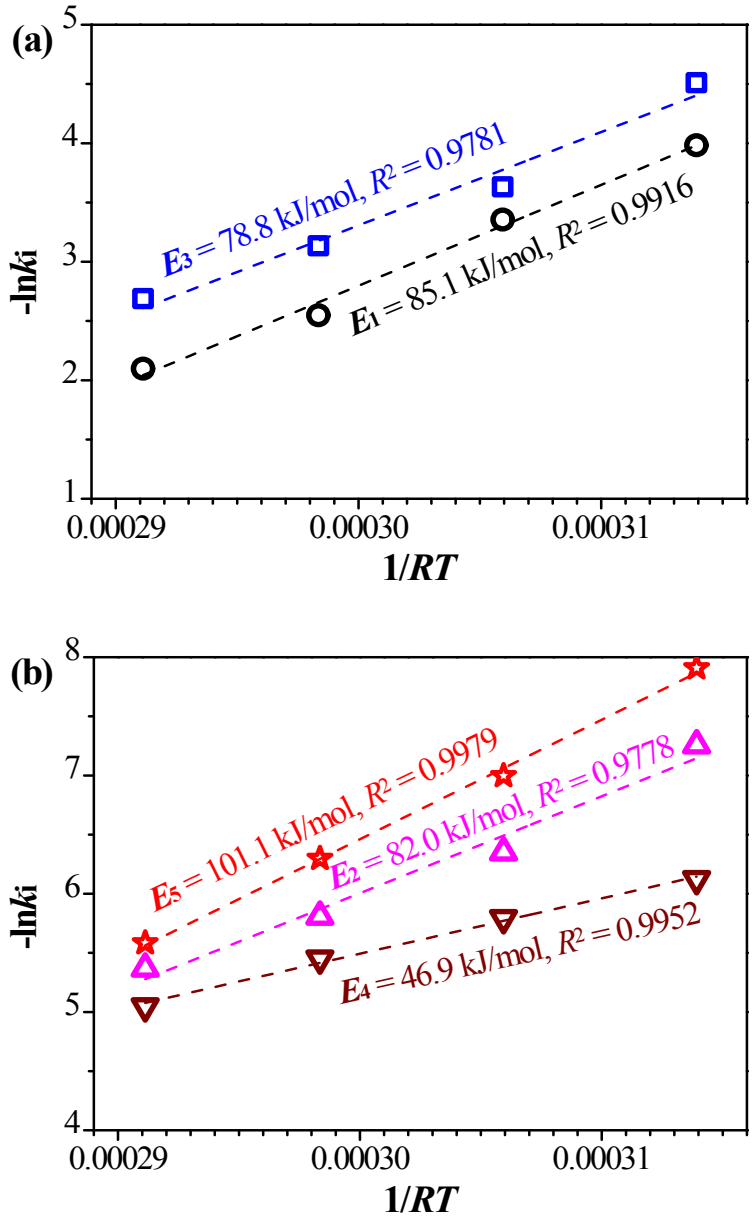

Fig. S8. Arrhenius plot of the main reactions (a) and side reactions (b) for the conversion of xylose to FA.

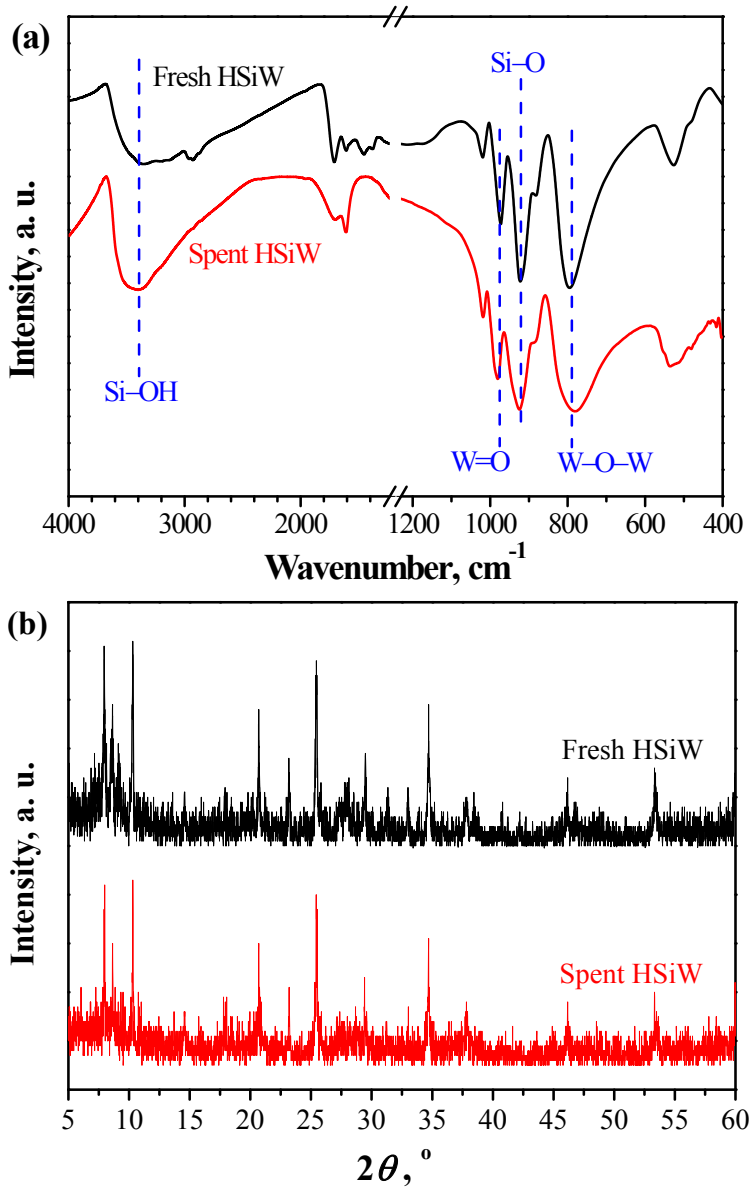

Fig. S9. FTIR (a) and XRD (b) results of the fresh and spent HSiW after five recycles.