



# A novel route to synthesize SAPO-11 molecular sieves with a high external surface area in the presence of ethylene glycol and supercritical carbon dioxide for 1-octene hydroisomerization to dimethylhexanes



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## ABSTRACT

The article proposes a novel and eco-friendly method for synthesizing SAPO-11 in ethylene glycol (EG) and supercritical carbon dioxide (ScCO<sub>2</sub>). The method incorporates ScCO<sub>2</sub> into EG to decrease the solubility of SAPO-11 precursors in EG and thereby forms a highly supersaturated solution of SAPO-11 precursors. The as-synthesized SAPO-11 possesses smaller particles, a larger external surface area, and a larger number of acid sites than the SAPO-11 synthesized in EG and the SAPO-11 synthesized in water and ScCO<sub>2</sub>, respectively. These advantages of the as-synthesized SAPO-11 endow the corresponding catalyst with superior dibranched isomer selectivity and low cracking selectivity during 1-octene hydroisomerization.

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## 1. Introduction

Hydrocarbon hydroisomerization is crucial for petroleum refining processes [1]. The branched isomers produced via hydroisomerization reduce the pour point of lubricant oils [2], improve the viscosity-temperature of diesel, and increase the octane number of gasoline [3–5]. Pt/SAPO-11, as a bifunctional catalyst that contains mild acidic sites and metallic sites, shows superior performance for the hydroisomerization of hydrocarbons [6–8]. As a material for silicoaluminophosphate molecular sieves, SAPO-11 crystals with an AEL zeotype structure [9] and a pore opening of  $0.39 \times 0.63$  nm consist of elliptical ten-membered rings [10]. However, conventional Pt/SAPO-11 catalysts with micropores and large particles mainly produce monobranched isomers with low octane numbers [11], limiting their application for improving the octane number of gasoline [12]. Pt/SAPO-11 catalysts with larger external surface areas possess a larger number of active sites than the conventional Pt/SAPO-11 [13]. Therefore, significant efforts have been devoted to enhancing the external surface area of SAPO-11. Blasco [14] noted that SAPO-11 with small particles could be obtained using hexadecylamine as a surfactant. Verma [15] proposed a route to synthesize hierarchically porous SAPO-11 with a high external surface area using octadecyldimethyl (3-trimethoxysilyl)propyl

ammonium chloride as a structure-directing agent. Kim [16] synthesized mesoporous SAPO-11 by carbon templating. However, a green synthesis process requires a minimum of templates and surfactants. Thus, a novel and eco-friendly route for synthesizing SAPO-11 with greater external surface area and small particles should be pursued.

Supercritical carbon dioxide (ScCO<sub>2</sub>), with the advantages of being nontoxic, inexpensive, and environmentally benign, is regarded as a green solvent [17–19]. Zhu [20] synthesized TS-1 molecular sieves with a high Ti content using ScCO<sub>2</sub>. Wang [21] synthesized Me (Me = Fe, Co)-substituted aluminophosphates, AlPO-5, with a small number of mesopores in CO<sub>2</sub>-in-water emulsions. Sun [22] synthesized silicalite-1 and ZSM-5 with a high silica content and low BET surface area in CO<sub>2</sub>-in-water emulsions. So far, the synthesis of silicoaluminophosphate molecular sieves in the presence of ScCO<sub>2</sub>, to which this investigation is addressed, has not been reported.

Here, we propose a novel route without any surfactants to synthesize SAPO-11 with smaller particles, larger external surface areas, a larger number of Brønsted acid sites, and more mesopores in the presence of ScCO<sub>2</sub> and ethylene glycol (EG) in comparison with the conventional SAPO-11. The Pt/as-synthesized SAPO-11 was assessed using the dibranched hydroisomerization reaction of 1-octene and compared with the Pt/SAPO-11 catalysts synthesized in EG and in ScCO<sub>2</sub>-water, respectively.

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## 2. Experimental

### 2.1. Materials

Phosphoric acid ( $\text{H}_3\text{PO}_4$ , 85 wt.%; Beijing Chemical Plant), tetraethyl orthosilicate (TEOS, 99 wt.%; Aladdin), di-n-propylamine (DPA, 99.5 wt.%; J&K Scientific Ltd.), aluminum isopropoxide (IPA, 98 wt.%; J&K Scientific Ltd.), ethylene glycol (EG, 99 wt.%; Alfa Aesar), chloroplatinic acid ( $\text{H}_2\text{PtCl}_6$ , 37 wt.%, Aladdin), 1-octene ( $\text{C}_8\text{H}_{16}$ , 98 wt.%; Aladdin), carbon dioxide, and distilled water were used without further purification.

### 2.2. Synthesis of different SAPO-11 molecular sieves

#### 2.2.1. Synthesis of SAPO-11-E/S in EG and $\text{ScCO}_2$

First, 6.25 g of IPA was dissolved in 51.70 g of EG under stirring for 1 h. Second, 7.62 g of DPA and 6.22 g of  $\text{H}_3\text{PO}_4$  were added to the solution and stirred for 2 h. Third, 0.64 g or 1.28 g of TEOS was added under stirring, and the synthesized gel was formed after 1.5 h. The molar composition of the synthesized gel was as follows:  $1.0 \text{ Al}_2\text{O}_3 : x \text{ SiO}_2 : 1.8 \text{ P}_2\text{O}_5 : 5.0 \text{ DPA} : 55.0 \text{ EG}$  ( $x = 0.2, 0.4$ ). Fourth, the synthesized gel was transferred into a 100 mL Teflon-coated autoclave and pressurized with carbon dioxide up to 900 psi. Fifth, the autoclave was heated at 200 °C for 144 h, and the pressure was increased autogenously to 1800 psi. Finally, after the temperature of the autoclave fell to 25 °C, the product was centrifuged, washed with distilled water, dried at 120 °C for 12 h, and calcined at 600 °C for 6 h. The as-synthesized SAPO-11 samples were named SAPO-11-E/S-0.2 and SAPO-11-E/S-0.4.

#### 2.2.2. Conventional solvothermal synthesis of SAPO-11-E

The solvothermal synthesis of SAPO-11 was carried out using the same procedure for SAPO-11-E/S, except for the absence of carbon dioxide. The as-synthesized SAPO-11 samples were named SAPO-11-E-0.2 and SAPO-11-E-0.4.

#### 2.2.3. Synthesis of SAPO-11-W/S in water and $\text{ScCO}_2$

First, 6.25 g of IPA was dissolved in 10.80 g of distilled water. After it was stirred for 1 h, 3.52 g of  $\text{H}_3\text{PO}_4$  and 1.83 g of DPA were added to the mixture and stirred for 2 h. Then 0.64 g or 1.28 g of TEOS was added under stirring, and the synthesized gel was formed after 1.5 h. The molar composition of the synthesized gel was as follows:  $1.0 \text{ Al}_2\text{O}_3 : x \text{ SiO}_2 : 1.0 \text{ P}_2\text{O}_5 : 1.2 \text{ DPA} : 40.0 \text{ H}_2\text{O}$  ( $x = 0.2, 0.4$ ). The obtained synthesized gel was transferred into a 100 mL Teflon-coated autoclave and pressurized with carbon dioxide up to 900 psi. The autoclave was heated at 200 °C for 24 h, and the pressure was increased autogenously to 1800 psi. Finally, after the autoclave was cooled to room temperature, the product in the autoclave was centrifuged, washed with distilled water, dried at 120 °C for 12 h, and calcined at 600 °C for 6 h. The as-synthesized SAPO-11 samples were named SAPO-11-W/S-0.2 and SAPO-11-W/S-0.4.

#### 2.2.4. Conventional hydrothermal synthesis of SAPO-11-W

The hydrothermal synthesis of SAPO-11 was carried out using the same procedure as for SAPO-11-W/S, except for the absence of carbon dioxide. The as-synthesized SAPO-11 with a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 0.4 was named SAPO-11-W-0.4.

### 2.3. Catalyst preparation

The synthesized SAPO-11 molecular sieves were extruded, manually crushed, and sieved through 20–40 meshes. Then, these shaped SAPO-11 samples were supported with 0.5 wt.% Pt after being impregnated with a solution of  $\text{H}_2\text{PtCl}_6$ . The Pt/SAPO-11

catalysts were obtained after being dried at 120 °C for 5 h and calcined at 500 °C for 4 h.

### 2.4. Characterizations

X-ray powder diffraction (XRD) studies of these SAPO-11 samples were conducted on a Bruker D8 Advance diffractometer with  $2\theta$  ranging from 5° to 50°, using Cu K $\alpha$  radiation and working at 30 mA and 40 kV.

The morphologies and particle sizes of SAPO-11 were observed via scanning electron microscopy, which was performed on a HITACHI SU8010 using Cu K $\alpha$  radiation and working at 1 kV.

The  $\text{N}_2$  adsorption–desorption experiments were recorded on a Micromeritics ASAP 2420. The Brunauer–Emmett–Teller method was used to calculate the surface area of the SAPO-11 samples, and the  $t$ -plot method was used to obtain the pore volumes of the SAPO-11 samples. The mesopore sizes of the SAPO-11 samples were obtained by the Barret–Joyner–Halenda method. Before the measurements, the SAPO-11 samples were pretreated under vacuum ( $1.3 \times 10^{-3}$  Pa) at 250 °C for 5 h to degas them.

The intercrystalline mesopore structures of the SAPO-11 samples and the sizes of Pt nanoparticles in the Pt/SAPO-11 catalysts were observed by transmission electron microscope (TEM) analysis, which was carried out on an FEI Tecnai G2 F20 machine.

The elemental compositions of the SAPO-11 samples were detected by X-ray fluorescence spectroscopy (XRF) on an Axios-mAX instrument.

Pyridine adsorbed infrared (Py-IR) spectra were recorded on a Bruker Tensor II to measure the acidity of the SAPO-11 samples, using almost the same weight and area as for the sample pellet. The SAPO-11 samples were dried under vacuum, purified at 400 °C for 1 h, and adsorbed with pyridine for 15 min under vacuum ( $1.3 \times 10^{-3}$  Pa) after cooling to room temperature. Then the SAPO-11 samples with pyridine were degassed at 200 and 300 °C, respectively. Finally, the Py-IR spectra were obtained after the background was deducted.

The solid-state  $^{29}\text{Si}$  MAS-NMR experiments on the SAPO-11 samples were conducted using an Avance III 400 MHz WB solid state NMR spectrometer. The  $^{29}\text{Si}$  spectra of the SAPO-11 samples were recorded with a pulse width of 4.0  $\mu\text{s}$ , frequency of 79.5 MHz, and delay of 2.0 s.

The Pt dispersion of the Pt/SAPO-11 catalysts was determined by  $\text{H}_2$  adsorption using a classical volumetric apparatus.

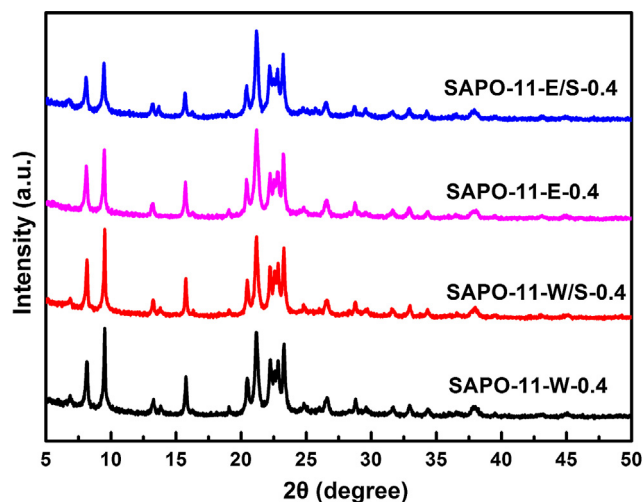


Fig. 1. XRD patterns of SAPO-11-E/S-0.4, SAPO-11-E-0.4, SAPO-11-W/S-0.4, and SAPO-11-W-0.4.

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