

## Supplementary Information

### **Facile synthesis of SAPO-34 nanocrystallites with excellent performance for carbohydrates dehydration to 5-hydroxymethylfurfural**

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**Table S1.** Comparison of textural properties and compositions of nanosized/hierarchical SAPO-34 catalysts directed by amine templates

Entry	Sample	Method	Microporous template <sup>a</sup>	Si content	Textural properties <sup>b</sup>					Ref.
					S <sub>BET</sub>	S <sub>micro</sub>	S <sub>ext</sub>	V <sub>micro</sub>	V <sub>meso</sub>	
1	S <sub>H3</sub>	soft-template PDADMAC	MOR	0.13	505	426	79	0.18	0.31	1
2	S <sub>H3</sub>	soft-template polyethylene glycol	TEA	0.08	513	320	193	0.15	0.31	2
3	SP34-MS	soft-template TPOAC	DEA	0.15	567	455	112	0.21	0.17	3
4	S <sub>2</sub>	soft-template polyethylene glycol	MOR	0.1	519	360	159	0.16	0.2	4
5	S-DEA-1/5	soft-template DPHAB	DEA	0.11	622	597	25	0.28	0.02	5
6	SP34-M3	soft-template PZPMS	TEA	0.12	604	497	107	0.24	0.17	6
7	S <sub>H2</sub>	soft-template TPOAC	MOR	0.16	507	384	123	0.18	0.26	7
8	S <sub>2</sub>	soft-template polyacrylamide	TEA	0.08	652	615	37	0.23	0.12	8
9	hierarchical SAPO-34-10wt	hard-template rapeseed pollen	TEA	-	683	609	74	0.24	0.1	9
10	S-1	nitric acid post-treatment	TEA	0.13	671	638	33	0.25	0.01	10
11	HZ-SAPO-34-Mor-60	HF-NH <sub>4</sub> F post-treatment	MOR	0.16	509	471	38	0.23	0.02	11
12	Sample 1.1	HF in-situ etching	TEA	0.09	544	533	11	0.26	-	12
13	SAPO-34 US30	NH <sub>4</sub> F post-treatment	TEA	0.04	488	416	72	0.21	0.24	13
14	SP34-S-2.0	seed assistant	MOR	0.16	600	580	20	0.28	-	14
15	S <sub>H3</sub>	seed assistant	TEA	0.1	556	536	20	0.27	-	15
16	S34-0.08	NaHCO <sub>3</sub> assistant	TEA	0.08	733	675	58	0.24	0.08	16
17	SP34-HEEP-s	amine HEEP assistant	TEA	0.09	583	548	35	0.27	0.12	17
18	SAPO-34-H1	vapor-phase transport method	TEA	0.12	712	679	33	0.25	0.12	18
19	Sample 2	post-synthesis milling and recrystallization method	TEA	0.14	530	479	51	0.22	0.2	19
20	S <sub>PT</sub> -80-12	mother liquid post-treatment	TEA	0.09	574	516	58	0.24	0.03	20

<sup>a</sup> TEA: triethylamine, MOR: morpholine, DEA: diethylamine. <sup>b</sup> S<sub>BET</sub>: BET surface area, S<sub>micro</sub>: micropore surface area, S<sub>ext</sub>: external surface area, V<sub>micro</sub>: micropore volume, V<sub>meso</sub>: mesopore volume

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**Table S2.** Thermal analysis results of the samples

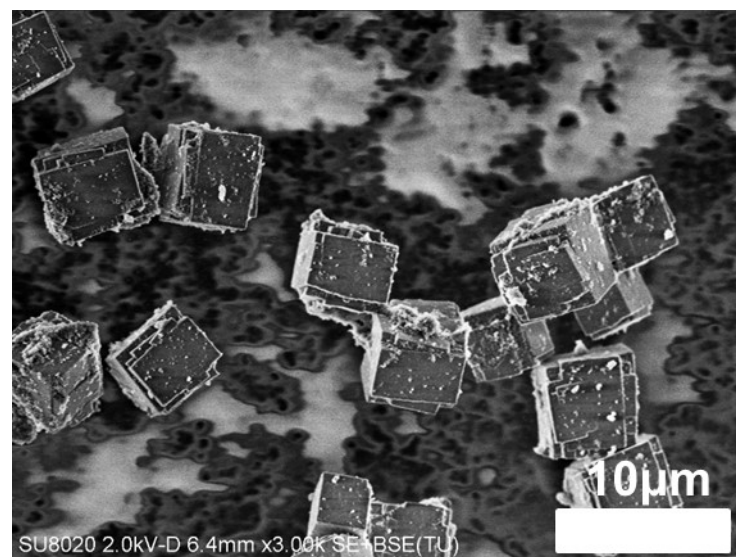
Sample	Weight loss (%)	
	Physical absorbed water (RT-200 °C)	Organic species (200- 900 °C)
SP-M1	6.7	12.6
SP-M2	8.9	13.9
SP-M3	9.7	16.0
SP-M4	9.4	16.3
SP-M5	10.5	16.9

**Table S3.** Textural properties of the aluminosilicate zeolites

Sample	Surface area (m <sup>2</sup> /g)			Pore volume (cm <sup>3</sup> /g)	
	S <sub>BET</sub> <sup>a</sup>	S <sub>micro</sub> <sup>b</sup>	S <sub>exter</sub> <sup>b</sup>	V <sub>micro</sub> <sup>b</sup>	V <sub>meso</sub> <sup>c</sup>
ZSM-5	323	227	96	0.11	0.05
MCM-22	499	357	142	0.18	0.58
Y	667	594	93	0.28	0.09
Beta	570	403	167	0.19	0.33

<sup>a</sup> Total surface area is determined by the BET equation. <sup>b</sup> Micropore surface area, micropore volume and external surface area are determined by the t-plot method. <sup>c</sup>

Mesopore volume is determined from the adsorption isotherm by the BJH method.



**Fig. S1** SEM image of calcined SP-C.

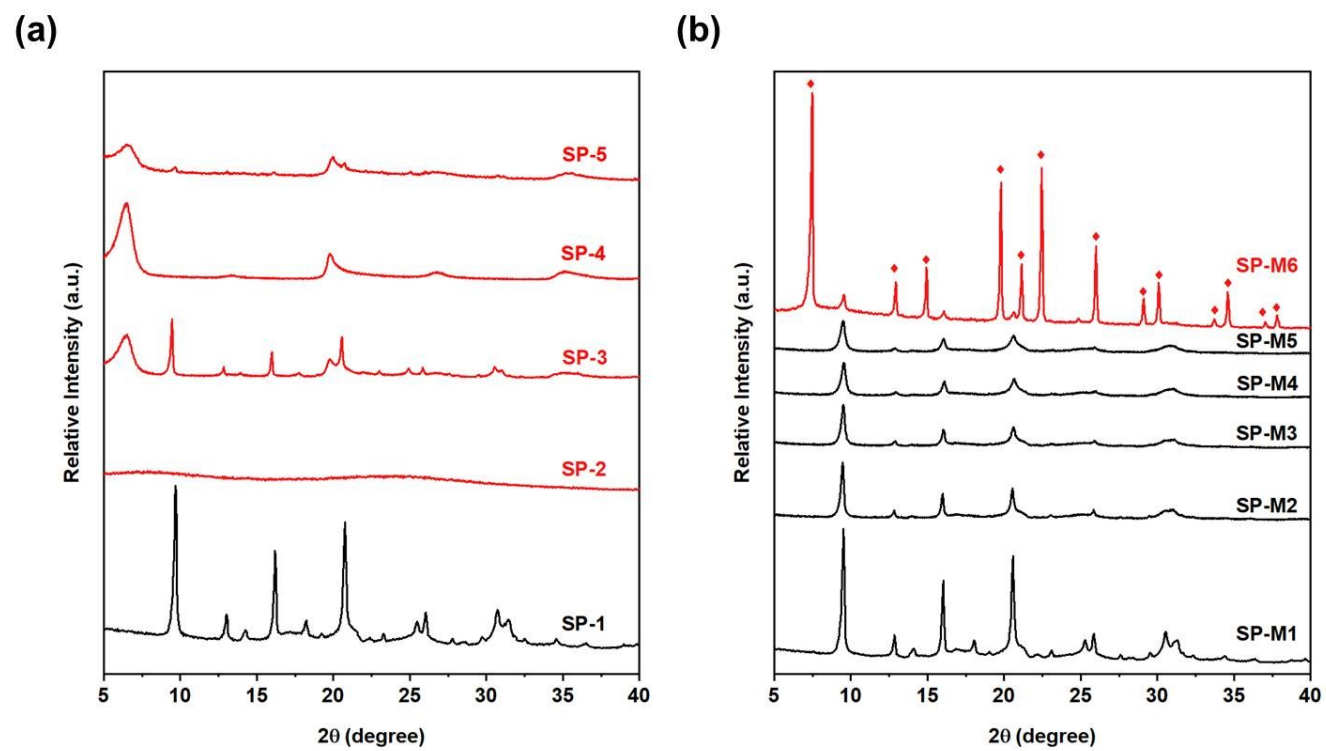


Fig. S2 XRD patterns of the as-synthesized SP-n (a) and SP-Mn (b). Diamonds indicate the AFI phase.

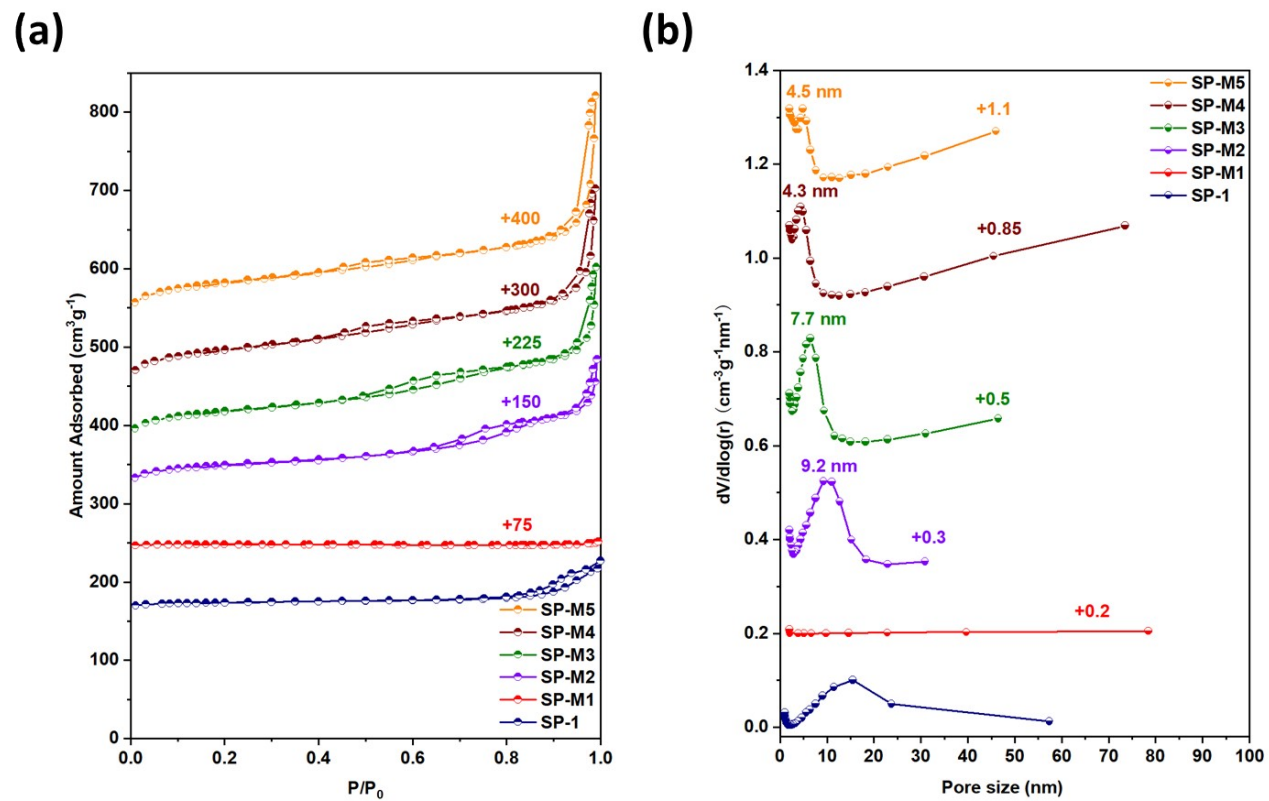


Fig. S3  $\text{N}_2$  sorption isotherms (a) and pore size distributions (b) of the samples.



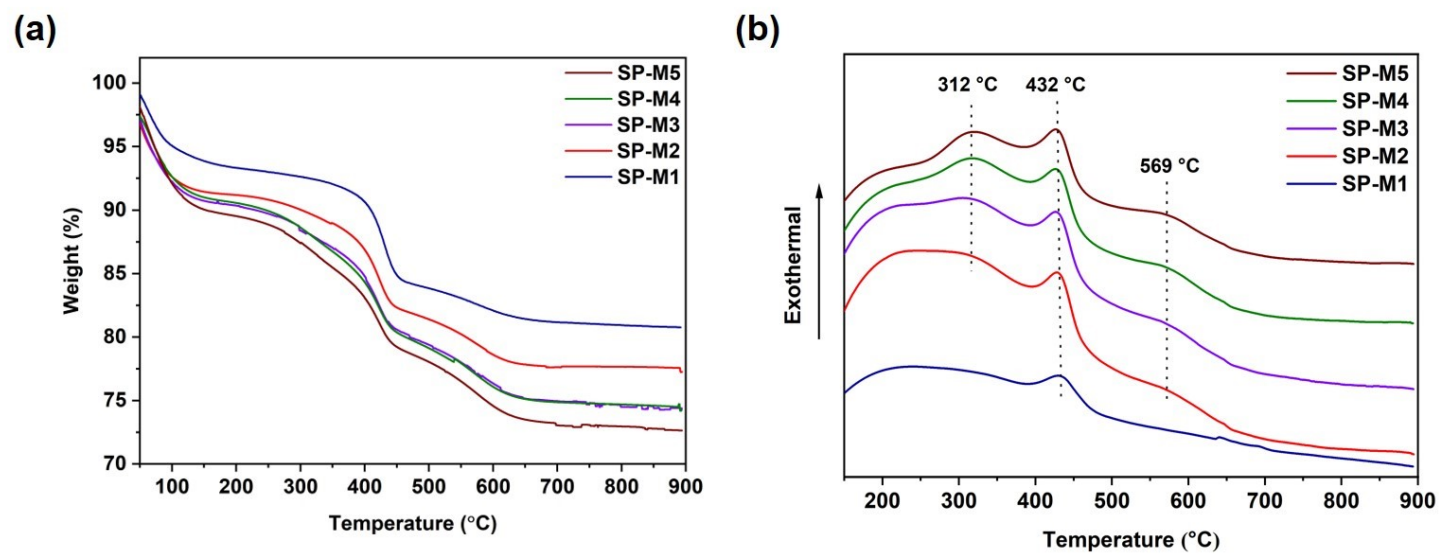
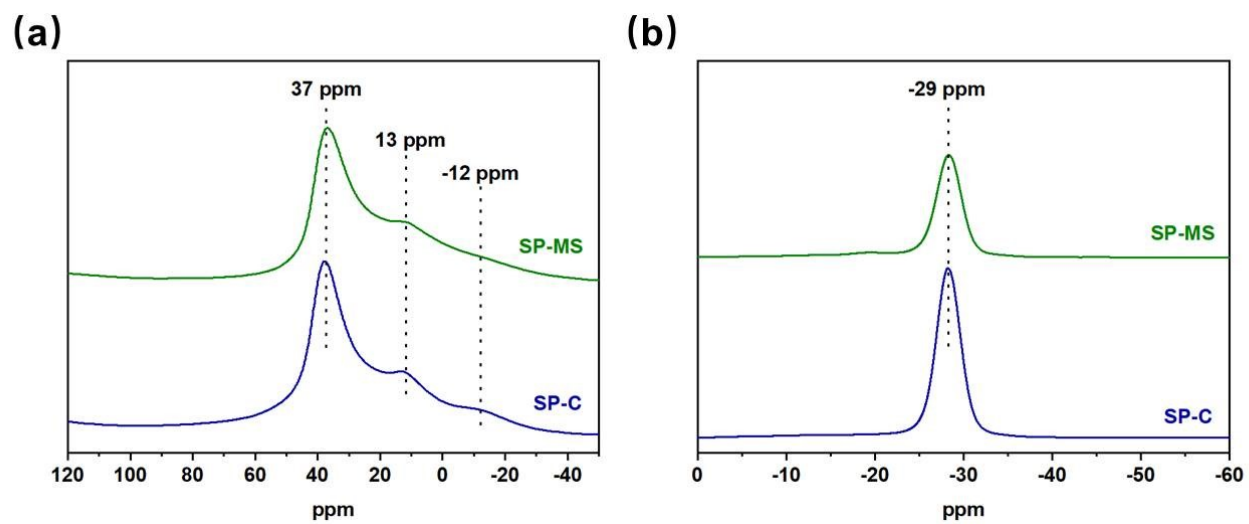
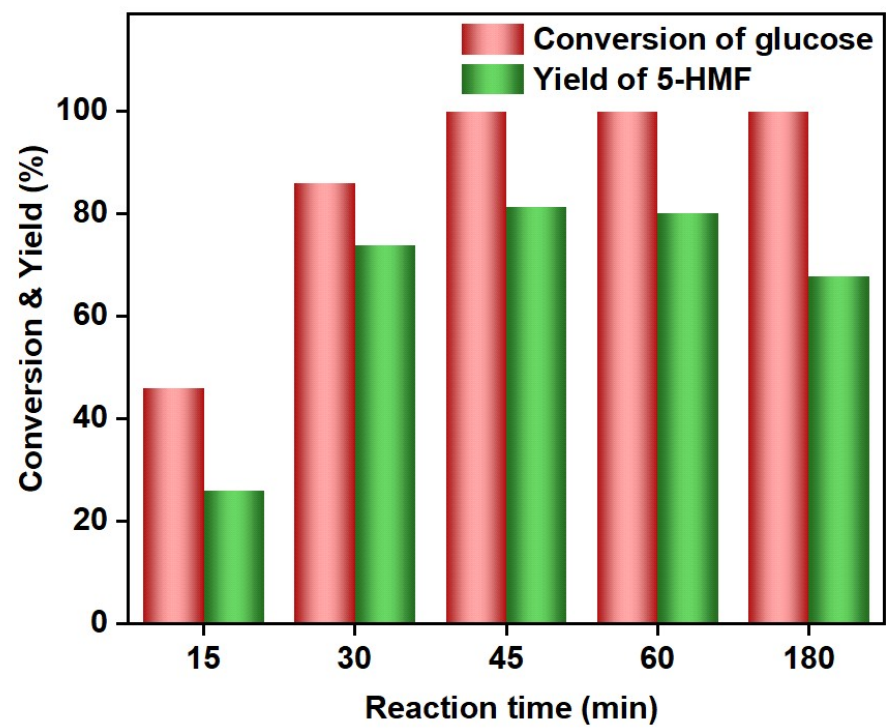


Fig. S4 TG (a) and DTA (b) curves of the as-synthesized samples.



**Fig. S5**  $^{27}\text{Al}$  MAS NMR spectra (a) and  $^{31}\text{P}$  MAS NMR spectra (b) of the as-synthesized samples.



**Fig. S6** Effect of reaction time on conversion of glucose and 5-HMF yield. Reaction condition: 0.1 g glucose, 0.1 g SP-MS, 2 mL NaCl-H<sub>2</sub>O + 8 mL MIBK, 170 °C.

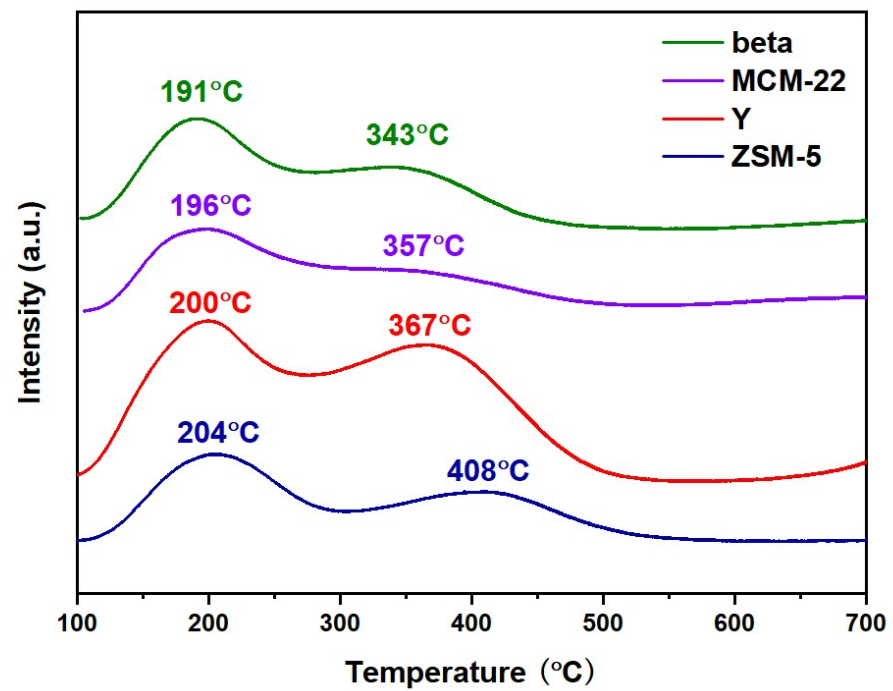
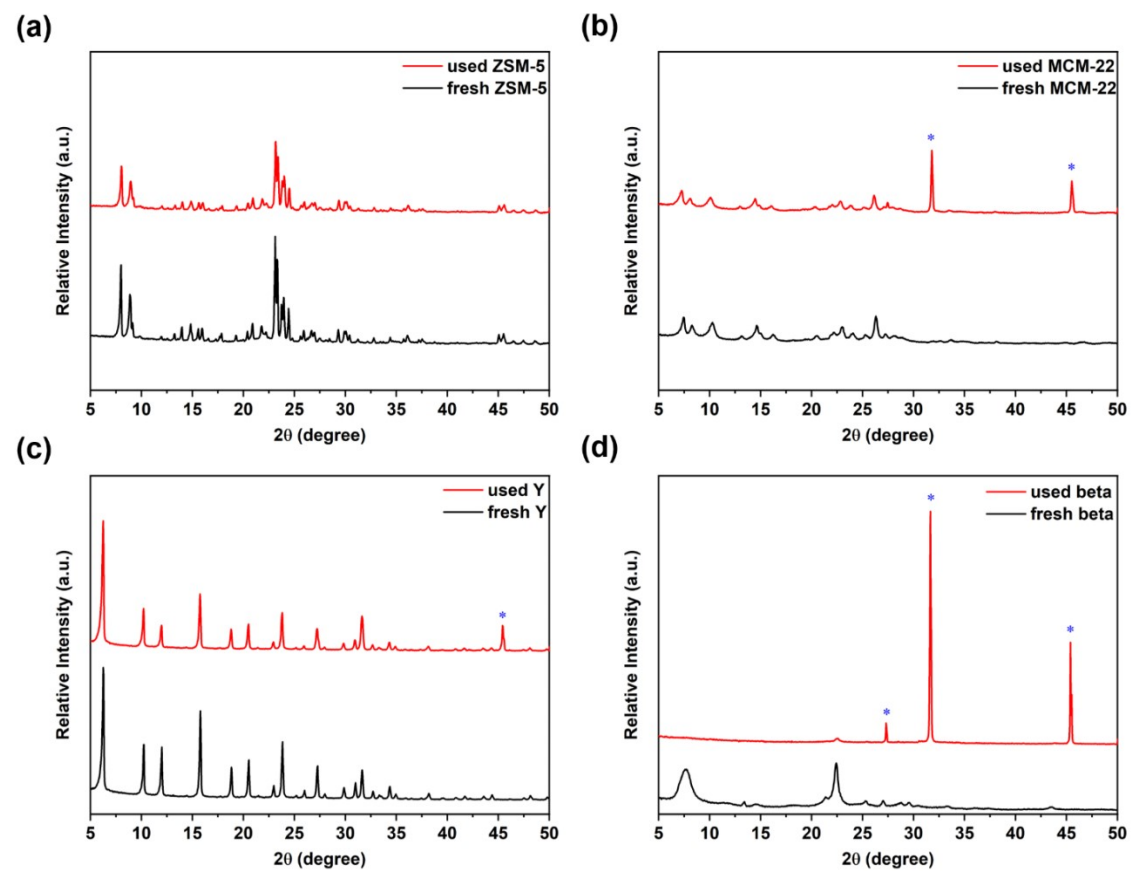
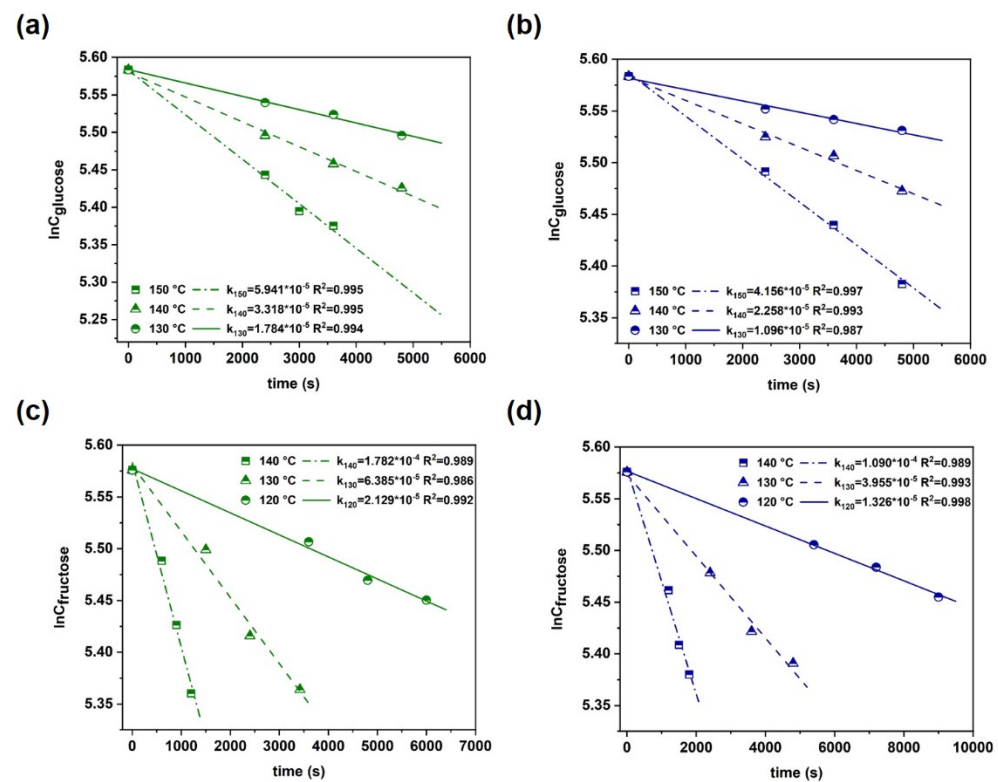


Fig. S7 NH<sub>3</sub>-TPD profiles of aluminosilicate zeolites.



**Fig. S8** XRD patterns of the fresh and used catalysts. Asterisk indicate the NaCl. All the used samples were washed with deionized water and dried overnight.



**Fig. S9** First order kinetic fit for the conversion of glucose over SP-MS (a), SP-C (b), and fructose over SP-MS (c), SP-C (d). Reaction condition: 0.1 g substrate, 2 mL saturated solution of NaCl + 8 mL MIBK, 0.1 g catalyst for glucose conversion, 0.02g catalyst for fructose conversion.