Electronic Supplementary Information for

Rapid synthesis of hierarchical SSZ-13 zeolite microspheres via fluoride-assisted in situ growth route using aluminum isopropoxide as aluminum source

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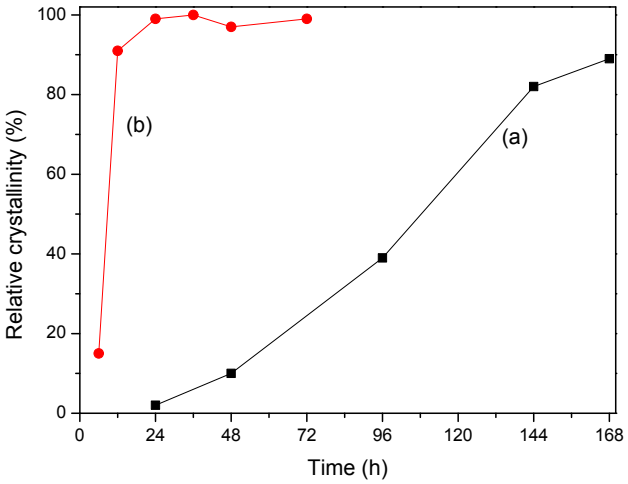

Fig. S1 Crystallization curves of SSZ-13 synthesized (a) without HF and (b) with HF/Al_2O_3 of 3.3

The relative crystallinity is based on the intensity of peak at 20.9° in XRD patterns, and fully crystallized SSZ-13 synthesized at 160 °C for 36 h with HF/Al_2O_3 of 3.3 was designated as 100 % crystallinity.

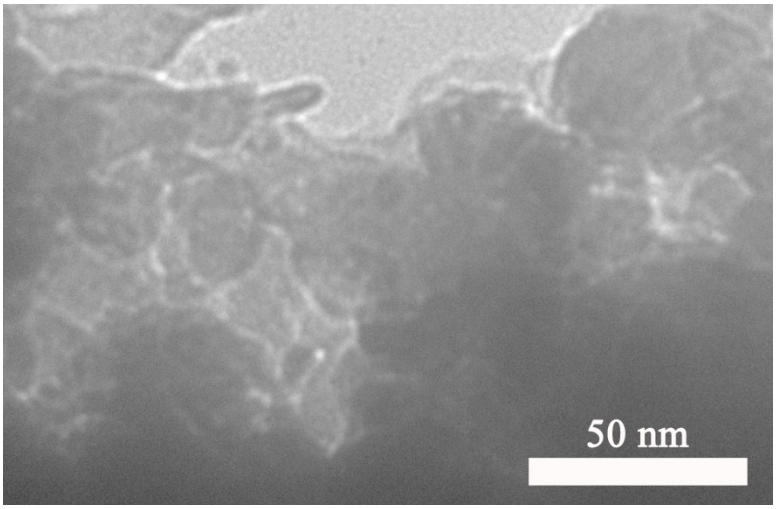

Fig. S2 TEM image of SH-12 zeolite microsphere.

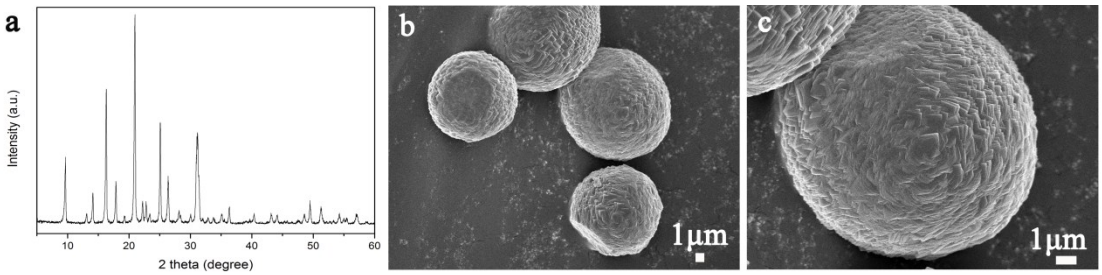

Fig. S3 (a) XRD pattern, (b) and (c) SEM images of SSZ-13 synthesized by using aluminum isopropoxide and fumed silica as aluminum and silicon sources, respectively.

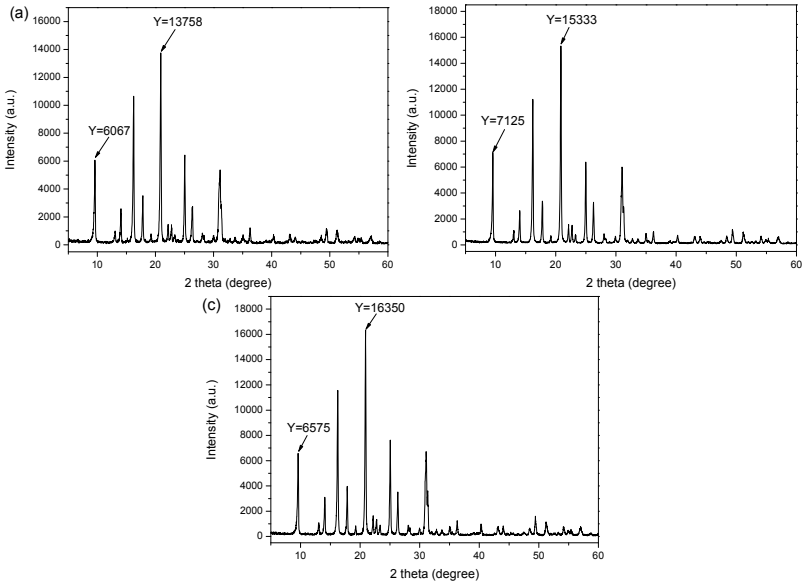

Fig. S4 XRD patterns of (a) SM-144, (b) SH-12 and SH-48.

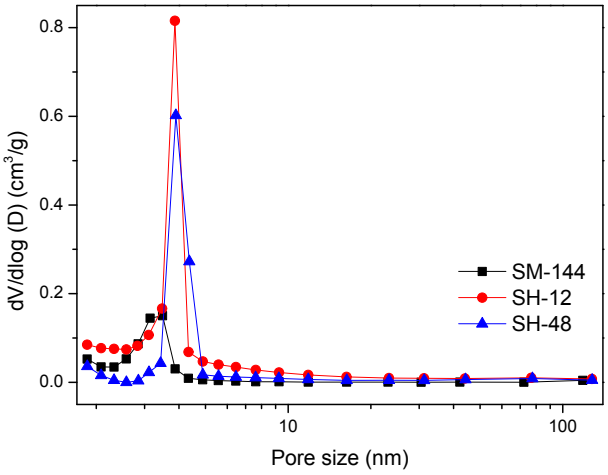

Fig. S5 Pore size distribution of conventional microporous SSZ-13 and hierarchical SSZ-13 samples.

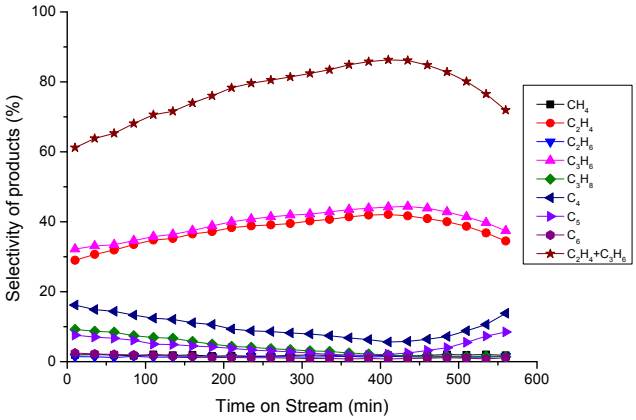

Fig. S6 Products distribution in the conversion of methanol at 450 ºC and WHSV = 3 h^{-1} on SM-144 catalysts.

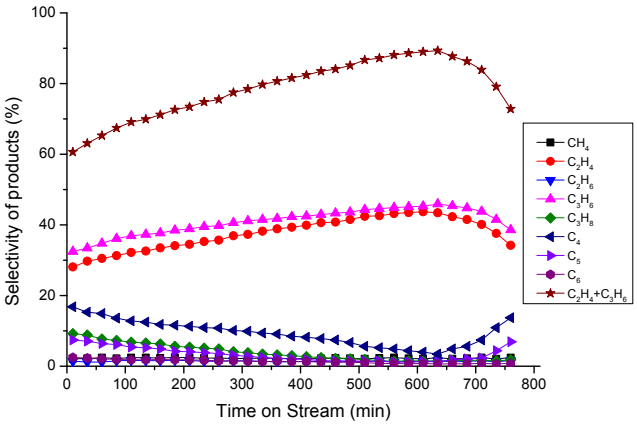

Fig. S7 Products distribution in the conversion of methanol at 450 ºC and WHSV = 3 h^{-1} on SH-12 catalyst.

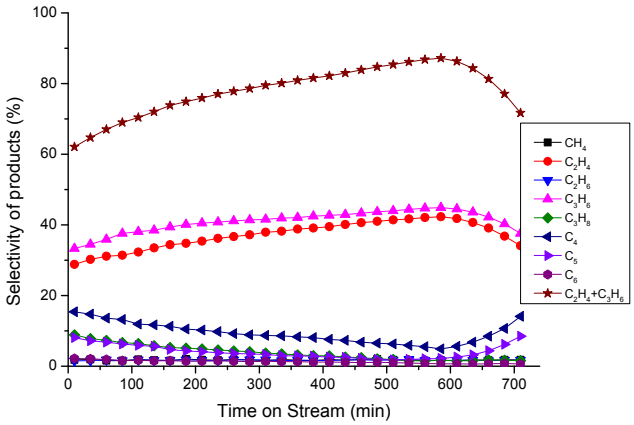

Fig. S8 Products distribution in the conversion of methanol at 450 ^{o}C and WHSV = 3 h^{-1} on SH-48 catalyst.

Table S1 Physico-chemical properties of the conventional SSZ-13 (SM-144) and hierarchical SSZ-13 samples (SH-12 and SH-48)

Sample	Si/Al	S_{BET} (m^2/g)	S_{micro} (m^2/g)	$S_{external}$ (m^2/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	V_{total} (cm^3/g)
SM-144	18	475	451	24	0.24	0.03	0.27
SH-12	20	591	507	84	0.28	0.16	0.44
SH-48	21	559	496	63	0.27	0.10	0.37

Table S2 MTO results over conventional microporous SSZ-13 (SM-144) and hierarchical porous SSZ-13 (SH-12 and SH-48) catalysts

Samples	TOS/min	Selectivity of products/%						
		CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4～C_6	C_2H_4+C_3H_6
SM-144	10	1.9	29.0	1.4	32.2	9.2	26.3	61.2
	260 [a]	1.6	39.1	1.4	41.4	3.7	12.8	80.5
SH-12	10	2.1	28.1	1.4	32.5	9.2	26.7	60.6
	485 [a]	2.2	41.5	1.3	43.6	2.1	9.3	85.1
SH-48	10	1.8	28.8	1.5	33.3	8.9	25.7	62.1
	410 [a]	1.9	39.5	1.6	42.7	2.9	11.4	82.2

[a] Catalyst lifetime is defined as the reaction time when methanol conversion less than 99%.