Supporting Information for:

Acetalization of Aldehydes and Ketones over $H_4[SiW_{12}O_{40}]$ and $H_4[SiW_{12}O_{40}]/SiO_2$

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Table S1. ICP analysis of of H-SiW_{12}, fresh H-SiW_{12}/SiO_2 and reused H-SiW_{12}/SiO_2.

Catalyst	Found (%)	Calcd. (%)
	W	W
H-SiW_{12}	76.48	76.65
fresh H-SiW_{12}/SiO_2	6.92	6.98
reused H-SiW_{12}/SiO_2	6.90	6.98

Table S2. Assignments of FT-IR spectra of H-SiW_{12}, SiO_2 and H-SiW_{12}/SiO_2.[a]

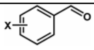
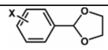
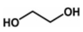
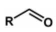
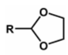
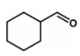
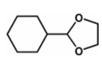
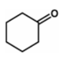
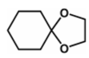
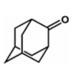
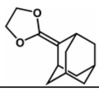
H-SiW_{12}	SiO_2	H-SiW_{12}/SiO_2	Assignments
3445	3448	3436	O-H asym. str.
2926	2925	2927	O-H scissoring
1100	1097	1102	Si-O asym. str.
1046			W-O_d scissoring
934		935	W-O_d asym. str.
891		893	W-O_b-W asym. str.
790		792	W-O_c-W asym. str.
715		716	W-O_c-W asym. str.
471	469	472	Si-O bending

[a] asym. str.: asymmetric stretching.

Table S3. Assignments of ^{29}Si CP/MAS NMR spectra of H-SiW_{12}, SiO_2 and H-SiW_{12}/SiO_2.

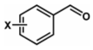
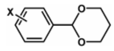
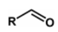
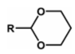
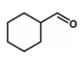
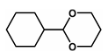
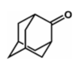
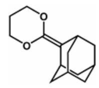
H-SiW_{12}/SiO_2 (ppm)	SiO_2 (ppm)	H-SiW_{12} (ppm)	Assignment
-86.032		-84.995	$H_4SiW_{12}O_{40}$
-102.880	-101.488		$(SiO)_3SiOH$ (Q^3)
-111.932	-110.800		$Si(OSi)_4$ (Q^4)

Table S4. The yields at different temperature and E_a for acetalization of various substrates with ethylene glycol catalyzed by $H\text{-}SiW_{12}$ under solvent-free conditions.[a]

Entry	Alcohol	Substrate	Product	Temperature (°C)	Yield (%)	Activation energy ($kJ \cdot mol^{-1}$)[b]
						
1		X = H	X = H	25	37	19.2
2				60	73	
3		X = 2-Me	X = 2-Me	25	49	15.9
4				60	81	
5		X = 3-Me	X = 3-Me	25	36	19.0
6				60	73	
7		X = 2-Cl	X = 2-Cl	25	73	8.8
8				60	95	
9		X = 3-Cl	X = 3-Cl	25	69	10.1
10				60	90	
11		X = 4-Cl	X = 4-Cl	25	58	13.3
12				60	80	
13		X = 2-Br	X = 2-Br	25	70	9.7
14				60	93	
15		X = 3-Br	X = 3-Br	25	67	10.6
16				60	85	
17		X = 4-Br	X = 4-Br	25	68	11.0
18				60	89	
19		X = 2-NO_2	X = 2-NO_2	25	81	6.6
20				60	93	
21		X = 3-NO_2	X = 3-NO_2	25	83	5.9
22				60	94	
		X = 4-NO_2	X = 4-NO_2	25	86	5.1
23				60	>99.9	
24						
25		R = *n*-C_5H_{11}	R = *n*-C_5H_{11}	25	89	4.2
26				60	>99.9	
27		R = *n*-C_6H_{13}	R = *n*-C_6H_{13}	25	85	5.4
28				60	98	
29		R = *n*-C_7H_{15}	R = *n*-C_7H_{15}	25	82	6.2
30				60	99	
31		R = *n*-C_8H_{17}	R = *n*-C_8H_{17}	25	79	7.6
32				60	99	
33		R = *n*-C_9H_{19}	R = *n*-C_9H_{19}	25	76	8.3
34				60	98	
35				25	88	4.6
36				60	97	
37				25	92	3.3
38				60	94	
39				25	75	8.7
40				60	99	

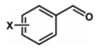
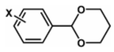
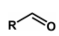
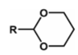
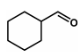
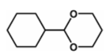
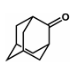
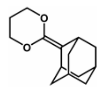
[a] Reaction conditions: substrate (1 mmol), $H\text{-}SiW_{12}$ (0.25 mol% to substrate), ethylene glycol (1.5 mmol), 6 hours. Yields were determined by GC analysis using reference standards. Assignments of corresponding products were analyzed by ^1H-NMR. [b] These values have been calculated by Arrhenius equation: lnk = (lnA –E_a)/RT.

Table S5. Acetalization of various aldehydes and ketones with 1,3-propanediol catalyzed by H-SiW_{12} at 60 ^{o}C under solvent-free conditions.[a]

Entry	Donor	Acceptor	Product	Yield(%)
				
1		X = H	X = H	95
2		X = 2-Me	X = 2-Me	96
3		X = 3-Me	X = 3-Me	96
4		X = 4-Me	X = 4-Me	92
5		X = 2-MeO	X = 2-MeO	87
6		X = 3-MeO	X = 3-MeO	95
7		X = 4-MeO	X = 4-MeO	75
8		X = 2-Cl	X = 2-Cl	99
9		X = 3-Cl	X = 3-Cl	99
10		X = 4-Cl	X = 4-Cl	99
11		X = 2-Br	X = 2-Br	99
12		X = 3-Br	X = 3-Br	99
13		X = 4-Br	X = 4-Br	99
14		X = 2-NO_2	X = 2-NO_2	>99.9
15		X = 3-NO_2	X = 3-NO_2	>99.9
16		X = 4-NO_2	X = 4-NO_2	87
				
17		R = n-C_5H_{11}	R = n-C_5H_{11}	>99.9
18		R = n-C_6H_{13}	R = n-C_6H_{13}	97
19		R = n-C_7H_{15}	R = n-C_7H_{15}	95
20		R = n-C_8H_{17}	R = n-C_8H_{17}	96
21		R = n-C_9H_{19}	R = n-C_9H_{19}	92
22				99
23				85

[a] Reaction conditions: substrate (1 mmol), H-SiW_{12} (0.25 mol% to substrate), 1,3-propanediol (1.5 mmol), 60 ^{o}C, 6 hours. Yields were determined by GC analysis using reference standards. Assignments of corresponding products were analyzed by ^{1}H-NMR.

Table S6. Acetalization of various aldehydes and ketones with 1,3-propanediol catalyzed by H-SiW_{12}/SiO_2 at 60 ^{o}C under solvent-free conditions.[a]

Entry	Donor	Acceptor	Product	Yield(%)[b]
				
1		X = H	X = H	95(91)
2		X = 2-Me	X = 2-Me	96(94)
3		X = 3-Me	X = 3-Me	96(93)
4		X = 4-Me	X = 4-Me	92(89)
5		X = 2-MeO	X = 2-MeO	87(83)
6		X = 3-MeO	X = 3-MeO	95(90)
7		X = 4-MeO	X = 4-MeO	75(71)
8		X = 2-Cl	X = 2-Cl	99(97)
9		X = 3-Cl	X = 3-Cl	99(98)
10		X = 4-Cl	X = 4-Cl	99(96)
11		X = 2-Br	X = 2-Br	99(98)
12		X = 3-Br	X = 3-Br	99(96)
13		X = 4-Br	X = 4-Br	99(98)
14		X = 2-NO_2	X = 2-NO_2	>99.9(99)
15		X = 3-NO_2	X = 3-NO_2	>99.9(99)
16		X = 4-NO_2	X = 4-NO_2	87(84)
				
17		R = n-C_5H_{11}	R = n-C_5H_{11}	>99.9(99)
18		R = n-C_6H_{13}	R = n-C_6H_{13}	97(94)
19		R = n-C_7H_{15}	R = n-C_7H_{15}	95(92)
20		R = n-C_8H_{17}	R = n-C_8H_{17}	96(94)
21		R = n-C_9H_{19}	R = n-C_9H_{19}	92(88)
22				99(96)
23				85(81)

[a] Reaction conditions: substrate (1 mmol), H-SiW_{12}/SiO_2 (0.0225 mol% to substrate), 1,3-propanediol (1.5 mmol), 60 ^{o}C, 6 hours. Yields were determined by GC analysis using reference standards. Assignments of corresponding products were analyzed by ^{1}H-NMR. [b] The values in parentheses are the isolated yields.

Table S7. ICP analysis of reaction filtrate before and after reaction catalyzed by H-SiW_{12}.[a]

Reaction filtrate	Si (ppm)	W (ppm)
Before reaction	<0.01	<0.01
After reaction	0.04	0.49

[a] Reaction condtions: benzaldehyde (1 mmol), H-SiW_{12} (0.25 mol% to substrate), 1,3-propanediol (1.5 mmol), 60 °C, 6 hours.

Table S8. ICP analysis of reaction filtrate before and after reaction catalyzed by H-SiW_{12}/SiO_2.[a]

Reaction filtrate	Si (ppm)	W (ppm)
Before reaction	<0.01	<0.01
After reaction	<0.01	<0.01

[a] Reaction condtions: benzaldehyde (1 mmol), H-SiW_{12}/SiO_2 (0.0225 mol% to substrate), 1,3-propanediol (1.5 mmol), 60 °C, 6 hours.

Table S9. H-SiW_{12}/SiO_2-recycling and reusing experiments of acetalization of benzaldehyde with 1,3-propanediol.[a]

Entry	Recycle time	Catalyst	Yield (%)	Catalyst Recovery (%)
1	1	H-SiW_{12}/SiO_2	94	98
2	2	H-SiW_{12}/SiO_2	94	98
3	3	H-SiW_{12}/SiO_2	94	98
4	4	H-SiW_{12}/SiO_2	94	98
5	5	H-SiW_{12}/SiO_2	94	97
6	6	H-SiW_{12}/SiO_2	94	97
7	7	H-SiW_{12}/SiO_2	93	97
8	8	H-SiW_{12}/SiO_2	93	96
9	9	H-SiW_{12}/SiO_2	93	96
10	10	H-SiW_{12}/SiO_2	93	96

[a] Reaction conditions: benzaldehyde (1 mmol), H-SiW_{12}/SiO_2 (0.0225 mol% to benzaldehyde), 1,3-propanediol (1.5 mmol), 60 °C, 6 hours. Yields were determined by GC analysis using reference standards. Assignments of corresponding products were analyzed by ^{1}H-NMR.

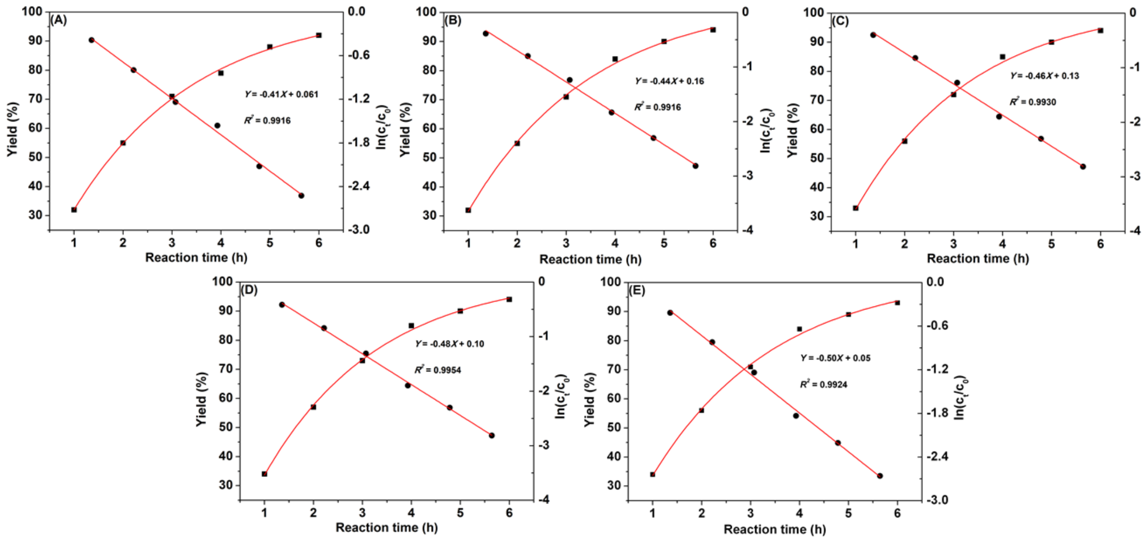


Figure S1. Yield and $\ln(C_t/C_0)$ as functions of reaction time at (A) 25 ^{o}C, (B) 40 ^{o}C, (C) 50 ^{o}C, (D) 60 ^{o}C and (E) 70 ^{o}C. Reaction conditions: cyclohexanone (1 mmol), H-SiW$_{12}$ (0.25 mol% to cyclohexanone), ethylene glycol (1.5 mmol), 6 hours.

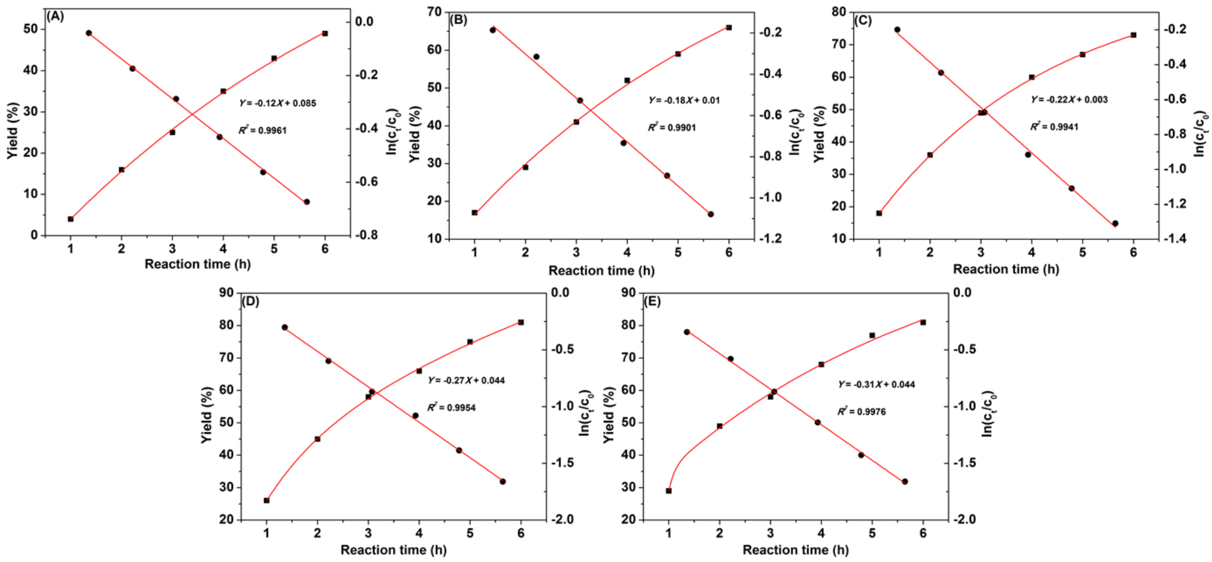


Figure S2. Yield and $\ln(C_t/C_0)$ as functions of reaction time at (A) 25 ^{o}C, (B) 40 ^{o}C, (C) 50 ^{o}C, (D) 60 ^{o}C and (E) 70 ^{o}C. Reaction conditions: 2-methylbenzaldehyde (1 mmol), H-SiW$_{12}$ (0.25 mol% to 2-methylbenzaldehyde), ethylene glycol (1.5 mmol), 6 hours.

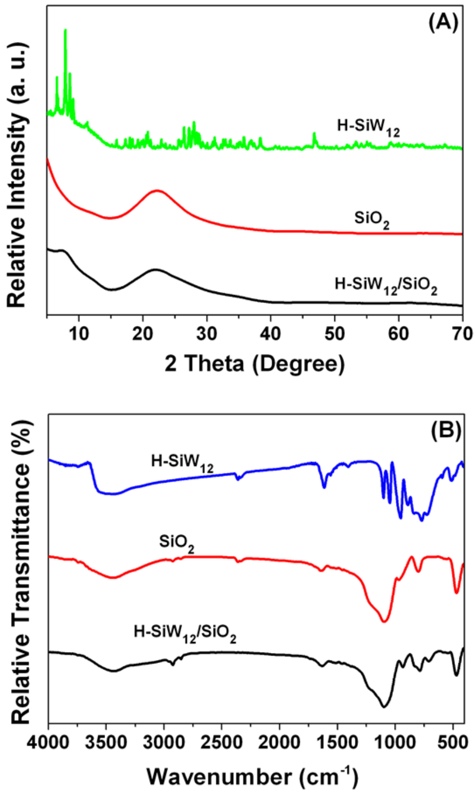


Figure S3. Powder XRD patterns (A) and FT-IR spectra (B) of H-SiW_{12}/SiO_2, SiO_2 and H-SiW_{12}.

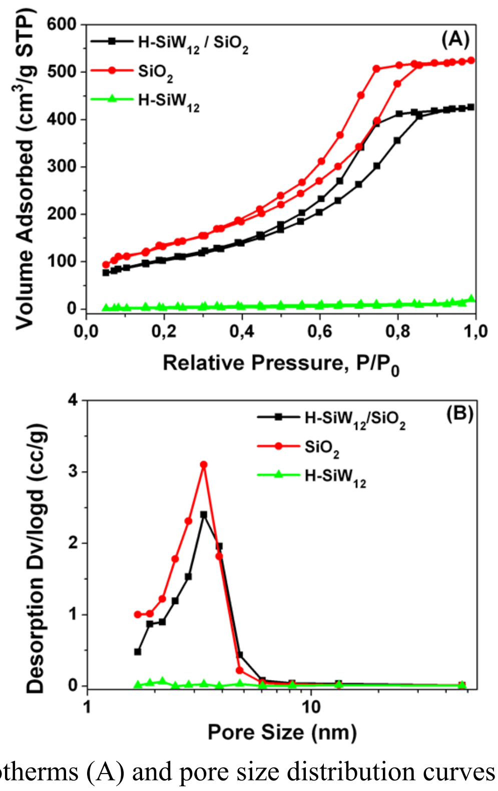


Figure S4. Adsorption-desorption isotherms (A) and pore size distribution curves (B) of H-SiW_{12}/SiO_2, SiO_2 and H-SiW_{12}.

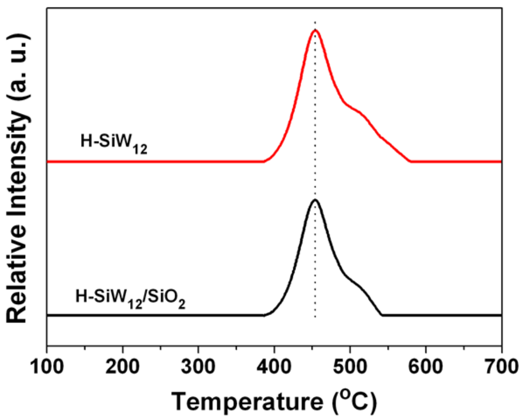


Figure S5. NH_3-TPD profiles of H-SiW_{12}/SiO_2 and H-SiW_{12}.

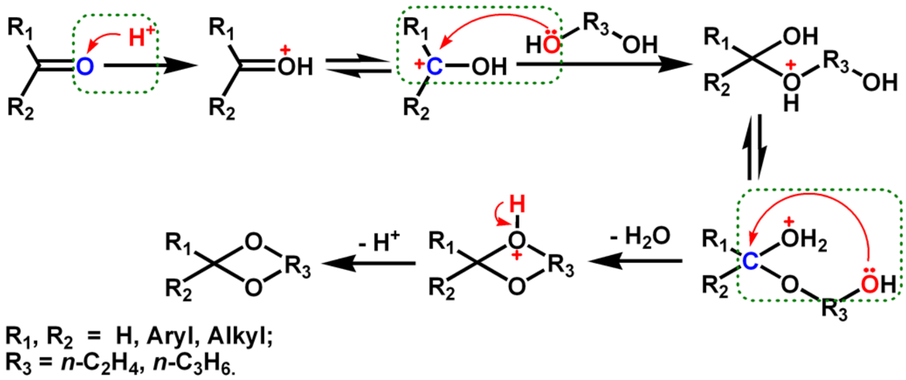


Figure S6. The proposed mechanism of acetalization of aldehydes and ketones with diols (ethylene glycol and 1,3-propanediol) catalyzed by H-SiW_{12} and H-SiW_{12}/SiO_2.