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Supporting Information

Hydrophilicity/hydrophobicity modulated synthesis of nanocrystalline and hierarchically structured TS-1 zeolites

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Experimental Section

Chemicals: Tetraethyl orthosilicate (TEOS, Sinopharm Chemical Reagent Co. (China)), tetrabutyl orthotitanate (TBOT, Sigma Aldrich), tetrapropylammonium hydroxide (TPAOH, 25wt% aqueous solution, Yixing Dahua Chemical Co. (China)), isopropanol (Sinopharm Chemical Reagent Co. (China)), and deionized water.

Catalyst synthesis: The molar composition of *un*-TS-1 precursor gel was SiO_2 : TiO_2 : TPAOH : H_2O : $CH_3CHOHCH_3$ = 50 : 1.0 : 13.5 : 1460 : 100. Typically, TEOS (10.4165 g), deionized water (18 g), and TPAOH solution (10.98 g) were mixed under stirring at 40 °C for 4 h. TBOT (0.34 g) and isopropanol (6 g) were mixed under stirring at ice bath in a separate wide neck flask. Subsequently, after both of them cooled down to below 4 °C the above two solutions were combined and stirred for another 4 h, then, stirred at 40 °C for adequate duration to remove the isopropanol until solid precursor gel powder were obtained. The resultant gel powder containing ~ 50% water amount was put into a crucible, then transferred to a 80 ml Teflon-lined stainless steel autoclave and crystallized at 180 °C for 10 h. After crystallization, the solid was washed with deionized water for three times and dried at 100 °C for 12 h. The sample was calcined in a muffle furnace to remove the microporous agents. From room temperature to 550 °C, a heating rate of 1 °C min^{-1} was adopted and then it was kept at 550 °C for 6 h. The resultant sample was denoted as *un*-TS-1***(x,T,t)***, which represents the precursor gel with a Si/Ti ratio of ***x*** was crystallized at ***T*** °C for ***t*** h.

The uniform silicalite-1 crystal was synthesized according to the similar recipe with that of *un*-TS-1 crystals. Typically, TEOS (10.4165 g), deionized water (18 g), and TPAOH solution (4.1 g) were mixed under stirring at 40 °C for adequate duration to obtained solid precursor gel. The resultant precursor gel containing ~ 50% water amount was put into a 80 ml Teflon-lined stainless steel autoclave and crystallized at 150 °C for 24 h. After crystallization, the solid was centrifugated and washed with deionized water for three times and dried at 100 °C for 12 h. The sample was calcined in a muffle furnace to remove the microporous agents. From room temperature to 550 °C, a heating rate of 1 °C min^{-1} was adopted and then it was kept at 550 °C for 6 h.

The aluminum and titanium co-doped silicalite-1 was synthesized according to the similar recipe with that of *un*-TS-1 crystals with additional aluminum source. Typically, TEOS (10.4165 g) and aluminium isopropoxide ($Al(PrO)_3$, 0.1021 g) were mixed at 40 °C for 2 h. Then deionized water (18 g), and TPAOH solution (4.1 g) were added dropwise under stirring at 40 °C for 4 h. TBOT (0.34 g) and isopropanol (6 g) were mixed under stirring at ice bath in a separate wide neck flask. Subsequently, after both of them cooled down to below 4 °C the above two solutions were combined and stirred for another 4 h, then, stirred at 40 °C for adequate duration to remove the isopropanol until solid precursor gel powder were obtained. The resultant gel powder containing ~ 50% water amount was put into a crucible, then transferred to a 80 ml Teflon-lined stainless steel autoclave and crystallized at 150 °C for 24 h. After crystallization, the solid was washed with deionized water for three times and dried at 100 °C for 12 h. The sample was calcined in a muffle furnace to remove the microporous agents. From room temperature to 550 ^{o}C, a heating rate of 1 ^{o}C min^{-1} was adopted and then it was kept at 550 ^{o}C for 6 h.

The Fe-doped silicalite-1 (Fe/Si=1.0:50) was synthesized according to that of *un*-TS-1, typically, TEOS (10.4165 g), deionized water (18 g), and $Fe(NO_3)_3 \cdot 9H_2O$ (0.404 g) were mixed at 20 ^{o}C for 2 h. Subsequently TPAOH solution (4.1 g) was added dropwise under stirring at 20 ^{o}C, then, stirred at 40 ^{o}C for adequate duration until solid precursor gel powder was obtained. The resultant gel powder containing ~ 50% water amount was put into a crucible, then transferred to a 80 ml Teflon-lined stainless steel autoclave and crystallized at 150 ^{o}C for 72 h. After crystallization, the solid was washed with deionized water for three times and dried at 100 ^{o}C for 12 h. The sample was calcined in a muffle furnace to remove the microporous agents. From room temperature to 550 ^{o}C, a heating rate of 1 ^{o}C min^{-1} was adopted and then it was kept at 550 ^{o}C for 6 h.

The Zr-doped silicalite-1 (Zr/Si=1.0:50) was synthesized according to that of *un*-TS-1. Typically, TEOS (10.4165 g), deionized water (18 g), and TPAOH solution (4.1 g) were mixed under stirring at 40 ^{o}C for 4 h. zirconium isopropoxide (0.3276 g) and isopropanol (6 g) were mixed under stirring at ice bath in a separate wide neck flask. Subsequently, after both of them cooled down to below 4 ^{o}C the above two solutions were combined and stirred for another 4 h, then, stirred at 40 ^{o}C for adequate duration to remove the isopropanol until solid precursor gel powder was obtained. The resultant gel powder containing ~ 50% water amount was put into a crucible, then transferred to a 80 ml Teflon-lined stainless steel autoclave and crystallized at 150 ^{o}C for 24 h. After crystallization, the solid was washed with deionized water for three times and dried at 100 ^{o}C for 12 h. The sample was calcined in a muffle furnace to remove the microporous agents. From room temperature to 550 ^{o}C, a heating rate of 1 ^{o}C min^{-1} was adopted and then it was kept at 550 ^{o}C for 6 h.

The conventional TS-1 was prepared using the same precursor gel composition and procedure without corresponding precursor aging step. Typically, TEOS (10.4165 g), deionized water (18 g), and TPAOH solution (10.98 g) were mixed under stirring at 40 °C for 4 h. TBOT (0.34 g) and isopropanol (6 g) were mixed under stirring at ice bath in a separate wide neck flask. Subsequently, after both of them cooled down to below 4 °C the above two solutions were combined and stirred for 4 h and, then, stirred at 40 °C for 4 h. The resultant precursor solution was transferred into a 80 ml Teflon-lined stainless steel autoclave and crystallized at 150 °C for 24 h. After crystallization, the solid was centrifugated and washed with deionized water for three times and dried at 100 °C for 12 h. The sample was calcined in a muffle furnace to remove the microporous agents. From room temperature to 550 °C, a heating rate of 1 °C min^{-1} was adopted and then it was kept at 550 °C for 6 h. The resultant sample was denoted as *ht*-TS-1.

Ti-MCM-41 was synthesized according to the previous literature reported by Lin *et al.*.[1] Typically, sodium hydroxide (1.24 g) was dissolved in deionized water (2115 ml), followed by the addition of CTAB (4.155 g). Then, the mixture of TEOS (22.5 ml) and TBOT (0.70 ml) was added dropwise under vigorous stirring at room temperature for 4 h. The resulting solid was filtered, washed with deionized water, and dried at 100 °C for 12 h. The sample was calcined in a muffle furnace to remove the microporous agents. From room temperature to 550 °C, a heating rate of 1 °C min^{-1} was adopted and then it was kept at 550 °C for 6 h.

Characterization: Power X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max 2200PC diffractometer, using Cu K_{α} X-ray source at a scanning rate of 6 degrees min^{-1} over the 2θ range between 5° and 50° (40 kV and 40 mA). The relative crystallinity was calculated based on the peak area in the range of 22-26° relative to hydrothermally synthesized *ht*-TS-1. TEM images were taken on a JEOL-2010F instrument with an acceleration voltage of 200 kV. The samples for TEM analysis were prepared by dipping the carbon-coated copper grid into ethanol solution of samples and dried at room temperature. The SEM images were obtained on a FEI-Magellan 400L instrument with an operating voltage of 1 kV. N_2 adsorption-desorption isotherms were recorded on a Micromeritics Tristar 3000 analyzer at 77 K. Prior to the measurement, the samples were degassed in vacuum at 300 °C for 12 h. The surface areas were calculated by the Brunauer-Emmett-Teller (BET) method and pore size distribution by the Barrett-Joyner-Halenda (BJH) method by using the desorption branch of the isotherms. Micropore volume and external surface area were calculated by the *t*-plot method. The particle size distribution of nanoparticles was characterized by dynamic light scattering (DLS) on a Malvern Zetasizer Nano-ZS90 instrument. UV-Vis spectra were recorded from 200 nm to 700 nm on a Shimadzu UV-3101 instruction using $BaSO_4$ as a reference. Si/Ti ratios were determined by the Agilent Technologies 725 inductively coupled plasma optical emission spectrometry (ICP-OES). Water adsorption measurement of *un*-TS-1 was conducted according to the adsorption capacity of saturated water vapor at atmosphere temperature and pressure. Prior to the measurement, the samples were degassed in vacuum at 300 °C for 12 h. Contact angle measurement were recorded on SL200C after tablet press processed under 10 MPa. ^{27}Al NMR were carried out with $Al(H_2O)_6^{3+}$ as the reference at 104.26 MHz, with the pulse of 0.5 μs ($< \pi/12$), and pulse interval of 60 s combined with a spinning speed of 4 kHz.

Catalytic reactions: The catalytic properties of the obtained *un*-TS-1 catalysts were tested using the well-known 1-hexene epoxidation as a probe reaction in a three-necked glass flask equipped with a condenser and vigorous stirring. Initially, 10 mmol 1-hexene and 50 mg catalyst were added into 10 ml methanol. Then, after heating the mixture to 60 °C, 10 mmol hydrogen peroxide (H_2O_2, 30 wt% aqueous solution) was added dropwise and reacted for 4 h. Before reaction, the catalyst was activated at 300 °C for 2 h. The products were analyzed by GC-MS (Agilent, 6890/5973N) with a 5 ms column (30 m × 0.25 mm). The conversion of 1-hexene and selectivity of 1,2-epoxyhexane were determined as follows:

$$X_{\text{1-hexene}} = (n_{\text{1-hexene,0}} - n_{\text{1-hexene}}) / n_{\text{1-hexene,0}} \times 100\%$$

$$S_{\text{1,2-epoxyhexane}} = n_{\text{1,2-epoxyhexane}} / (n_{\text{1,2-epoxyhexane}} + n_{\text{by-products}})$$

The $n_{1\text{-hexene},0}$ and $n_{1\text{-hexene}}$ represent the molar amount of 1-hexene in the reactants and products, respectively. $n_{1,2\text{-epoxyhexane}}$ and $n_{\text{by-products}}$ represent the molar amount of 1,2-epoxyhexane and by-products in the products, respectively.

For liquid-phase hydroxylation of phenol, 5 mmol of phenol, 15 ml of water, and 50 mg of catalyst were mixed in a three-necked glass flask under vigorous stirring and heated to 80 °C. Then, 170 µl hydrogen peroxide (H_2O_2, 30 wt% aqueous solution) was added dropwise. Before reaction, the catalyst was activated at 300 °C for 2 h. After reacting for 4 h, the products were analyzed using GC/2010 plus (Shimadzu, Rtx® -Wax capillary column) with flame ionization detector (FID). The conversion (*X*) of phenol and selectivity (*S*) of hydroquinone, catechol, and *p*-benzoquinone were determined as follows:

$X_{\text{phenol}} = (n_{\text{phenol},0} - n_{\text{phenol}}) / n_{\text{phenol},0} \times 100\%$

$S_{\text{hydroquinone}} = n_{\text{hydroquinone}} / (n_{\text{hydroquinone}} + n_{\text{catechol}} + n_{p\text{-benzoquinone}})$

$S_{\text{catechol}} = n_{\text{catechol}} / (n_{\text{hydroquinone}} + n_{\text{catechol}} + n_{p\text{-benzoquinone}})$

$S_{p\text{-benzoquinone}} = 1 - S_{\text{hydroquinone}} - S_{\text{catechol}}$

The $n_{\text{phenol},0}$ and n_{phenol} represent the molar amount of phenol in the reactants and products, respectively. $n_{\text{hydroquinone}}$, n_{catechol}, and $n_{p\text{-benzoquinone}}$ represent the molar amount of hydroquinone, catechol, and *p*-benzoquinone in the products, respectively.

1 K. F. Lin, P. P. Pescarmona, H. Vandepitte, D. Liang, G. Van Tendeloo, P. A. Jacobs, *J. Catal.* 2008, **254**, 64.

Table S1. Textural properties and elemental compositions of *ht*-TS-1 and *un*-TS-1 synthesized under different crystallization temperatures and durations

Sample	theoretical Si/Ti [mol/mol]	Si/Ti[a] [mol/mol]	Particle size (nm)	S_{BET} ($m^2 g^{-1}$)	S_{micro} ($m^2 g^{-1}$)	S_{ext} ($m^2 g^{-1}$)	V_{pore} ($cm^3 g^{-1}$)	V_{micro} ($cm^3 g^{-1}$)	relative crystallinity (%)
ht-TS-1	50	53	250	440	282	158	0.22	0.13	100
silicalite-1[b]	-	-	~2000	462	197	266	0.22	0.09	-
un-TS-1***(30,120,36)***	30	33	80	500	245	255	0.54	0.11	82.8
un-TS-1***(50,120,36)***	50	50	80	499	234	265	0.54	0.11	88.7
un-TS-1***(80,120,36)***	80	88	80	520	258	262	0.55	0.12	90.8
un-TS-1***(150,120,36)***	150	168	70	497	260	237	0.54	0.12	91.0
un-TS-1***(50,150,24)***	50	48	100	515	248	267	0.55	0.11	88.4
un-TS-1***(50,150,24)***[*]	50	-	2000	472	321	151	0.23	0.15	94.8
un-TS-1***(50,150,24)***[*1]	50	-	1000	496	204	294	0.45	0.10	-
un-TS-1***(50,150,24)***[&]	50	-	800	486	296	190	0.31	0.14	92.4
un-TS-1***(50,150,24)***[#]	50		105	490	231	259	0.48	0.13	90.1
un-TS-1***(50,180,6)***	50	52	-	536	324	212	0.41	0.15	93.8
un-TS-1***(50,180,10)***	50	57	140	468	294	174	0.38	0.14	95.2
Zr-silicalite-1[c]	50	-	-	434	233	201	0.24	0.11	-
Fe-silicalite-1[d]	50	-	-	354	161	193	0.54	0.07	-

[a] Si/Ti ratio determined by ICP-OES; [b] Synthesized at 150 °C for 24 h; [c] Synthesized with a Zr/Si ratio of 1.0:50; [d] Synthesized with a Fe/Si ratio of 1.0:50; [*] Synthesized from a TPAOH/Si ratio of 0.1; [*1] Synthesized from a TPAOH/Si ratio of 0.1 and an Al/Ti/Si ratio of 0.75:1:50; [&] Synthesized from a TPAOH/Si ratio of 0.16; [#] Scale-up synthesized in a 12 ml autoclave; S_{BET}, S_{micro}, S_{ext}, V_{pore}, and V_{micro} represent the total surface area, micropore surface area, external surface area, total pore volume, and micropore volume, respectively.

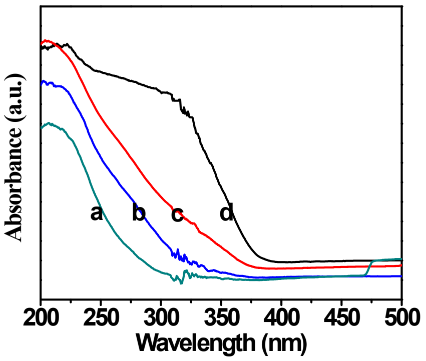

Figure S1. UV-Vis spectra of *un*-TS-1***(50,120,36)*** with different Si/Ti ratio of (a) 150, (b) 80, (c) 50, (d) 30.

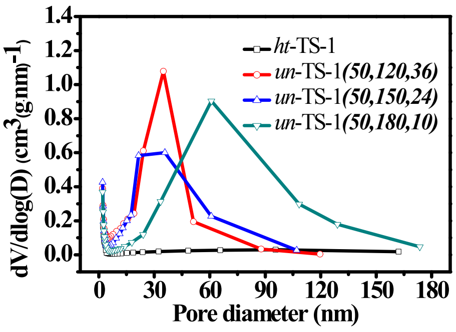

Figure S2. Pore size distributions of synthesized *un*-TS-1 and *ht*-TS-1.

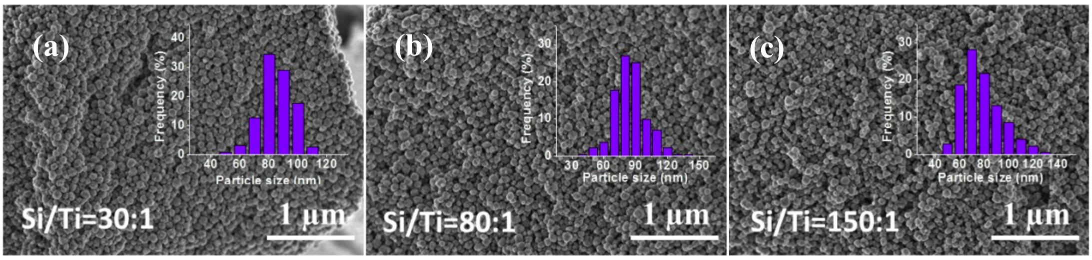

Figure S3. SEM images of *un*-TS-1***(x,120,36)*** with different Si/Ti ratios (a) 30, (b) 80, (c) 150, and the corresponding particle size distributions (inset).

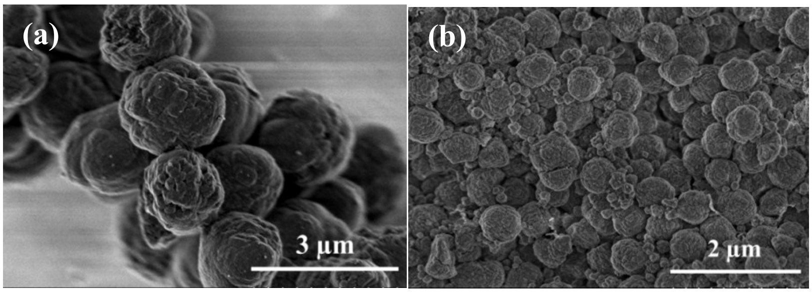

Figure S4. SEM images of *un*-TS-1***(50,150,24)*** synthesized with different TPAOH amounts (a) TPAOH / Si = 0.1, (b) TPAOH / Si = 0.16.

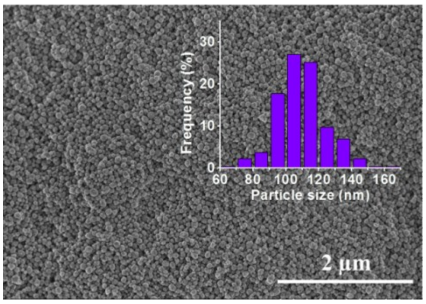

Figure S5. SEM image of *un*-TS-1***(50,150,24)***$^{\#}$ obtained in a scaled-up synthesis in a 12 ml reactor.

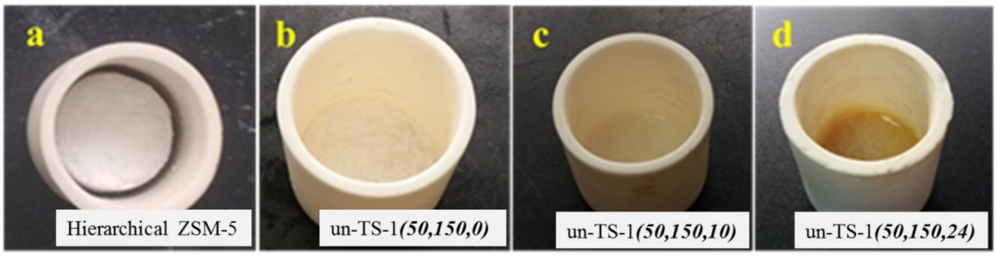

Figure S6. (a) Digital photographs of hierarchical ZSM-5, (b-d) *un*-TS-1 after SAC treatment but without drying.

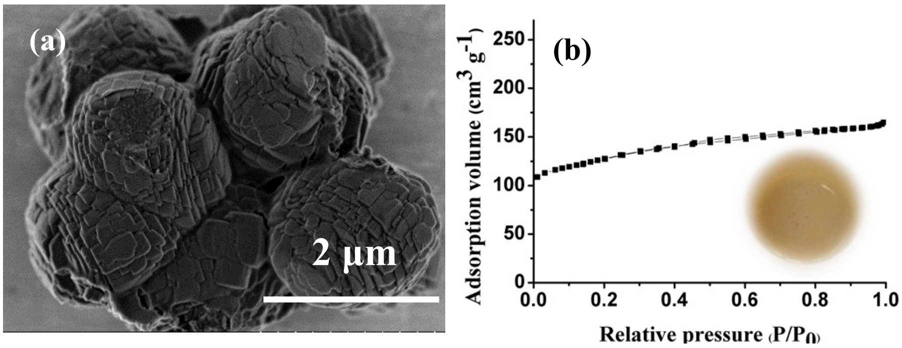

Figure S7. (a) SEM image, and (b) N_2 sorption isotherm of silicalite-1 synthesized at 150 ^{o}C for 24 h (inset is the digital photograph of as-synthesized silicalite-1 in the crucible).

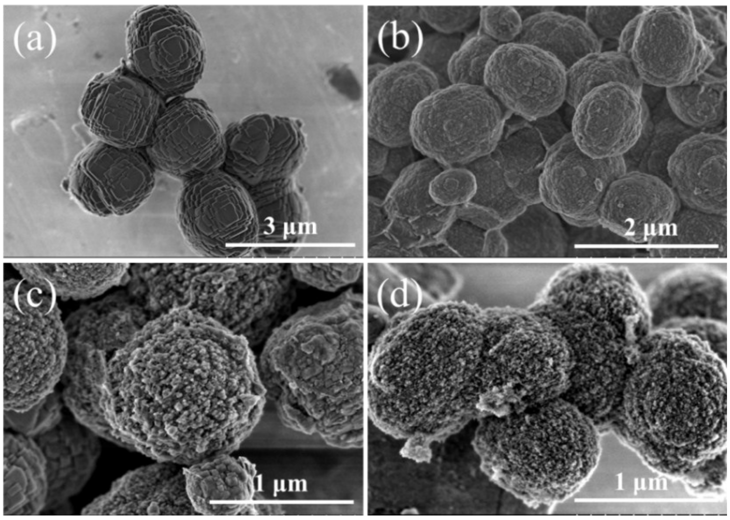

Figure S8. SEM images of *un*-TS-1***(50,150,24)**** with varied Al doping amounts (a) Al / Ti / Si of 0 : 1.0 : 50, (b) 0.25 : 1.0 : 50, (c) 0.5 : 1.0 : 50, (d) 0.75 : 1.0 : 50.

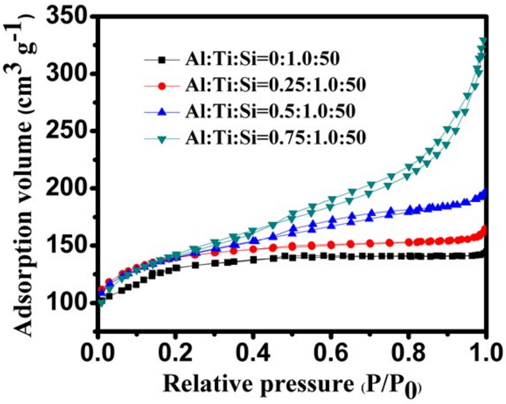

Figure S9. N_2 isotherms of *un*-TS-1***(50,150,24)**** samples with varied Al doping amounts.

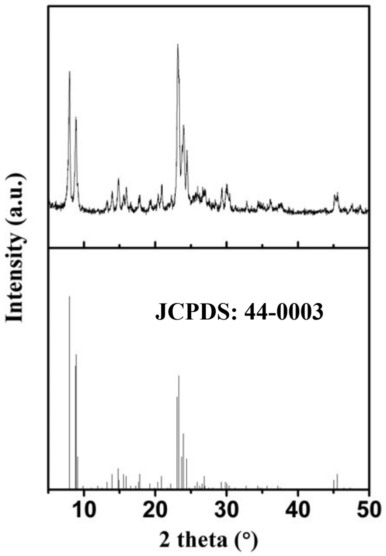

Figure S10. XRD pattern of Al-doped *un*-TS-1***(50,150,24)**** sample with Al / Ti / Si ratio of 0.75 : 1.0 : 50.

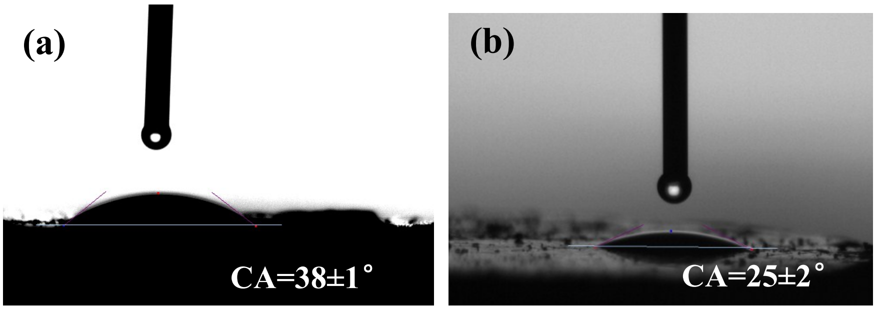

Figure S11. Contact angle (CA) measurement of (a) *un*-TS-1***(50,150,24)**** and (b) Al-doped *un*-TS-1***(50,150,24)**** sample with a Al / Ti / Si ratio of 0.75 : 1.0 : 50.

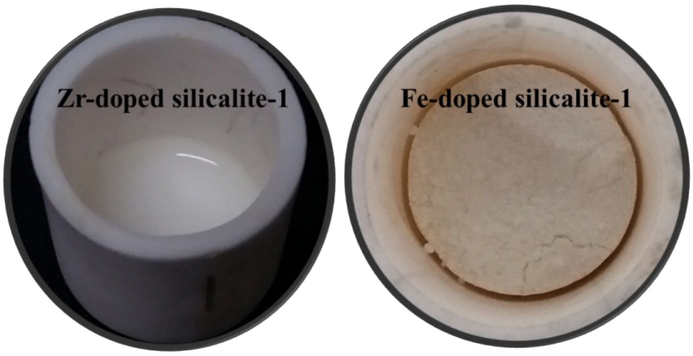

Figure S12. Digital photographs of precursor after crystallization at 150 ^{o}C for 24 h of Zr-doped silicalite-1 with a Zr / Si ratio of 1.0 : 50 and Fe-doped silicalite-1 with a Fe / Si ratio of 1.0:50.

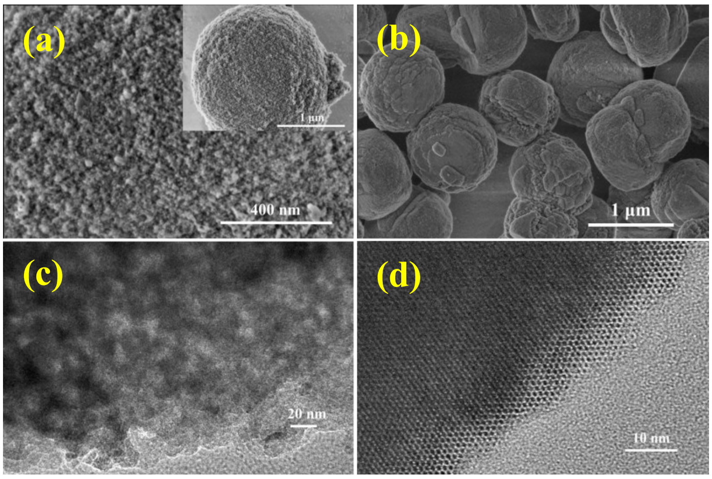

Figure S13. SEM images of (a) Fe-doped silicalite-1 with a Fe / Si ratio of 1.0 : 50 (inset is the low magnification SEM image), (b) Zr-doped silicalite-1 with a Zr / Si ratio of 1.0 : 50, and (c, d) the corresponding high resolution TEM images of (a, b).

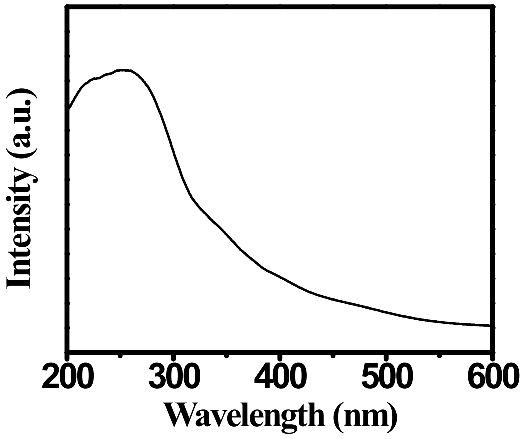

Figure S14. UV-Vis spectrum of Fe-doped silicalite-1 sample with a Fe / Si ratio of 1.0 : 50.

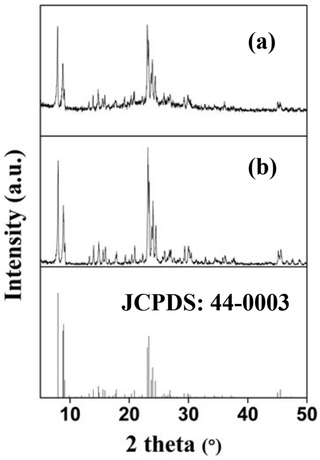

Figure S15. XRD patterns of (a) Fe-doped silicalite-1 sample with a Fe / Si ratio of 1.0 : 50, (b) Zr-doped silicalite-1 with a Zr / Si ratio of 1.0 : 50.