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Supplementary Information

Mesoporogen-Free Synthesis of Nano-Sized Hierarchical ITQ-21 zeolites

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Experimental section

Materials

All reagents were used as purchased commercially without any further purification. The source materials used in the synthesis of ITQ-21 were germanium dioxide (>99.99%, Yunnan Lincang Xinyuan Germanium Industrial Co., Ltd), Ludox (SiO_2, 40%, Sigma-Aldrich), HF (40%, Beijing Chemical Works), Al $(OH)_3$ (99%, Beijing Chemical Works), N, N-dicyclohexylmethylamine (98%, J&K Scientific Ltd) and methyl iodide (98%, Aladdin Industrial Co., Ltd). Heptanal (97%), 2-phenylpropanal (95%), diphenylacetaldehyde (97%) and trimethylorthoformate (98%) were purchased from Energy Chemical Co.

Catalytic tests

The reaction conditions of carbonyl compound (heptanal, 2-phenylpropanal, or diphenylacetaldehyde) with trimethylorthoformate (TOF) were as follows: 30 mg of catalyst, 3 mmol of carbonyl compound, 15 mmol of TOF, at 120 °C for 6 h. The products were analyzed by Gas chromatography-mass spectrometry (GC-MS, Thermo Fisher Trace ISQ, equipped with TG-5MS column, 60m × 320μm × 25μm).

Characterizations.

Material Characterizations

Powder X-ray diffraction analysis (XRD) of the samples was carried out on a Rigaku D-Max 2550 diffractometer using Cu Kα radiation (λ = 1.5418 Å, 50 kV). The scanning electron microscope (SEM) images were obtained with a JSM-6700F electron microscope. Transmission electron microscopy (TEM) images were JEM-2100 electron microscope. Nitrogen adsorption-desorption measurements were carried out on a Micromeritics ASAP 2020 Plus analyser at 77 K. All the samples were activated by degassing in-situ at about 573 K for 10 h. Chemical compositions were determined with Inductively Coupled Plasma Optical Emission Spectrometry (ICP-AES) analysis performed on an iCAP 7000 SERIES. The temperature-programmed desorption of ammonia (NH_3-TPD) experiments were carried out with a Micromeritics AutoChem II 2920 automated chemisorption analysis unit with a thermal conductivity detector (TCD) under helium flow. ^{27}Al magic-angle spinning (MAS) NMR spectrum was recorded on a Varian Infinity plus 400 spectrometer at resonance frequencies of 104.2 MHz with spinning rates of 6 KHz. ^{1}H NMR spectrum was recorded on a Varian Mercury spectrometer operating at frequencies of 300 MHz.

Captions

Fig. S1. ^{13}C NMR spectrum of the organic structure-directing agent OSDABr.

Fig. S2 TEM images of nanosized hierarchical germanosilicate ITQ-21 samples crystallized at different crystallization time (a) I-1, (b) I-1.5, (c) I-2, (d) I-12, (e)I-48, and (f) I-72.

Fig. S3 TEM images of calcined Al-containing samples of (a) Al-ITQ-21/150, (b) Al-ITQ-21/100, and (c) Al-ITQ-21/15 (The T/Al ratios in the starting gels are 150, 100, and 15).

Fig. S4 ^{27}Al MAS NMR spectrum of the calcined Al-ITQ-21/15 sample.

Fig. S5 NH_3-TPD analyses of germanosilicate sample with crystallization time of 72 h and different Al-containing samples (T/Al of 15, and 100, T=Si+Ge)

Table S1 Elemental analyses and product yields of the calcined ITQ-21 zeolites with different crystallization time.

Table S2 Textural properties of the ITQ-21 zeolites with crystallization time of 1 h, 2 h, 12 h, 48 h, and 72 h and Al-containing samples of Al-ITQ-21/15 and Al-ITQ-21/100.

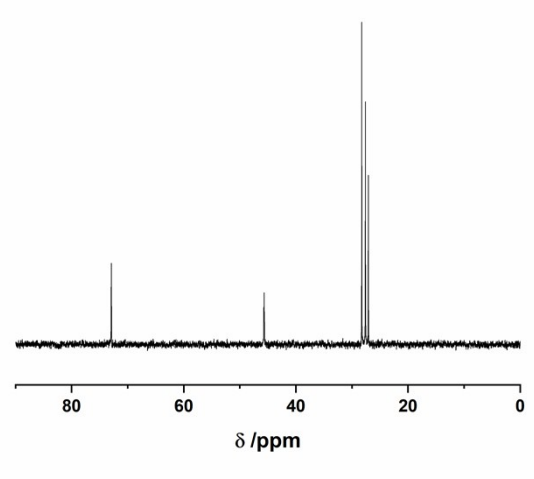

Fig. S1. ^{13}C NMR spectrum of the organic structure-directing agent OSDABr.

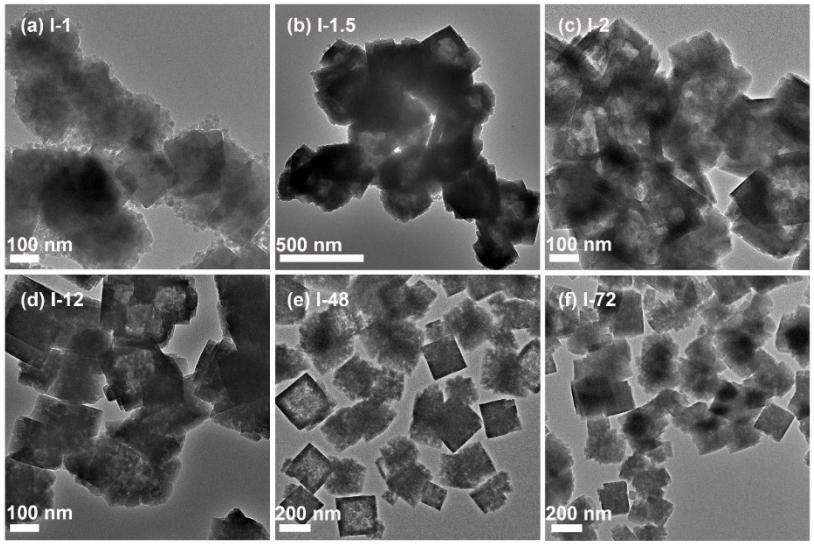

Fig. S2 TEM images of nanosized hierarchical germanosilicate ITQ-21 samples crystallized at different crystallization time (a) I-1, (b) I-1.5, (c) I-2, (d) I-12, (e)I-48, and (f) I-72.

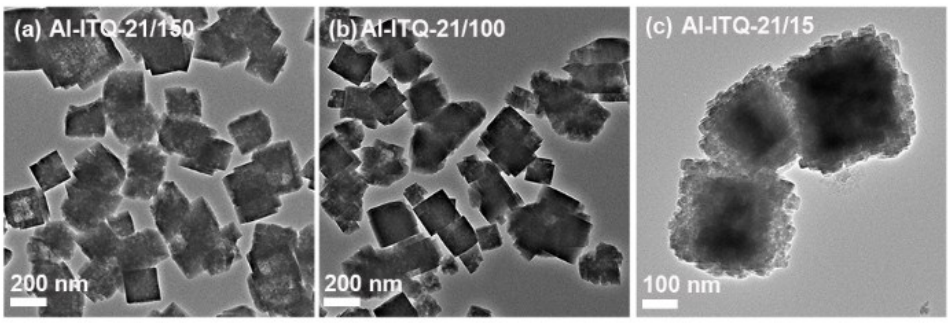

Fig. S3 TEM images of calcined Al-containing samples of (a) Al-ITQ-21/150, (b) Al-ITQ-21/100, and (c) Al-ITQ-21/15. (The T/Al ratios in the starting gels are 150, 100, and 15).

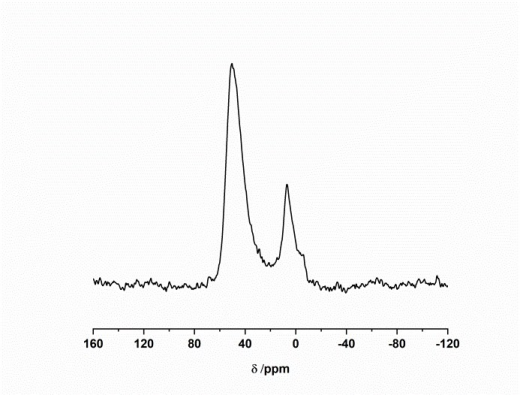

Fig. S4. ^{27}Al MAS NMR spectrum of the calcined Al-ITQ-21/15 sample.

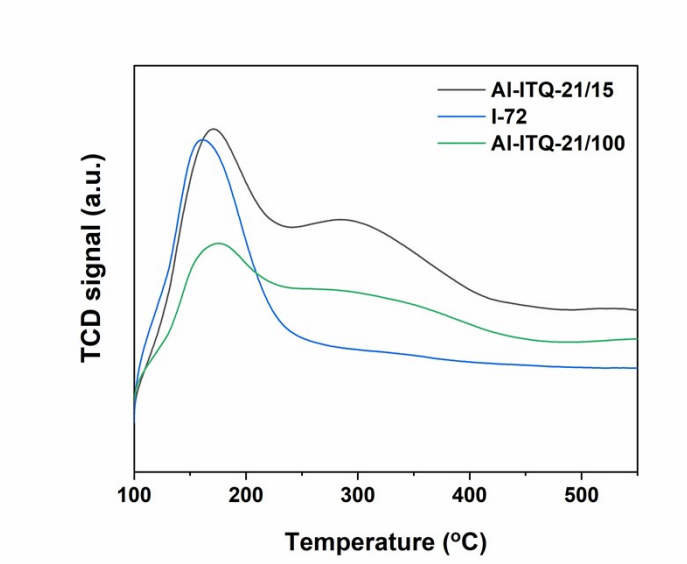

Fig. S5. NH_3-TPD analyses of germanosilicate sample with crystallization time of 72 h and different molar ratio Al-containing samples, T/Al of 15 and 100. (T=Si+Ge)

Table S1 Elemental analyses and product yields of the calcined ITQ-21 zeolites with different crystalline time.

Samples	Si/Ge[a]	T/Al[b]	Yield[c] (%)
I-1	1.78	/	73.8
I-1.5	1.75	/	78.6
I-2	1.68	/	82.3
1-9	1.67	/	94.7
I-12	1.69	/	93.1
I-18	1.71	/	93.5
I-24	1.69	/	92.7
I-48	1.93	/	93.2
I-72	1.91	/	93.0
Al-ITQ-21/100	/	84	/
Al-ITQ-21/15	/	17	/

[a,b] Measured by inductively coupled plasma (ICP-AES). [c] Yield = w1/w2*100%, where w1 and w2 are the weight of the calcined sample and theoretical ITQ-21 sample, respectively.

Table S2 Textural properties of the ITQ-21 zeolites with crystallization time of 1 h, 2 h, 9 h, 12 h, 48 h, and 72 h and Al-containing samples of Al-ITQ-21/15 and Al-ITQ-21/100.

Samples	S_{BET} (m^2/g)[a]	S_{micro} (m^2/g)[b]	S_{ext} (m^2/g)[b]	V_{micro} (cm^3/g)[b]	V_{meso} (cm^3/g)[c]
I-1	168	127	40	0.06	0.08
I-2	341	257	83	0.12	0.15
I-12	360	296	64	0.12	0.06
I-48	416	348	67	0.16	0.10
I-72	462	362	101	0.17	0.19
Al-ITQ-21/100	516	416	98	0.19	0.11
Al-ITQ-21/15	575	356	219	0.17	0.30

[a] S_{BET} (total surface area) is calculated by applying the BET equation using the linear part ($0.05<P/P_o<0.30$) of the adsorption isotherm; [b] S_{micro} (micropore area), Sext (external area), and V_{micro} (micropore volume) are calculated using the t-plot method; [c] V_{meso} (mesoporous volume) is calculated using the BJH method (from desorption).