

SUPPORTING INFORMATION

Solvent-Free Synthesis of Mg-incorporated Nanocrystalline SAPO-34 Zeolites via Natural Clay for Chloromethane-to- Olefin Conversion

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Experimental Section

Chemicals and materials: Tetraethylammonium hydroxide (TEAOH, 25 wt%) was used as structure-directing agents (SDAs). After being pretreated at 900 °C for 2 h, commercial Mg-rich clay (Figure S4, Shanghai Richjoint Chemical Reagents) was selected as combinational metal, silicon, and aluminum precursors. Phosphoric acid (85 wt%) provides the phosphorous source. Other Al and Si sources were supported by pseudo-boehmite (69 wt% Al_2O_3 , Shandong Aluminum Co. Ltd., China) and Ludox AS-30 (30 wt%, Merck), respectively. Nano-sized magnesium oxide powder (MgO , 98.0 wt%) was purchased from Sigma-Aldrich.

Synthesis of zeolite MgAPSO-34: All the SAPO-34 and MgAPSO-34 zeolites were synthesized with significantly reduced SDAs consumption by a solvent-free method. The dry gel has a molar ratio of $1.0 \text{ Al}_2\text{O}_3 : 0.3 \text{ SiO}_2 : 1.0 \text{ P}_2\text{O}_5 : 1.0 \text{ TEAOH} : x \text{ MgO} : 50.0 \text{ H}_2\text{O}$, where x is 0, 0.18, and 0.35, and the resulting zeolite products were marked as SAPO-34, MgAPSO-34-C1, and MgAPSO-34-C2, respectively. When the clay is used as half or all of the silicon source, the corresponding x in the formula is 0.18 and 0.35, respectively. In a typical synthesis of MgAPSO-34-C2, quantitative clay was firstly mixed with TEAOH solution under stirring for 2 h to develop a homogeneous solution A. Then, solution A was added dropwise into the mixture of weighted phosphoric acid and pseudo-boehmite. Finally, SAPO-34 crystals were added into the reaction mixture as seeds with a mass ratio of SAPO-34 to Al_2O_3 of 1/100. After drying at 80 °C for 12 h, the acidic dry gel was

transferred into a sealed autoclave, followed by being reacted at 220 °C for 24 h before cooling down. The solid-state products were dried at 100 °C for 12 h and then calcined in air at 600 °C for 5 h to remove SDAs.

For comparison, conventional MgAPSO-34 zeolite denoted as MgAPSO-34-M1 was prepared with the same procedure but using MgO powder as individual Mg sources.

Characterization: Powder XRD patterns were collected by a Rigaku Ultima IV X-ray diffractometer with Cu K α X-radiation (tube voltage: 40 kV and tube current: 40 mA). Scanning electron micrographs (SEM) were taken on a ZEISS SUPRA55 SAPPHIRE field emission scanning electron microscope at 2 kV. Samples for SEM analysis were coated using a Shanghai Fudi sputter coater with a gold-palladium target. Transmission electron microscopy (TEM) images were collected on a Tecnai F20 electron microscope. ^{29}Si MAS NMR measurements were performed on a Bruker Advance-400 spectrometer operating at 99 MHz. The NMR spectra with high-power proton decoupling were recorded using a sample-rotation rate of 5 kHz and a 4 mm MAS probe head. Infrared spectra were collected on a Thermo Scientific Nicolet 6700 Fourier-transform infrared spectrometer (FT-IR). Nitrogen (N_2) sorption measurements were carried out on a Micromeritics physisorption analyzer, ASAP 2020 instrument. The analyses of the calcined samples were acquired after outgassing at 300 °C. Thermogravimetric (TG) analysis was performed on a TGA NETZSCH, STA449F3 unit in air at a heating rate of 10 °C min $^{-1}$ from room temperature to 900 °C in air. Chemical compositions were determined with an X-ray fluorescence

(XRF) spectrometer (ZSX Primus). The temperature-programmed desorption of ammonia (NH_3 -TPD) experiments was performed using a Tianjin Xianquan TP-5080 automated chemisorption analysis unit with a thermal conductivity detector (TCD) under helium flow. The UV-visible diffuse reflectance spectrum of the samples was determined by Shimadzu UV-2700.

Testing of Catalytic Performance: CMTO reaction was performed in a fixed bed reactor at atmospheric pressure. 1.0 g of catalyst (20-40 mesh) was loaded into the middle of stainless steel with an inner diameter of 1 cm. The sample was pretreated in a flow of dry nitrogen at 500 °C for 1 h and then the temperature of the reactor was adjusted to 400 °C and the atmosphere was replaced by N_2 and CH_3Cl where the molar ratio of N_2 to CH_3Cl was 20. The weight hourly space velocity (WHSV) was 0.15 h^{-1} for CH_3Cl . The reaction products were analyzed every 30 min by a gas chromatograph (Shimadzu GC-2014C), equipped with a flame ionization detector (FID) and Plot-Q column. The conversion was defined as the percentage of CH_3Cl consumed during the reaction, and the selectivity of each product was calculated as the percentage amount (in moles) of CH_3Cl converted to hydrocarbons. The carbon and chlorine balances were higher than 95%.

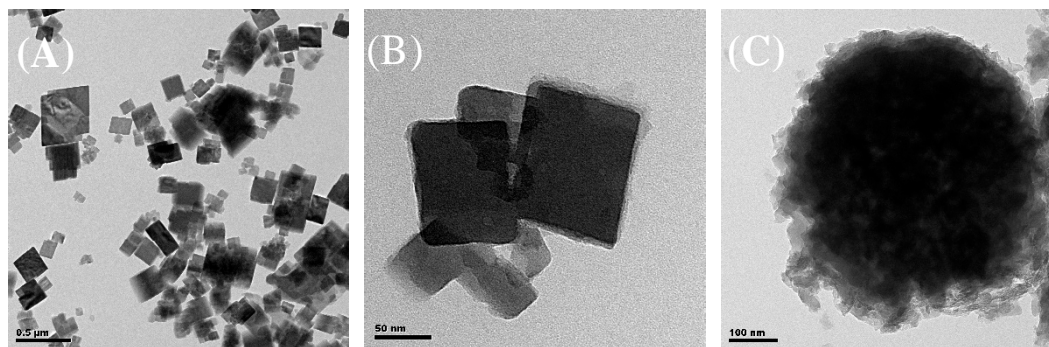


Figure S1. TEM of (A) SAPO-34, (B) MgAPSO-34-C1, and (C) MgAPSO-34-M1.

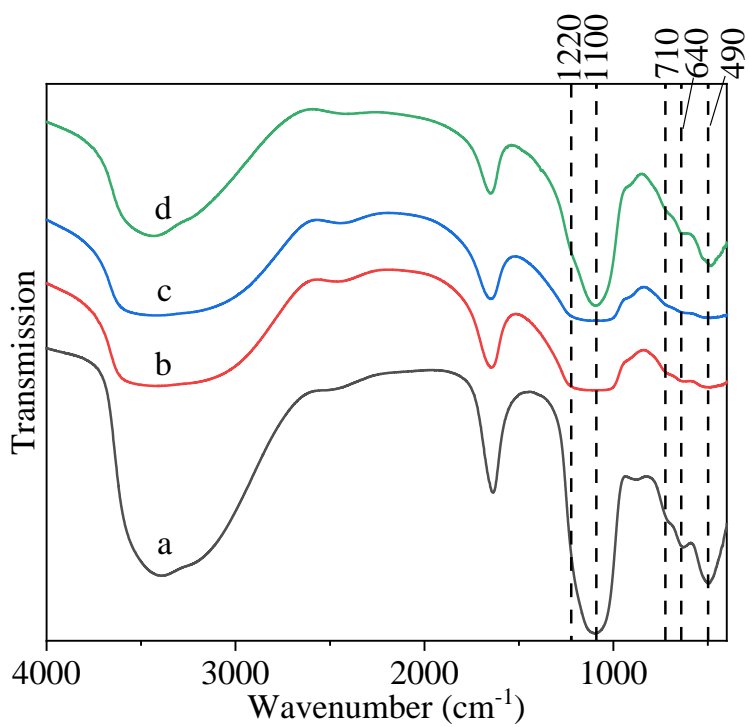


Figure S2. FT-IR spectra of (a) SAPO-34, (b) MgAPSO-34-C1, (c) MgAPSO-34-C2, (d) MgAPSO-34-M1.

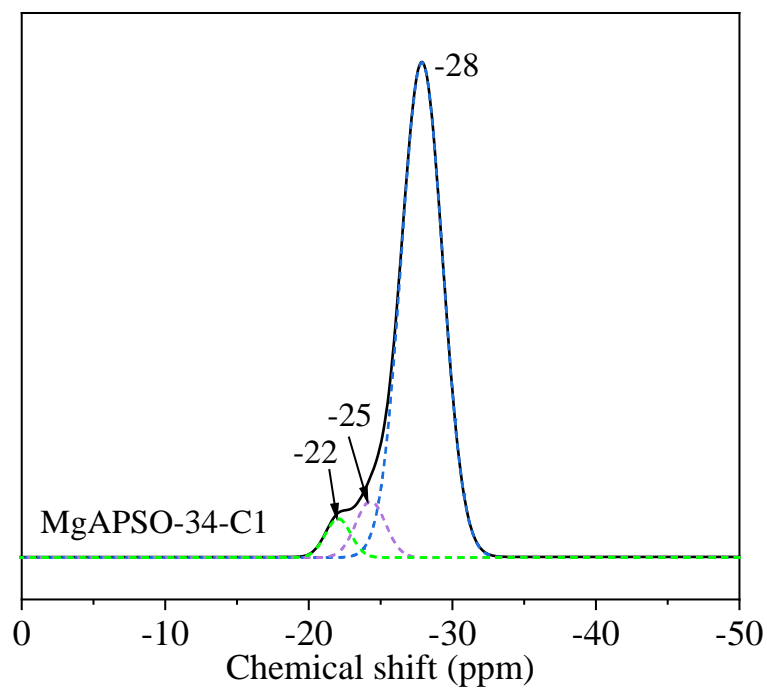


Figure S3. ^{31}P MAS NMR spectra of the calcined MgAPSO-34-C1.

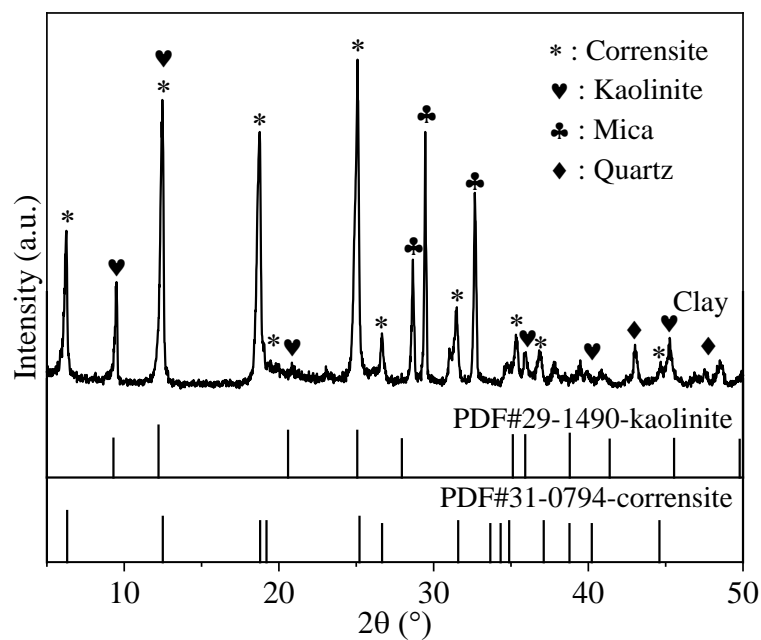


Figure S4. Powder XRD patterns of natural magnesium-rich clay mineral with atomic percentage of Mg, Al, and Si of 41.8, 22.6, and 35.6, respectively.

Table S1. Deconvolution results of the ^{31}P MAS NMR spectra of MgAPSO-34-C1, C2, and M1 via the normalized peak areas of the different P species

Sample	P(4Al, 0Mg)	P(3Al, 1Mg)	P(2Al, 2Mg)
	–28 ppm	–25, –22 ppm	–18 ppm
MgAPSO-34-C1	91.10%	8.90%	0
MgAPSO-34-C2	80.43%	17.01%	2.56%
MgAPSO-34-M1	90.61%	9.39%	0

Table S2. Deconvolution results of the ^{29}Si MAS NMR spectra of MgAPSO-34-C2 and SAPO-34-M1 via the normalized peak areas of the different Si species

Sample	Si(OH) or Si(OH) $_2^a$	Si(4Al)	Si(3Al)	Si(2Al)	Si(1Al)	Si(0Al)
	–85 ppm	–91 ppm	–97 ppm	–102 ppm	–108 ppm	–112 ppm
MgAPSO-34-C2	11.58%	16.77%	50.55%	11.06%	10.04%	0
MgAPSO-34-M1	4.50%	27.28%	39.88%	26.41%	0.55%	1.39%

$^a(\text{AlO})_3\text{Si}(\text{OH})$ or $(\text{SiO})(\text{AlO})\text{Si}(\text{OH})_2$

Table S3. Detailed CMT0 results of the four catalysts (400°C, 0.15 h⁻¹, 0.1 MPa)

Sample	Conv./%	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	C ₄ H ₈	C ₄ H ₁₀	C ₅ ⁺	C ₂ ⁼ + C ₃ ⁼
SAPO-34	77.79	1.64	48.27	0.36	30.27	1.19	9.07	2.14	6.22	78.54
MgAPSO-34-C1	99.68	1.39	44.67	0.22	37.03	0.88	6.39	2.20	5.82	81.70
MgAPSO-34-C2	61.76	1.16	40.62	0.14	40.18	0.93	6.37	2.62	6.44	80.81
MgAPSO-34-M1	51.90	1.89	43.68	0.22	36.75	0.62	7.27	3.71	4.47	80.43