Supplementary Information

Sustainable one-pot preparation of full-crystalline and shaped zeolites catalysts

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Experimental

Synthesis of shaped silicalite-1 zeolite extrudate/pellets

3.8 g of $Na_2SiO_3 \cdot 9H_2O$, 7.5 g of the silica gel, and 1.5 g of silicalite-1 zeolite seeds were mixed and ground for 5 min, followed by addition of 24 g of colloidal silica (31.5 wt% SiO_2 in water) to form a mixture, which was used for shaping. Then, the resultant extrudates and pellets were dried at 50 °C for 10 h and calcined at 550 °C for 4 h, which was used as a starting solid silica for the preparation of the shaped silicalite-1 zeolite.

As a typical run, 0.88 g of the shaped silica extrudate/pellet, 0.06 g of H_2O, and 0.99 g of ethanol were put into a Teflon-lined autoclave and sealed, then crystallized at 180 °C for 4 d at static condition. The final products were obtained by filtering, washing with deionized water, and subsequently drying overnight at 100 °C. Na^+ in the product was removed by exchanging with HCl solution.

Synthesis of shaped MTT zeolite extrudates

As a typical run, 1.309 g of $NaAlO_2$ was dissolved in 3.0 g of H_2O, then added into 63 g of colloidal silica (31.5 wt% SiO_2 in water) under stirring conditions. After stirring for another 2 h, the mixture was heated in an oven at 150 °C for 12 h to evaporate the water to obtain the aluminosilicate precursor. Furthermore, 2.4 g of $Na_2SiO_3 \cdot 9H_2O$, 3.75 g of the aluminosilicate precursor, and 0.75 g of MTT zeolite seeds were mixed and ground for 5 min, followed by the addition of 12 g of colloidal silica (31.5 wt% SiO_2 in water) to form a mixture, which was used for shaping. Then, the resulting extrudates and pellets were dried at 50 °C for 10 h and calcined at 550 °C for 4 h, which was used as the starting aluminosilicate solids for the preparation of the shaped MTT zeolite catalyst. Finally, 0.88 g of the shaped aluminosilicate extrudate, 0.14 g of H_2O and 0.99 g of ethanol were put into a Teflon-lined autoclave and sealed, then crystallized at 140 °C for 6 d at static condition. After filtering, washing with deionized water, and subsequently drying overnight at 100 °C, and removing Na^+ in the product by exchanging with HCl solution, it was obtained the shaped MTT zeolite extrudate.

Synthesis of shaped TON zeolite extrudates

As a typical run, 1.309 g of $NaAlO_2$ was dissolved in 3.0 g of H_2O, then added into 63 g of colloidal silica (31.5 wt% SiO_2 in water) under stirring conditions. After stirring for another 2 h, the mixture was heated in an oven at 150 °C for 12 h to evaporate the water to obtain the aluminosilicate precursor. Furthermore, 3 g of $Na_2SiO_3 \cdot 9H_2O$, 3.75 g of the aluminosilicate precursor, and 0.75 g of TON seeds were mixed and ground for 5 min, followed by the addition of 12 g of colloidal silica (31.5 wt% SiO_2 in water) to form a mixture, which was used for shaping. Then the resulting extrudates and pellets were dried at 50 °C for 10 h and calcined at 550 °C for 4 h, which was used as the starting solid material for the preparation of the shaped TON zeolite catalyst. Finally, 0.88 g of shaped aluminosilicate extrudate, 0.14 g of H_2O and 0.99 g of methanol were put into a Teflon-lined autoclave and sealed, then crystallized at 140 °C for 6 d at static condition. The final products were obtained by filtering, washing with deionized water, and subsequently drying overnight at 100 °C. Na^+ in the product was removed by exchanging with HCl solution, it was obtained the shaped TON zeolite extrudate.

Synthesis of conventional shaped ZSM-5 zeolite

In a typical run for synthesis of conventional shaped aluminosilicate ZSM-5 zeolite, 0.0218 g of isopropyl alcohol aluminum and 4.875 g of TPAOH (40 wt%) were added to 5.1 g of H_2O, resulting in a clear solution. After addition of 4.2 g of TEOS, a mixture was formed. After stirring for 6 h, the mixture was transferred into an autoclave and heated at 200 °C for 48 h. The final products were obtained by filtering, washing with deionized water, subsequently drying overnight at 100 °C, and calcined at 550 °C for 4 h. Then ZSM-5 zeolite and silica binder were mixed for preparation of conventional shaped ZSM-5 catalyst.

Supplementary Figures & Table Captions

Fig. S1. Photograph of the shaped aluminosilicate extrudate before crystallization.

Fig. S2. SEM images of the shaped aluminosilicate extrudate before crystallization.

Fig. S3. XRD patterns of the shaped aluminosilicate extrudate (a) before and (b) after crystallization.

Fig. S4. N_2 sorption isotherms of the shaped aluminosilicate extrudate before crystallization.

Fig. S5. ^{29}Si MAS NMR spectrum of the shaped aluminosilicate extrudate before crystallization: experimental curve (solid line) and deconvoluted curves (dotted lines).

Fig. S6. ^{29}Si MAS NMR spectra of the conventional shaped ZSM-5 zeolite catalyst: experimental curve (solid line), deconvoluted curves (dotted lines).

Fig. S7. XRD patterns of the full-crystalline and shaped ZSM-5 zeolite extrudates with different Si/Al ratios of (a) 37, (b) 118, (c) 151, (d) 240, and (e) 317, respectively.

Fig. S8. Photographs of the full-crystalline and shaped ZSM-5 zeolite pellets (a) before and (b) after crystallization.

Fig. S9. SEM images of the full-crystalline and shaped ZSM-5 zeolite pellet.

Fig. S10. XRD pattern of the full-crystalline and shaped ZSM-5 zeolite pellet.

Fig. S11. XRD pattern of the full-crystalline and shaped silicalite-1 zeolite extrudate.

Fig. S12. SEM images of the full-crystalline and shaped silicalite-1 zeolite extrudate.

Fig. S13. XRD pattern of the full-crystalline and shaped silicalite-1 zeolite pellet.

Fig. S14. SEM images of the full-crystalline and shaped silicalite-1 zeolite pellet.

Fig. S15. Methanol conversion and product selectivities over the shaped aluminosilicate extrudate before crystallization at 480 °C (◆, Conv.; ■, $C_2^=$; ●, $C_3^=$; ▲, $C_4^=$; ▼, C_5^+).

Fig. S16. Methanol conversion and product selectivities over the conventional shaped ZSM-5 zeolite catalyst at 480 °C (◆, Conv.; ■, $C_2^=$; ●, $C_3^=$; ▲, $C_4^=$; ▼, C_5^+).

Fig. S17. XRD pattern of the conventional shaped ZSM-5 zeolite catalyst.

Fig. S18. N_2 sorption of the conventional shaped ZSM-5 zeolite catalyst.

Fig. S19. Schematic representation of the formation of core-shell structures.

Fig. S20. Al2p XPS spectra of full-crystalline and shaped ZSM-5 zeolite catalysts by parallel tests for five times (a-e).

Table S1. Mechanical strength tests for 100 shaped ZSM-5 extrudates.

Table S2. ^{29}Si MAS NMR data of the shaped extrudates.

Table S3. Si/Al ratios of the shaped aluminosilicate extrudates and the ZSM-5 zeolite catalysts.

Fig. S1. Photograph of the shaped aluminosilicate extrudate before crystallization.

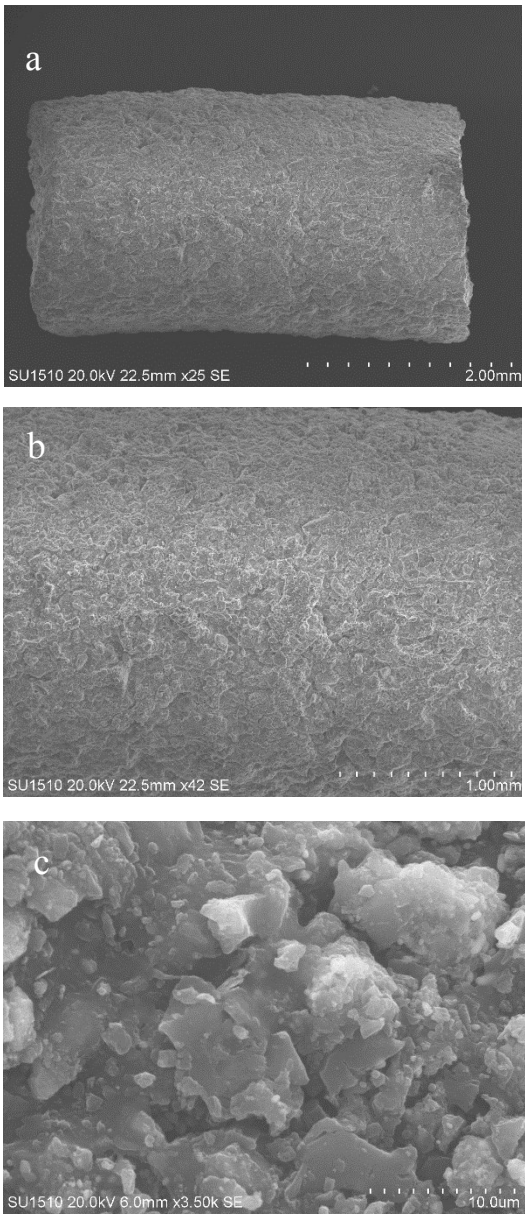

Fig. S2. SEM images of the shaped aluminosilicate extrudate before crystallization.

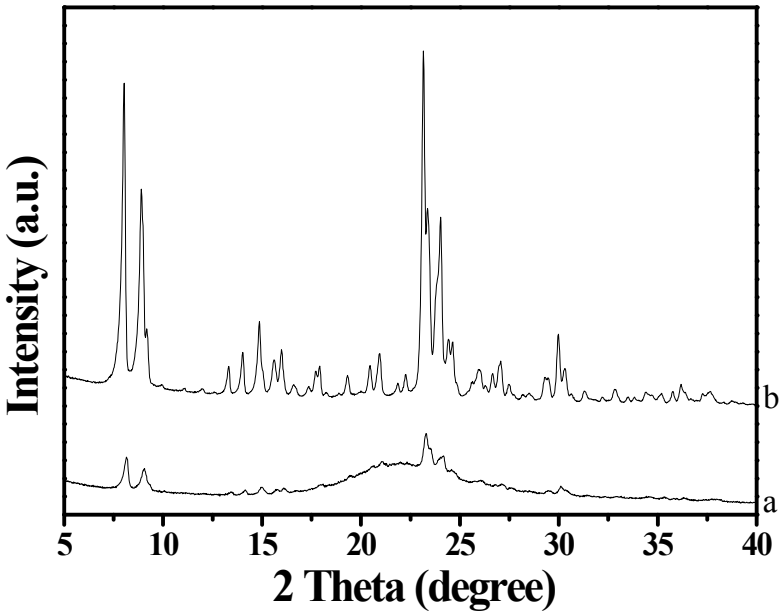

Fig. S3. XRD patterns of the shaped aluminosilicate extrudate (a) before and (b) after crystallization.

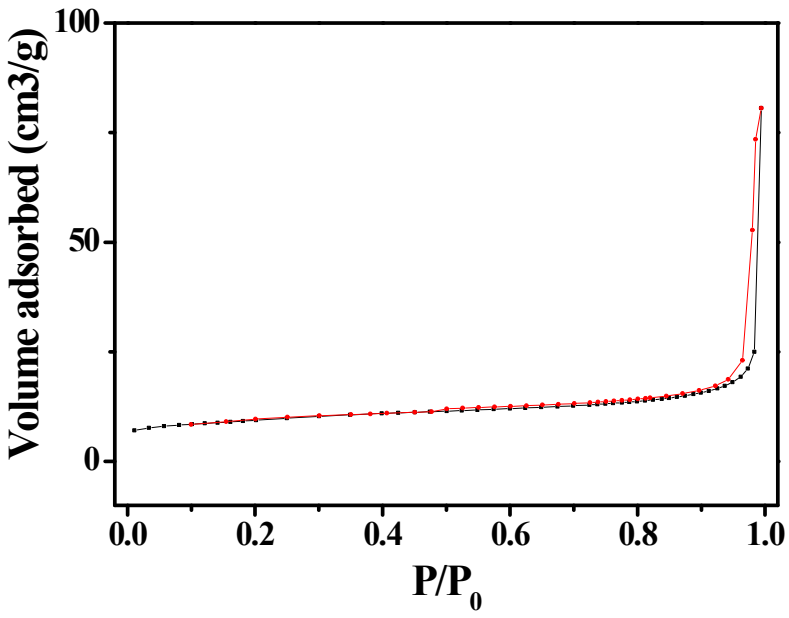

Fig. S4. N_2 sorption isotherms of the shaped aluminosilicate extrudate before crystallization.

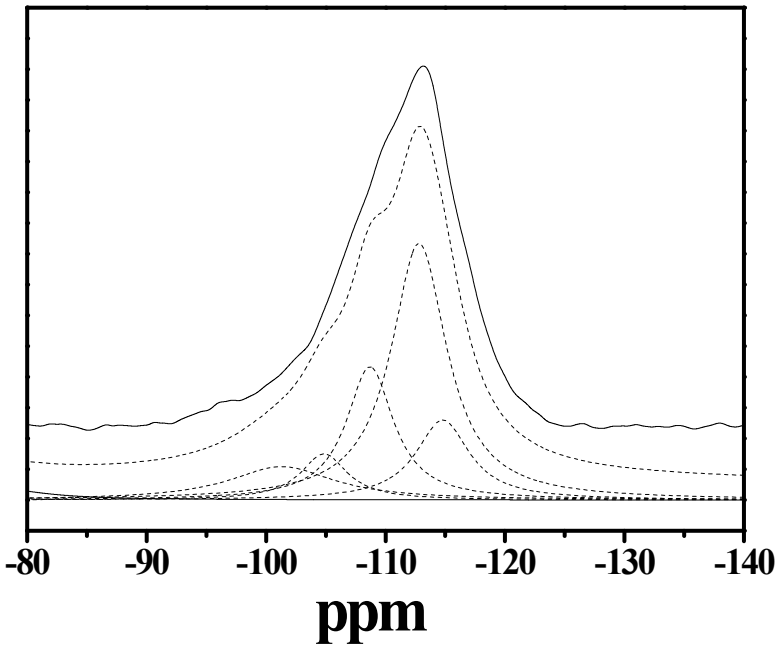

Fig. S5. ^{29}Si MAS NMR spectrum of the shaped aluminosilicate extrudate before crystallization: experimental curve (solid line) and deconvoluted curves (dotted lines).

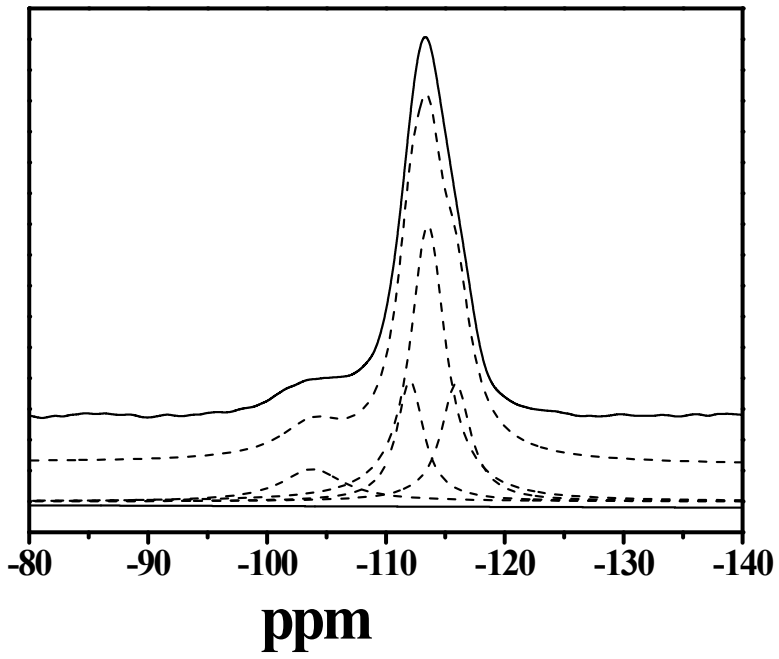

Fig. S6. ^{29}Si MAS NMR spectrum of the conventional shaped ZSM-5 zeolite catalyst: experimental curve (solid line) and deconvoluted curves (dotted lines).

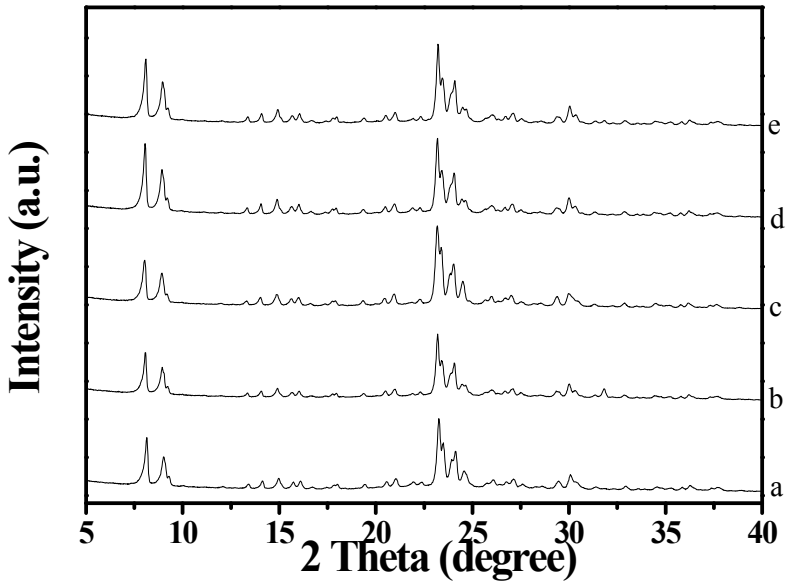

Fig. S7. XRD patterns of the full-crystalline and shaped ZSM-5 zeolite extrudates with different Si/Al ratios of (a) 37, (b) 118, (c) 151, (d) 240, and (e) 317, respectively.

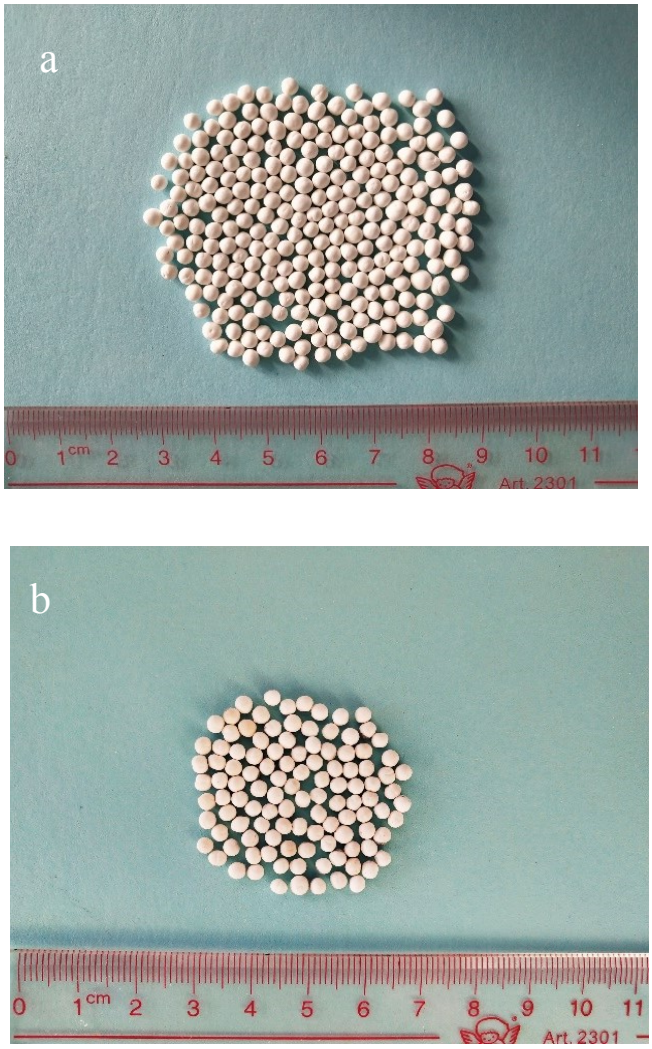

Fig. S8. Photographs of the full-crystalline and shaped ZSM-5 zeolite pellets (a) before and (b) after crystallization.

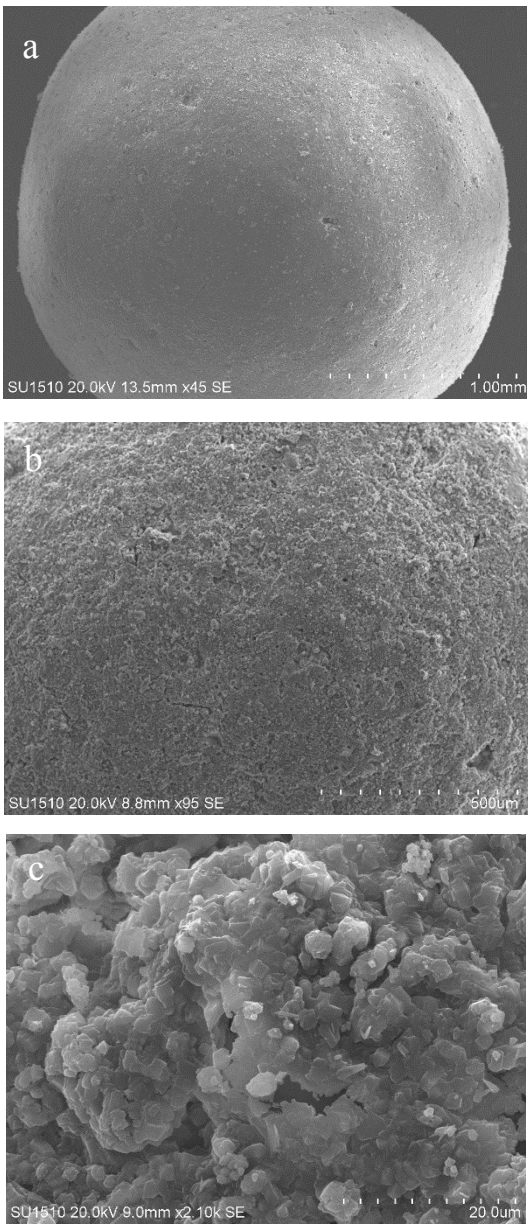

Fig. S9. SEM images of the full-crystalline and shaped ZSM-5 zeolite pellet.

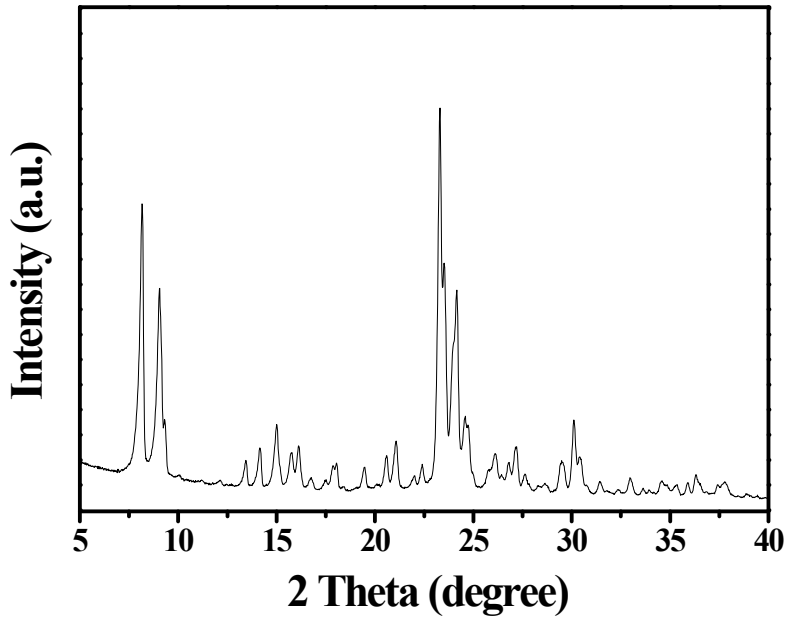

Fig. S10. XRD pattern of the full-crystalline and shaped ZSM-5 zeolite pellet.

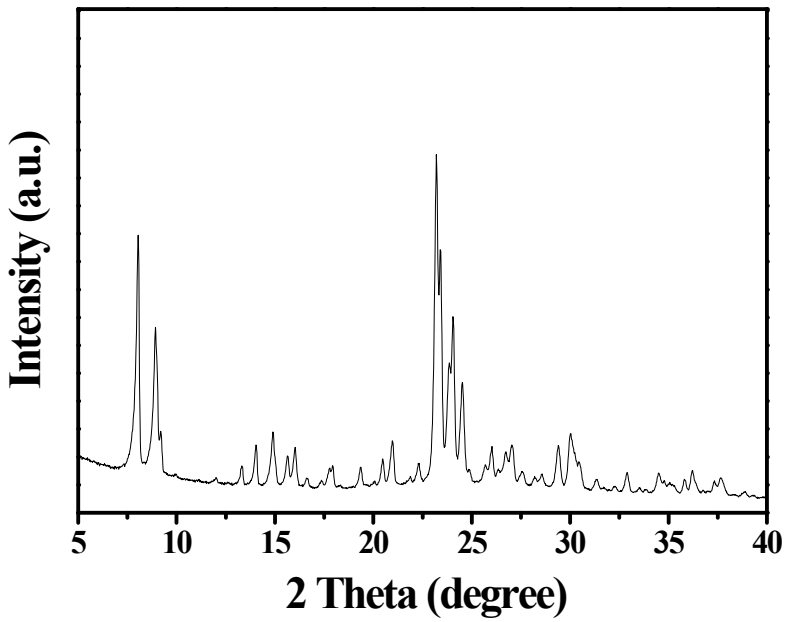

Fig. S11. XRD pattern of the full-crystalline and shaped silicalite-1 zeolite extrudate.

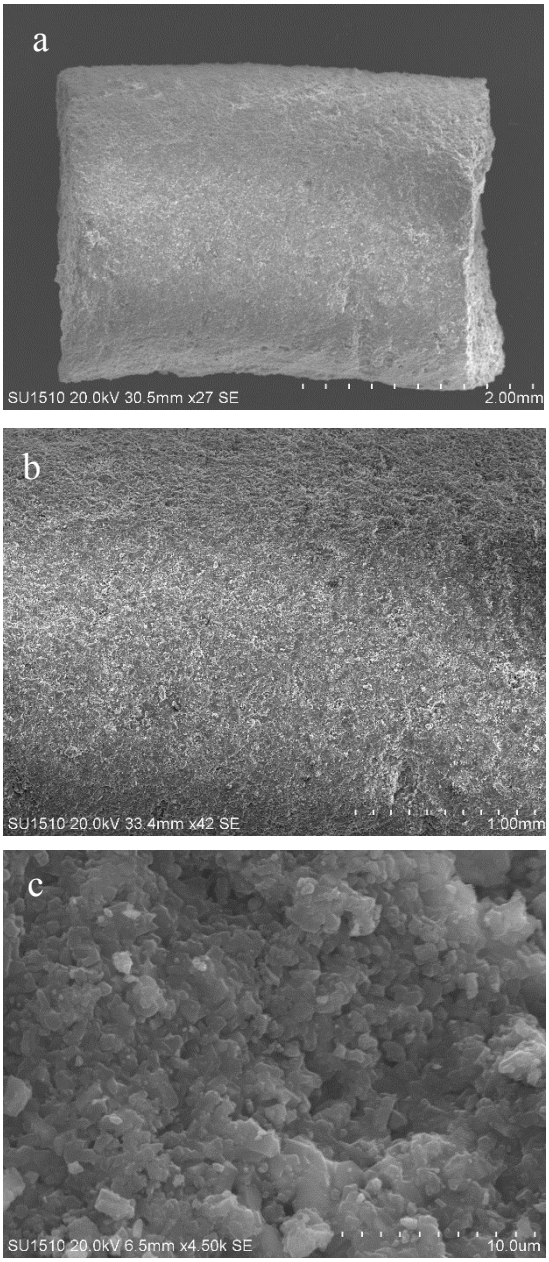

Fig. S12. SEM images of the full-crystalline and shaped silicalite-1 zeolite extrudate.

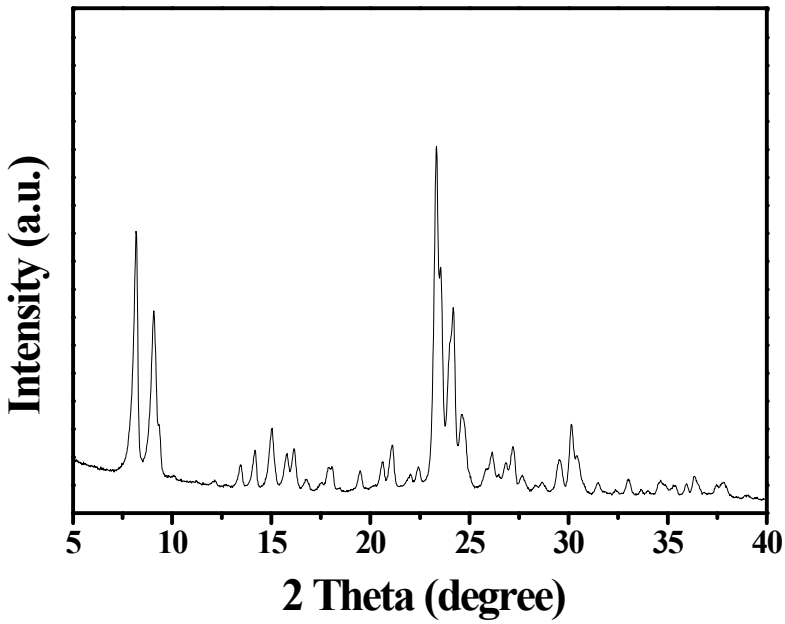

Fig. S13. XRD pattern of the full-crystalline and shaped silicalite-1 zeolite pellet.

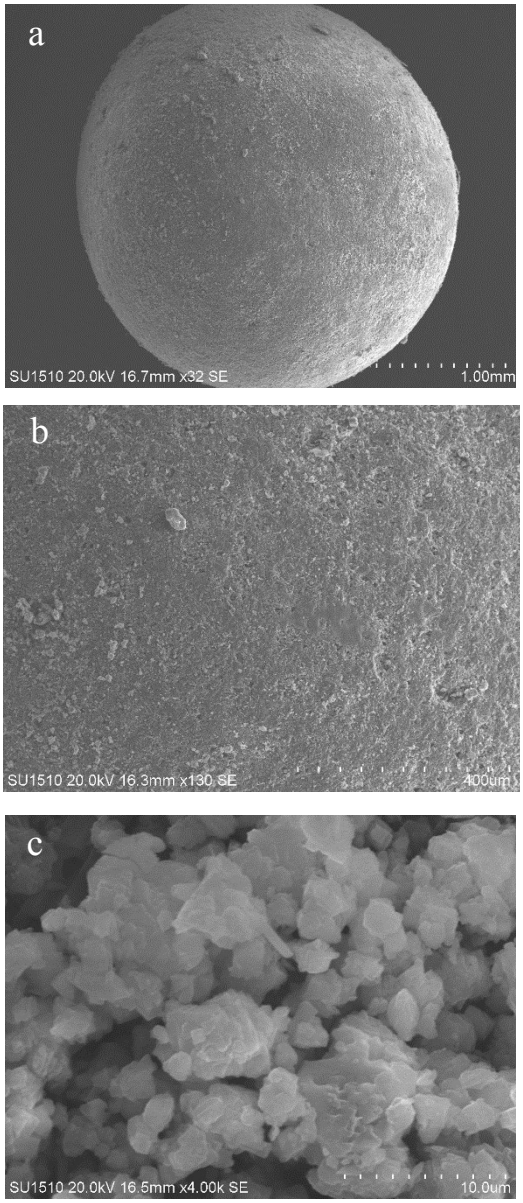

Fig. S14. SEM images of the full-crystalline and shaped silicalite-1 zeolite pellet.

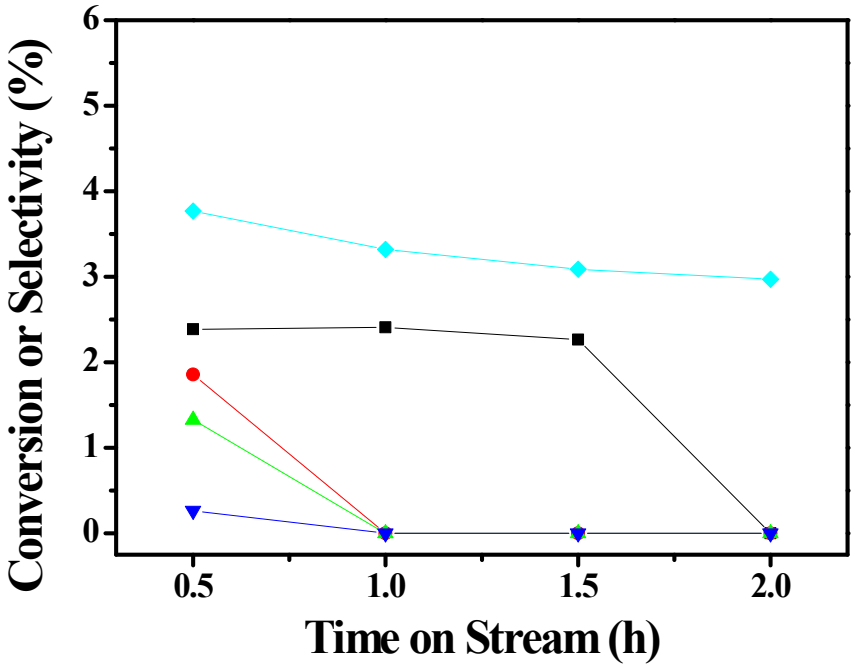

Fig. S15. Methanol conversion and product selectivities over the shaped aluminosilicate extrudate before crystallization at 480 °C (◆, Conv.; ■, $C_2^=$; ●, $C_3^=$; ▲, $C_4^=$; ▼, C_5^+).

Note: Before crystallization, the shaped aluminosilicate extrudate is almost inactive.

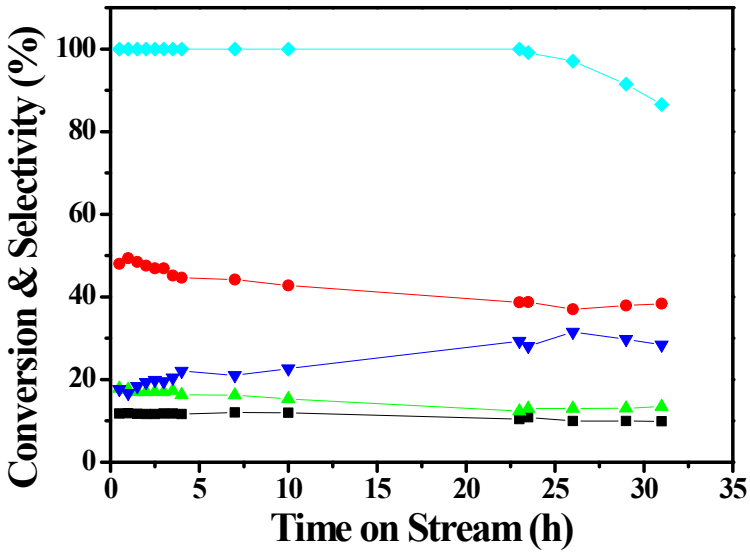

Fig. S16. Methanol conversion and product selectivities over the conventional shaped ZSM-5 zeolite catalyst at 480 °C (◆, Conv.; ■, $C_2^=$; ●, $C_3^=$; ▲, $C_4^=$; ▼, C_5^+).

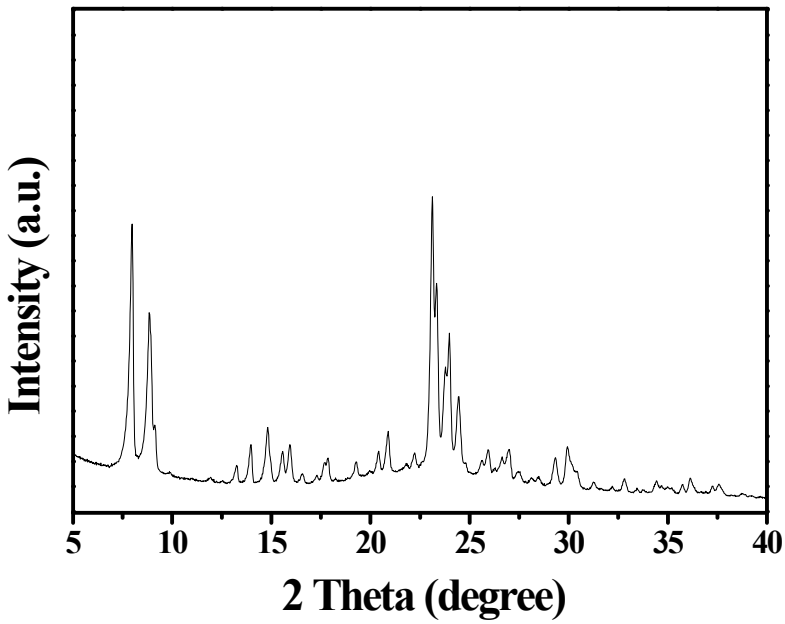

Fig. S17. XRD pattern of the conventional shaped ZSM-5 zeolite catalyst.

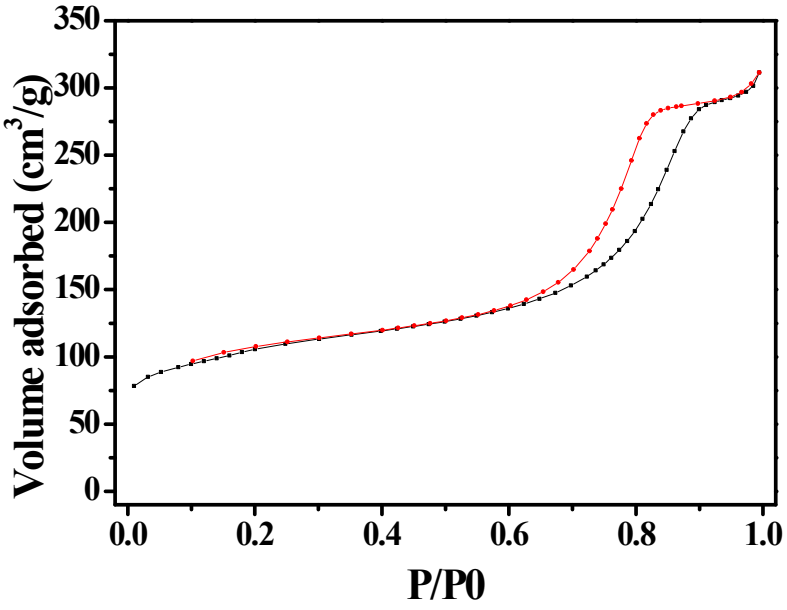

Fig. S18. N_2 sorption of the conventional shaped ZSM-5 zeolite catalyst.

Note: The BET surface area and micropore volume are 368 m^2/g and 0.059 cm^3/g.

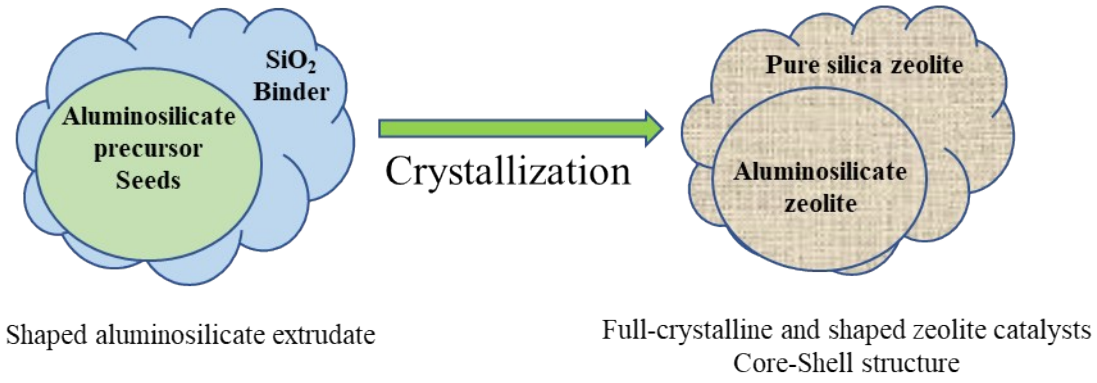

Fig. S19. Schematic representation of the formation of core-shell structures.

Note: After full crystallization of the extrudate, the colloidal silica was transformed into the pure silica zeolite shell, while the aluminosilicate precursor nanoparticles were transformed into the aluminosilicate zeolite core, which formed a "core-shell structure".

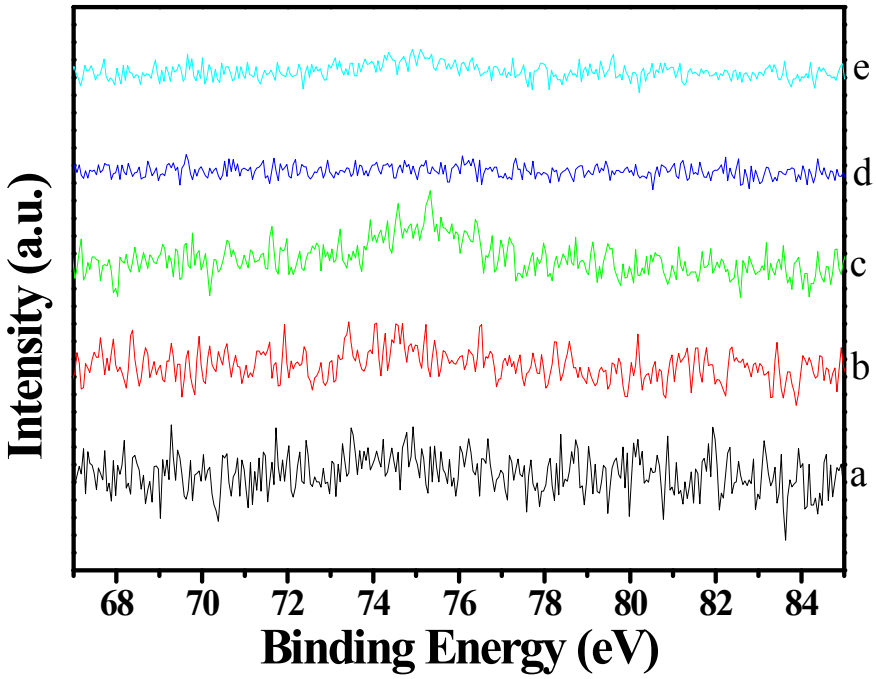

Fig. S20. Al2p XPS spectra of full-crystalline and shaped ZSM-5 zeolite catalysts by parallel tests for five times (a-e).

Note: Because XPS is a surface technique, it is reasonable to measure the surface composition of the samples. During these measurements, the Al signal in the sample d was undetectable, and the Al signals in the other samples were very weak, which are in good agreement with the proposed "core-shell structure", where core structure is aluminosilicate zeolite and shell structure is pure silica zeolite transformed from inorganic binder of colloidal silica.

Table S1. Mechanical strength tests for 100 shaped ZSM-5 extrudates.

20-30 N	**30-40 N**	**40-50 N**	**50-60 N**	**＞60 N**
24.3, 20.0,	38.7, 34.0,	45.4, 46.3,	50.2, 52.0,	60.1, 60.7,
28.2, 26.0,	39.5, 38.1,	43.0, 48.0,	51.5, 50.5,	66.0, 62.0,
27.3, 27.2,	37.2, 39.2,	41.9, 43.0,	51.0, 58.9,	63.0, 60.0,
22.2, 27.0,	36.6, 38.4,	40.0, 44.0,	52.7, 51.8,	71.0, 61.2
24.5, 29.6,	36.9, 35.0,	46.3, 48.1,	52.0, 54.0,	
21.6	37.0, 36.0,	48.4, 47.8,	53.1, 50.0,	
	32.3, 33.0,	42.3, 44.7,	52.0, 58.0,	
	31.0, 34.2,	47.0, 44.7,	56.0, 57.0,	
	30.0, 31.0,	48.2, 45.2,	50.0, 50.7,	
	38.0, 30.1,	42.0, 44.4,	52.0, 51.6,	
	38.8, 36.9,	40.0, 46.8,	50.1	
	35.2, 36,	41.0, 40.0,		
	35	47.1, 44.3,		
		49.0, 43.3,		
		46.0, 48.1,		
		40.3, 46.3,		
		40.0, 43.8,		
		43.8		

Table S2. ^{29}Si MAS NMR data of the shaped extrudates.

Sample	Si(0Al) (%)	Si(0Al) (%)	Si(0Al) (%)	Si(1Al) (%)
Full-crystalline and shaped ZSM-5 zeolite catalyst	11	36	49	4
Shaped aluminosilicate extrudate	14	47	21	18
Conventional shaped ZSM-5 zeolite catalyst	20	52	18	10

Table S3. Si/Al ratios of the shaped aluminosilicate extrudates and the ZSM-5 zeolite catalysts.

Run	Si/Al ratios of aluminosilicate precursors	Si/Al ratios of the shaped aluminosilicate extrudates	Si/Al ratios of the shaped ZSM-5 zeolite catalysts
1	17	28	37
2	50	107	118
3	80	134	151
4	132	202	240
5	234	272	317