Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Facile creation of hierarchical nano-sized ZSM-5 with large external surface via desilication-recrystallization of silicalite-1 for conversion of methanol to hydrocarbons

Supplementary material

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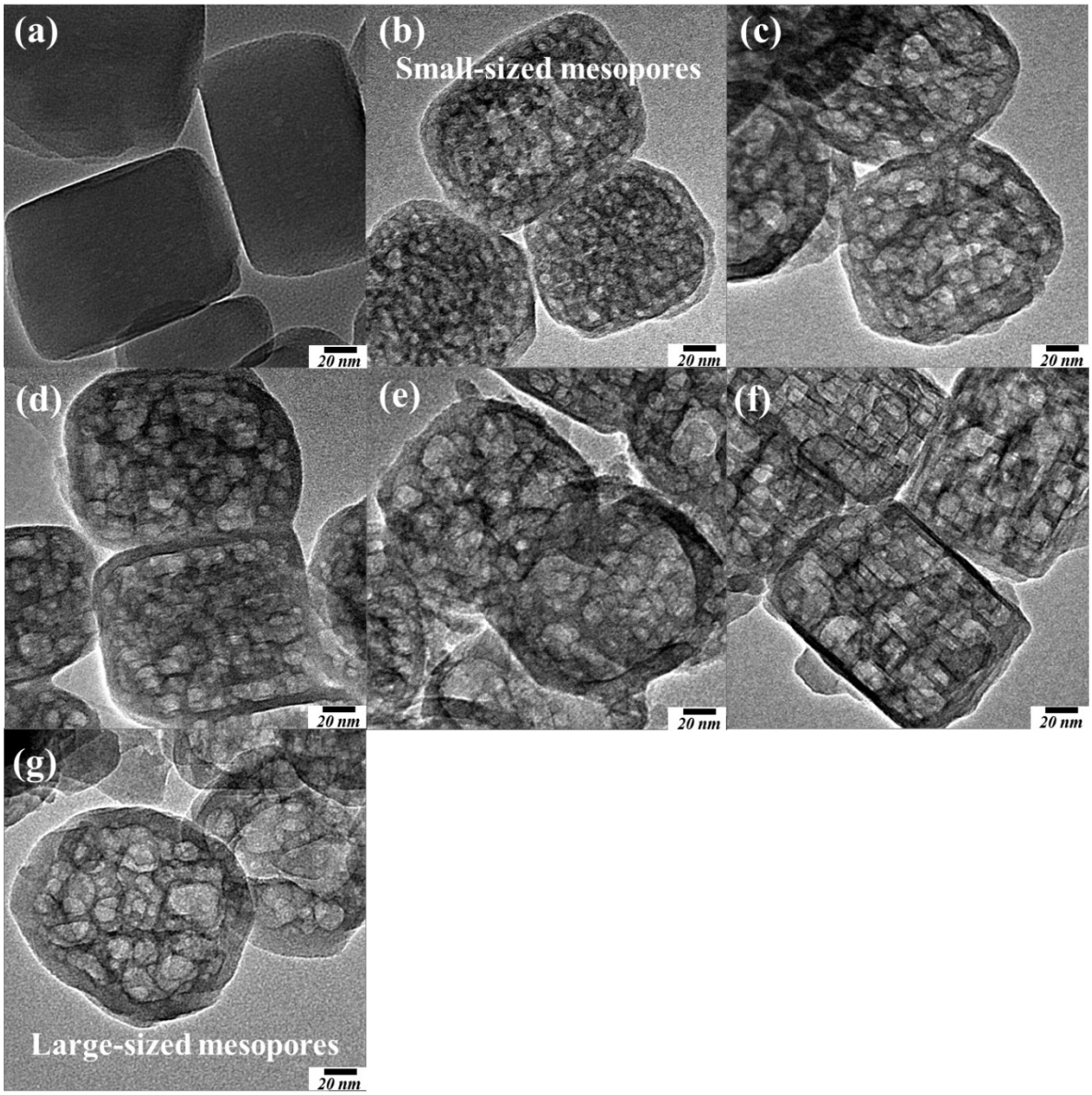

Fig. S1. TEM images of the silicalite-1(a), HZ-150-0.5 (b), HZ-150-3 (c), HZ-150-6 (d), HZ-150-12 (e), HZ-150-24 (f) and HZ-150-72 (g) by prolonging the desilication-recrystallization time with the particle size of about 150 nm.

The detailed description of chemical shift of $Q^4(0Al)$, $Q^4(1Al)$ and $Q^3(0Al)$ sites in ^{29}Si MAS NMR spectra.

The ^{29}Si MAS NMR spectra of silicalite-1 shows $Q^4(0Al)$, $Q^3(0Al)$ sites in Figure 6, there are four crystallographically different $Q^4(0Al)[Si(OSi)_4]$ silicon sites at -117 ppm, -115 ppm -113 ppm and -111 ppm, and $Q^3(0Al)[Si(OSi)(OH)]$ site at -103 ppm. While the ^{29}Si MAS NMR spectra of HZSM-5 samples by different time of desilication-recrystallization show $Q^4(0Al)$, $Q^4(1Al)$, $Q^3(0Al)$ sites. There are three crystallographically different $Q^4(0Al)[Si(OSi)_4]$ silicon sites at -116 ppm, -113 ppm and -111 ppm, respectively. $Q^4(1Al)[Si(OSi)_3OAl]$ site at -107 ppm and $Q^3(0Al)[Si(OSi)(OH)]$ site at -103 ppm are seen in ^{29}Si MAS NMR spectra of HZSM-5 samples by different time of desilication-recrystallization.

Table S1. N_2 physisorption characteristics of different deactivated nano-ZSM-5 zeolites.

Samples	S_{BET} ($m^2 g^{-1}$)	S_{Micro} ($m^2 g^{-1}$)	S_{Exter} ($m^2 g^{-1}$)	V_{Total} ($cm^3 g^{-1}$)	t-plot V_{Micro} ($cm^3 g^{-1}$)	V_{Meso} ($cm^3 g^{-1}$)
De HZ-0.5	378	176	202	0.92	0.09	0.83
De HZ-3	206	130	76	0.42	0.07	0.35
De HZ-6	171	100	71	0.37	0.05	0.32
De HZ-12	164	103	61	0.26	0.05	0.21
De HZ-24	96	48	48	0.22	0.02	0.20
De HZ-72	112	60	52	0.22	0.02	0.20

Table S2. The variation of N_2 physisorption characteristics between fresh and used nano-HZSM-5 zeolites prepared by desilication-recrystallization with the time extension.

Samples	ΔS_{BET} ($m^2 g^{-1}$)	ΔS_{Micro} ($m^2 g^{-1}$)	ΔS_{Exter} ($m^2 g^{-1}$)	ΔV_{Total} ($cm^3 g^{-1}$)	t-plot ΔV_{Mircro} ($cm^3 g^{-1}$)	ΔV_{Meso} ($cm^3 g^{-1}$)
HZ-0.5	85	0	85	0.19	0.00	0.19
HZ-3	197	54	143	0.55	0.03	0.52
HZ-6	258	106	152	0.61	0.06	0.55
HZ-12	306	128	178	0.66	0.07	0.59
HZ-24	370	212	158	0.71	0.11	0.60
HZ-72	345	212	133	0.66	0.11	0.55

The proportion of coke deposition in the micropores or on the external surface was analyzed by $R_{\Delta SMicro}$, $R_{\Delta SMeso}$, $R_{\Delta VMicro}$, $R_{\Delta VMeso}$, which calculated through the relative variation degree of surface area and volume of micropores and mesopores. The calculated formulations were based on the textural properties from deactivated and fresh catalysts, and were listed as follows.

$$R_{\Delta SMicro} = (\Delta S_{Micro} / \Delta S_{BET}) \times 100\%$$

$$R_{\Delta SMeso} = (\Delta S_{Meso} / \Delta S_{BET}) \times 100\%$$

$$R_{\Delta VMicro} = (\Delta V_{Micro} / \Delta V_{Total}) \times 100\%$$

$$R_{\Delta VMeso} = (\Delta V_{Meso} / \Delta V_{Total}) \times 100\%$$

Table S3. The proportion of coke location in microporous or mesoporous structure.

Samples	$R_{\Delta SMicro}$ (%)	$R_{\Delta SMeso}$(%)	$R_{\Delta VMicro}$(%)	$R_{\Delta VMeso}$(%)
HZ-0.5	0	100	0	100
HZ-3	28	72	5	95
HZ-6	41	59	10	90
HZ-12	42	58	11	89
HZ-24	57	43	14	86
HZ-72	61	39	15	85

Table S4. N_2 physisorption characteristics of fresh, deactivated and regenerated HZ-24 zeolites prepared by desilication-recrystallization 24 h.

Samples	S_{BET} ($m^2 g^{-1}$)	S_{Micro} ($m^2 g^{-1}$)	S_{Exter} ($m^2 g^{-1}$)	V_{Total} ($cm^3 g^{-1}$)	t-plot V_{Micro} ($cm^3 g^{-1}$)	V_{Meso} ($cm^3 g^{-1}$)
HZ-24	466	260	206	0.93	0.13	0.80
De HZ-24	96	48	48	0.22	0.02	0.20
Re HZ-24	266	135	131	0.65	0.07	0.58

Table S5. Acidic properties of fresh, deactivated and regenerated HZ-24 prepared by desilication-recrystallization 24 h.

Samples	Total acidic amount [c] (mmol g^{-1})	Weak acidic amount (mmol g^{-1})	Medium acidic amount (mmol g^{-1})	Strong acidic amount (mmol g^{-1})
HZ-24	0.58	0.20	0.14	0.24
De HZ-24	0.01	-	-	-
Re HZ-72	0.17	0.06	0.04	0.07