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# Synthesis of hierarchical SAPO-34 to improve the catalytic performance of bifunctional catalysts for syngas-to-olefins reactions



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Mengheng Wang<sup>a</sup>, Ziwei Wang<sup>a</sup>, Suhan Liu<sup>a</sup>, Runtian Gao<sup>a</sup>, Kang Cheng<sup>a,\*</sup>, Lei Zhang<sup>b</sup>, Guoquan Zhang<sup>b</sup>, Xiaojian Min<sup>b</sup>, Jincan Kang<sup>a</sup>, Qinghong Zhang<sup>a</sup>, Ye Wang<sup>a,\*</sup>

<sup>a</sup> State Key Laboratory of Physical Chemistry of Solid Surfaces, Collaborative Innovation Center of Chemistry for Energy Materials, National Engineering Laboratory for Green Chemical Productions of Alcohols, Ethers and Esters, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, People's Republic of China <sup>b</sup> State Energy Key Lab of Clean Coal Grading Conversion, Shaanxi Coal and Chemical Technology Institute Co., Ltd., Xi'an 710070, People's Republic of China

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### 1. Introduction

# ABSTRACT

Bifunctional process integrating methanol synthesis and methanol-to-olefins conversion provides a new synthetic strategy for lower olefins ( $C_2$ — $C_4$ ), whereas designing matchable zeolite components is still challenging due to the harsh reaction conditions. Here, a hierarchical SAPO-34 zeolite with a sandglass-like hollow structure is synthesized from an aluminum-rich precursor gel, which provides an abundance of crystal defects during zeolite crystallization. The bifunctional catalyst obtained by integrating the hierarchical SAPO-34 and ZnO—ZrO<sub>2</sub> oxide offers a  $C_2$ — $C_4^{--}$  selectivity of 80% at 25% CO conversion with excellent stability in syngas conversion. We demonstrate that in the presence of high-pressure hydrogen, a moderate density of acid sites is the prerequisite for obtaining high  $C_2$ — $C_4^{---}$  selectivity in syngas/methanol conversion, because the olefins are easily hydrogenated into alkanes by excessive Brønsted acid sites. The hierarchical architecture significantly prolongs the lifetime of bifunctional catalysts, by facilitating  $C_2$ — $C_4^{----}$  desorption and slowing down the coking rate.

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Lower olefins  $(C_2-C_4)$  are key building blocks and have wide applications in the chemical industry, ranging from packing materials to plastics, solvents, and coatings [1,2]. Lower olefins are mainly produced through the thermal cracking of naphtha or fluid catalytic cracking (FCC) [3]. In recent years, dehydrogenation of ethane and propane has also been commercialized for producing ethene and propene [4,5]. Because of the increasing global population, together with rising living standards, the demand for lower olefins is expected to increase steadily [6]. This situation has been driving numerous efforts to develop alternative and more sustainable processes for the production of lower olefins. In this context, the conversion of syngas (H<sub>2</sub>/CO), which can be produced from natural gas, coal, biomass, and even CO<sub>2</sub> and organic waste, to  $C_2-C_4^$ has recently drawn great attention in both academia and industry [6–10].

The traditional process for direct conversion of syngas to lower olefins is Fischer–Tropsch (FT) synthesis using Fe catalysts. However, the hydrocarbon products of FT synthesis follow the

\* Corresponding authors. E-mail address: kangcheng@xmu.edu.cn (K. Cheng).

Anderson-Schulz-Flory (ASF) distribution, and the maximum selectivity for  $C_2$ — $C_4$  hydrocarbons is around 60% [11–13]. Recently, significant progress has been made on FT catalysts through using promoters or design of specific catalyst structures [14–21]. Zhai et al. developed a Zn–Na modulated  $Fe_5C_2$  catalyst for olefin synthesis, where Zn served as the structural promoter and Na altered the electronic structure [14]. This well-designed catalyst rendered the catalyst more than 79% selective for olefins in hydrocarbons, and the selectivity for  $C_2-C_4^-$  was around 30%. Jiang et al. reported a zeolite capsule catalyst with a core (Fe/ SiO<sub>2</sub>)-shell (Silicalite-1) structure, which exhibited 35% selectivity for  $C_2$ — $C_4^{-}$  in hydrocarbons [15]. Torres Galvis et al. reported that iron nanoparticles (promoted by sulfur and sodium) dispersed on inert supports such as  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and carbon nanofibers resulted in superior selectivity, around 60%, to  $C_2$ — $C_4^{-}$  [16,17]. Zhong et al. found that Co<sub>2</sub>C nanoprisms with exposed facets of (101) and (020) exhibited high selectivity toward the formation of  $C_2 - C_4^{-1}$ (60.8%) [18,19]. Generally, the selectivity for  $C_2 - C_4^{-1}$  by the FT route reported in the literature is still governed by the ASF distribution due to the polymerization mechanism.

Another newly developed route for direct transformation of syngas to  $C_2$ — $C_4^-$  is bifunctional catalysis, coupling methanol/ketene synthesis and C—C coupling reactions in one catalyst [22–

25]. This idea is inspired by one of the commercialized processes for the production of  $C_2$ — $C_4$ , which separates methanol synthesis from syngas and methanol (or dimethyl ether, DME) to  $C_2 - C_4^{-1}$ (MTO) [8–11]. Typical bifunctional catalysts are composed of mixed oxides and zeolites, which are responsible for CO activation and C-C coupling reactions, respectively. In 2016, Jiao et al. reported a bifunctional catalyst consisting of reducible ZnCrO<sub>x</sub> oxide and SAPO-34 zeolite, over which a  $C_2$ -- $C_4^{=}$  selectivity of 80% at a CO conversion of 17% was achieved [23]. Ketene (CH<sub>2</sub>CO) formed on ZnCrO<sub>x</sub> oxide was proposed as a reaction intermediate, which can be converted to  $C_2$ — $C_4^{-}$  within zeolite micropores. In parallel, our group developed a series of bifunctional catalysts composed of ZnO-ZrO<sub>2</sub> oxide and SAPO-34 (or SSZ-13) zeolite that bridged methanol synthesis and the MTO reaction, which was named the SMO route (syngas via methanol intermediate to olefin) [24,25]. The selectivity for  $C_2$ — $C_4^{-}$  could reach 87% at a CO conversion of 10%, or 77% by increasing CO conversion to 29%. Methanol and DME were confirmed to be the key reaction intermediates. These two pieces of work have set off a new wave of research for the selective synthesis of lower olefins and aromatic hydrocarbons with high selectivity [26-33], which are hardly achieved by traditional FT synthesis. Meanwhile, more kinds of oxide components other than reducible  $ZnCrO_x$  and  $ZnO-ZrO_2$  have been reported, such as MnO, ZnO, ZnAlO<sub>x</sub>, CeZrO<sub>x</sub>, InZrO<sub>x</sub>, and MoZrO<sub>x</sub> [34–38].

Compared with the emerging research on active phases for CO activation and how to combine them with zeolites, less attention has been paid to engineering zeolite structure and their characteristics under conditions of syngas conversion. It is generally accepted today that the methanol conversion in zeolites follows a hydrocarbon pool (HP) mechanism, and deactivation is caused by the formation of bulky hydrocarbons or graphitic species [26,39,40]. Although most knowledge of MTO reactions can be applied to SMO processes, we still need to consider the differences from MTO catalysts when designing matchable acidic zeolites for bifunctional catalysts (Fig. 1) [41-43]. First, syngas conversion must be conducted at high pressure to provide productivity, and the MTO reaction must be operated at high temperature to initiate the C–C coupling reaction and decrease the rate of coke formation. Thus, the typical reaction conditions for this bifunctional reaction are generally at ~400 °C and 2-5 MPa. However, in bifunctional systems, hydrogen in feedstock at high pressure can impose deep hydrogenation of lower olefins to alkanes, especially at MTO temperature and in the presence of hydrogenation components (mixed oxides and zeolites with strong Brønsted acid sites) [24,44,45]. Second, the elevated pressure might cause high surface coverage of reaction intermediates and products, or even capillary condensation of hydrocarbon products in micropore channels [46], resulting in more severe mass transfer limitation than for the MTO reaction at atmospheric pressure. A fluidized bed reactor with high throughput was considered superior to a fixed bed reactor because of its excellent heat transfer performance and good fluidity of the catalyst [47], while all the bifunctional catalysts have been tested using a fixed-bed reactor [23–38]. In this context, a zeolite component with a well-developed pore structure is indispensable for building efficient bifunctional catalysts.



Fig. 1. General differences and similarities for MTO and SMO reactions.

SAPO-34 is the most widely used catalyst for the MTO reaction and also for conversion of syngas to lower olefins via a bifunctional process, owing to its shape selectivity and the matching of sizes of its pore window with those of lower olefin molecules [39,40,47]. However, the structure of SAPO-34 is not as robust as that of ZSM-5, Beta, and Y zeolites, which can undergo acid, alkaline, and hydrothermal treatment for constructing hierarchical structure and adjusting acid properties [48,49]. Also, the synthesis of SAPO-34 with low silicon content and moderate acidity is guite difficult due to the complicated synthesis recipes and the formation of mixed crystal phases [50-52]. It remains a challenge to obtain high crystallinity of SAPO-34 with well-developed porosity and moderate acidity [53–55]. In this work, we report a simple method for synthesizing a SAPO-34 zeolite with abundant porosity and moderate acidity to match up with an oxide catalyst to achieve direct conversion of syngas to lower olefins. A preoptimized  $ZnO-ZrO_2$  oxide is used as the active component of the syngasto-methanol reaction [25]. Particularly, we focus on the evolution of porosity and acidity of SAPO-34 during hydrothermal synthesis. The impact of SAPO-34 porosity and acidity on the performance of bifunctional ZnO-ZrO<sub>2</sub>/SAPO-34 is discussed in detail. We intend to provide a universal criterion for the rational design of an efficient and stable zeolite component for the emerging bifunctional processes.

# 2. Experimental

# 2.1. Catalyst preparation

The reagents used were pseudoboehmite (Al<sub>2</sub>O<sub>3</sub>, 72 wt%, Beijing Reagents Company), piperidine (99%, Aldrich), silica solution (30 wt%, Aldrich,) and tetraethylammonium hydroxide (TEAOH, 25 wt%, Aldrich). Orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>, 85 wt%), triethylamine (TEA, 99 wt%), aluminum isopropoxide (Al(OPri)<sub>3</sub>, 99 wt %), hydrofluoric acid (HF, 40 wt%), zirconium nitrate (Zr(NO)<sub>4</sub>·5H<sub>2</sub>-O), zinc nitrate (Zn(NO)<sub>2</sub>·9H<sub>2</sub>O), polyethylene glycol (PEG-6000), and citric acid were purchased from Sinopharm Chemical Reagent.

Conventional microporous SAPO-34 with different densities of acid sites was synthesized by a hydrothermal method from a gel with a molar ratio of 3.0 TEA:0.03 TEAOH:1.0 Al<sub>2</sub>O<sub>3</sub>:x SiO<sub>2</sub>:1.0  $P_2O_5$ :50  $H_2O$  (x = 0.04, 0.06, 0.07, 0.10, 0.21, 0.32, and 0.44) [52]. The as-prepared SAPO-34 zeolites were denoted as SP1(n), where *n* was the molar ratio Si/(Si + Al + P) analyzed using X-ray fluorescence (XRF). Specifically, 4.7 g pseudoboehmite was dissolved in 50 mL deionized water to form an alumina sol after stirring for 2 h. Then a certain amount of silica sol was added to the prepared alumina sol under stirring for 2 h. Next, 14.2 g TEA and 0.81 g TEAOH were added slowly under continual stirring for another 2 h. After that, 7.3 g H<sub>3</sub>PO<sub>4</sub> was added to the prepared mixture and stirred for 12 h until a homogeneous gel mixture was attained. The gel mixture was sealed in a 200-mL Teflon-lined stainless steel autoclave and heated from room temperature to 200 °C at a rate of 2 °C min<sup>-1</sup>. The crystallization was carried out at 200 °C under autogenic pressure for 72 h. After crystallization, as-synthesized samples were obtained after centrifugal separation, washing, and drying at 100 °C for 6 h. Finally, calcination was carried out from room temperature to 550 °C at 2 °C min<sup>-1</sup> and kept at 550 °C for 6 h to remove the organic template. In this work, SP1 is the abbreviation for SP1(0.06) when x = 0.21, unless otherwise mentioned.

Hierarchical SAPO-34 was synthesized using an Al-rich method from a gel molar composition of the ratio of 6.0 TEA:0.06 TEAOH:mAl<sub>2</sub>O<sub>3</sub>:0.21 SiO<sub>2</sub>:1.0 P<sub>2</sub>O<sub>5</sub>:50 H<sub>2</sub>O) and denoted as SP2 (m = 1.2) and SP3 (m = 1.5), respectively. The method of hydrothermal synthesis and thermal treatment for SP2 and SP3 was the same for SP1. To investigate the crystallization of SP3, solid zeolites with different crystallization times were collected. AlPO-34 without silicon was synthesized by a hydrothermal method from a gel with a molar ratio of 2.0 piperidine:1.0 Al<sub>2</sub>O<sub>3</sub>:1.0 P<sub>2</sub>O<sub>5</sub>:1.0 HF:100 H<sub>2</sub>O [50]. The gel mixture was prepared by successive addition of H<sub>3</sub>PO<sub>4</sub>, HF, and piperidine to a suspension of Al(OPri)<sub>3</sub> in water with constant stirring. The crystallization was carried out at 190 °C under autogenic pressure for 96 h. Finally, calcination was carried out from room temperature to 550 °C at 2 °C min<sup>-1</sup> and kept at 550 °C for 6 h to remove the organic template.

Nanosheet SAPO-34 was synthesized from a gel molar composition in the ratio 4.0 TEAOH:1.0 Al<sub>2</sub>O<sub>3</sub>:0.3 SiO<sub>2</sub>:2.0 P<sub>2</sub>O<sub>5</sub>:50 H<sub>2</sub>O:0.0016 PEG-6000 [56] and denoted as ns-SP. Pseudoboehmite (2.5 g) and silica sol (1.0 g) were dissolved in a mixture of 36.9 g TEAOH and 9.0 g H<sub>2</sub>O. Subsequently, 0.7 g PEG-6000 and 8.4 g H<sub>3</sub>PO<sub>4</sub> was added slowly. After being stirred for 12 h, the homogeneous mixture was transferred a 200-mL Teflon-lined stainless steel autoclave and heated from room temperature to 180 °C at 2 °C min<sup>-1</sup>. The crystallization was carried out at 180 °C under autogenic pressure for 72 h. After crystallization, as-synthesized samples were obtained after centrifugal separation, washing, and drying at 120 °C for 6 h. Finally, calcination was carried out from room temperature to 550 °C at 2 °C min<sup>-1</sup> and kept at 550 °C for 6 h to remove the organic template.

Zn-doped ZrO<sub>2</sub> (ZnO–ZrO<sub>2</sub>) was synthesized by a reported solgel method with a Zn/Zr ratio of 1:12 (at/at) [25]. Specifically, 8.6 g Zr(NO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O, 0.5 g Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, and 7.5 g citric acid were dissolved in 100 mL deionized water. The mixture was evaporated at 90 °C until a viscous gel was obtained. Then the mixture was heated to 180 °C for 3 h and calcined at 500 °C in air for 5 h. The bifunctional catalyst composed of ZnO–ZrO<sub>2</sub> and SAPO-34 was prepared by a physical mixing method in an agate mortar for 10 min. The mass ratio of ZnO–ZrO<sub>2</sub> and SAPO-34 was fixed at 1:2 in this work. The mixture powders were pressed, crushed and sieved to granules of 30–60 meshes (grains, 250–600 µm) before reaction.

#### 2.2. Catalyst characterization

X-ray powder diffraction (XRD) patterns were recorded on a Rigaku Ultima IV diffractometer. The CuKa radiation  $(\lambda = 0.15406 \text{ nm})$  generated at 40 kV and 30 mA was used as the X-ray source. The relative crystallinity of SAPO-34 was normalized by integrating the peak area at  $2\theta = 9.5^{\circ}$ . The mean size of ZnO–ZrO<sub>2</sub> crystallite was estimated by the Scherrer equation using a [0 1 1] tetragonal ZrO<sub>2</sub> XRD peak at  $2\theta$  = 30.27°. N<sub>2</sub> physisorption measurements were carried out on a Micromeritics Tri-Star II 3020 surface area analyzer. Prior to N<sub>2</sub> adsorption, the sample was degassed under vacuum at 150 °C for 3 h. Scanning electron microscopy (SEM) measurements were performed on a Hitachi S-4800 operated at 15 kV. The sample was dispersed ultrasonically in ethanol for 10 min and then was dropped onto a silicon pellet, followed by drying for 30 min. Transmission electron microscopy (TEM) measurements were carried out on a Phillips Analytical FEI Tecnai20 electron microscope operated at an acceleration voltage of 200 kV. The sample was dispersed ultrasonically in ethanol for 10 min, and a drop of solution was deposited onto a carboncoated copper grid.

NH<sub>3</sub> temperature-programmed desorption (NH<sub>3</sub>-TPD) measurements were performed on a Micromeritics AutoChemII 2920 instrument. Typically, the sample was pretreated in a quartz reactor with a high-purity He flow at 400 °C for 1 h. The adsorption of NH<sub>3</sub> was performed at 100 °C in an NH<sub>3</sub>—He mixture (10 vol% NH<sub>3</sub>) for 1 h, and after purging with He for an additional 1 h, the temperature was raised from 50 to 600 °C at 10 °C min<sup>-1</sup>. The NH<sub>3</sub>-TPD profile was recorded by a mass spectrometer with a signal of *m*/ *z* = 16. Fourier-transform infrared (FT-IR) studies of adsorbed NH<sub>3</sub> were carried out on a Nicolet 6700 instrument equipped with an MCT detector. The sample was pressed into a self-supported wafer and placed in an *in situ* IR cell. After being pretreated under vacuum at 400 °C for 30 min, the sample was cooled to 100 °C. Then NH<sub>3</sub> was introduced at 100 °C for 30 min. FT-IR spectra were recorded after gaseous or weakly adsorbed NH<sub>3</sub> molecules were removed by evacuation at 100 °C. The FT-IR studies of adsorbed pyridine were also carried out on the same infrared instrument. After being treated under vacuum at 400 °C for 60 min, the sample was cooled to 100 °C. Then pyridine vapor was introduced at 100 °C for 10 min. FT-IR spectra were recorded after gaseous or weakly adsorbed pyridine molecules were removed by evacuation at 100 °C. C<sub>3</sub>H<sub>6</sub>-TPD and C<sub>3</sub>H<sub>8</sub>-TPD were carried out for SAPO-34 zeolites on a Micromeritics AutoChemII 2920 instrument. In brief. the zeolite was first treated at 400 °C in a He flow for 3 h. Then the adsorption of gaseous  $C_3H_6$  or  $C_3H_8$  was performed at 50 °C for 1 h. After purging with He for an additional 1 h, the temperature was raised from 50 to 700 °C at 10 °C min<sup>-1</sup>. The C<sub>3</sub>H<sub>6</sub>-TPD and C<sub>3</sub>H<sub>8</sub>-TPD profiles were recorded by a mass spectrometer with a signal of m/e = 41 (C<sub>3</sub>H<sub>6</sub>) or m/e = 43 (C<sub>3</sub>H<sub>8</sub>).

<sup>27</sup>Al and <sup>31</sup>P MAS NMR measurements were conducted using a Varian Infinity plus AS400 spectrometer (Varian Inc.). <sup>27</sup>Al MAS NMR spectra were recorded using a one-pulse sequence with a spinning rate of 12 kHz. One hundred scans were accumulated with a  $\pi/8$  pulse width of 0.75  $\mu$ s and a 2-s recycle delay. The chemical shifts were referenced to (NH<sub>4</sub>)Al(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O at -0.4 ppm. <sup>31</sup>P MAS NMR spectra were recorded using highpowered proton decoupling with a spinning rate of 12 kHz. Forty-eight scans were accumulated with a  $\pi/4$  pulse width of 2 µs and a 10-s recycle delay. The chemical shifts were referenced to 85% H<sub>3</sub>PO<sub>4</sub> at 0 ppm. XRF spectroscopy was carried out with a Panalytical Axios-Petro XRF instrument with rhodium target (50 kV, 50 mA). X-ray photoelectron spectroscopy (XPS) was carried out with a Quantum 2000 Scanning ESCA Microprobe instrument (Physical Electronics) with an AlKa radiation source (1846.6 eV).

The amount of generated coking species in used catalysts was determined by thermal gravimetric (TG) analysis on a TGA Q500 instrument. The temperature was first raised to 150 °C for 30 min to remove physically adsorbed water, followed by raising the temperature to 900 °C at 10 °C min<sup>-1</sup> under air flow. The occluded organic species of the used catalysts were analyzed by GC-MS (Agilent 7890A/5975C) with a capillary column of HP-5, an FID detector, and a mass-sensitive detector. A HF solution (40 wt%) was used to digest the used catalysts, after which the organic compounds were extracted using CH<sub>2</sub>Cl<sub>2</sub>. Diffuse reflectance UV/vis spectra (DR UV/vis) were recorded with a Varian Cary5000 spectrophotometer to characterize the deposited coking species on the catalysts.

#### 2.3. Catalyst evaluation

The syngas conversion was performed on a high-pressure fixedbed reactor built by Xiamen HanDe Engineering Co. Typically, 0.50 g catalyst with grain size 250–600  $\mu$ m was loaded into a titanium reactor (inner diameter 8 mm). Syngas with a H<sub>2</sub>/CO ratio of 2:1 and a pressure of 3.0 MPa was introduced into the reactor. Nitrogen with a concentration of 4.0 vol% in the syngas was used as an internal standard for the calculation of CO conversion. The temperature was raised to typically 400 °C to start the reaction. The catalytic reaction for methanol conversion was performed in the same reactor. Typically, 0.34 g catalyst was first activated at 400 °C in a carrier gas (N<sub>2</sub> or H<sub>2</sub>, 30 mL min<sup>-1</sup>) for 1 h. Then liquid methanol with WHSV was fed by a Series II pump together with the carrier gas (N<sub>2</sub> or H<sub>2</sub>, 30 mL min<sup>-1</sup>) to start the reaction. For both reactions, products were analyzed by an online GC equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The TDX-01 packed column was connected to the TCD, while the RT-Q-BOND-PLOT capillary column was connected to the FID. The selectivity presented in this work was calculated on a molar carbon basis for CO hydrogenation without considering CO<sub>2</sub>. The selectivity of CO<sub>2</sub> was calculated separately. Carbon balances were all better than 95%.

# 3. Results and discussion

# 3.1. Structure of SAPO-34 zeolites

Three SAPO-34 zeolites, denoted as SP1, SP2, and SP3, were synthesized from precursor gels with different compositions (Table 1). The XRD patterns (Fig. S1 in the Supplementary Materials) confirm that these three SAPO-34 zeolites exhibit characteristic diffraction peaks of pure CHA structure. SP1, with typical Al/P ratio of 1.0 (at/at), shows the best crystallinity among three zeolites. The SEM and TEM images suggest that all the zeolites possess characteristic cubic-like morphology with particle sizes ranging from 1 to 4  $\mu$ m (Fig. 2). Differently from the conventional microporous SP1 crystals with a smooth crystal surface, SP2 and SP3 zeolites synthesized via an Al-rich method exhibit hollow structures like a sandglass inside the crystal. The hollow structures can provide the zeolite with both intracrystalline mesoporosity and macroporosity. However, these porosities are created at the expense of microporosity to some extent, which is in line with XRD results (Fig. S1).

N<sub>2</sub> physisorption was used to determine the porosity of asprepared SAPO-34 zeolites (Fig. 3a). The porosities of these three SAPO-34 zeolites are listed in Table S1. SP1 displays the characteristic type I N<sub>2</sub> isotherms, while SP2 and SP3 zeolites exhibit combined I and IV isotherms with hysteresis loops in the region  $0.45 < P/P_0 < 0.95$ , indicating the existence of a hierarchical porous system [57]. Pore size distribution curves derived from the adsorption branches prove the existence of mesopores around 13 nm in SP2 and SP3 zeolites (inset in Fig. 3a). Compared with isotherms of SP1, more significant uptakes were observed near saturation pressure in the isotherms of SP2 and SP3 zeolites, indicating the coexistence of macropores in these two samples. The BET surface area of SP3 (379 m<sup>2</sup> g<sup>-1</sup>) is close to that of SP1 (429 m<sup>2</sup> g<sup>-1</sup>), but the mesopore volume of SP3 (0.26 cm<sup>3</sup> g<sup>-1</sup>) is five times larger than that of SP1 (0.04 cm<sup>3</sup> g<sup>-1</sup>). To illuminate the structure of macropores, we carried out mercury intrusion porosimetry for asprepared SAPO-34 zeolites (Fig. 3b). The results show that the size of macropores in the SP2 and SP3 zeolites is in a wide range of 0.2-3  $\mu$ m, and the most probable pore sizes of SP2 and SP3 concentrate around 1.5 and 2.5  $\mu$ m, respectively, while SP1 zeolite only shows a small quantity of macropores corresponding to the intercrystalline macropores. These results prove the existence of macroporosity in SP2 and SP3 zeolites, which mostly originates from their intracrystalline structure (Fig. 2). Mercury intrusion porosimetry also confirms the existence of mesoporosity with pore size around 10 nm in SP2 and SP3 samples. These findings provide concrete proof that the as-prepared SP2 and SP3 zeolites possess a hierarchical structure with trimodal pores.

#### 3.2. Acidity of as-prepared SAPO-34 zeolites

The Brønsted acid sites (BAS) are assumed to be the active sites to catalyze the MTO reaction [24]. The BAS of SAPO-34 zeolite is generated by the surface bridge hydroxyl groups, which originate from protons compensating for the unbalanced electric charges due to Si incorporation into the neutral framework of AlPO-34 [58]. Even so, the density of BAS of SAPO-34 is not strictly in proportion to the silicon content, because the silicon islands may form during synthesis [59]. NH<sub>3</sub>-TPD was used to quantify the acidity densities of as-prepared SAPO-34 zeolites (Fig. 4a). Based on different desorption temperatures, the profile of NH<sub>3</sub>-TPD were deconvoluted to three peaks, which can be assigned to weak, medium, and strong acid sites [60]. The strong acid sites are probably from BAS in zeolites. Although the silicon content of three SAPO-34 zeolites ranges from 0.69 to 0.99 mmol  $g^{-1}$  (Table 1), the quantitation of the density of strong acid sites for three SAPO-34 zeolites is similar in a narrow range of 0.24–0.26 mmol g<sup>-1</sup>.

To distinguish the types of acid sites in as-prepared SAPO-34 zeolites, ammonia, with a kinetic diameter of 0.26 nm, which is smaller than pore window of SAPO-34 (0.38  $\times$  0.38 nm), was used as a probe molecule for FT-IR studies (Fig. 4b). The bands at 1457 and 1619 cm<sup>-1</sup> can be assigned to Brønsted and Lewis acid sites in the forms of -Si-OH…NH<sub>3</sub> and -M-O-M…NH<sub>3</sub>, respectively [61,62]. No significant difference in acid types can be observed between these three zeolites. Moreover, pyridine, with a kinetic diameter of 0.57 nm, was used to determine the type of acid sites on the outer surface of SAPO-34 [62]. It was found that both Brønsted and Lewis acid sites existed on the outer surfaces of microporous SP1 and hierarchical SP3 (Fig. S2). The intensity of Lewis acid sites on the outer surface of SP3 was higher than that on SP1, indicating more defective sites (probably extraframework alumina). However, the number of acid sites on the SAPO-34 surface is hard to quantify by infrared spectroscopy. Overall, these three SAPO-34 zeolites, with the densities of BAS being similar, allow us to evaluate the impact of porosity on both MTO and SMO reactions.

#### 3.3. The formation mechanism of hierarchical SAPO-34

To unveil the mechanism of formation of hollow structures with trimodal porosity, we conducted detailed investigation of SP3 samples with different crystallization times. The time-consuming experiments present growing crystallinity in a 72 h reaction, and no impure phases besides CHA structure can be found (Fig. 5a). Along with the crystallization time, the density of strong acid sites continually increased from 6 to 48 h and reached a plateau of 0.25 mmol  $g^{-1}$  (Fig. 5b). One should note that SP3 (6 h) with 18% crystallinity (Fig. 5a), which is similar to that of SP3 (18 h), exhibits almost no medium or strong acid sites (Fig. 5b). This might indicate that the crystallization process starts from the formation of AlPO-34, followed by the incorporation of silicon, which is actually supposed to be a consensus for SAPO-34 synthesis [57]. By XRF quantification, we found that the content of Si and P in the bulk phase increased steadily in the whole crystallization process, while the content of Al presented the opposite trend (Fig. 5c). Differently

Table 1

Aola	r ratio of	'Al, S	i, and	P sources in the	precursor g	gels and	the final	compositions	of obtained	l SAPO-34 zeolites.
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Zeolite	Molar composition in gel	Al content $(mmol g^{-1})^a$	Si content (mmol g <sup>-1</sup> ) <sup>a</sup>	Product composition <sup>a</sup>
SP1	1.0Al <sub>2</sub> O <sub>3</sub> :0.21SiO <sub>2</sub> :1.0P <sub>2</sub> O <sub>5</sub>	8.3	0.99	Si <sub>0.060</sub> Al <sub>0.504</sub> P <sub>0.435</sub> O <sub>2</sub>
SP2	1.2Al <sub>2</sub> O <sub>3</sub> :0.21SiO <sub>2</sub> :1.0P <sub>2</sub> O <sub>5</sub>	9.0	0.82	Si <sub>0.050</sub> Al <sub>0.544</sub> P <sub>0.405</sub> O <sub>2</sub>
SP3	$1.5Al_2O_3:0.21SiO_2:1.0P_2O_5$	9.8	0.69	$Si_{0.042}Al_{0.591}P_{0.365}O_2$

<sup>a</sup> Obtained from XRF.



Fig. 2. Morphology of SAPO-34 zeolites: (a-c) SEM images of SP1, SP2, and SP3, respectively; (d-f) TEM images of SP1, SP2, and SP3, respectively.

from the conventional recipe for synthesizing SAPO-34 with Al/ P = 1.0 (at/at), the starting precursor for SP3 contained much more Al than needed. Therefore, solidification of the products seems to start from the aluminum source, resulting from Al-rich mesoporous SP3 or mesoporous  $Al_2O_3$  at the beginning of the crystallization process (Table 2).

Based on these findings, we deem that P atoms, followed by Si atoms, gradually incorporate into the Al-rich mesoporous structure, forming a CHA structure of SAPO-34 and acid sites. In addition, the mesoporous area and volume of SP3 (72 h) before calcination (Table 2) are very close to those of its counterpart SP3 (72 h) after calcination, which means that mesoporosity has already formed before the organic template is removed. The SEM image (Fig. S3) also confirms the formation of macropores of SP3 (72 h) solid without removing the organic template. Moreover, to explore the Al distribution along the zeolite crystals, we performed additional XPS analysis for SP3 with crystallization times of 30 h and 72 h (Table S2). It was found that the Al content in the outer surface of SP3 was higher than that in the bulk, indicating that alumina species added in excess amounts were enriched on the outer surface of SP3.

To investigate the coordination environment of Al and P during crystallization, we performed solid-state MAS NMR spectroscopy for SP3 samples with different crystallization times. In <sup>27</sup>Al MAS NMR spectra (Fig. 5d), the weak and broad peak with a chemical

shift of 66 ppm indicates the presence of tetrahedral coordination aluminum atoms from Al<sub>2</sub>O<sub>3</sub> owing to the excess aluminum atoms in the precursor gel. As the crystallization proceeded, this peak disappeared after 48 h, indicating the absence of Al<sub>2</sub>O<sub>3</sub> clusters in the final SP3 catalyst (72 h). The peak with a chemical shift of 36-40 ppm arises from tetrahedral framework aluminum atoms (Al  $(OP)_4$ ) when the crystallization time is over 30 h. The small peak with a chemical shift of 12 ppm represents pentacoordinated extra-framework aluminum atoms formed by the additional coordination of one water molecule (Al(OP)<sub>4</sub>(H<sub>2</sub>O)), while that of -10 ppm is attributed to octahedral aluminum atoms formed by the additional coordination of two water molecules (Al(OP)<sub>4</sub>  $(H_2O)_2$  [63]. The peaks with a chemical shift of 12 ppm existed in the whole crystallization process even after 72 h of crystallization, indicating the existence of extra-framework Al species. The spectra of <sup>31</sup>P MAS NMR (Fig. 5e) display two distinct peaks at around -11 and -29 ppm. The peak at -11 ppm can be ascribed to phosphorus atoms in amorphous aluminophosphate materials, and the peak at -29 ppm can be attributed to framework (P (OAl)<sub>4</sub>) species [63,64]. After 48 h of crystallization, most of the P atoms incorporate into the SAPO-34 structure. These findings further confirm the good crystallinity of SP3 with a hierarchical structure, and a small fraction of aluminum source added in excess amounts was present as extra-framework Al species, such as pentacoordinated aluminum atoms.



**Fig. 3.** (a) N<sub>2</sub> physisorption analysis and Barrett–Joyner–Halenda (BJH) pore size distributions derived from the adsorption branches of the isotherms (inset). (b) Pore size distribution determined by mercury intrusion porosimetry of as-prepared SAPO-34 zeolites.

Based on these results, we propose a formation mechanism for SP3 with a hierarchical structure, in contrast to that for conventional microporous SP1 (Fig. 5f). In the crystallization process, cubic SAPO-34 crystals are generated from amorphous aggregates or nanocrystals in the presence of the organic template. With a typical Al/P ratio of 1.0, a smooth cubic SAPO-34 with a regular array of Al, P, and Si can be produced, while in the presence of an excess Al source (Al/P = 1.5), more crystal defects in the form of terminal groups are induced, leading to the formation of both mesopores and macropores even before the organic template is removed. After calcination, a SAPO-34 with a hierarchical structure, good crystallinity, and moderate acidity can be obtained.

# 3.4. Structure of bifunctional ZnO-ZrO<sub>2</sub>/SAPO-34

X-ray diffraction measurements for ZnO–ZrO<sub>2</sub> and pure ZnO reveal the formation of tetragonal ZrO<sub>2</sub>, and no obvious ZnO phase can be detected (Fig. S4). The mean size of ZnO–ZrO<sub>2</sub> particles, estimated by TEM, is 7.0 nm with a narrow distribution (Fig. 6a). The fringe spacings of 0.295 and 0.257 nm can be attributed to the (011) and (002) planes of tetragonal ZrO<sub>2</sub> (Fig. 6b). No fringe spacings belonging to hexagonal ZnO could be found over HRTEM images. The ZnO–ZrO<sub>2</sub> catalyst was also analyzed using STEM coupled with EDX to confirm the distribution of Zn species in ZrO<sub>2</sub>. Although the HAADF-STEM image could not provide a clear contrast difference between Zn and Zr, an overlapping of Zn and Zr by EDX mapping can be observed (Fig. 6c–e), indicating a uniform distribution of Zn species in ZrO<sub>2</sub>. The results of XRD and electron microscopy suggest that a ZnO–ZrO<sub>2</sub> solid solution might be formed with low Zn content (Zn/Zr = 1:12). SAPO-34 zeolites with



Fig. 4. (a)  $NH_3$ -TPD profiles and (b)  $NH_3$ -IR spectra of as-prepared SAPO-34 zeolites with different porosity.

different porosity were then integrated with the ZnO–ZrO<sub>2</sub> catalyst for the SMO reaction. The SEM and TEM images of the ZnO–ZrO<sub>2</sub>/SP1 catalyst clearly show the ZnO–ZrO<sub>2</sub> aggregates well dispersed on the surface of cubic SP1 zeolite (Fig. 6f and g), providing a physical interaction between the two components without disturbing their chemical properties.

# 3.5. Impact of acid density and porosity on catalysis

The densities of BAS of microporous SP1(n) zeolites without mesopores and macropores were well controlled by silicon content in the precursor gels (Table S3 and Fig. S5), which allowed us to investigate the effect of acid density on the performance of bifunctional catalysts in the conversion of syngas (Fig. 7 and Table S4). The ZnO–ZrO<sub>2</sub> and SAPO-34 wt ratio was fixed at 1/2, which was preoptimized (Table S5). The ZnO-ZrO<sub>2</sub>/AlPO-34 catalyst without BAS displays the lowest CO conversion, accompanied by 88% selectivity of methanol and DME. The formation of methanol and DME from syngas is strongly restricted by thermodynamics at high temperature. As the densities of BAS increased, the CO conversion increased significantly from 5% to 30%, along with a decrease in the selectivity of methanol/DME. Because the BAS cannot catalyze CO hydrogenation, the significant increase in CO conversion should be attributed to the thermodynamic driving force because of the rapid consumption of methanol/DME to form lower olefins by acidic zeolites. The selectivity of  $C_2$ — $C_4^=$  exhibited a volcano curve. Only if the acid densities were in a narrow range could we obtain both high activity and  $C_2 - C_4^{-}$  selectivity. For example, the selectivity of  $C_2$ — $C_4^{-}$  could reach 80% at CO conversion of 24% when the



**Fig. 5.** Physicochemical properties of SP3 with different crystallization times: (a) XRD patterns and relative crystallinities in parentheses; (b) NH<sub>3</sub>-TPD profiles; (c) element distribution (total content of Al, P, and Si is normalized to 100%) in the bulk vs. crystallization time; (d) <sup>27</sup>Al MAS NMR spectra; (e) <sup>31</sup>P MAS NMR spectra; (f) proposed crystallization mechanisms of SP1 (Al/P = 1.0) and SP3 (Al/P = 1.5) zeolites with different porosities.

Table 2	
The relative crystallinity, pore volume, and surface characteristics of SP3 zeolites with different crystallization times.	

Time (h)	Relative crystallinity (%) <sup>a</sup>	Al content (mmol g <sup>-1</sup> ) <sup>b</sup>	$S_{total}$ $(m^2 g^{-1})^c$	$S_{ m micro} \ (m^2 g^{-1})^{ m d}$	$S_{meso}$ $(m^2 g^{-1})^d$	$(\mathrm{cm}^3\mathrm{g}^{-1})^\mathrm{e}$	$V_{ m micro}$ $( m cm^3 g^{-1})^{ m d}$	$V_{\rm meso}$ $({\rm cm}^3 {\rm g}^{-1})^{\rm f}$
6	18	15	253	20	233	0.57	0	0.57
18	18	14	299	63	236	0.41	0.02	0.39
30	41	12	325	103	222	0.37	0.10	0.27
48	80	11	342	227	115	0.36	0.11	0.25
72	100	9.8	379	278	101	0.39	0.13	0.26
72 <sup>g</sup>	_	_	94	4	90	0.20	0	0.20

<sup>a</sup> Obtained from XRD.

<sup>b</sup> Obtained from XRF.

<sup>c</sup> BET surface area.

<sup>d</sup> Micropore surface area, mesopore surface area, and micropore volume evaluated by the *t*-plot method.

<sup>e</sup> Single point desorption total pore volume of pores,  $P/P_0 = 0.99$ .

<sup>f</sup> Pore volume for mesopores evaluated by the BJH method.

<sup>g</sup> Represents as-synthesized samples without calcination.

density of BAS was 0.22 mmol g<sup>-1</sup>. However, a further increase in the acid density was detrimental to the selectivity of  $C_2-C_4^-$  and resulted in the formation of  $C_2-C_4$  paraffins.

NH<sub>3</sub>-TPD suggests similarities of acid density and strength among SP1, SP2, and SP3, and therefore allows us to investigate the role of porosity in both SMO and MTO reactions. The  $C_2-C_{\mp}^-$ 



**Fig. 6.** Structures of ZnO–ZrO<sub>2</sub> and ZnO–ZrO<sub>2</sub> combined with SAPO-34. (a) TEM image of ZnO–ZrO<sub>2</sub> with particle size distribution. (b) HRTEM image of ZnO–ZrO<sub>2</sub>. (c-e) HAADF-STEM images of ZnO–ZrO<sub>2</sub>. (f) SEM image of ZnO–ZrO<sub>2</sub>/SP1. (g) TEM image of ZnO–ZrO<sub>2</sub>/SP1. Yellow arrows mark ZnO–ZrO<sub>2</sub> aggregates on the SP1 surface.

selectivity for three bifunctional catalysts composed of different SAPO-34 zeolites is around 75% at CO conversion of ~30% (Fig. 8a), indicating that the initial catalytic performance of our bifunctional catalysts is mainly dependent on zeolite acidities. However, during the course of the syngas reaction, the three catalysts showed very different catalytic behavior. The ZnO-ZrO<sub>2</sub>/SP1 with microporous SAPO-34 deactivated rapidly: the CO conversion decreased from 27% (10 h) to 17% (98 h), while the  $C_2$ - $C_4^{-}$  selectivity decreased from 75% (10 h) to 66% (98 h; Fig. 8a and Table S6). The ZnO–ZrO<sub>2</sub>/SP3 with hierarchical SAPO-34 shows better stability: the CO conversion decreases slightly from initial 29% (10 h) to 25% (100 h), while the  $C_2$ — $C_4^{=}$  selectivity is sustained at ~75%. Since methanol/DME have been confirmed to be the intermediates for our bifunctional catalysts [24,25], we also performed the MTO reaction over SP1, SP2, and SP3 to verify the effect of porosity. The methanol conversion and  $C_2 - C_4^{-}$  selectivity vs. time on stream (TOS) over the SAPO-34 catalysts are shown in Fig. 8b and c. Compared with the microporous SP1 catalyst, SP2 and SP3 exhibit longer lifetimes, which is in line with their performance in the SMO reaction (Fig. 8a). These findings illustrate the superiority of hierarchical SAPO-34 in both SMO and MTO reactions. Besides, the deactivation behavior of SAPO-34 catalysts in SMO and MTO of SAPO-34 catalysts is quite different. The bifunctional catalysts in the SMO reaction show much better stability (Fig. 8a) than the zeolite catalysts in the MTO reaction (Fig. 8b), hinting at a different deactivation mechanism.

The introduction of hierarchical structure significantly shortens the length of micropores and the distance between two catalyst components, thus facilitating the diffusion of methanol/DME intermediates between the ZnO–ZrO<sub>2</sub> catalyst and SAPO-34 or along the SAPO-34 micropores. To validate this point, we synthesized a small SAPO-34 (ns-SP) with a nanosheet morphology and acidity similar to that of SP1 (Figs. S6 and S7 and Table S1). With the combination with ZnO–ZrO<sub>2</sub>, ZnO–ZrO<sub>2</sub>/ns-SP and ZnO–ZrO<sub>2</sub>/SP1 showed similar initial CO conversion and the selectivity for lower olefins were very close (Fig. S8). However, like ZnO–ZrO<sub>2</sub>/SP3 (Fig. 8a), ZnO–ZrO<sub>2</sub>/ns-SP showed better stability than ZnO–ZrO<sub>2</sub>/ SP1. Therefore, the catalytic improvement in syngas conversion



**Fig. 7.** Effect of density of BAS on syngas conversion over bifunctional ZnO–ZrO<sub>2</sub>/SAPO-34 catalysts. The colored columns refer to product selectivity. The ZnO–ZrO<sub>2</sub> and SAPO-34 wt ratio was fixed at 1/2. Reaction conditions: catalyst, 0.50 g;  $H_2/CO = 2:1$ ; 3 MPa; 30 cm<sup>3</sup> min<sup>-1</sup>; time on stream 10 h; 400 °C.  $C_2-C_4^{-}$ ,  $C_2-C_4^{-}$ , and  $C_{5+}$  denote  $C_2-C_4^{-}$  olefins,  $C_2-C_4$  paraffins, and hydrocarbons with carbon numbers  $\geq$  5, respectively. Detailed product selectivity including CO<sub>2</sub> is listed in Table S4.



**Fig. 8.** (a) Stability of bifunctional ZnO–ZrO<sub>2</sub>/SAPO-34 catalysts in the SMO reaction. SMO reaction conditions: catalyst, 0.50 g;  $H_2/CO = 2:1$ ; 30 mL min<sup>-1</sup>; 3 MPa; time on stream 100 h; 400 °C. (b) CH<sub>3</sub>OH conversion of the MTO reaction over SAPO-34 zeolites with different porosity. (c) Selectivity of  $C_2-C_4$  olefins in the gaseous hydrocarbon product of the MTO reaction. MTO reaction conditions: catalyst, 0.34 g; flow N<sub>2</sub>, 30 cm<sup>3</sup>min<sup>-1</sup>; liquid CH<sub>3</sub>OH, 0.01 cm<sup>3</sup> min<sup>-1</sup>; 0.1 MPa; 400 °C.

when SP2 and SP3 are used can eventually be attributed to the enhanced mass transport properties.

The CO<sub>2</sub> selectivity for all bifunctional catalysts was in a narrow range of 40–43%, and independent of CO conversion (Tables S4 and S6). Recently, we have proved that CO<sub>2</sub> formation is caused by the water–gas-shift (WGS) reaction, and CO<sub>2</sub> selectivity is governed by thermodynamics [25,65].

To obtain a more intrinsic relation between the physicochemical properties of SAPO-34 and the  $C_2 - C_4^{\scriptscriptstyle =}/C_2 - C_4^{\scriptscriptstyle 0}$  ratio, we performed propene-TPD and propane-TPD for SAPO-34 with different acid strength and porosity (Fig. S9). The quantity of  $C_{3}H_{6}$  desorption was found to increase linearly with the density of BAS (Fig. S9a), which indicates a chemical interaction force between C=C bonds and BAS by the formation of  $\pi$ -complex and alkoxide [66]. Relatively, adsorption of  $C_3H_8$  on zeolites due to van der Waals force was much less than that of C<sub>3</sub>H<sub>6</sub> due to chemisorption (Fig. S9b). Regarding the impact of porosity, it seems that C<sub>3</sub>H<sub>6</sub> desorbs more easily from SP3 and SP2 than from SP1, because the temperature peak of C<sub>3</sub>H<sub>6</sub> desorption increases in the order SP3 < SP2 < SP1. Based on this, we believe that the hierarchical architecture can improve mass transfer behavior more than the microporous structure, and facilitate the escape of lower olefins from acid sites of zeolites.

### 3.6. MTO reaction in the presence of $H_2$

Differently from the typical MTO reaction, which takes place under atmospheric pressure with inert carrier gas, the conversion of a methanol intermediate over a bifunctional catalyst has to be conducted in the presence of high-pressure H<sub>2</sub>. From A thermodynamic view, saturated paraffins are much more stable than olefins, and from kinetics, olefins are easily hydrogenated into paraffins. Preventing the formation of paraffins is one of the priorities in achieving the SMO process. We have previously clarified the importance of hydrogenation ability over mixed oxides, which significantly impacts the CO conversion and  $C_2-C_4^-$  selectivity in the SMO reaction [24,25]. In this work, we try to disentangle the role of the hydrogenation reaction on a transition-metal-free SAPO-34 zeolite in methanol conversion.

Methanol conversion was performed at 400 °C in a fixed-bed reactor over microporous SAPO-34 zeolites with different densities of BAS and different carrier gases including N<sub>2</sub> (0.1 MPa), H<sub>2</sub> (0.1 MPa), and H<sub>2</sub> (1 MPa; Table S7). Under 0.1 MPa of N<sub>2</sub>, the C<sub>2</sub>-C<sub>4</sub><sup>--</sup> selectivity can reach 91% when the BAS densities of the SAPO-34 zeolite are 0.16 and 0.26 mmol g<sup>-1</sup> (Fig. 9a). The C<sub>2</sub>-C<sub>4</sub><sup>--</sup>

selectivity can still be sustained at 85% when the acid density rose to 0.44 mmol  $g^{-1}$ . Generally, the C<sub>2</sub>-C<sub>4</sub> selectivity is not very sensitive to the BAS densities. When the gas is switched to 0.1 MPa  $H_{2}$ , the product distribution of hydrocarbons did not change obviously (Fig. 9a), but the ratio  $C_2 - C_4^{-1}/C_2 - C_4^{-0}$  decreased remarkedly (Fig. 9b). Further increasing the H<sub>2</sub> pressure is detrimental to the ratio  $C_2 - C_4^-/C_2 - C_4^0$ , especially over SAPO-34 with high density of BAS. Differently from SAPO-34 with acid density of 0.44 mmol g<sup>-1</sup> (Fig. 9a), the product distribution over SAPO-34 zeolites with acid densities no more than 0.26 mmol  $g^{-1}$  did not change significantly, and the ratio  $C_2 - C_4^{-1}/C_2 - C_4^{0}$  is still as high as 8.3 in the presence of 1 MPa H<sub>2</sub>. Since the acid strength also decreased with the decrease of acid density (Fig. S5), we believe that a zeolite with strong and high density of BAS can catalyze the deep hydrogenation of olefins. Recently, a hydride-transfer mechanism was confirmed to catalyze olefins to paraffins by strong BAS in zeolites [26]. Therefore, a zeolite with low Brønsted acid strength and adequate density is highly desired for the SMO reaction.

Furthermore, the presence of high-pressure  $H_2$  was recently proved to be beneficial for MTO stability, with small influence on  $C_2-C_4^-$  selectivity [41,42]. In this work, we also evaluated the effect of carrier gas (N<sub>2</sub> or H<sub>2</sub>) on the MTO lifetime at 0.5 MPa (Fig. 10). Compared with N<sub>2</sub>, the lifetime of the catalyst (SP1 with a BAS density of 0.26 mmol g<sup>-1</sup>) was prolonged nearly two times under H<sub>2</sub>, while the selectivity for  $C_2-C_4^-$  at steady state decreased slightly from 80 to 90% to 75–80%. These results indicated that the evolution pathways of coke species in the MTO reaction are markedly influenced by the carrier gas.

#### 3.7. Coking species in used catalysts

The content of coking species over three bifunctional catalysts after syngas conversion of ~100 h was evaluated by TG measurements (Fig. 11a). In general, a broad combustion peak at 350–650 °C might suggest the oxidative decomposition of different coking species or a nonhomogeneous location of the coke that causes combustion at different temperatures. Su et al. confirmed that most coking species originated from the zeolite component, not from mixed oxides [26]. The total weight losses are 9.5, 4.5, and 4.3 wt% for used catalysts ZnO–ZrO<sub>2</sub>/SP1, ZnO–ZrO<sub>2</sub>/SP2, and ZnO–ZrO<sub>2</sub>/SP3, respectively. ZnO–ZrO<sub>2</sub>/SP1 with microporous SAPO-34 shows the greatest content of coking species. Instead, coke species were generated much slowly over ZnO–ZrO<sub>2</sub>/SP3, which could be due to the hierarchical architecture of SP3. We further analyzed the deposited coke species in the deactivated SAPO-



**Fig. 9.** Effect of (a) Brønsted acid density of SAPO-34 and (b) carrier gas on product selectivity and the ratio of lower olefins to paraffins on CH<sub>3</sub>OH conversion. MTO reaction conditions: catalyst, 0.34 g; carrier gas, 30 cm<sup>3</sup> min<sup>-1</sup>; liquid CH<sub>3</sub>OH, 0.01 cm<sup>3</sup> min<sup>-1</sup>; time on stream, 2 h; 400 °C.



**Fig. 10.** Effects of carrier gas  $(H_2 \text{ or } N_2)$  on the MTO lifetime over the SP1 catalyst. MTO reaction conditions: catalyst, 0.50 g; carrier flow  $(H_2 \text{ or } N_2)$ , 30 cm<sup>3</sup>min<sup>-1</sup>; liquid CH<sub>3</sub>OH, 0.005 cm<sup>3</sup> min<sup>-1</sup>; 0.5 MPa; 420 °C.

34 zeolites after the MTO reaction and used bifunctional catalysts after the SMO reaction using the GC-MS method (Fig. 11b). The differences in peak area indicate that the deposited coking species in used ZnO-ZrO<sub>2</sub>/SP3 after the SMO reaction are much less than those on the deactivated SP3 zeolite after the MTO reaction. Although the cumulative amount of coking species on  $ZnO_{-}ZrO_{2}$ SP3 increased as the reaction proceeded from 10 to 100 h (Fig. 11b), the catalytic performance did not change significantly (Fig. 8a). Besides, compared with deactivated SP3 after MTO reaction of 11 h, which shows a broad distribution of one-ring to four-ring polycyclic aromatics (Fig. 11b), ZnO-ZrO<sub>2</sub>/SP3 after 100 h of SMO reaction has much fewer polycyclic aromatic hydrocarbons with four rings. According to recent literature [67–69], the largest polycyclic aromatic hydrocarbon that CHA cages ( $0.70 \times 0$ .) 74 nm) can host is pyrene (four-ring aromatics,  $0.51 \times 0.73$  nm); therefore, most occluded organic species in used catalysts should be inside the SAPO-34 cages. The UV/vis studies of organic compounds also suggest that used ZnO-ZrO2/SP3 catalyst contains smaller organic molecules than deactivated SP3 catalyst after the MTO reaction (Fig. S11), in line with GC-MS results. On the basis of the observations described above, we believe that in the presence of high-pressure H<sub>2</sub>, the coking rate can be lowered by sup-



**Fig. 11.** (a) TG analysis of reacted bifunctional  $ZnO-ZrO_2/SAPO-34$  catalysts, (b) GC-MS chromatograms of occluded organic species in deactivated SP3 after 11 h of MTO reaction and reacted  $ZnO-ZrO_2/SP3$  after 10, 20, and 100 h of the SMO reaction.

pressing the formation of polyaromatics. Thus, the SMO reaction exhibits much better stability than the MTO reaction.

# 4. Conclusions

A SAPO-34 zeolite with a hierarchical structure and moderate acidity was successfully synthesized by a simple Al-rich method. The characterizations suggest that the Al-rich method using triethylamine and a small amount of TEAOH as template would result

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in crystal defects to generate trimodal porous structures. With the combination of  $ZnO-ZrO_2$  oxides with the hierarchical SAPO-34 for the syngas-to-lower-olefins reaction,  $ZnO-ZrO_2/SAPO-34$  exhibited a high and stable  $C_2-C_4^-$  selectivity of 75% at CO conversion of 30% due to the improvement of mass transport.

Our studies point out that compared with that in the MTO reaction, the  $C_2 - C_4^{-}$  selectivity in the SMO reaction is more sensitive, due to the presence of high-pressure H<sub>2</sub>. It is a contradiction that the syngas-to-methanol reaction needs hydrogenation sites, which may also hydrogenate  $C_2$ — $C_4$  olefins to saturated  $C_2$ — $C_4$  paraffins. This requires tailored design of bifunctional components to match up for the SMO reaction. Compared with that of metal oxides, the hydrogenation ability of transition-metal-free zeolites has been neglected. In this work, we have clarified the importance of the density of Brønsted acid sites for  $C_2-C_4^{-}$  selectivity: an appropriate density is required for the formation of  $C_2 - C_4^-$  and to drive CO conversion, while excessive Brønsted acid sites would catalyze deep hydrogenation of  $C_2$ — $C_4^=$ . The introduction of a hierarchical structure of SAPO-34 significantly decreased the coke rate in the SMO reaction, and the formation of polyaromatics was especially markedly suppressed owing to the hierarchical pore structure and the presence of high-pressure H<sub>2</sub>. Thus, SAPO-34 with a hierarchical structure would be potentially an excellent component in the application of the bifunctional syngas-to-hydrocarbon reaction. We can expect higher CO conversion per pass and  $C_2-C_4^{-}$  selectivity in this SMO reaction if a zeolite component with weak acid sites and adequate density is prepared.

# **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary material

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