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# Impact of cationic surfactant chain length during SAPO-11 molecular sieve synthesis on structure, acidity, and *n*-octane isomerization to di-methyl hexanes

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#### 1. Introduction

Hydroisomerization of n-alkanes to their branched isomers is one of the important processes in the modern petroleum refining industry [1] that has been widely applied in producing high-octane gasoline [2], reducing the pour point of diesel, and improving the viscosity-temperature property of lubricant basestocks [3,4]. In particular, with the ever-increasing demand for high-octane gasoline due to the rapid development of the automobile industry, searching for catalysts to isomerize  $C_5-C_8$  *n*-alkanes of low octane rating into multi-branched isomers of high octane rating has been the subject of many investigations around the world [5,6]. Among the numerous catalytic materials explored for *n*-alkane isomerization, SAPO-11 molecular sieve as an acidic carrier of bifunctional catalysts has attracted much attention due to its outstanding isomerization performance [7–9]. As a member of the silicoaluminophosphate molecular sieve family, SAPO-11 with a one-dimensional 10-membered-ring channel system of 0.39 nm  $\times$  0.63 nm [10] has shown its advantages in *n*-alkane isomerization [11.12] due to its distinct pore structure and mild acidity [13–15]. However, it is also noted that the channels of conventional SAPO-11 can only produce mono-branched isomers [16-18] but hardly allow the formation of di-branched isomers with higher research octane numbers (RONs) [19]. Sinha et al. [20] has pointed out that the active sites near the pore mouths of SAPO-11

#### ABSTRACT

The structure, acidity, and *n*-octane di-branched isomerization of SAPO-11 synthesized with surfactants of different chain lengths in water-propanol system were investigated. The results showed that with the increasing chain length of surfactants, the crystallite size of SAPO-11 firstly decreased and then increased, but the external surface area and the active B acid sites of SAPO-11 firstly increased and then decreased. The smallest crystallite, the highest external surface area, and the most B acid sites were obtained simultaneously with the surfactant of 12 carbon atoms. The isomerization results of *n*-octane indicated that among the series Pt/SAPO-11 catalysts, the catalyst with DoTAB-directed SAPO-11 as support had the highest selectivity to di-branched isomers and the lowest cracking selectivity due to the largest external surface area that created more active sites to promote the formation of di-branched isomers by the key-lock mechanism and improve the diffusion of intermediates and products for reducing cracking reactions. © 2012 Elsevier Inc. All rights reserved.

contribute to the formation of di-branched isomers and the number of pore mouths is closely related to the external surface area of SAPO-11. Recently, in the presence of hexadecyltrimethyl ammonium bromide (CTAB) and alcohol, Franco et al. [21] obtained a SAPO molecular sieve with larger external surface area and more acid sites compared with those of conventional SAPO-11, similar to the results obtained by Blasco et al. [22] and Huang et al. [23], demonstrating the enhancing effect of surfactant introduction into the wateralcohol synthesis system on the external surface area of the resultant SAPO-11. However, the effects of chain length of surfactants on the structure and acidity of resulting SAPO-11 molecular sieve as well as its di-branched isomerization performance have not been reported to our best knowledge, to which this work is addressed.

JOURNAL OF CATALYSIS

Herein, a series of SAPO-11 were hydrothermally synthesized with cationic surfactants of different chain lengths in the waterpropanol system. The chain length of surfactants was correlated with the structure and acidity of the SAPO-11 synthesized and the corresponding Pt/SAPO-11 catalysts were assessed with the di-branched isomerization of *n*-octane as a model reaction. The optimal surfactant was determined according to the discussed relationship between the physicochemical properties and the isomerization performances.

#### 2. Experimental

#### 2.1. Materials

Tetrapropyloxy silane ( $C_{12}H_{28}O_4$ Si, Aladdin), pseudoboehmite (containing 73% Al<sub>2</sub>O<sub>3</sub>, Tianjin Hengmeilin Chemical Corporation),

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and ortho-phosphoric acid (85%, Beijing Chemical Reagents Company) were used as the sources of Si, Al and P, respectively. Di-*n*propylamine (DPA, C<sub>6</sub>H<sub>15</sub>N, Beijing Chemical Reagents Company) was used as the template, and *n*-propanol (C<sub>3</sub>H<sub>7</sub>OH, Beijing Chemical Reagents Company) was used as the co-solvent. The cationic surfactants used include decyltrimethyl ammonium bromide (DeTAB, C<sub>10</sub>H<sub>21</sub>(CH<sub>3</sub>)<sub>3</sub>NBr, Aladdin), dodecyltrimethyl ammonium bromide (DoTAB, C<sub>12</sub>H<sub>25</sub>(CH<sub>3</sub>)<sub>3</sub>NBr, Aladdin), tetradecyltrimethyl ammonium bromide (TTAB, C<sub>14</sub>H<sub>29</sub>(CH<sub>3</sub>)<sub>3</sub>NBr, Aladdin), and hexadecyltrimethyl ammonium bromide (CTAB, C<sub>16</sub>H<sub>33</sub>(CH<sub>3</sub>)<sub>3</sub>NBr, Aladdin), which have different hydrophobic chain lengths. All of the above chemicals were used as purchased without any further purification.

## 2.2. Synthesis of SAPO-11 without and with different cationic surfactants

First, the SAPO-11 was synthesized by using *n*-propanol as cosolvent without adding any surfactant, as shown by Route 1 in Fig. 1. A typical synthesis procedure was detailed as follows: first, 13.6 g of phosphoric acid and 40.0 g of deionized water were well mixed, and then, 9.0 g of pseudoboehmite was slowly added under stirring: second, after the formation of homogeneous gel, 5.0 g of tetrapropyloxy silane and 11.3 g of *n*-propanol were added dropwise, and the resulting mixture was stirred vigorously for 4 h in order to dissolve the silica species and yield a homogeneous gel; third, 7.6 g of DPA was slowly added and the synthesis system was stirred for 1 h; fourth, the resulting gel with the molar composition of 1.0 Al<sub>2</sub>O<sub>3</sub>:0.95 P<sub>2</sub>O<sub>5</sub>:0.3 SiO<sub>2</sub>:3.0 *n*-propanol:1.2 DPA:40 H<sub>2</sub>O was transferred into a 150 mL stainless steel autoclave lined with polytetrafluorethylene (PTFE) and kept in an oven at 458 K for 24 h; finally, the as-synthesized SAPO-11 was collected by centrifugation, washing with deionized water, and drying at 393 K overnight. To remove the organic template, the as-synthesized SAPO-11 was calcined in flowing air at 873 K for 6 h. The synthesized sample was named as SAPO-11-P, where P stands for the co-solvent *n*-propanol.

The synthesis of SAPO-11 with different cationic surfactants was the same as Route 1 in Fig. 1 used for synthesizing sample SAPO-11-P except for adding different cationic surfactants of the identical amount with the template DPA together, as shown by Route 2 in Fig. 1. The molar ratio of the surfactants to SiO<sub>2</sub> was 0.01. The resulting samples were denoted as SAPO-11-P-De, SAPO-11-P-Do, SAPO-11-P-T, and SAPO-11-P-C, respectively, where *De*, *Do*, *T*, and *C* stand for cationic surfactants DeTAB, DoTAB, TTAB and CTAB, respectively.

#### 2.3. Preparation of Pt/SAPO-11 catalysts

The above SAPO-11 samples were extruded, crushed, and sieved to obtain the particles of 20–40 mesh in size. Then, these SAPO-11 particles were impregnated with an aqueous solution of  $H_2PtCl_6$ 

according to 0.5 wt% Pt loading and dried at 383 K for 2 h and calcined in air at 723 K for 2 h to yield a series of Pt/SAPO-11 catalysts.

#### 2.4. Characterizations

The phase structure of the SAPO-11 samples was characterized by powder X-ray diffraction (XRD) conducted on a Shimadzu 6000 diffractometer (Kyoto, Japan) that used CuKa radiation and was operated at 40 kV and 30 mA with  $2\theta$  in 5–40° and scanning speed at 5°/min. The morphology and size of the SAPO-11 samples were determined by means of scanning electron microscopy (SEM) conducted on a Cambridge S-360 instrument (England). Nitrogen adsorption-desorption measurements were performed on an ASAP 2020 instrument (Micromeritics, USA). The surface area and pore volume of the SAPO-11 samples were determined according to the Brunauer–Emmett–Teller (BET) method and the *t*-plot method, respectively, and the most probable pore sizes in the ranges of 0-2 nm and 2–50 nm were calculated by the Horvath–Kawazoe (HK) method and the Barret-Joyner-Halenda (BJH) method, respectively. The surface zeta potentials of the SAPO-11 samples were determined by a zeta-sizer instrument (Malvern, England). The acidic properties of the SAPO-11 samples were measured by the pyridine-adsorbed infrared (Py-IR) spectra and 2.6-dimethylpyridine-adsorbed infrared (2.6-DMPv-IR) spectra on a MAGNA-IR 560 instrument (Nicolet Co., USA). The samples were dehydrated at 773 K for 4 h under a vacuum of  $1.33 \times 10^{-3}$  Pa and the adsorption of pure pyridine or 2,6-dimethylpyridine vapor at room temperature for 20 min was followed. After reaching equilibrium, the pyridine-adsorbed system was evacuated at 473 K and 573 K, respectively, and the 2,6-dimethylpyridine-adsorbed system was evacuated at 423 K and 573 K, and finally, the IR spectra were recorded. <sup>29</sup>Si solid-state magic-angle-spinning nuclear magnetic resonance (MAS NMR) spectra were recorded on a Bruker MSL-300 NMR spectrometer with frequency at 59.6 MHz, pulse width at 4.5 ms, and delay at 30 s.

#### 2.5. Catalytic performance assessment

Isomerization of *n*-octane  $(n-C_8)$  was carried out in a flowingtype microreactor under the conditions of 573 K, 1.5 MPa, volumetric H<sub>2</sub>/*n*-octane ratio 400, and different weight hour space velocities (WHSVs). In each run, 3.0 g of the catalyst to be assessed was loaded into the reactor, and the *n*-octane was fed into the reactor by a syringe pump at a predetermined flow rate. Before the reaction, each catalyst was reduced in hydrogen flowing at 673 K for 4 h and then the temperature was lowered to the reaction temperature. After steady state was achieved, the products were analyzed by an Agilent 1790 gas chromatograph installed with a flame ionization detector and a HP-PONA capillary column (50 m × 0.2 mm), and the data were processed by a GC99 software (Research Institute of Petroleum Processing, SINOPEC, China).



Fig. 1. Schematic diagram for the synthesis procedure of SAPO-11. Route 1: in water-propanol system; Route 2: in water-propanol-surfactant system.

#### 3. Results and discussion

#### 3.1. Phase structure

Fig. 2 shows the XRD patterns of the SAPO-11 samples synthesized by the different methods. All the samples synthesized with and without the cationic surfactants present the diffraction peaks at  $2\theta = 8.1$ , 9.4, 13.1, 15.6, 20.3, and 22.1–23.2° attributed to the typical SAPO-11 phase with AEL structure [24,25]. These results demonstrate that the addition of cationic surfactants in the synthesis system well preserves the crystal structure of SAPO-11.



Fig. 2. XRD patterns of the SAPO-11 samples.

#### 3.2. Morphology

The SEM images of the samples at different magnifications are presented in Fig. 3. All the SAPO-11 samples display the spherical particles (Fig. 3A), and the single spherical aggregate of each sample consists of many crystallites assembled layer by layer (Fig. 3B). The SAPO-11 samples synthesized with surfactants have smaller particle and crystallite sizes than those without surfactants. For the SAPO-11 samples synthesized with surfactants, the particle and crystallite sizes decrease in the order of SAPO-11-P-C > SAPO-11-P-T > SAPO-11-P-De > SAPO-11-P-Do, indicating that the surfactants with different chain lengths reduce the particle and crystallite sizes of the resulting SAPO-11 samples to different degrees and SAPO-11-P-Do with the 12-carbon surfactant has the smallest crystallite size of about 150 nm imes 200 nm among the different samples. Generally, these small crystallites are initially formed during the crystallization of SAPO-11, and then, they aggregate into large spheres among which intercrystal pores are generated [26,27].

#### 3.3. Pore structure

The nitrogen adsorption-desorption isotherms of the SAPO-11 samples are shown in Fig. 4. For SAPO-11-P-x series (x = De, Do, T, C), the adsorption-desorption isotherm of each sample has a large hysteresis loop at the high relative pressure attributed to mesopores in addition to the characteristics of microporous materials at the low relative pressure [28]. For SAPO-11-P, however, there exists an isotherm typical for pure microporous materials. These results clearly reveal that the involvement of different



Fig. 3. SEM images of the SAPO-11 samples at low (A) and high (B) magnifications.



Fig. 4. Nitrogen adsorption-desorption isotherm curves of the SAPO-11 samples.

cationic surfactants in the SAPO-11 synthesis system can generate bimodal pore structure.

The microporous and mesoporous size distributions of the samples are shown in Figs. 5 and 6, respectively. The micropore diameters of all the samples are narrowly centered at about 0.50 nm that is comparable to the diameter of a crystallographic 10-membered-oxygen ring (Fig. 5). In the mesopore distribution curves of



Fig. 5. Micropore size distributions of the SAPO-11 samples.



Fig. 6. Mesopore size distributions of the SAPO-11 samples.

the SAPO-11-P-x samples in Fig. 6, there are two maxima: one is centered at ca. 4.0 nm, usually attributed to the so-called tensile strength effect [29]; the other is centered at ca. 10.0 nm representing real mesopores. The above results indicate that the SAPO-11-P-x series have a hierarchical pore structure, with the micropores coming from microcrystallines and the mesopores from the intercrystal voids. Furthermore, in view of the similar mesopore distributions of the different SAPO-11-P-x samples, it can be concluded that the length of hydrophobic chain in the cationic surfactants hardly changes the mesopore size of the resulting SAPO-11. The SAPO-11-P sample has only a so-called tensile peak at ca. 4.0 nm in its mesoporous distribution curve, indicating its property of pure micropores.

Table 1 gives the textural parameters of all the SAPO-11 samples. Compared with the SAPO-11 synthesized without any surfactant, the SAPO-11-P-x samples have much higher external surface area and mesopore volumes, showing the promoting effect of cationic surfactants on the mesopore formation. By combining the pore structure results with the above morphology results, it can be inferred that the greatly increased external surface area and mesopore volume result from the decreased crystallite size accompanied with the formation of more intercrystal mesopores. Therefore, SAPO-11-P-Do with the smallest crystallite has the highest mesopore structure among all the samples.

#### 3.4. Surface zeta potential

It is well known that in zeolite synthesis, the aggregation of zeolitic precursors is a spontaneous process owing to their colloidal nature [30]. Therefore, conventional SAPO-11 usually has large crystallite size. In this study, we found that the presence of the cationic surfactants can significantly reduce the crystallite size of the obtained SAPO-11 samples. According to the DLVO (Deriaguin-Landau-Verwey-Overbeek) theory [31], the dispersion behavior of crystallites is in good coincidence with their zeta potential, so the higher absolute value of zeta potential on crystallite surface leads to the better dispersion of crystallites. To clarify the effect of different surfactants on the crystallite size of SAPO-11, the surface zeta potentials of the synthetic gel system at different crystallization times were measured and the results are shown in Fig. 7. The zeta potentials for all the samples are firstly negative and then increase from a negative value to a positive one with the increasing crystallization time. These phenomena can be explained as follows: as shown in Fig. 8, at first, SAPO-11 precursors are negatively charged because Si atoms are introduced into the neutral AIPO<sub>4</sub> framework, so the cationic surfactants can be easily adsorbed on the surface of the SAPO-11 precursors due to the electrostatic attraction between them, which gradually decreases the negative charge number on the precursor surface and thus weakens the electrostatic repulsion between the precursor crystallites. Hence, the absorption of cationic surfactants on the precursor surface leads to the crystallite flocculation. After the negative charges of precursors are neutralized completely by the cations of surfactants, the cationic surfactant in solution will be further bridged onto the precursor surface through the formed bilayer micelles resulting

Table 1		
Pore structure parameters	of the SAPO-11	samples.

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Sample	$S_{\text{BET}}$	S <sub>external</sub>	V <sub>micropore</sub>	V <sub>mesopore</sub>
	(m <sup>2</sup> /g)	(m <sup>2</sup> /g)	(cm <sup>3</sup> /g)	(cm <sup>3</sup> /g)
SAPO-11-P	218	64	0.09	0.12
SAPO-11-P-De	290	217	0.06	0.42
SAPO-11- P-Do	330	261	0.05	0.51
SAPO-11- P-T	270	180	0.07	0.27
SAPO-11- P-C	259	170	0.07	0.25



Fig. 7. The surface zeta potential of the synthetic gel system with different crystallization time.

from the association of its hydrophobic groups, which continuously increases the positive charge number on the precursor surface until reaching stability. Therefore, the electrostatic repulsion between positive charges gradually increases and thus the dispersion effect from the cationic surfactant rather than the flocculation effect is predominant.

On the basis of the surfactant adsorption model on the solid surface [32], the adsorption capacity of a specified surfactant increases

with its increasing concentration, but reaches the adsorption equilibrium at the critical micelle concentration (cmc) of the surfactant. As shown in Fig. 7, the SAPO-11 samples synthesized with four different surfactants present different zeta potentials, suggesting that the chain length is of critical importance in determining the adsorption behavior of a surfactant. Indeed, the surfactant with longer hydrocarbon chain has a much lower cmc [33], which affects its adsorption behavior dramatically. Herein, the concentration of each cationic surfactant is  $2.75 \times 10^{-3}$  mol/L, which is higher than  $cmc_{TTAB}$  (2.1  $\times$  10  $^{-3}$  mol/L) and  $cmc_{CTAB}$  $(9.2\times10^{-4}\ mol/L),$  but lower than  $cmc_{DeTAB}\ (6.5\times10^{-2}\ mol/L)$ and cmc<sub>DoTAB</sub>  $(1.6 \times 10^{-2} \text{ mol/L})$  [34]. As a result, the effective adsorptive concentrations for the four surfactants are in the order of DeTAB  $(2.75 \times 10^{-3} \text{ mol/L}) = \text{DoTAB} (2.75 \times 10^{-3} \text{ mol/L}) > \text{TTAB}$  $(2.1 \times 10^{-3} \text{ mol/L}) > \text{CTAB} (9.2 \times 10^{-4} \text{ mol/L})$ . Hence, it is reasonable to believe that DeTAB and DoTAB with the higher effective adsorptive concentrations have the higher adsorption capacity than the other two surfactants. According to the surfactant adsorption theory that the adsorption capacity of the long-chain surfactant is higher than that of the short-chain surfactant under the same conditions [33], it can be concluded that DoTAB with longer hydrophobic chain has the higher adsorption capacity compared with DeTAB in the case of the same effective adsorptive concentrations and crystallization time.

In line with the above analyses, the zeta potentials of the SAPO-11 samples synthesized with the different surfactants decrease in the order of SAPO-11-P-Do > SAPO-11-P-De > SAPO-11-P-T > SAPO-11-P-C (Fig. 7) when the stable adsorption state is



Fig. 8. The dispersion and flocculation effects of cationic surfactants on the negatively charged SAPO-11 precursors.

reached. The SAPO-11 crystallites adsorbed by DoTAB shows the highest positive potential among all the samples, so their dispersion is optimal due to the greatly enhanced electrostatic repulsion between them. Therefore, SAPO-11-P-Do has much smaller crystallites and much higher external surface area than the other samples with the weak electrostatic repulsion, as evidenced by the SEM and nitrogen adsorption–desorption results.

#### 3.5. Acidity

The Py-IR spectra of all the SAPO-11 samples are shown in Fig. 9. For Py-IR spectra, the bands located at  $1540 \text{ cm}^{-1}$  and  $1450 \text{ cm}^{-1}$  can be assigned to pyridine adsorbed on Brönsted (B) and Lewis (L) acid sites, respectively [35,36]. Total B acid sites and total L acid sites, and medium and strong B acid sites and medium and strong L acid sites can be obtained from the Py-IR measurement results at 473 and 573 K, respectively. The quantitative calculation of B and L acidity by Py-IR analysis is based on the integrated Lambert–Beer Law [25]:

$$C_{sw} = AS/m\varepsilon \tag{1}$$

where  $C_{sw}$  (µmol/g) is the concentration of B or L acid sites in reference to a unit weight of dry sample, A (cm<sup>-1</sup>) is the integrated absorbance, S (cm<sup>2</sup>) is cross sectional area of the sample wafer, m(g) is the weight of the dry sample, and  $\varepsilon$  is the integrated molar extinction coefficient. According to the literature reported [37], for B acid sites,  $\varepsilon_B = 0.059 \pm 0.004$  (cm/µmol); for L acid sites,  $\varepsilon_L = 0.084 \pm 0.003$  (cm/µmol).

The 2,6-DMPy-IR spectra of all the SAPO-11 samples are shown in Fig. 10. For 2,6-DMPy-IR spectra, the bands located at 1630– $1650 \text{ cm}^{-1}$  can be assigned to 2,6-dimethylpyridine adsorbed on



Fig. 9. IR spectra of pyridine adsorbed on the SAPO-11 samples at 473 K (A) and 573 K (B).



Fig. 10. IR spectra of 2,6-dimethylpyridine adsorbed on the SAPO-11 samples at 423 K (A) and 573 K (B).

B acid sites [38,39]. The kinetic diameter of 2,6-dimethylpyridine (0.67 nm) [40] is too large to enter the pore channel of SAPO-11 (0.39 nm  $\times$  0.63 nm) [10], so only B acid sites at the pore mouths of SAPO-11 are accessible for 2,6-dimethylpyridine [41]. Similar to the quantitative calculation of B acid sites by Py-IR analysis, the total B acid sites and the medium and strong B acid sites at the pore mouths of SAPO-11 can be obtained from the 2,6-DMPy-IR measurement results at 423 K and 573 K [42], respectively. The integrated molar extinction coefficient of 2,6-dimethylpyridine given by Onfroy et al. [43] was used here.

Table 2 gives the quantitative results about the acid properties of the different samples from Py-IR and 2,6-DMPy-IR. Compared with SAPO-11-P, the SAPO-11-P-x series have similar amount of L acid sites but more amount of B acid sites, indicating the promotion effect of cationic surfactants on the exposure of B acid sites [22]. For the SAPO-11-P-x series, the amounts of medium and strong B acid sites at the pore mouths decrease in the order of SAPO-11-P-Do > SAPO-11-P-De > SAPO-11-P-T > SAPO-11-P-C, showing that the suitable chain length of cationic surfactants is necessary for more detected B acid sites. Combining the acidity results and the above SEM and nitrogen adsorption–desorption results, it can be inferred that the smaller crystallites of SAPO-11 with higher external surface area can produce more amount of medium and strong B acid sites at the pore mouths of SAPO-11.

It has been well recognized that the acidity of a SAPO-11 molecular sieve originates from Si atoms incorporated into the AlPO<sub>4</sub>-11 framework, so the manners of Si substitution directly determine the acidity properties of SAPO-11 [44]. Generally, the incorporation of Si atoms into the AlPO<sub>4</sub>-11 structure follows two different mechanisms [22]: the one is the so-called SM2 mechanism, that is, one Si atom substitutes for one P atom to form a Si(4Al) site; the other is the so-called SM3 mechanism, that is, two Si atoms

Table 2
Acidity properties of the SAPO-11 samples determined by Py-IR and 2,6-DMPy-IR characterizations.

Sample	Acidity (µmol/g)						
	Weak acid sites (Py-IR)		Medium and strong sites (Py-IR)		Weak acid sites (2,6-DMPy-IR)	Medium and strong sites (2,6-DMPy-IR)	
	L	В	L	В	В	В	
SAPO-11-P	43.3	50.9	25.5	72.3	12.4	15.7	
SAPO-11-P-De	45.2	68.7	26.2	123.6	49.6	57.6	
SAPO-11- P-Do	45.9	85.9	26.0	130.8	48.1	70.4	
SAPO-11- P-T	44.2	66.7	25.4	96.4	37.4	38.9	
SAPO-11- P-C	43.8	61.5	25.1	85.9	38.0	35.2	

simultaneously substitute adjacent one P atom and one Al atom. According to the theory of Martens et al. [45], the SAPO domains originate from Si incorporated into AlPO<sub>4</sub> framework by SM2 mechanism with the Si(4Al) environment of each Si atom, and all the second nearest neighbors of Si are P atoms. Different from SAPO domains, the aluminosilicate (SA) domains formed by SM3 and SM2 mechanisms do not contain P atoms. To understand the chemical surroundings of Si in the different SAPO-11 samples synthesized, the <sup>29</sup>Si MAS NMR spectroscopy characterization was carried out and the results are shown in Fig. 11. The <sup>29</sup>Si MAS NMR spectra of both SAPO-11-P and SAPO-11-P-Do show a broad band in the range of -80 to -120 ppm. The resonance peak at around -90 ppm is attributed to Si(4Al) species in SAPO domains, and those at -86, -95, -99, -106, and -112 ppm represent Si(4Al), Si(3Al), Si(2Al), Si(1Al), and Si(4Si) in SA domains, respectively [14,45]. The experimentally determined <sup>29</sup>Si MAS NMR spectra were deconvolved into six distinct peaks by using Gaussian curves, and the results are shown in Table 3. Si(1Al) and Si(2Al) in SA domains, and Si(3Al) located at the interface between SA and SAPO domains have medium and strong B acidity that promotes the skeletal isomerization of hydrocarbons, so the SAPO-11-P-Do sample with more Si(nAl)(0 < n < 4) has more amounts of medium and strong B acid sites [46] than the SAPO-11-P sample as confirmed by the above Py-IR characterization results.



Fig. 11. <sup>29</sup>Si MAS NMR spectra of the selected SAPO-11 samples.

#### 3.6. Catalytic performance

Höchto et al. [44] pointed out that the loading of 0.5 wt% Pt on an acidic support could meet the requirement for the hydrogenation-dehydrogenation function of bifunctional catalysts. Thereby, a series of 0.5 wt% Pt/SAPO-11 catalysts were prepared with the above SAPO-11 samples as supports and assessed with *n*-octane isomerization as a model reaction herein. *n*-Octane isomerization results are shown in Fig. 12. Both of selectivity to di-branched isomers and cracking selectivity over different Pt/SAPO-11 catalysts increase with the increasing  $n-C_8$  conversion, suggesting that the increase in *n*-octane conversion not only promotes the formation of di-branched isomers but also enhances the undesirable cracking reactions. At the same conversion of *n*-octane, the Pt/SAPO-11-P-x catalysts are always found to exhibit higher selectivity to dibranched isomers and lower cracking selectivity than the Pt/ SAPO-11-P catalyst, indicating the improving effect of the cationic surfactants on the di-branched isomerization of SAPO-11-based catalysts. As to the Pt/SAPO-11-P-x catalysts, at the same conversion of *n*-octane, the selectivity to di-branched isomers decreases in the order of Pt/SAPO-11-P-Do > Pt/SAPO-11-P-De > Pt/SAPO-11-P-T > Pt/SAPO-11-P-C while the cracking selectivity increases in the order of Pt/SAPO-11-P-Do < Pt/SAPO-11-P-De < Pt/SAPO-11-P-T < Pt/SAPO-11-P-C, demonstrating that the suitable chain length of cationic surfactants is critical for improving the dibranched isomerization and restraining the cracking reactions over SAPO-11-based catalysts.

The detailed results of *n*-octane isomerization over all the catalvsts are listed in Table 4. 2-methyl heptane (2-MC<sub>7</sub>) and 3methyl heptane (3-MC<sub>7</sub>) are the major mono-branched products over all the catalysts, in good agreement with the product shape selectivity in SAPO-11 [47], while the selectivity to di-branched isomers decreases in the order of 2,5-dimethylhexane (2,5  $DMC_6$  > 2,4-dimethylhexane (2,4  $DMC_6$  ) > 2,3-dimethylhexane  $(2,3 \text{ DMC}_6) > 3,4$ -dimethylhexane  $(3,4 \text{ DMC}_6) > 2,2$ -dimethylhexane  $(2,2 \text{ DMC}_6)$  over all the catalysts, implying the prior isomerization of terminal alkyls of n-octane over the above SAPO-11 catalysts. Among the Pt/SAPO-11-P-x catalysts, the highest activity for n-octane conversion reflected by the k and TOF values, the highest selectivity to di-branched isomers, and the lowest cracking selectivity are realized over Pt/SAPO-11-P-Do, displaying the remarkable advantage of DoTAB in balancing high-efficient isomerization and minimal cracking.

Table 3

Deconvolution results of the <sup>29</sup>Si MAS NMR spectra of SAPO-11-P and SAPO-11-Do based on the normalized peak areas of the different Si species.

Sample	SAPO domain	SA domain	SA domain				
	Si (4Al) (%)	Si (4Al) (%)	Si (3Al, 1Si) (%)	Si (2Al, 2Si) (%)	Si (1Al,3Si) (%)	Si (4Si) (%)	
	–90 ppm	-86 ppm	–95 ppm	–99 ppm	–106 ppm	–112 ppm	
SAPO-11-P	3.3	2.3	7.2	16.4	25.1	45.7	
SAPO-11-P-Do	15.8	8.0	21.5	26.8	15.5	12.4	



**Fig. 12.** Selectivity to di-branched isomers (A) and cracking selectivity (B) versus *n*-octane conversion over Pt/SAPO-11-P (a), Pt/SAPO-11-P-De (b), Pt/SAPO-11-P-Do (c), Pt/SAPO-11-P-T (d), and Pt/SAPO-11-P-C (e).

On the basis of the isomerization mechanism of *n*-alkanes over bifunctional catalysts [48], for Pt/SAPO-11 catalysts, *n*-octane is first dehydrogenated into *n*-octene on Pt centers, and the resulting *n*-octene molecules with a critical molecular diameter of 0.56 nm [6] diffuse onto the B acid sites of SAPO-11 where the intermediates of mono-branched  $C_8$  isomers are formed; then, the monobranched  $C_8$  intermediates can be further converted into the di-branched  $C_8$  intermediates on the B acid sites in the case of no steric hindrance; finally, the di-branched  $C_8$  isomers of *n*-octane are generated by the hydrogenation on Pt centers. For microporous

 Table 4

 Results of *n*-octane isomerization over the different Pt/SAPO-11 catalysts.

Pt/SAPO-11-P with the largest crystallites among all the catalysts (Fig. 13), its longest pore channels lead to the greatly increased residence time of the intermediates of mono-branched C<sub>8</sub> isomers and thus result in their further cracking on medium and strong acid sites, so Pt/SAPO-11-P presents the highest cracking selectivity among all the catalysts. Due to the larger size of di-branched  $C_8$ isomers (0.71 nm) [19] than the pore diameter (0.63 nm) of SAPO-11 [19], the di-branched C<sub>8</sub> isomers can be formed only near the pore mouths rather than in the microporous channels according to the "pore mouth and key-lock" concept [49]. As a result, SAPO-11 with more amounts of medium and strong B acid sites at the pore mouths should be beneficial to produce more di-branched isomers. In view of the direct proportion relationship between the amount of B acid sites at the pore mouths and the external surface area of SAPO-11 [50], SAPO-11-P with the lowest external surface area has the least B acid sites at the pore mouths among all the SAPO-11 samples, so the corresponding catalyst Pt/ SAPO-11-P produces the least di-branched C<sub>8</sub> isomers.

The Zeta potential analysis results have clarified that the suitable chain length in cationic surfactants can maximize the dispersion of SAPO-11 crystallites. The SEM, nitrogen adsorption-desorption, and acidity results have confirmed that incorporating the cationic surfactant with the optimal chain length in the synthesis system can produce the SAPO-11 with the smallest crystallite, the highest external surface area and the most amounts of active B acid sites at the pore mouths among the SAPO-11 samples synthesized with different surfactants. DoTAB has just the above-mentioned suitable chain length and thus the corresponding catalyst Pt/SAPO-11-P-Do presents the best di-branched isomerization performance among all the catalysts.

As illustrated in Fig. 13, Pt/SAPO-11-P-Do with smaller crystallites and higher external surface area has abundant and accessible B acid sites at the pore mouths that guarantee the efficient monobranched isomerization of two terminal alkyls of *n*-octane near the two adjacent pore mouths, so more di-branched  $C_8$  isomers are produced over it. However, the other catalysts with larger crystallites and lower external surface area have less B acid sites at the pore mouths that reduce the di-branched isomerization of *n*-octane near pore mouths, so these catalysts show lower di-branched isomer selectivity.

The results of the <sup>29</sup>Si MAS NMR and acidity characterizations have demonstrated that the SAPO-11-P-Do sample has more borders of Si domains and thus more amount of medium and strong B acid sites compared with the other samples. For isomerization

	Pt/SAPO-11-P	Pt/SAPO-11-P-De	Pt/SAPO-11-P-Do	Pt/SAPO-11-P-T	Pt/SAPO-11-P-C
$k^{\rm a}$ (10 <sup>-6</sup> mol g <sup>-1</sup> s <sup>-1</sup> )	3.9	19.4	26.5	12.0	9.1
$TOF^{b} (10^{-2} s^{-1})$	16.6	22.7	30.5	21.8	18.8
S <sub>MB</sub> <sup>c</sup> (%)	84.7	78.1	74.7	82.6	83.1
S <sub>DB</sub> <sup>c</sup> (%)	1.7	15.5	23.1	8.9	8.1
<i>PS</i> <sup>c</sup> (%)					
2-MC <sub>7</sub>	40.3	33.7	30.2	38.5	38.1
3-MC <sub>7</sub>	35.4	35.5	36.9	35.6	36.4
4-MC <sub>7</sub>	9.0	8.9	7.6	8.5	8.6
2,5-DMC <sub>6</sub>	1.3	8.0	10.8	6.1	5.9
2,4-DMC <sub>6</sub>	0.2	5.4	9.2	2.2	2.3
2,3-DMC <sub>6</sub>	0.1	1.5	2.1	0.5	0.5
3,4-DMC <sub>6</sub>	0.1	0.4	0.8	0.1	0.1
2,2-DMC <sub>6</sub>	0.0	0.2	0.2	0.0	0.0
$S_{c}^{c}(\%)$	13.6	6.4	2.2	8.5	8.8

<sup>a</sup> Reaction rate constant obtained by assuming a pseudo-first-order reaction for *n*-octane isomerization at 573 K, 1.5 MPa, H<sub>2</sub>/octane volumetric ratio of 400, and 7.0 WHSV.

<sup>b</sup> Number of reacted *n*-octane molecules per second and per medium and strong B acid site at the pore mouths.

<sup>c</sup> S<sub>MB</sub>, S<sub>DB</sub>, PS, and S<sub>c</sub> correspond to the total selectivity to mono-branched C<sub>8</sub> isomers, the total selectivity to di-branched C<sub>8</sub> isomers, the product selectivity, and the cracking selectivity, respectively, at 54% conversion of *n*-octane.



Fig. 13. Reaction locations and diffusion pathways for *n*-octane isomerization over the Pt/SAPO-11 catalysts based on large-sized and small-sized SAPO-11 crystallites, respectively.



**Fig. 14.** External surface area versus crystallite size and selectivity to di-branched isomers over the Pt/SAPO-11 catalysts with the conversion of *n*-octane at 54%.

of *n*-alkanes, the medium and strong B acid sites are considered as the active sites for the skeletal isomerization and C–C bond cracking of hydrocarbons [19], so the increase in their number can efficiently promote not only the mono- and di-branched sequential isomerization of *n*-octane but also accelerate the cracking of *n*-octane. However, Pt/SAPO-11-P-Do with more amounts of medium and strong B acid sites has not only better di-branched isomer selectivity, but also lower cracking selectivity compared with the other catalysts at the same conversion of *n*-octane (Fig. 12 and Table 4). This distinct feature can be attributed to the shortened diffusion paths because of the greatly decreased crystallite size of Pt/SAPO-11-P-Do, accelerating mass transport and thus suppressing the cracking of *n*-octane.

To better understand the relationship between the physicochemical properties of the SAPO-11 samples and their isomerization performances, the external surface areas of the SAPO-11 samples were correlated with their crystallite sizes and dibranched isomer selectivities, and the results are shown in Fig. 14. Decreasing the crystallite size of the SAPO-11 samples can increase their external surface areas [50], and the increased external surface area of the SAPO-11 samples can increase the medium and strong B acid sites at the pore mouths (Tables 1 and 2) [51], which enhances the di-branched isomerization of *n*-octane (Table 4). In summary, the superior di-branched isomerization of *n*-octane can be accomplished over the Pt/SAPO-11 catalyst with small crystallite and high external surface area.

#### 4. Conclusions

A series of SAPO-11 molecular sieves with different crystallite sizes, pore structures, and acidities were successfully synthesized via incorporating the cationic surfactants of different chain lengths in water-propanol system, and their di-branched isomerization performances were assessed. The results showed that increasing chain length of surfactants could firstly decrease and then increase the crystallite size of SAPO-11, while the external surface area and the active B acid sites of SAPO-11 firstly increased and then decreased with the increasing chain length. Dodecyltrimethyl ammonium bromide (DoTAB) could maximize the dispersion of SAPO-11 crystallites and thus produced the smallest crystallite, the highest external surface area, and the most amounts of medium and strong B acid sites at the pore mouths of SAPO-11 among the four cationic surfactants investigated, endowing the corresponding catalyst with superior di-branched isomer selectivity and minimal cracking selectivity. The findings obtained herein highlight the development of novel catalysts for boosting high octane-rating gasoline via the di-branched isomerization of long *n*-alkanes with low octane rating.

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