Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary Information

Efficient catalytic oxidation of biomass to formic acid coupled with low-energy formaldehyde production from methanol

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Supplementary Tables

Table S1 Literature review on catalytic aerobic oxidation of biomass with vanadium-based catalyst[a]

Substrate	Catalyst	Solvent	Additive	FA (ester) yield (%)	Ref.
Cellulose	HPA-5 + H_2SO_4	H_2O	CH_3OH (value-added)	76	This work
	$VOSO_4$	H_2O		39	[1]
	$NaVO_3$-H_2SO_4	H_2O		65	[2]
	$NaVO_3$-$FeCl_3$-H_2SO_4	H_2O		67	[3]
	HPA-1	H_2O		68	[4]
	HPA-2 + TSA[b]	H_2O		19	[5]
	HPA-5 + TSA	H_2O		28	[6]
	HPA-2 + H_2SO_4	H_2O		61	[7]
	$Co_{0.6}H_{3.8}PMo_{10}V_2O_{40}$	H_2O		66	[8]
	$[MIMPS]_3[HPVMo_{11}O_{40}]$	H_2O		51	[9]
	$VOSO_4$	$H_2O + C_2H_5OH$		70	[1]
	$NaVO_3$-H_2SO_4	H_2O	DMSO[c] (consumed)	68	[10]
Glucose	HPA-5	H_2O	CH_3OH (value-added)	85	This work
	$VOSO_4$	H_2O		53	[1]
	$NaVO_3$-H_2SO_4	H_2O		68	[2]
	HPA-1	H_2O		55	[4]
	HPA-2	H_2O		49	[11]
	HPA-3	H_2O		56	[6]
	HPA-4	H_2O		52	[6]
	HPA-5	H_2O		57	[6]
	HPA-6	H_2O		56	[6]
	$VOSO_4$	$H_2O + CH_3OH$		75	[1]
	HPA-2	$H_2O + CH_3OH$		78	[12]
	HPA-5	CH_3OH		99	[13]

Substrate	Catalyst	Solvent	Additive	FA (ester) yield (%)	Ref.
Glucose	HPA-5	H_2O + 1-Hexanol (two-phase)		85	[14]
	$NaVO_3$-H_2SO_4	H_2O	DMSO (consumed)	77	[10]
	HPA-2	H_2O	IPA[d] (consumed)	92	[15]
Xylan	HPA-5	H_2O	CH_3OH (value-added)	80	This work
	$NaVO_3$-H_2SO_4	H_2O		64	[2]
	HPA-2	H_2O		33	[11]
	HPA-2 + TSA	H_2O		53	[5]
	HPA-5 + TSA	H_2O		58	[6]
	$K_5V_3W_3O_{19}$	H_2O		25	[16]
	$NaVO_3$-H_2SO_4	H_2O	DMSO (consumed)	67	[10]
	HPA-2	H_2O	IPA (consumed)	64	[15]
Xylose	HPA-5	H_2O	CH_3OH (value-added)	89	This work
	$NaVO_3$-H_2SO_4	H_2O		64	[2]
	HPA-2	H_2O		54	[11]
	$NaVO_3$-H_2SO_4	H_2O	DMSO (consumed)	74	[10]
	HPA-2	H_2O	IPA (consumed)	72	[15]

[a] Blue fill color represents the normal catalytic aerobic oxidation. Orange fill color represents the catalytic aerobic oxidation in alcohol-water solvents. Green fill color represents the catalytic aerobic oxidation with additives. [b] TSA: *p*-toluenesulfonic acid. [c] DMSO: dimethyl sulfoxide. [d] IPA: isopropanol.

Table S2 Proximate and ultimate analyses of enzymatic lignin[a]

Proximate analysis (wt%)			Ultimate analysis (wt%, in daf. basis)				
M_{ad}	A_d	V_{daf}	C	H	O[b]	N	S
2.48	1.60	63.78	63.97	5.54	29.55	0.79	0.15

[a] ad: air-dry basis; d: dry basis; daf: dry-and-ash-free basis. *M*: moisture; *A*: ash; *V*: volatile matter content. [b] By difference.

Table S3 Elemental analysis of the corn stalk

Element	C	H	O[a]	N	S
100 *w*	43.28	5.86	49.76	1.07	0.03

[a] By difference.

Table S4 Lignocellulose component analysis of the corn stalk[a]

Component	Cellulose	Hemicellulose	Lignin	Ash	Extraction
100 *w*	36.52	29.14	4.40	1.57	28.36

[a] The components of corn stalk were analyzed according to the Van Soest method.

Table S5 ICP-OES and TG analyses of HPA-*n*

Compound	Molecular composition	P/V/Mo ratio	Hydration Water[a] (mole)
HPA-0	$H_3[PMo_{12}O_{40}]$	1/−/12.27	9
HPA-1	$H_4[PVMo_{11}O_{40}]$	1/0.87/10.89	10
HPA-2	$H_5[PV_2Mo_{10}O_{40}]$	1/1.82/10.27	10
HPA-3	$H_6[PV_3Mo_9O_{40}]$	1/2.86/9.15	11
HPA-4	$H_7[PV_4Mo_8O_{40}]$	1/4.06/8.33	12
HPA-5	$H_8[PV_5Mo_7O_{40}]$	1/5.24/6.83	13
HPA-6	$H_9[PV_6Mo_6O_{40}]$	1/5.82/6.28	14

[a] Moles of hydration water determined via TG.

Table S6 The stabilities of FA and FAld in the catalytic system[a]

Substrate	Conv. (%)	Yield (%)		
		FA	CO_2	CO
FA	18.7		16.8	1.7
FAld	59.2	48.6	6.7	2.3

[a] Reaction conditions: substrate, 0.32 g; HPA-5, 5.4 mM; H_2SO_4, 0.15 M; H_2O, 20 mL; O_2 pressure, 3 MPa; temperature, 180 °C; reaction time, 20 min.

Table S7 Conversions of substrates in the coupling oxidations showed in molar amount

Substrate	Molar amount (mmol)	Conversion (%)	Converted molar amount (mmol)
Cellulose[a]	11.85	97.56	11.56
Methanol	52.13	20.10	10.48

[a] The molar amount of cellulose was the molar amount of C atoms in it.

Table S8 Yields of products in the coupling oxidations showed in molar amount

Product	Molar amount (mmol)	Calculations of FA-1 and FA-2 (mmol)
Formic acid	11.32	
Methyl formate	0.12	
Cellobiose	0.0004	FA-2 = converted methanol − FAld − dimethyl ether
Glycolic aldehyde	0.0027	= 10.48 – 7.65 – (0.21 × 2) = 2.41
Levulinic acid	0.008	
Acetic acid	0.077	
CO	0.28	FA-1 = FA − FA-2 = (11.32 + 0.12) – 2.41 = 9.03
CO_2	1.57	
Formaldehyde[a]	7.65	
Dimethyl ether	0.21	

[a] Formaldehyde exist in the form of formaldehyde hydrate and methoxymethanol in the methanol-water solution.

Table S9 TOFs of FA and FAld production in the separate oxidations and the coupling oxidations[a]

Substrate	FA (mmol)	FAld (mmol)	HPA-5 (mmol)	TOF_{FA} (h^{-1})	TOF_{FAld} (h^{-1})
Cellulose	4.50	0.14	0.11	122.7	3.8
Methanol	1.37	4.54	0.11	37.4	123.8
Cellulose + Methanol	11.44	7.65	0.11	312.0	208.6

[a] Reaction conditions: cellulose, 0.32 g; methanol, 1.6 g; HPA-5, 5.4 mM; H_2SO_4, 0.15 M; H_2O, 20 mL; O_2 pressure, 3 MPa; temperature, 180 ^oC; reaction time, 20 min.

Table S10 ICP-OES analysis of HPA-5 before and after the recycling experiments

HPA-5	P/V/Mo ratio
Before recycle	1/5.24/6.83
After recycle	1/5.27/6.79

Table S11 Gram-scale reaction of the coupling oxidations[a]

Cellulose conv. (%)	Yield (%)			Methanol conv. (%)	Yield (%)		
	FA-1	CO_2	Others[b]		FAld	FA-2	Dimethyl ether
100	64.1	20.2	11.6	15.7	13.4	0.7	1.6

[a] Reaction conditions: cellulose, 1 g; methanol, 5 g; HPA-5, 17.0 mM; H_2SO_4, 0.05 M; H_2O, 20 mL; O_2 pressure, 5 MPa; temperature, 190 ^oC; reaction time, 30 min. [b] Other products include acetic acid and carbon monoxide.

Supplementary Figures

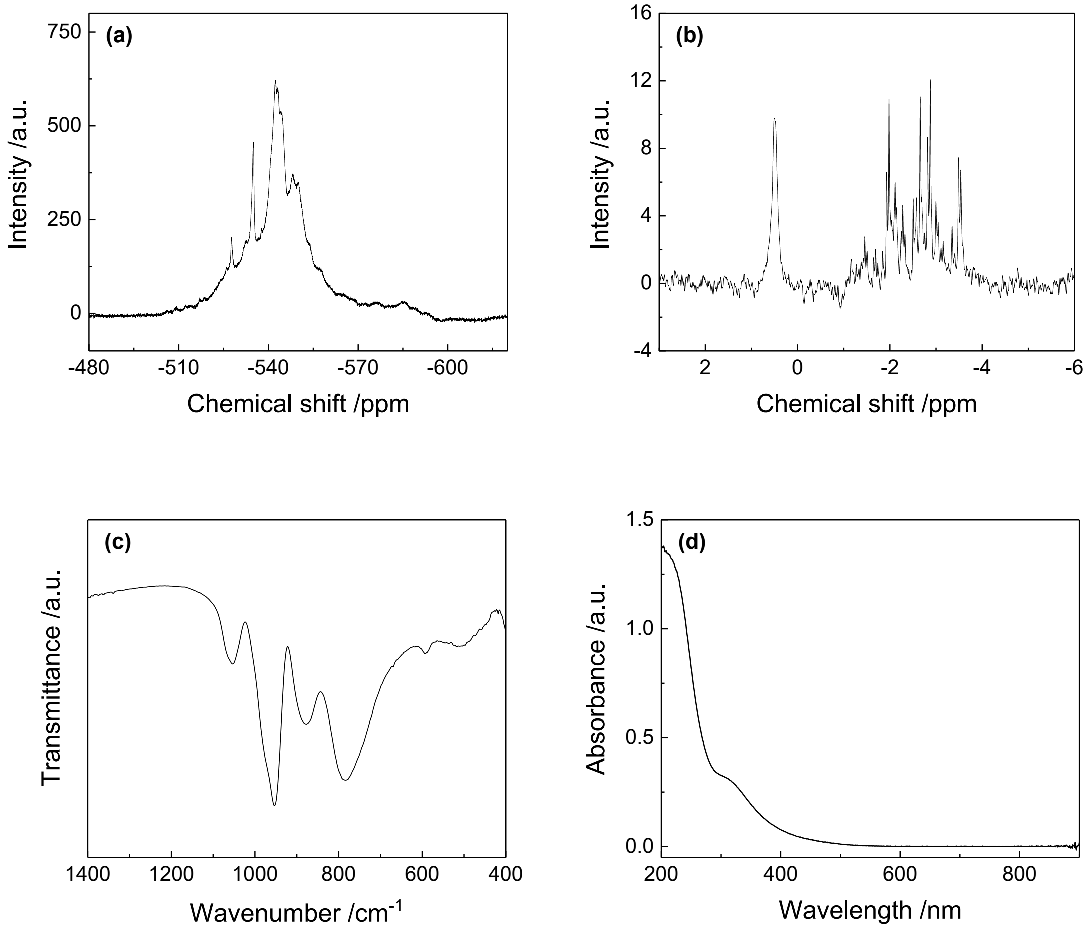


Fig. S1 (a) ^{51}V NMR spectrum shows all characteristic peaks for the pentavalent vanadium species derived from HPA-5 in aqueous solution, including −533 ppm (V-1 species), −528, −535, −537 ppm (V-2 species), −540 to −560 ppm (V-3 and VO_2^+ species), −560 to −620 ppm (V-4, V-5 and V-6 species).[17] (b) ^{31}P NMR spectrum shows characteristic peaks for the multiple positional isomers at −4 to −1 ppm and the free PO_4^{3-} anion at +0.5 ppm.[6] (c) FT-IR spectrum shows four characteristic peaks for the Keggin structure at 1053 cm^{-1}, 955 cm^{-1}, 877 cm^{-1} and 783 cm^{-1}, assigned to P-O$_a$ (inner oxygen), M-O$_d$ (terminal oxygen), M-O$_b$-M (corner-sharing oxygen) and M-O$_c$-M (edge-sharing oxygen), respectively (M = Mo, V). (d) UV-Vis spectrum displays ligand-to-metal charge transfer bands associated to the oxygen-Mo^{6+} transition in octahedral coordination around 217 nm and 300 nm.

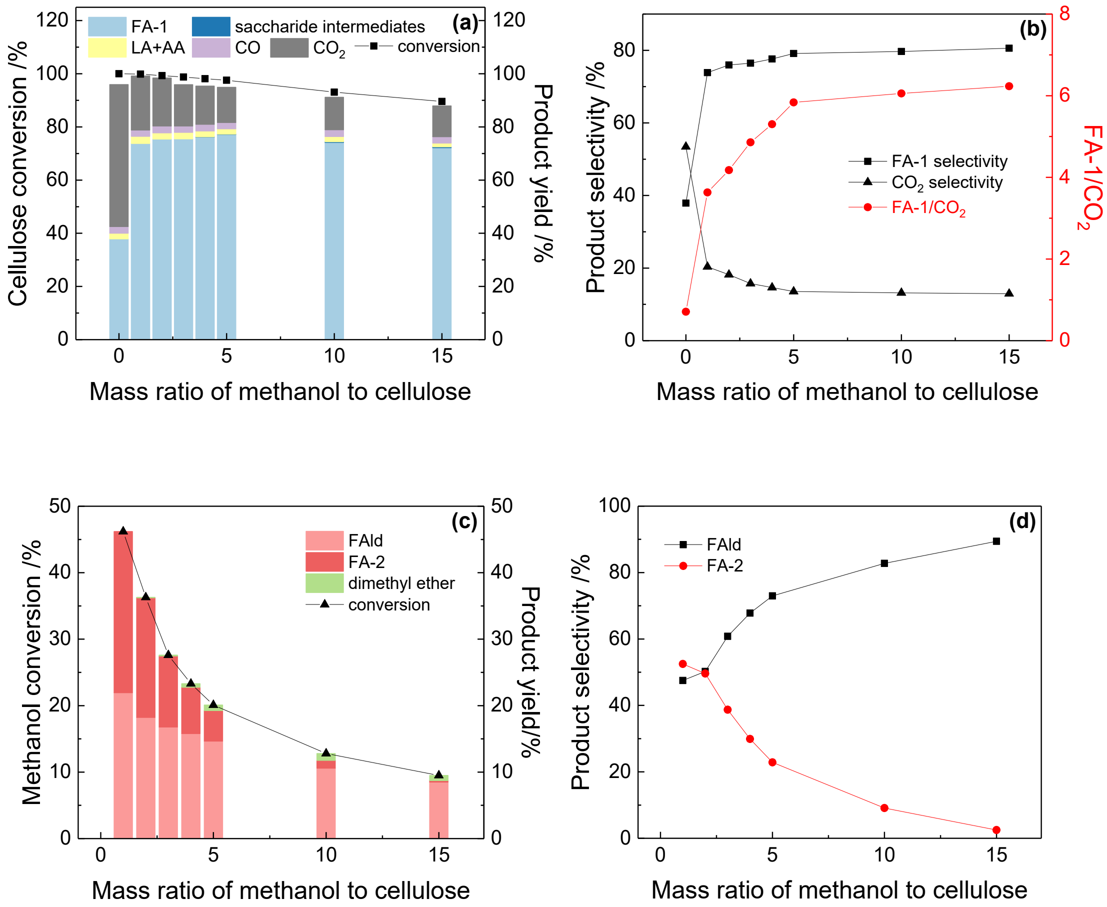


Fig. S2 Effect of mass ratio of methanol to cellulose on (a) the conversion of cellulose and the yields of products from cellulose, (b) the selectivities of products from cellulose and the molar ratio of FA-1 to CO_2, (c) the conversion of methanol and the yields of products from methanol, (d) the selectivities of products from methanol. Reaction conditions: cellulose, 0.32 g; HPA-5, 5.4 mM; H_2SO_4, 0.15 M; H_2O, 20 mL; O_2 pressure, 3 MPa; temperature, 180 °C; reaction time, 20 min.

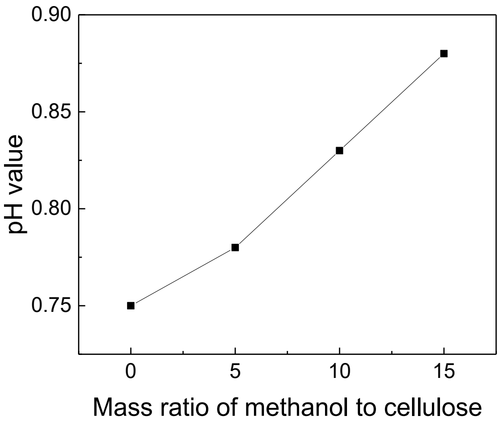


Fig. S3 Effect of mass ratio of methanol to cellulose on pH value of the catalytic system.

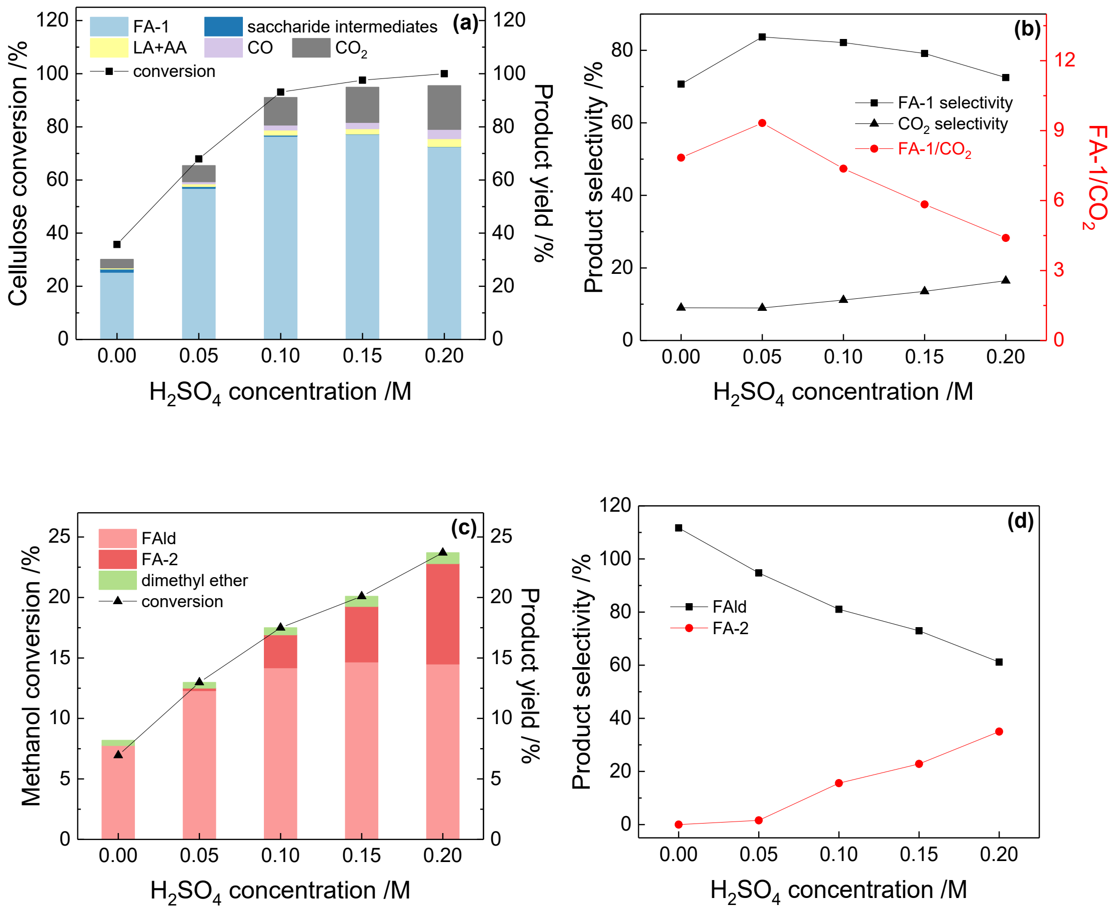


Fig. S4 Effect of H_2SO_4 concentration on (a) the conversion of cellulose and the yields of products from cellulose, (b) the selectivities of products from cellulose and the molar ratio of FA-1 to CO_2, (c) the conversion of methanol and the yields of products from methanol, (d) the selectivities of products from methanol. Reaction conditions: cellulose, 0.32 g; methanol, 1.6 g; HPA-5, 5.4 mM; H_2O, 20 mL; O_2 pressure, 3 MPa; temperature, 180 °C; reaction time, 20 min.

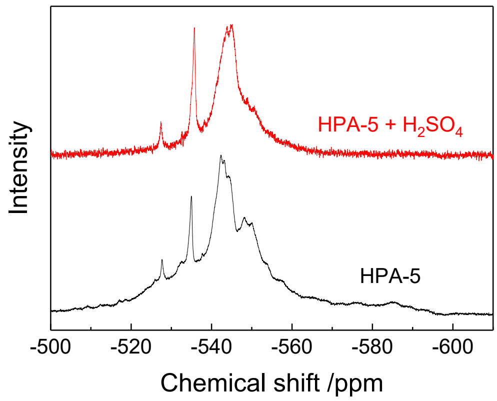


Fig. S5 ^{51}V NMR spectra of HPA-5 in aqueous solutions with and without H_2SO_4. The characteristic peaks of various pentavalent vanadium species were shown, including −533 ppm (V-1 species), −528, −535, −537 ppm (V-2 species), −540 to −560 ppm (V-3 and VO_2^+ species), −560 to −620 ppm (V-4, V-5 and V-6 species).[17] V-*n* (*n* = 1−6) denote heteropoly anions of various vanadium-substitution numbers.

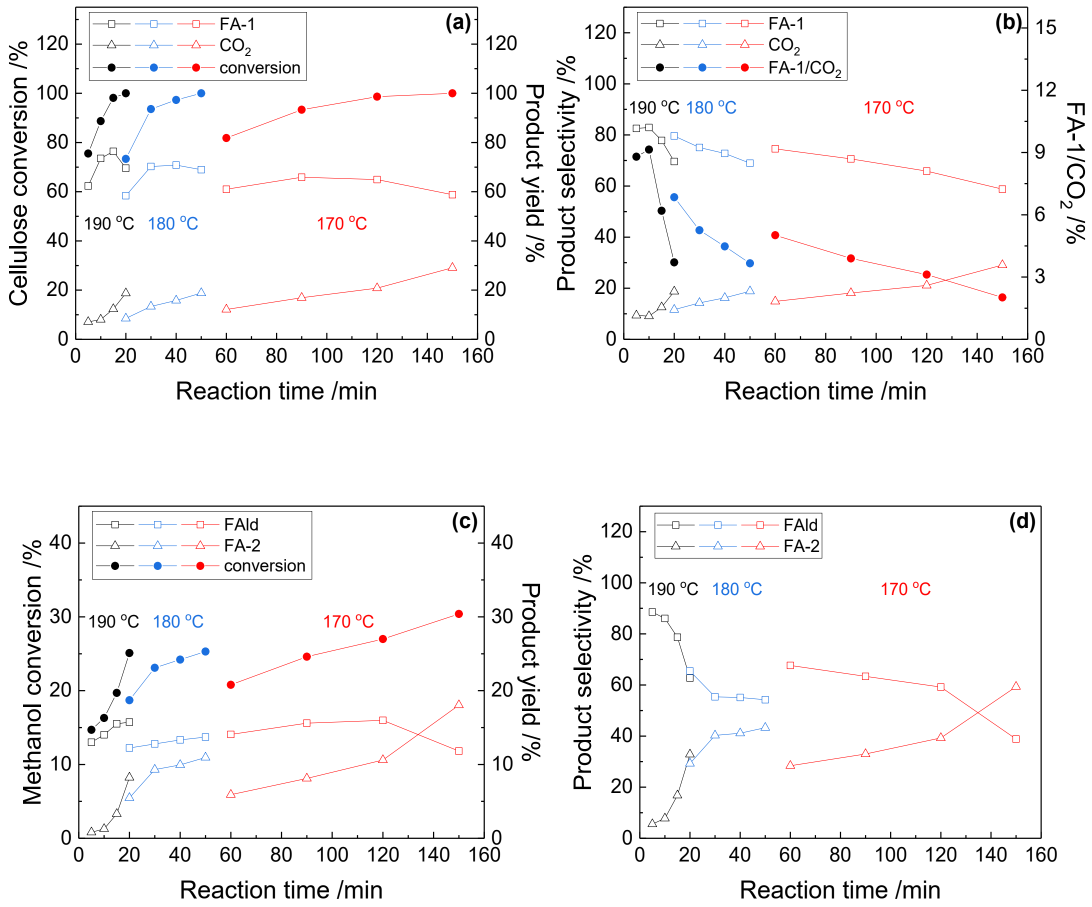


Fig. S6 Effects of reaction temperature and time on (a) the conversion of cellulose and the yields of products from cellulose, (b) the selectivities of products from cellulose and the molar ratio of FA-1 to CO_2, (c) the conversion of methanol and the yields of products from methanol, (d) the selectivities of products from methanol. Reaction conditions: cellulose, 0.32 g; methanol, 1.6 g; HPA-5, 5.4 mM; H_2SO_4, 0.05 M; H_2O, 20 mL; O_2 pressure, 3 MPa.

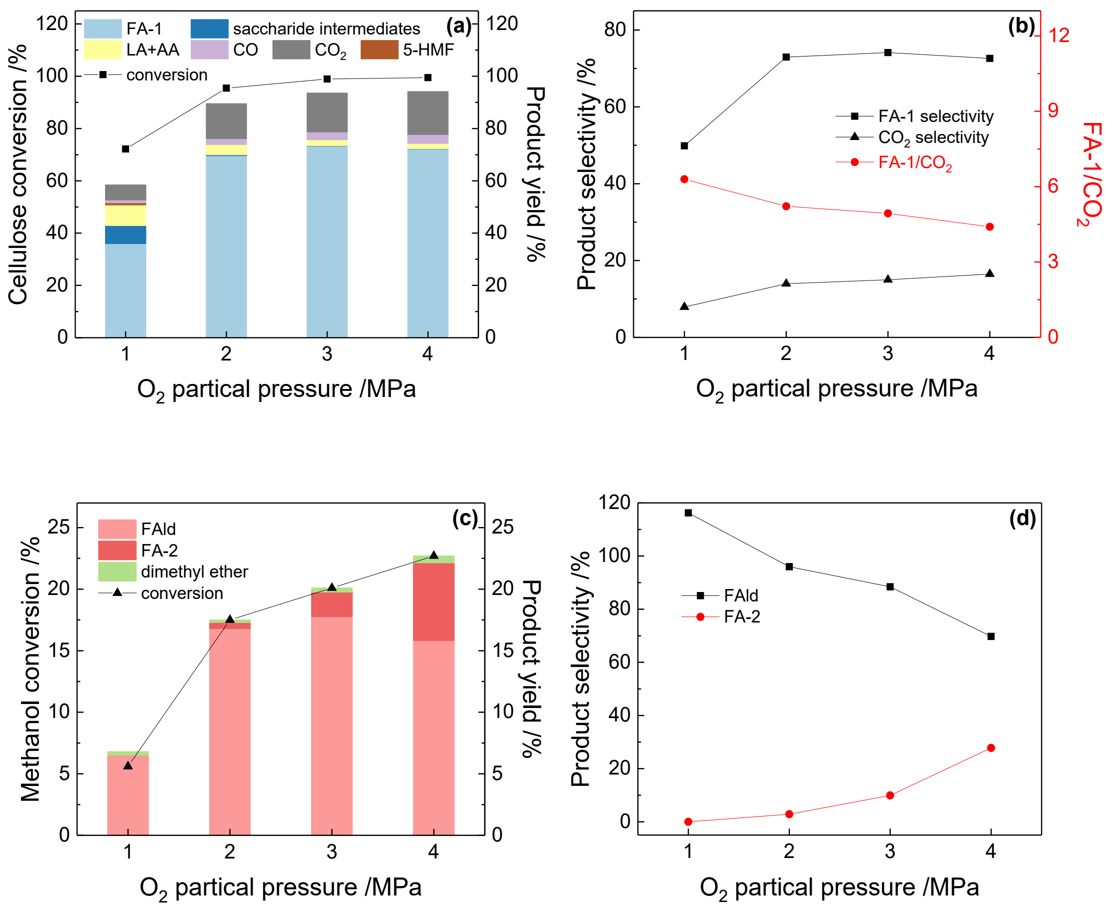
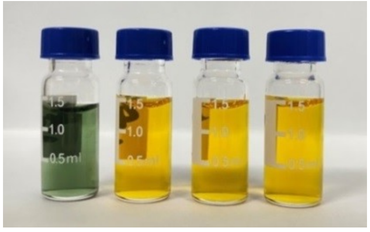


Fig. S7 Effect of O_2 partial pressure on (a) the conversion of cellulose and the yields of products from cellulose, (b) the selectivities of products from cellulose and the molar ratio of FA-1 to CO_2, (c) the conversion of methanol and the yields of products from methanol, (d) the selectivities of products from methanol. Reaction conditions: cellulose, 0.32 g; methanol, 1.6 g; HPA-5, 5.4 mM; H_2SO_4, 0.05 M; H_2O, 20 mL; total gas pressure, 4 MPa; temperature, 190 ^{o}C; reaction time, 15 min.



(a) (b) (c) (d)

Fig. S8 Colors of solutions after reactions at the O_2 partial pressures of (a) 1 MPa, (b) 2 MPa, (c) 3 MPa, (d) 4 MPa. The tetravalent and pentavalent vanadiums show blue and yellow, respectively, and the partially reduced HPA-5 (containing tetravalent and pentavalent vanadiums) shows green.[6,18] Reaction conditions: cellulose, 0.32 g; methanol, 1.6 g; HPA-5, 5.4 mM; H_2SO_4, 0.05 M; H_2O, 20 mL; total gas pressure, 4 MPa; temperature, 190 °C; reaction time, 15 min.

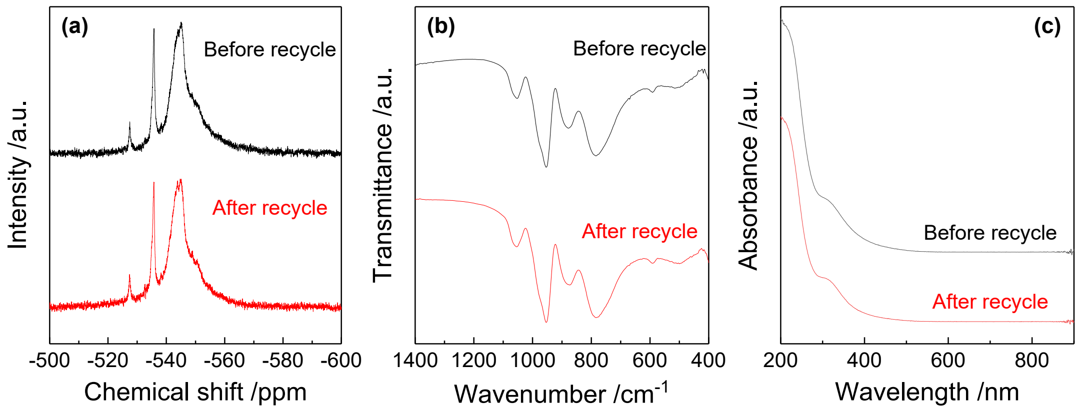


Fig. S9 (a) ^{51}V NMR, (b) FT-IR and (c) UV-Vis spectra of HPA-5 + H_2SO_4 catalyst before and after the recycling experiments.

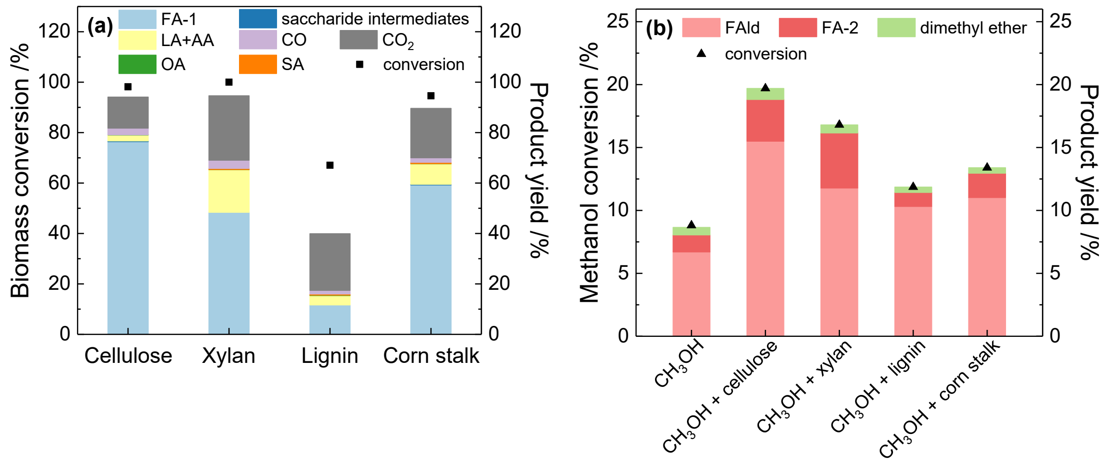


Fig. S10 Coupling oxidations of different biomass and methanol and the separate oxidation of methanol. (a) The conversion of biomass and the yields of products from biomass. (b) The conversion of methanol and the yields of products from methanol. Reaction conditions: biomass, 0.32 g; methanol, 1.6 g; HPA-5, 5.4 mM; H_2SO_4, 0.05 M; H_2O, 20 mL; O_2 pressure, 3 MPa; temperature, 190 ^oC; reaction time, 15 min. OA: oxalic acid; SA: succinic acid.

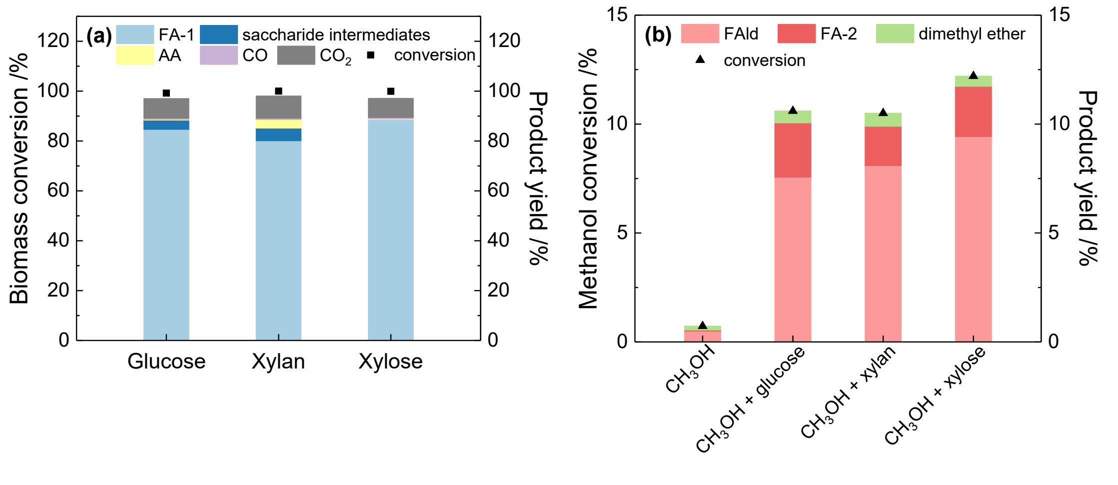


Fig. S11 Coupling oxidations of various water-soluble biomass and methanol and the separate oxidation of methanol. (a) The conversion of biomass and the yields of products from biomass. (b) The conversion of methanol and the yields of products from methanol. Reaction conditions: biomass, 0.32 g; methanol, 1.6 g; HPA-5, 5.4 mM; H_2O, 20 mL; O_2 pressure, 3 MPa; temperature, 90 ^oC; reaction time, 28 h.

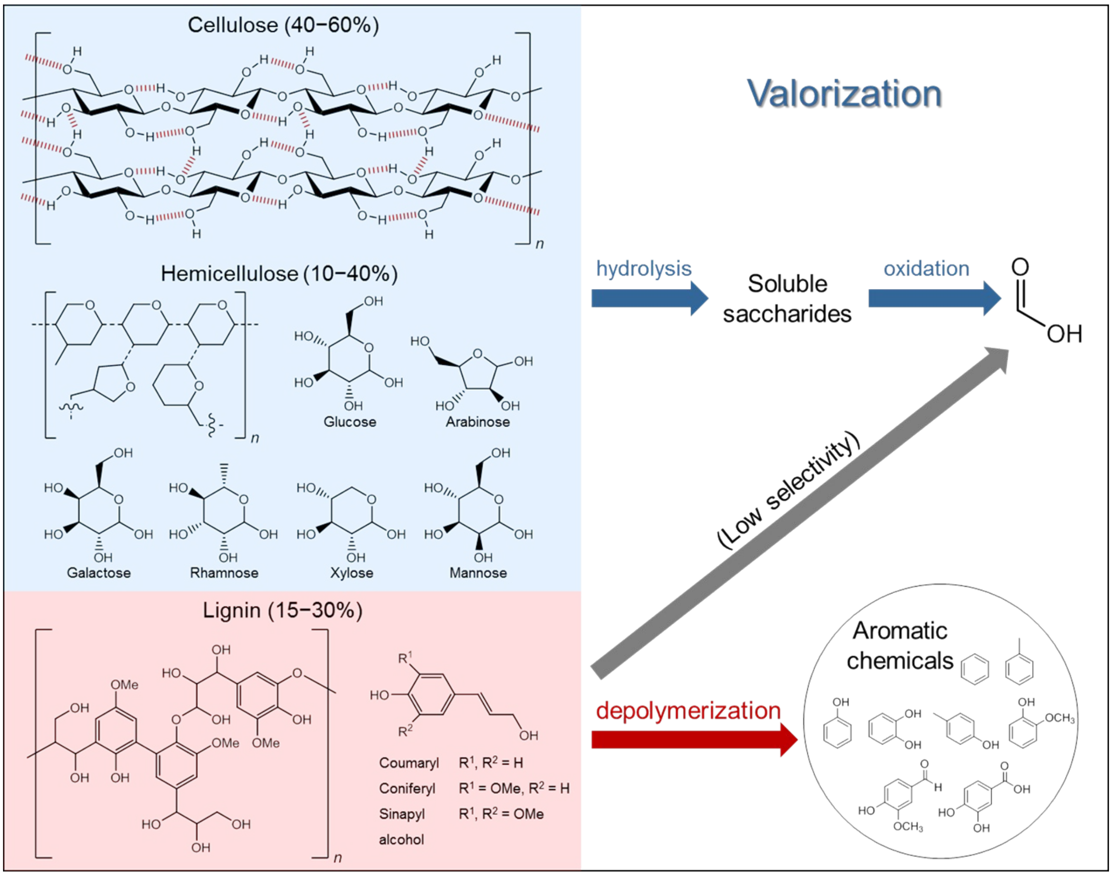


Fig. S12 The structural components of lignocellulose and their proper valorizations.

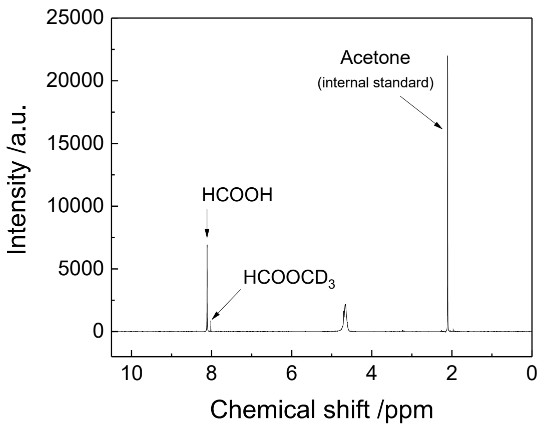


Fig. S13 ^{1}H NMR spectrum of liquid products in the coupling oxidations of cellulose and CD_3OD. Reaction conditions: cellulose, 0.32 g; CD_3OD, 0.05 mmol (1.8 g); HPA-5, 5.4 mM; H_2SO_4, 0.05 M; H_2O, 20 mL; O_2 pressure, 3 MPa; temperature, 190 ^{o}C; reaction time, 15 min.

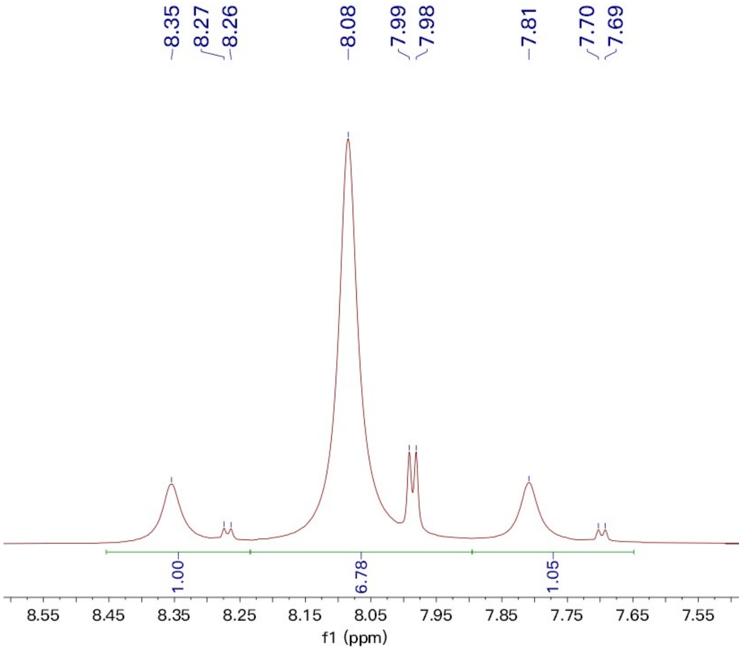


Fig. S14 ^{1}H NMR spectrum of liquid products in the coupling oxidations of cellulose and $^{13}CH_3OH$. Reaction conditions: mass ratio of methanol to cellulose, 5:1; $^{13}CH_3OH$, 0.2 g; HPA-5, 5.4 mM; H_2SO_4, 0.05 M; H_2O, 2.4 mL; O_2 pressure, 3 MPa; temperature, 190 °C; reaction time, 15 min.

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