Electronic Supplementary Information

Organophosphorous surfactant-assistant synthesis of SAPO-34

molecular sieve with special morphology and improved MTO

performance

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Sample Preparation

Synthesis of conventional SAPO-34 with TEAOH

Al(i-C₃H₇O)₃, water, TEAOH, TEOS and H₃PO₄ were mixed in sequence with a gel composition of 2.0 TEAOH:1.2 P₂O₅:1.0 Al₂O₃:0.5 SiO₂:150 H₂O. The crystallization was conducted in a stainless steel autoclave at 200 °C for 3 days under autogeneous pressure. The product was filtrated, washed and dried in air. The product is denoted as S-TEAOH-0.

Synthesis of conventional SAPO-34 with DEA/TEA

Al(i-C₃H₇O)₃, water, organic amines, TEOS and H₃PO₄ were mixed in sequence with a gel composition of x R:1.0 P₂O₅:1.0 Al₂O₃:0.5 SiO₂:50 H₂O (x = 2.0 for R = DEA and x = 3.0 for R = TEA). The crystallization was conducted in a stainless steel autoclave at 200 °C for 3 days under autogeneous pressure. The products were filtrated, washed and dried in air. The products are denoted as S-R-O, where R refers to the type of the template.

Synthesis of SAPO-34 with hexadecyltrimethyl ammonium bromide

A certain amount of N(CH₃)₃C₁₆H₃₃Br (CTAB) was firstly added into deionized water and stirred well. Then, desired amount of aluminium isopropoxide, TEAOH, etraethyl orthosilicate and phosphoric acid were added in sequence. After further stirring for 2-5 h, the obtained gel with the molar composition of 2.0 TEAOH:0.8 P₂O₅:0.4 CTAB:1.0 Al₂O₃:0.5 SiO₂:150 H₂O was transferred into a stainless steel autoclave and heated at 200 °C for 6 days under autogeneous pressure. The products were recovered by filtration, washed with deionized water and dried in air.



Scheme S1 Synthesis of [2-(diethoxylphosphono)propyl]hexadecyldimethylammonium bromide.



Fig. S1 ¹H (a), ¹³C (c) and ³¹P (e) NMR spectra of the intermediate product $(C_2H_5O)_2P(O)-C_3H_6Br$; ¹H (b), ¹³C (d) and ³¹P (f) NMR spectra of the final product $[(C_2H_5O)_2P(O)-C_3H_6-N(CH_3)_2-C_{16}H_{33}]Br$ in CDCl₃.



Fig. S2 XRD patterns of as-synthesized samples prepared with TEAOH and different DPHAB/H $_3PO_4$.



Fig. S3 XRD patterns of as-synthesized samples prepared with DEA and different DPHAB/H $_3PO_4$.



Fig. S4 XRD patterns of as-synthesized samples prepared with TEA and different DPHAB/H $_3PO_4$.



Fig. S5 The modeled position of the TEAOH (a), DEA (b) and TEA (c) in the CHA structure.



Fig. S6 SEM images of as-synthesized samples S-DEA-0 (a) and S-TEA-0 (b).



Fig. S7 Nitrogen adsorption/desorption isotherms of calcined S-DEA-1/6, S-DEA-1/5, S-TEA-1/6 and S-TEA-1/5.



Fig. S8 (A) ²⁷Al NMR spectra of as-synthesized S-TEAOH-1/2 (a), S-DEA-1/6 (b) and S-TEA-1/6 (c). (B) 29 Si NMR spectra of as-synthesized S-TEAOH-1/2 (a), S-DEA-1/6 (b) and S-TEA-1/6 (c).



Fig. S9 FT-IR spectra of as-synthesized S-DEA-0 and S-DEA-1/6 (a), and S-TEA-0 and S-TEA-1/6 (b).



Fig. S10 XRD pattern of sample synthesized with $N(CH_3)_3C_{16}H_{33}Br$ (CTAB) instead of DPHAB.



Fig. S11 NH₃-TPD profiles of S-TEAOH-0, S-TEAOH-1/9 and S-TEAOH-1/2.