## ELECTRONIC SUPPLEMENTARY INFORMATION

# Cationic Surfactant-Assisted Hydrothermal Synthesis: an Effective Way to Tune the Crystalline Phase and Morphology of SAPO Molecular Sieves

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#### Synthesis of nano-sized DNL-6

Conventional DNL-6 was first hydrothermally crystallized in a reactant of  $0.8H_3PO_4$ :  $1.0Al(i-C_3H_7O)_3$ : 0.2TEOS: 1.0DEA:  $50H_2O$ :  $0.15C_{16}TAB$  at 200 °C for 24h. The solid product was washed thoroughly with distilled water and dried at 110 °C overnight. The sample was further calcined at 600 °C for 5 hours to remove organic template, and then milled by using a planetary ball mill with water as a dispersing phase. The obtained powder has a very low crystallinity, which was used as a seed. To prepare nano-sized DNL-6, 1.3 wt% milled DNL-6 was charged into a reactant gel of  $0.8H_3PO_4$ :  $1.0Al(i-C_3H_7O)_3$ : 0.6TEOS: 1.5DEA:  $50H_2O$  with stirring, and then the gel was transferred into a stainless-steel autoclave and heated up to 200 °C under rotation. After a 24h reaction, the product was washed thoroughly with distilled water, separated by centrifugation and dried at 110 °C overnight. The obtained product was named as Nano-DNL-6, which can be used directly as DNL-6 seeds to synthesize nano sized DNL-6 continuously under the same condition. The procedure is the same with above one except using nano-sized DNL-6 as a seed. The product is named as nano-sized DNL-6-R, and the particle size is still in nanoscale. The XRD pattern and SEM image are shown in Figure S2, and the textural properties and compositions of these samples are listed in Table S1.

#### Synthesis of SAPO-35, SAPO-44 and SAPO-16 by HMI template

A certain amount of Al(i-C<sub>3</sub>H<sub>7</sub>O)<sub>3</sub>, TEOS, HMI and H<sub>2</sub>O was added in sequence into a static stainless steel autoclave with stirring. If necessary, cationic surfactant C<sub>18</sub>TAB was charged subsequently. The autoclave was sealed and heated at 200 °C for 24h under rotation. After the reaction, the autoclave was cooled down by cold water, and the solid product was washed thoroughly with distilled water, recovered by centrifugation and dried at 110 °C overnight. The reaction conditions are shown in Table S2. The XRD patterns and SEM images of the corresponding products are shown in Figure S3 and Figure S4 respectively.

#### NMR characterization

<sup>1</sup>H and <sup>13</sup>C NMR signals of the main product 4-Chloromethyl-1,3-dioxolan-2-one: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): d = 3.68 (m, 1 H), 3.82 (m, 1H), 4.37 (m, 1H), 4.54 (m, 1 H), 4.99 ppm (m, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): d = 44.23, 66.78, 74.51, 154.61 (C=O) ppm.

#### Table S1. Textural properties and compositions of the synthesized DNL-6 molecular sieves

Sample	Surface area (m <sup>2</sup> /g)			Pore Volume(m <sup>3</sup> /g)		Composition
	S <sub>total</sub> <sup>a</sup>	S <sub>mic</sub> (m <sup>2</sup> /g)	S <sub>ext</sub> (m <sup>2</sup> /g) <sup>b</sup>	V <sub>mic</sub> (m <sup>3</sup> /g) <sup>c</sup>	$V_{\text{total}}$	- composition*
Sample 8	747	640	106	0.33	0.48	$Si_{0.263}AI_{0.442}P_{0.295}O_2$
Nano-DNL-6	800	720	80	0.34	0.51	$Si_{0.253}AI_{0.386}P_{0.360}O_2$
Nano-DNL-6-R	771	668	103	0.35	0.44	$Si_{0.267}AI_{0.449}P_{0.283}O_2$
Conventional DNL-6 <sup>e</sup>	828	777	51	0.36	0.42	$Si_{0.135}AI_{0.496}P_{0.369}O_2$

<sup>a</sup> BET surface area, <sup>b</sup> t-plot external surface area, <sup>c</sup> t-plot micorpore volume. <sup>d</sup> The compositions are analyzed by XRF.

<sup>*e*</sup> The relative data is taken from reference 21.

### Table S2. Synthetic conditions of SAPO-35, SAPO-16 and SAPO-44 molecular sieves<sup>a</sup>

Entry	x TEOS	Cationic	Product	
		surfactant		
S1	0.1	0	SAPO-35	
S2	0.1	0.2C <sub>18</sub> TAB	SAPO-35	
S3	0.15	0.2 C <sub>18</sub> TAB	SAPO-35	
S4	0.5	0.2 C <sub>18</sub> TAB	SAPO-16	
S5	0.5	0	SAPO-44	

<sup>*a*</sup>The initial gel molar composition: 0.8H<sub>3</sub>PO<sub>4</sub>: 1.0Al(i-C<sub>3</sub>H<sub>7</sub>O)<sub>3</sub>: xTEOS: 1.51HMI: 50H<sub>2</sub>O: 0.2 or 0 C<sub>18</sub>TAB; Reaction condition: 200 °C, 24h.



Figure S1. XRD patterns of the synthesized DNL-6 samples corresponding to Table 1.



Figure S2 XRD patterns and SEM images of DNL-6s synthesized by using as-synthesized micrometer sized DNL-6 (bottom) and nano-DNL-6 (top) as seeds. The XRD peaks belong to SAPO-34 impurity was labeled by "\*".



Figure S3 XRD patterns of the synthesized SAPO-35(S1-S3), SAPO-16(S4) and SAPO-44(S5) corresponding to Table S2.



Figure S4 SEM images of the synthesized SAPO-35(S1-S3), SAPO-16(S4) and SAPO-44(S5) corresponding to Table S2.