Supporting Information

For

Direct synthesis of V-containing all silica Beta zeolite for efficient one-pot and one-step conversion of carbohydrates into 2,5-diformylfuran

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Supplementary Experimental

Synthesis of V_2O_5@Si-Beta

Si-Beta supported V_2O_5 (V_2O_5@Si-Beta) with the same Si/V molar ratio as the one of VSi-Beta(100) was prepared through wet-impregnation. Typically, quantitative ammonium metavanadate (NH_4VO_3, Zhejiang Yuda) was dissolved in water (1 mL) and then mixed with Si-Beta (1 g). The mixture was stirred at 80 °C for 0.5 h and then evaporated to remove water. After that, the solid were dried at 100 °C in an oven and then calcined at 550 °C for 5 h to give the final product V_2O_5@Si-Beta.

Synthesis of VAlSi-Beta

VAlSi-Beta with the same Si/V molar ratio as VSi-Beta(100) was synthesized with the similar procedure to VSi-Beta(100) except that sodium aluminate ($NaAlO_2$, 41 wt% Al_2O_3, Shanghai Chem. Reagent Co., AR) was added before the addition of TEAOH and NaOH.

Supplementary Figures

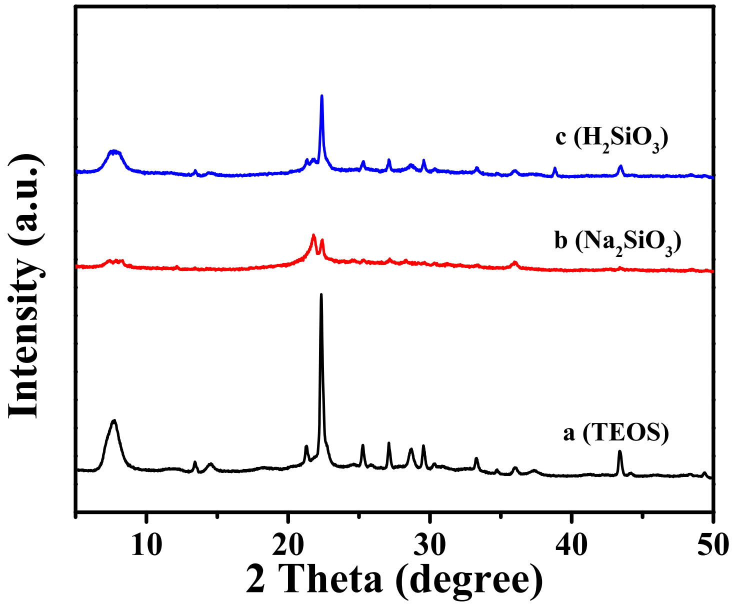

Figure S1. XRD patterns of the samples synthesized with different silica source. The gel molar composition was 1 SiO_2: 0.27 $(TEA)_2$: 0.01 V: 0.54 HF: 9.4 H_2O. Silica source: TEOS. The pH value in the initial acid hydrolysis step: 0.8. Crystallization: 180 °C, 3 d, pH=12.3.

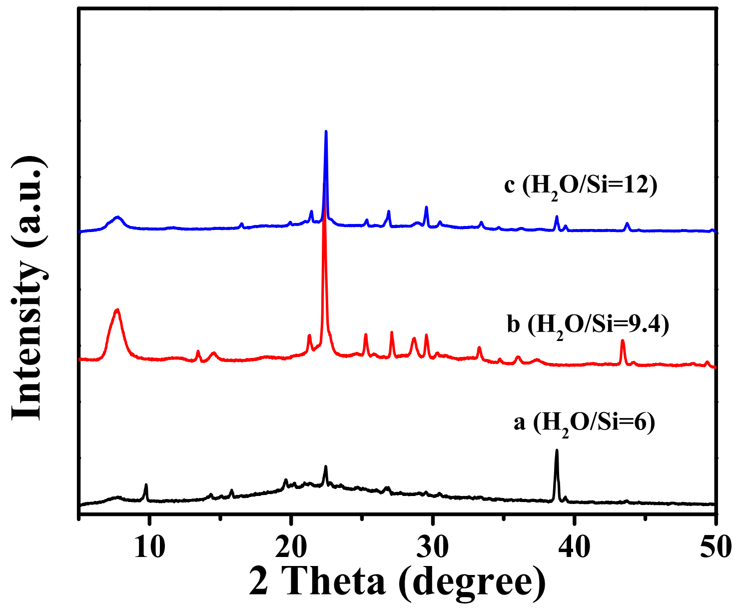

Figure S2. XRD patterns of the samples synthesized with different H_2O/SiO_2 molar ratios. The gel molar composition was 1 SiO_2: 0.27 $(TEA)_2$: 0.01 V: 0.54 HF: 9.4 H_2O. Silica source: TEOS. The pH value in the initial acid hydrolysis step: 0.8. Crystallization: 180 °C, 3 d, pH=12.3.

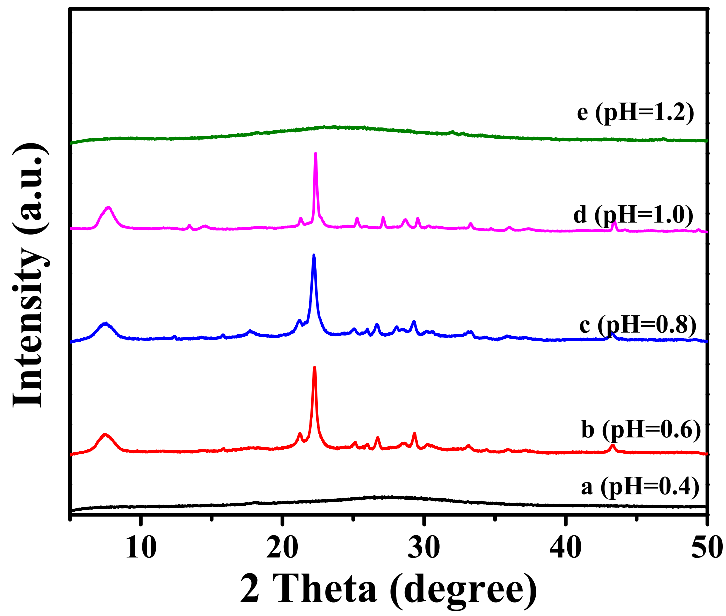

Figure S3. XRD patterns of the samples synthesized with initial acid hydrolysis pH values. The gel molar composition was 1 SiO_2: 0.27 $(TEA)_2$: 0.01 V: 0.54 HF: 9.4 H_2O. Silica source: TEOS. Crystallization: 180 °C, 3 d, pH=12.3.

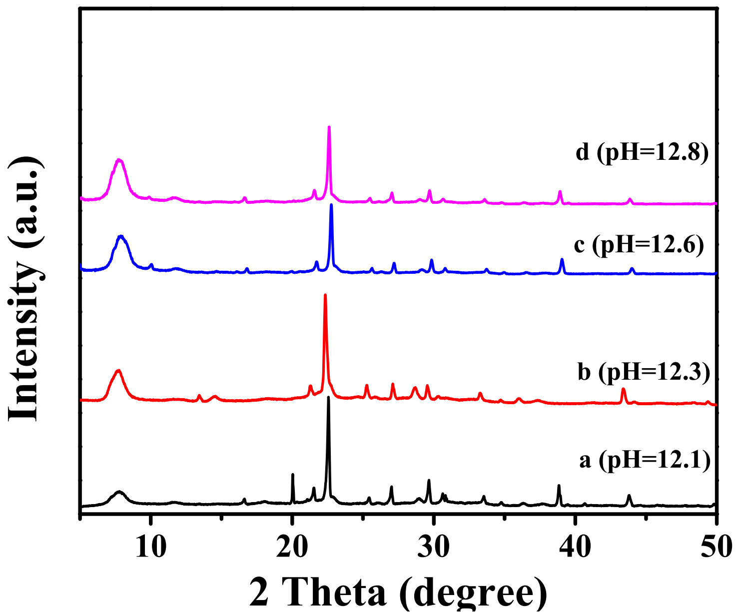

Figure S4. XRD patterns of the samples synthesized with different crystallization pH values. The gel molar composition was 1 SiO_2: 0.27 $(TEA)_2$: 0.01 V: 0.54 HF: 9.4 H_2O. Silica source: TEOS. The pH value in the initial acid hydrolysis step: 0.8. Crystallization: 180 °C, 3 d.

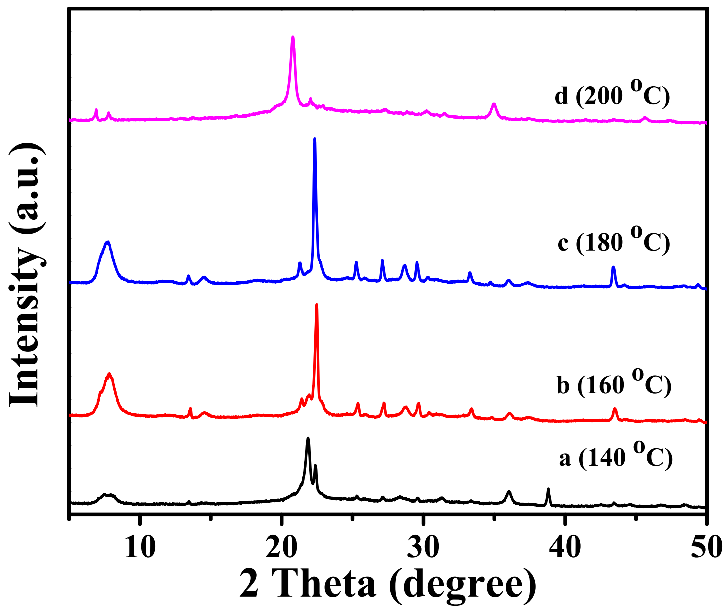

Figure S5. XRD patterns of the samples synthesized with crystallization at (a) 140, (b) 160, (c) 180 and (d) 200 °C. The gel molar composition was 1 SiO_2: 0.27 $(TEA)_2$: 0.01 V: 0.54 HF: 9.4 H_2O. Silica source: TEOS. The pH value in the initial acid hydrolysis step: 0.8. Crystallization: 3 d, pH=12.3.

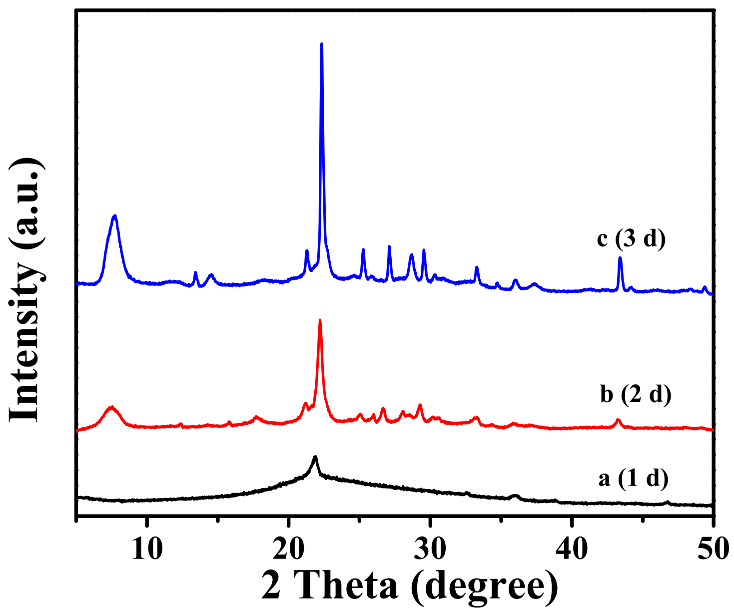

Figure S6. XRD patterns of the samples synthesized with the crystallization for (a) 1, (b) 2 and (c) 3 d. The gel molar composition was 1 SiO_2: 0.27 $(TEA)_2$: 0.01 V: 0.54 HF: 9.4 H_2O. Silica source: TEOS. The pH value in the initial acid hydrolysis step: 0.8. Crystallization: 180 °C, pH=12.3.

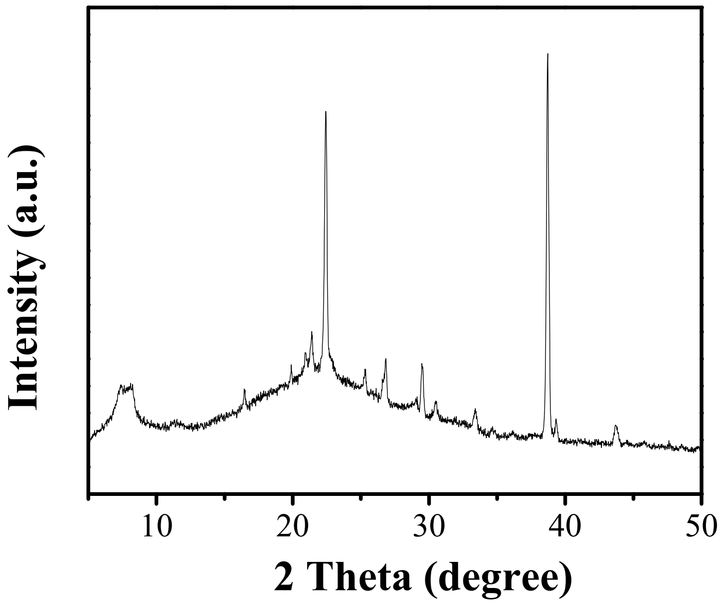

Figure S7. XRD pattern of VSi-Beta(33). The gel molar composition was 1 SiO_2: 0.27 $(TEA)_2$: 0.03 V: 0.54 HF: 9.4 H_2O. Silica source: TEOS. The pH value in the initial acid hydrolysis step: 0.8. Crystallization: 180 °C, 3 d, pH=12.3.

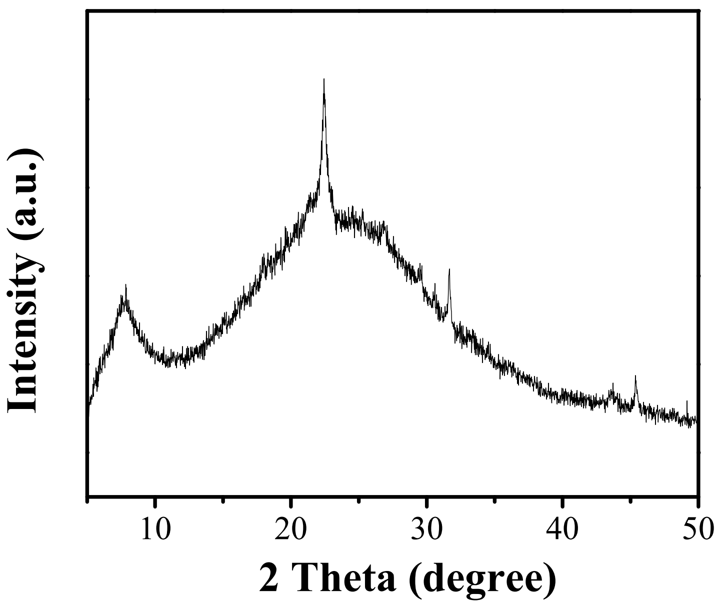

Figure S8. XRD pattern of VSi-Beta-basic synthesized in basic hydrolysis route. The gel molar composition is 1 SiO_2: 0.27$(TEA)_2$:0.01 V: 0.54 HF: 9.4 H_2O. Crystallization: 180 °C, 3 d, pH=12.3.

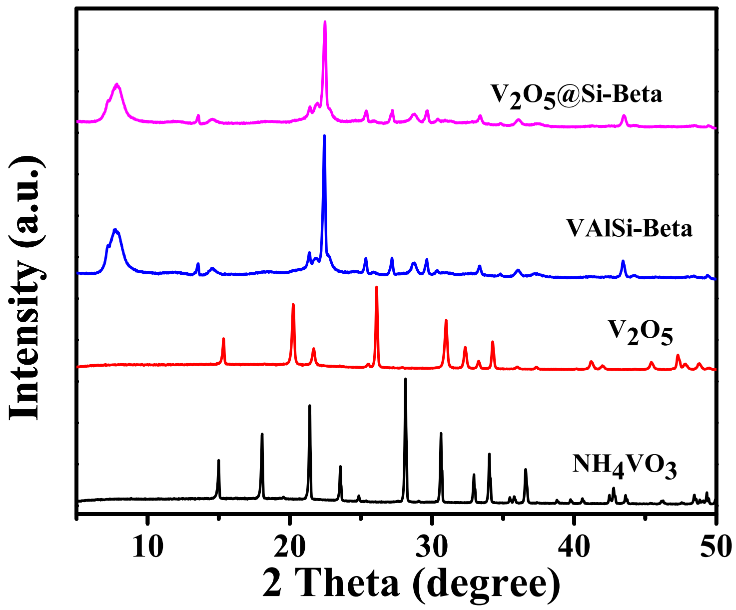

Figure S9. XRD patterns of control samples.

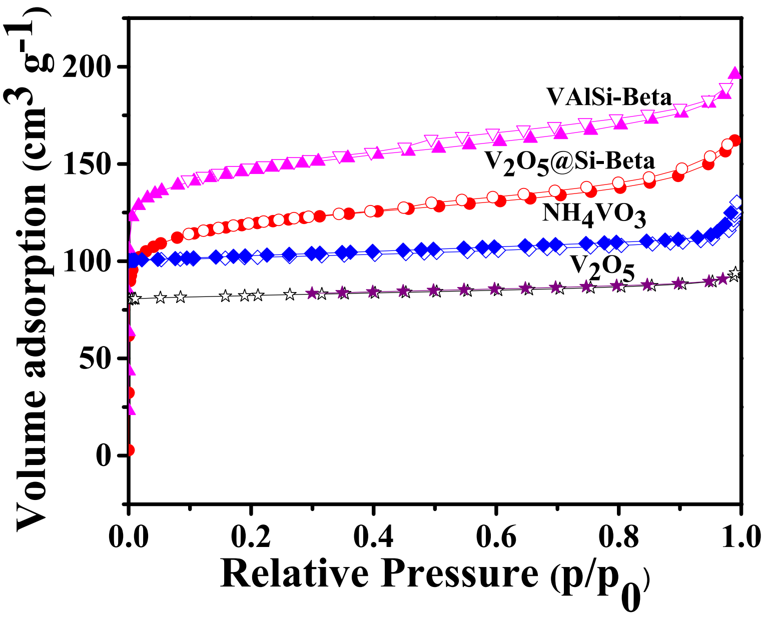

Figure S10. N_2 sorption isotherms of control samples.

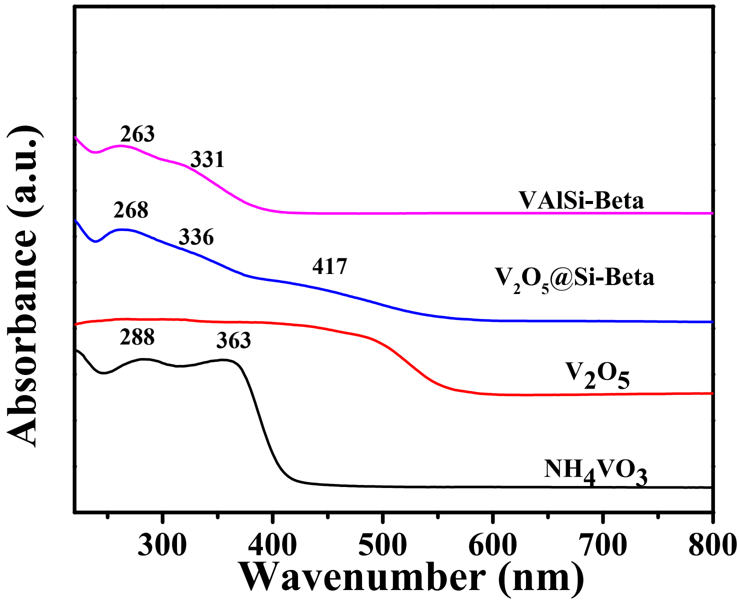

Figure S11. UV-vis spectra of control samples.

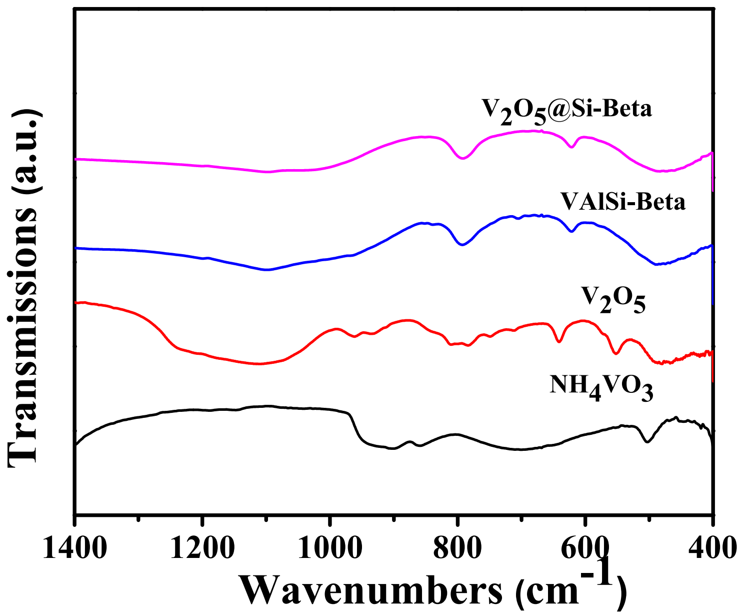

Figure S12. FTIR spectra of control samples.

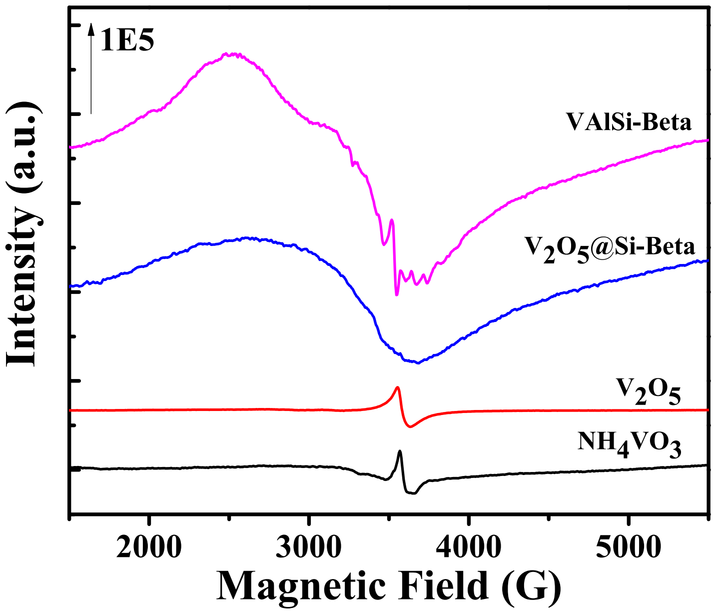

Figure S13. EPR spectra of control samples.

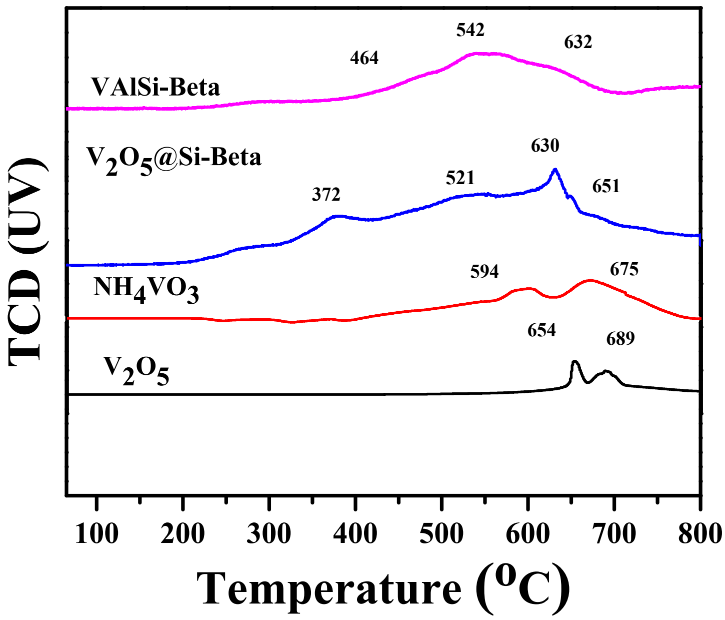

Figure S14. H_2-TPR profiles of control samples.

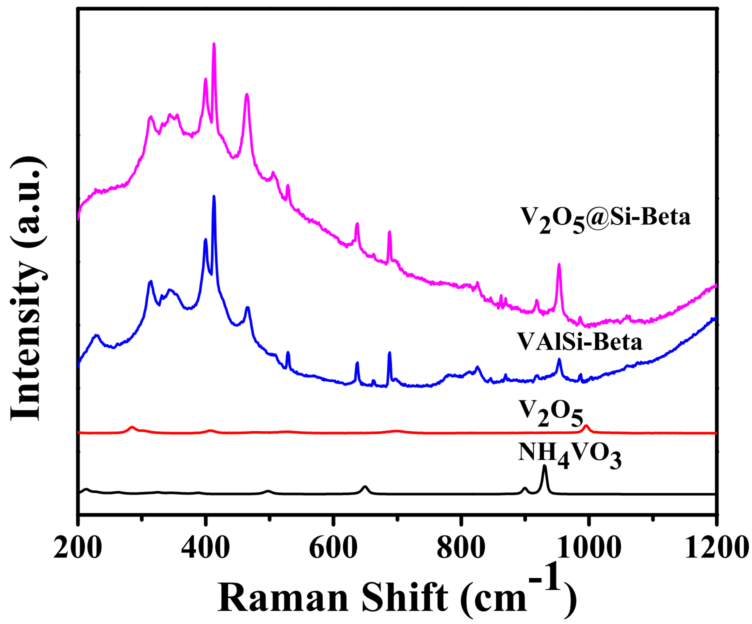

Figure S15. Raman spectra of control samples.

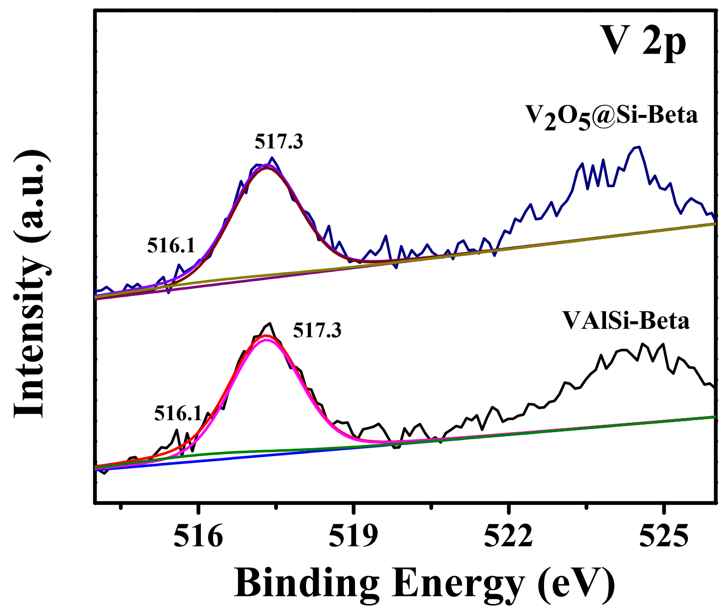

Figure S16. V 2p XPS spectra of control samples.

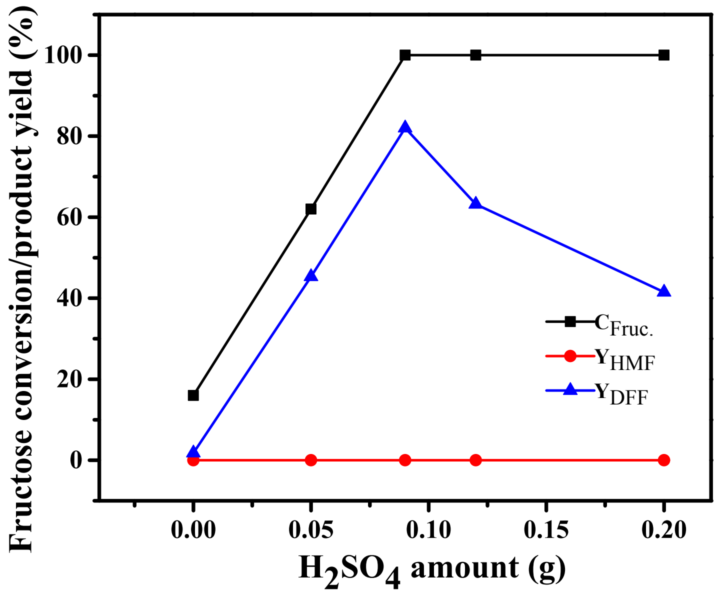

Figure S17. Influence of H_2SO_4 amount in the VSi-Beta(100) catalyzed one-pot and one-step conversion of fructose into DFF. Reaction conditions: 0.1 g fructose, 0.02 g catalyst, 5 mL DMSO, 130 °C, 4 h, O_2 balloon.

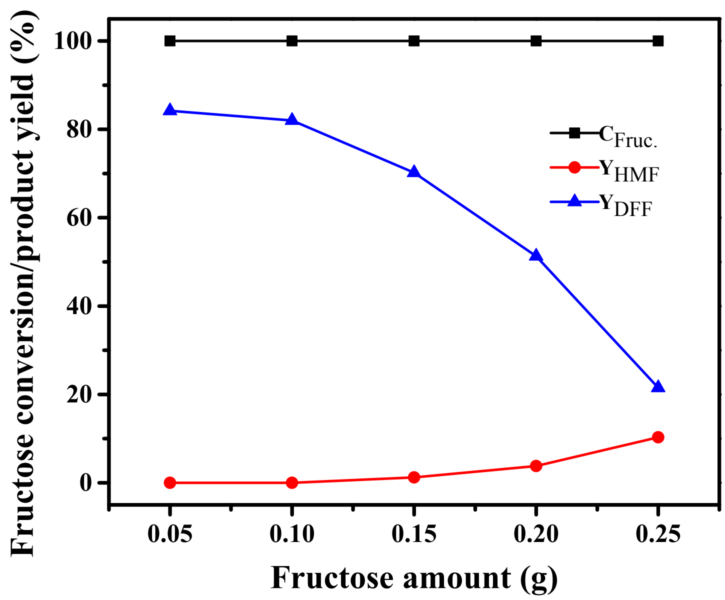

Figure S18. Influence of fructose amount in the VSi-Beta(100) catalyzed one-pot and one-step conversion of fructose into DFF. Reaction conditions: 0.02 g catalyst, 0.09 g H_2SO_4, 5 mL DMSO, 130 °C, 4 h, O_2 balloon.

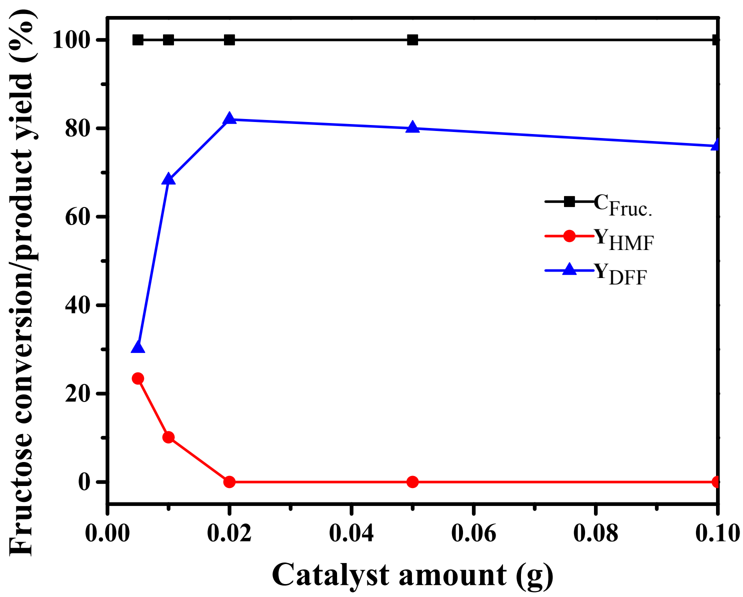

Figure S19. Influence of catalyst amount in the VSi-Beta(100) catalyzed one-pot and one-step conversion of fructose into DFF. Reaction conditions: 0.1 g fructose, 0.09 g H_2SO_4, 5 mL DMSO, 130 °C, 4 h, O_2 balloon.

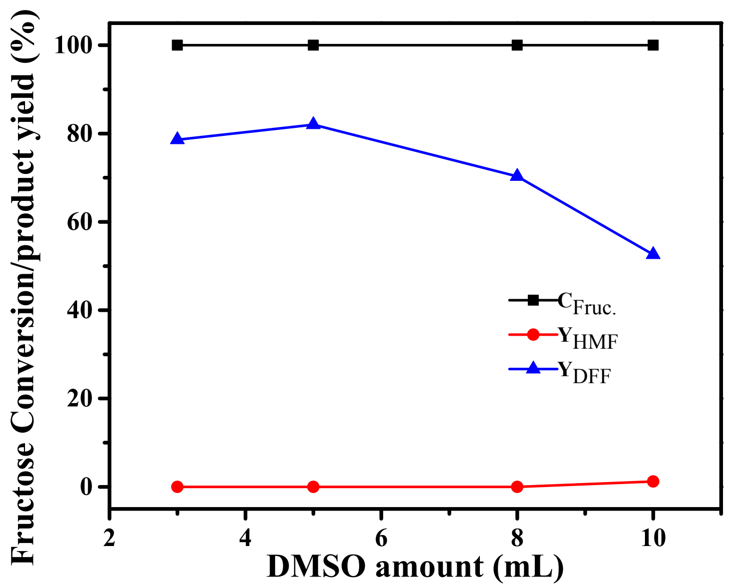

Figure S20. Influence of DMSO amount in the VSi-Beta(100) catalyzed one-pot and one-step conversion of fructose into DFF. Reaction conditions: 0.1 g fructose, 0.02 g catalyst, 0.09 g H_2SO_4, 130 °C, 4 h, O_2 balloon.

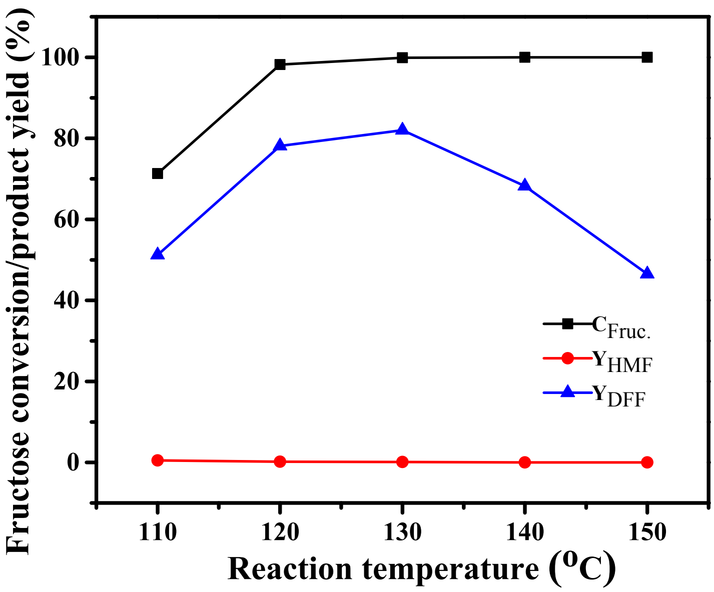

Figure S21. Influence of reaction temperature in the VSi-Beta(100) catalyzed one-pot and one-step conversion of fructose into DFF. Reaction conditions: 0.1 g fructose, 0.02 g catalyst, 0.09 g H_2SO_4, 5 mL DMSO, 4 h, O_2 balloon.

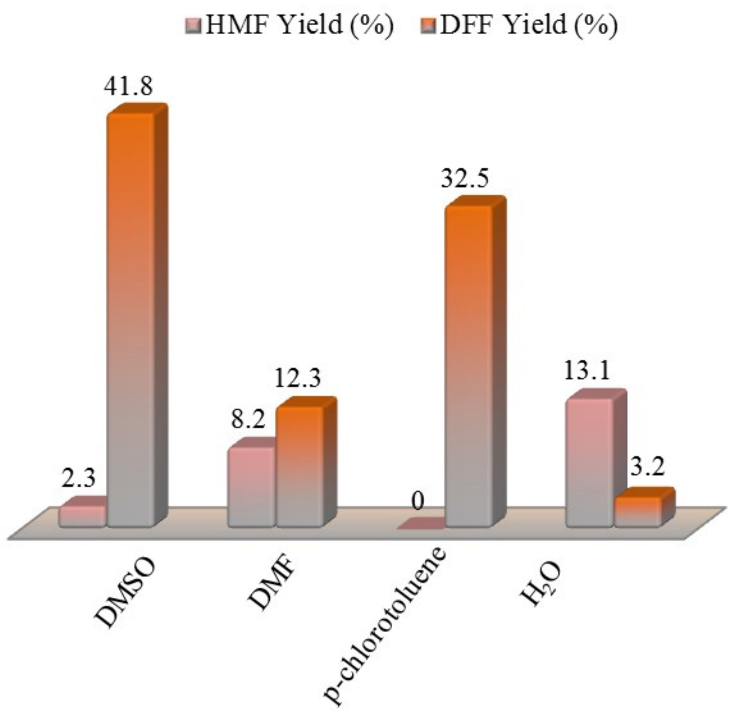

Figure **S22.** Influence of solvents in the VSi-Beta(100) catalyzed one-pot and one-step conversion of fructose into DFF. Reaction conditions: 0.1 g fructose, 0.02 g catalyst, 0.09 g H_2SO_4, 100 °C, 4 h, O_2 balloon.

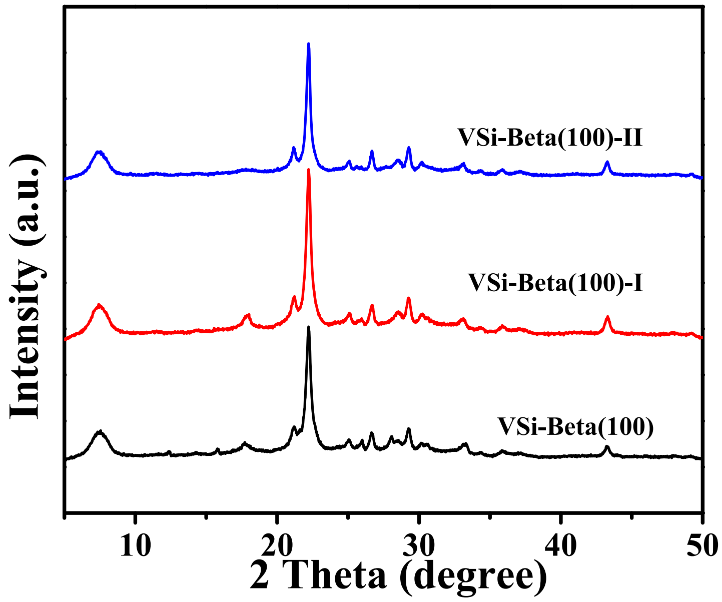

Figure S23. XRD patterns of VSi-Beta(100), VSiBeta(100)-I and VSiBeta(100)-II. VSiBeta(100)-I and VSiBeta(100)-II were the recovered VSi-Beta(100) after 5th run before and after calcination.

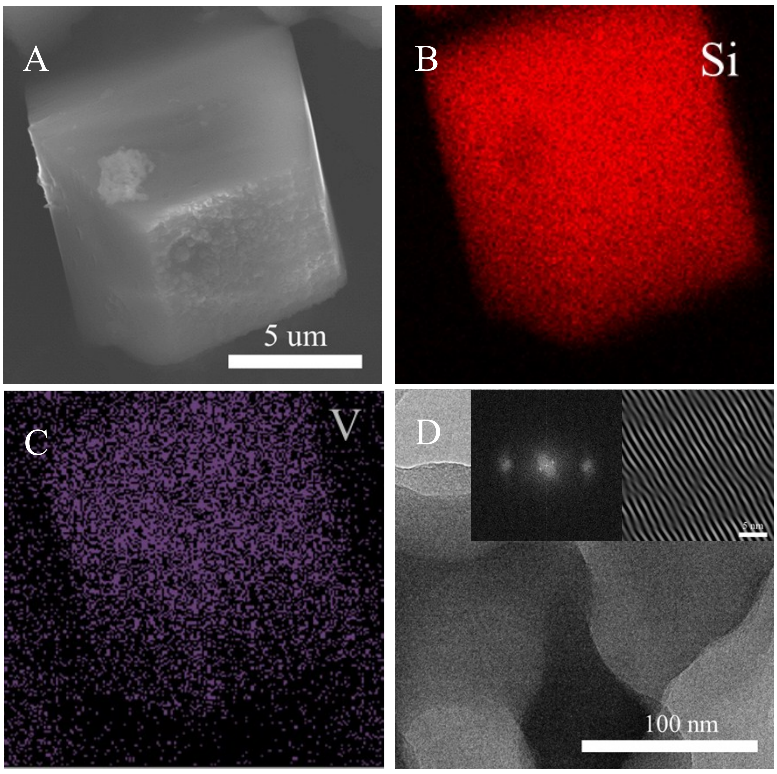

Figure S24. (A) SEM image with EDS elemental mapping images of (B) Si and (C) V element and (D) TEM image of VSi-Beta(100)-II.

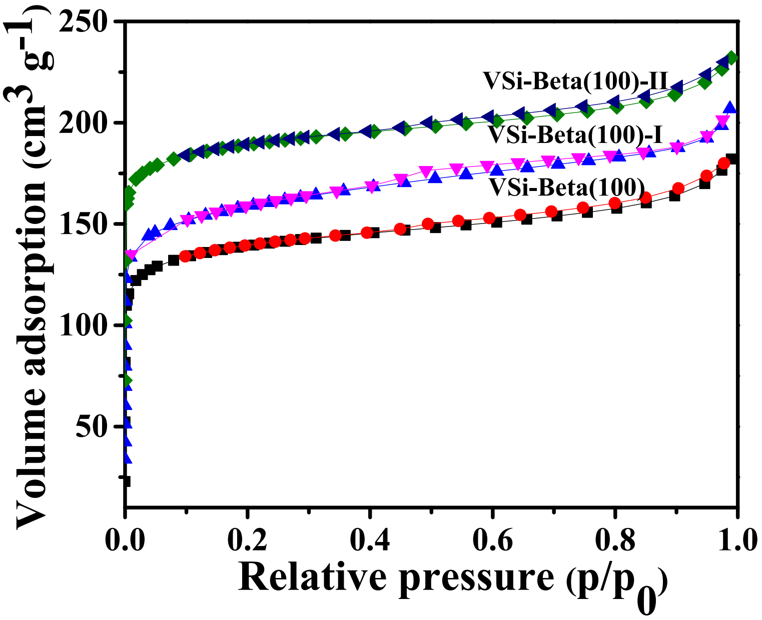

Figure S25. Nitrogen sorption isotherms of VSi-Beta(100), VSiBeta(100)-I and VSi-Beta(100)-II.

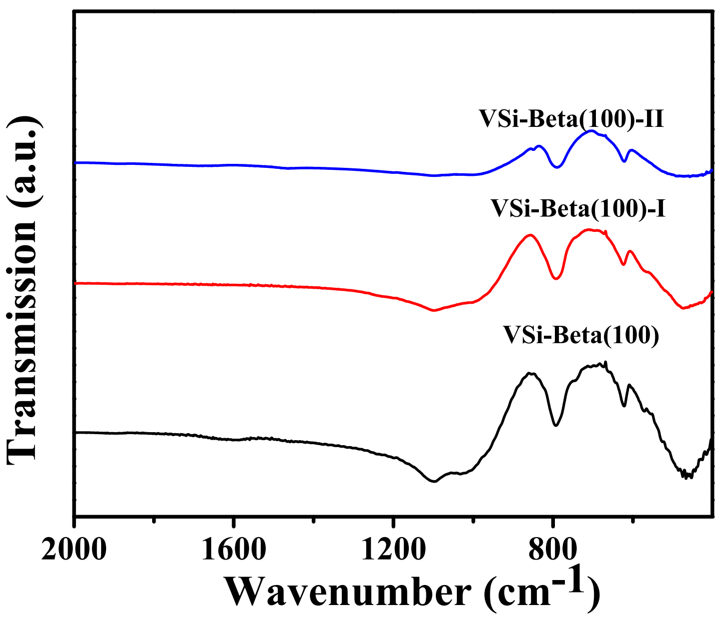

Figure S26. FTIR spectra of VSi-Beta(100), VSiBeta(100)-I and VSi-Beta(100)-II.

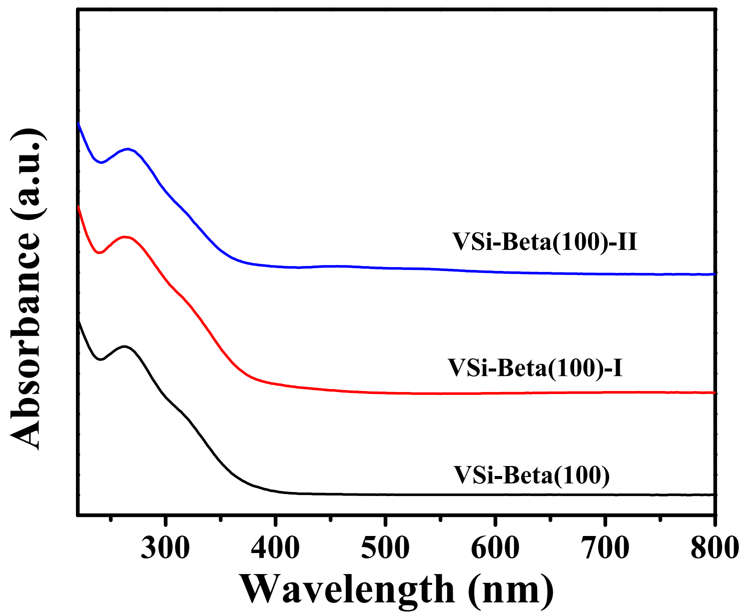

Figure S27. UV spectra of VSi-Beta(100), VSiBeta(100)-I and VSi-Beta(100)-II.

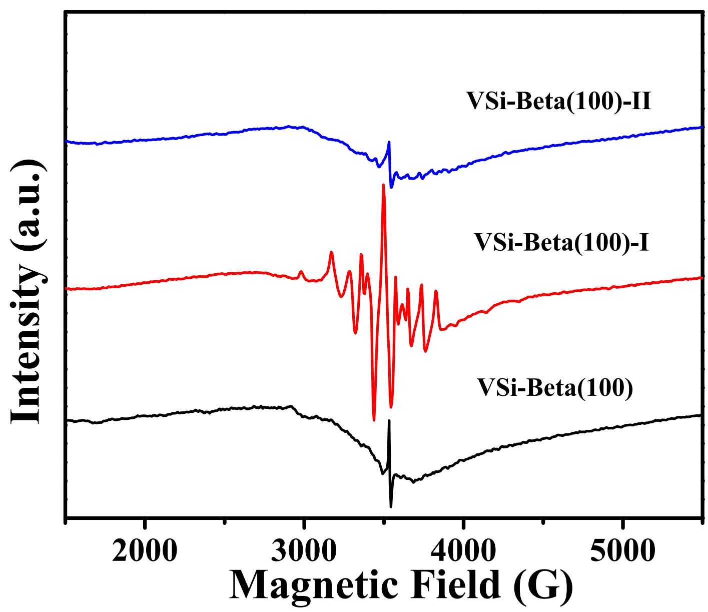

Figure S28. EPR spectra of VSi-Beta(100), VSiBeta(100)-I and VSi-Beta(100)-II.

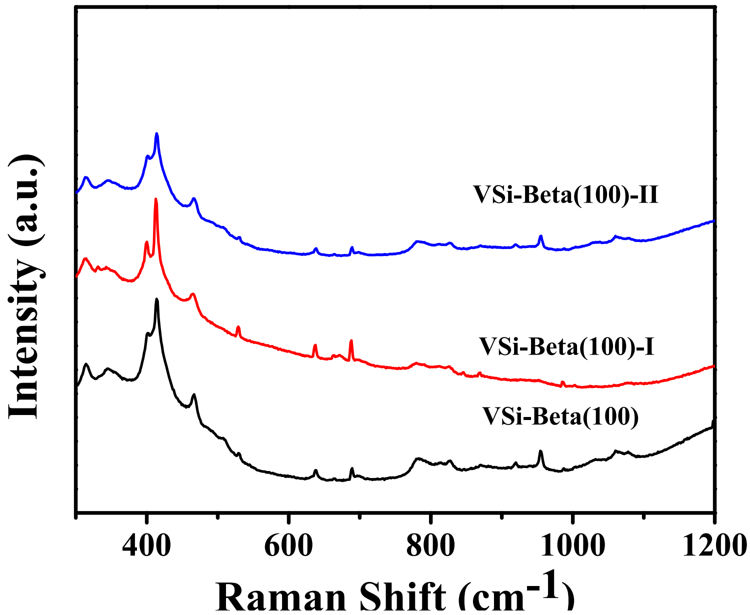

Figure S29. Raman spectra of VSi-Beta(100), VSiBeta(100)-I and VSi-Beta(100)-II.

Supplementary Tables

Table S1 Textural properties

Sample	V (wt%)[a]	Surface area ($m^2 \cdot g^{-1}$)	Pore volume ($cm^3 \cdot g^{-1}$)
V_2O_5@Si-Beta	0.68	507	0.25
VAl-Beta	0.73	532	0.28
NH_4VO_3	43.5	8	0.04
V_2O_5	55.9	4	0.01
VSi-Beta(100)-I	0.68	527	0.28
VSi-Beta(100)-II	0.69	532	0.28

[a] V content of the final solid products.

Table S2 V XPS data of VSi-Beta(100) and control samples

Catalyst	V^{4+}		V^{5+}	
	BE (eV)	Area (%)	BE (eV)	Area (%)
VSi-Beta(100)	516.1	1.9	517.2	98.1
VSi-Beta(50)	516.2	2.8	517.3	97.2
VAl-Beta	516.3	10.2	517.3	89.8
V_2O_5@Si-Beta	516.3	8.0	517.3	92.0

Table S3 One-pot synthesis of 2,5-diformylfuran from carbohydrates

Catalyst	Substrate	$P(O_2)$ [a]	Method	Y_{DFF} (%)[b]	TON	TOF (h^{-1})	Ref
$g\text{-}C_3N_4(H^+)$, $V\text{-}g\text{-}C_3N_4(H^+)$	fructose	0.1 MPa	Two-step	63	6.1	0.7	S1
$V\text{-}g\text{-}C_3N_4\,(H^+)$	fructose		One-Step	45	6.4	0.8	S1
Amberlyst-15 and Ru/HT	fructose	20 mL/min	Two-step	49	12.5	1.3	S2
$Fe_3O_4@SiO_2\text{-}SO_3H$, r-$Fe_2O_3$@HAP-Ru	fructose	20 mL/min	Two-step	79.1	21.3	0.8	S3
$Cs_3HPMo_{11}VO_{40}$	fructose fructose	0.1 MPa	Two-step One-step	60 (53) 39	9.7 6.3	1.2 0.9	S4 S4
$Cs_{0.5}H_{2.5}PMo_{12}$	fructose glucose sucrose inulin	air (0.1 MPa)	One-step	69.3 (65.3) 8.4 28.9 32.0	3.6 0.8 1.6 2.2	0.9 0.4 0.8 1.1	S5
Amberlyst-15, polyaniline-$VO(acac)_2$	fructose fructose	20 mL/min	Two-step One-step	71.1 42.1	5.8 3.4	0.4 0.2	S6 S6
$Fe_3O_4\text{−}RGO\text{−}SO_3H$, $ZnFe_{1.65}Ru_{0.35}O_4$	fructose	20 mL/min	Two-step	73.3	2.9	0.3	S7
Amberlyst 15, SBA-15-Biimidazole-Ru	fructose	20 bar	Two-step	72.4	36.6	2.6	S8
Fe-S/C (S 8 wt%)	fructose	1 bar	Two-step	>99 (>99)	3.3	0.6	S9
f-Ce_9Mo1O_δ	fructose	10 mL/min	One-step Two-step	45 74	12.3 7.5	1.0 0.6	S10
VSi-Beta	fructose glucose sucrose inulin raffinose maltose starch	1 bar	One-step	82(82) /86.3[c] 38.2 32.1 39.3 20.1 18.1 28.2	162 /270[c] 15.1 41.6 15.5 28.4 7.6 11.1	40.5 /67.5[c] 2.5 6.9 2.6 4.7 1.3 1.2	***This work***

[a] Pressure of O_2. [b] DFF yield; the value in the bracket is the yield after several recycles. [c] The maximum value for yield, TON and TOF, respectively.

Table S4 Dehydration of fructose into HMF[a]

Entry	Catalyst	Con (%)[b]	Y_{HMF} (%)[c]	Y_{DFF} (%)[d]
1[e]	-	100	94.0	0
2	-	100	91.0	0
3	VSi-Beta(100)	100	90.2	4.8
4	V_2O_5@Si-Beta	100	82.2	2.3

[a] Reaction conditions: 5 mL DMSO, 0.1 g fructose, 130 °C, 1 h, 0.09 g H_2SO_4, 0.02 g catalyst, O_2 balloon. [b] Conversion of fructose. [c] Yield of HMF. [d] Yield of DFF. [e] N_2 balloon.

Table S5 Oxidation of HMF to DFF[a]

Entry	Catalyst	C_{HMF} (%)[b]	Y_{DFF} (%)[c]
1[d]	-	25.3	7.2
2	-	>99.9	29.1
3	VSi-Beta(100)	>99.9	92.9
4	V_2O_5@Si-Beta	>99.9	80.3

[a] Reaction conditions: 5 mL DMSO, 0.07 g HMF, 130 °C, 3 h, 0.09 g H_2SO_4, 0.02 g catalyst, O_2 balloon. [b] Conversion of HMF. [c] Yield of DFF. [d] Without H_2SO_4.

References

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