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Article

Investigation of synthesis and hydroisomerization performance of SAPO-11/Beta composite molecular sieve

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ABSTRACT

The SAPO-11/Beta composite molecular sieve was synthesized by the hydrothermal method with zeolite Beta as the silicon source. The physicochemical properties of SAPO-11, Beta molecular sieve, the composite molecular sieve, and the mechanical mixture of SAPO-11 and Beta molecular sieve were characterized by X-ray diffraction, N₂ adsorption-desorption, scanning electron microscopy, transmission electron microscopy-energy dispersive spectroscopy, magic-angle spinning nuclear magnetic resonance, and pyridine adsorption infrared spectroscopy. In addition, the catalytic performance of platinum-loaded zeolite samples in the hydroisomerization of *n*-dodecane was investigated. The results indicate that the properties and catalytic performance of the composite molecular sieve were quite different from those of the pure zeolites and the mechanical mixture. Compared with the mechanical mixture, the combination of SAPO-11 and Beta by chemical bonds was more tightly bound in the composite molecular sieve with a core-shell structure. The acidity and pore structure of the composite were favorable for catalytic performance in the hydroisomerization of *n*-dodecane. The composite catalyst was superior to the other catalysts, especially in the yield of multibranched isomers.

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1. Introduction

The skeletal isomerization of *n*-alkanes can enhance the octane number of gasoline fractions, reduce the cloud point of diesel fractions, and improve the low-temperature performance of paraffin products. As indirect coal liquefaction (Fischer-Tropsch (F-T) synthesis) in China reaches large-scale industrialization, F-T products are of interest to produce high-quality diesel oil by isomerization technology. At present, the preferred catalysts are zeolite-based. Beta [1], MOR [2], SAPO-11, SAPO-41, and ZSM-22 [3] zeolites show high activity and selectivity in the isomerization reaction of *n*-alkanes. To further improve the isomerization catalyst performance, the investiga-

tion of binary carrier catalysts has attracted considerable attention [4–9]. Parton et al. [10] prepared a series of mechanical mixtures of bifunctional catalysts based on ZSM-22 and Y zeolites to investigate the synergism of ZSM-22 and Y zeolites in the bifunctional conversion of *n*-decane, and proposed the mechanism for the synergism between ZSM-22 and Y zeolites. Sun et al. [11] used *n*-hexadecane to study the isomerization performance of the mixture of SAPO-11 and Beta zeolites. The results indicated that the mixed catalyst consisting of Beta and SAPO-11 with similar acidity was favorable for the formation of multibranched isomers. Generally, the mechanical mixture will have poor connections because of the large spaces between the zeolites. However, composite molecular sieves synthesized by

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chemical methods not only exhibit the structural characteristics of zeolites [12], but also combine the frameworks of zeolites by chemical bonds. Composite molecular sieves have a reasonable distribution of acidity, good shape-selective performance, and hydrothermal stability, so the composite molecular sieves have potential applications in isomerization processes [13]. Liu et al [5] reported a composite zeolite catalyst (Pt/ β -MCM-41) and a mechanical mixture (Pt/ β + MCM-41) with higher activities for the hydroisomerization of *n*-heptane than Pt/H β . Furthermore, the isomerization selectivity of Pt/ β -MCM-41 was superior to Pt/ β + MCM-41.

At present, composite molecular sieves for the isomerization of long-chain alkanes have not been adequately investigated. The diffusion and reaction mechanisms of *n*-alkanes with different numbers of carbon atoms are different on the catalysts, so the chemical and physical properties of the composite molecular sieves have a great influence on the isomerization performance. Beta is a type of large-pore high-silica crystalline aluminosilicate zeolite, and is an excellent catalyst for light paraffin isomerization reactions [14,15]. Because of its medium acidity and suitable pore size, SAPO-11 shows better performance than other zeolites in lowering the pour point of diesel [16–21]. Thus, the composite molecular sieve of SAPO-11 and Beta is one of the most promising supports for bifunctional catalysts for the hydroisomerization reaction. Wang et al. [22] synthesized the H β (core)/SAPO-11 (shell) composite molecular sieve with the hydrothermal method, in which H β was a seed for the crystallization. Zhang et al. [23] reported that the SAPO-11/Beta composite molecular sieve with a mosaic structure was synthesized in weakly alkaline conditions.

Herein, we present a method to synthesize SAPO-11 (shell)/Beta (core) composite molecular sieves in weakly acidic conditions using zeolite Beta nanoclusters as the silica source and the seed for the crystallization of the composite. For comparison, a mechanical mixture of Beta and SAPO-11 was prepared by full blending. The physicochemical properties of Beta, SAPO-11, the composite, and the mechanical mixture were characterized by X-ray diffraction (XRD), N₂ adsorption-desorption, scanning electron microscopy (SEM), transmission electron microscopy-energy dispersive spectroscopy (TEM-EDS), magic-angle spinning (MAS) nuclear magnetic resonance (NMR), and pyridine adsorption-infrared spectroscopy (Py-IR). In addition, the catalytic performances of these samples were investigated for the hydroisomerization of *n*-dodecane.

2. Experimental

2.1. Synthesis of zeolites

The SAPO-11/Beta composite zeolite was synthesized by the hydrothermal method. The synthesis procedure was as follows: 25 g Beta zeolite ($n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3) = 20$, Catalyst Plant of Nankai University, Tianjin, China) was added to 40 mL of distilled water and the mixture was stirred for 30 min with pH = 8.0. H₃PO₄ (85 wt%, Sinopharm Co., Shanghai, China), pseudoboehmite (70 wt% Al₂O₃, Chinalco, Beijing, China), and dis-

tilled water was mixed and stirred for 10 min. The above slurries were mixed with hybrid template, which was a mixture of di-*n*-propylamine and di-*iso*-propylamine ($m_{\text{DPA}}:m_{\text{DIPA}} = 1$, Sinopharm Co., Shanghai, China), and stirred for 0.5 h to form a homogeneous slurry with pH = 6.0. The gel was moved to autoclaves with capacity 2 L and heated at 200 °C for 24 h. After crystallization, the products were washed, dried at 120 °C overnight, and then calcined at 550 °C for 15 h to completely remove the template. This product was SAPO-11/Beta.

The mechanical mixture of SAPO-11 + Beta was prepared by blending Beta with SAPO-11 ($m_{\text{Beta}}:m_{\text{SAPO-11}} = 3:17$). SAPO-11 was synthesized in accordance with the literature with some modification [24,25]. H₃PO₄ (85 wt%, Sinopharm Co., Shanghai, China), pseudoboehmite (70 wt% Al₂O₃, Chinalco, Beijing, China) and distilled water were mixed and stirred for 10 min. Silica sol and hybrid template were then successively added. The mixture was stirred for 0.5 h at pH = 6.0. The crystallization process and post-treatment of SAPO-11 were the same as that of composite zeolite.

The weight fraction of SAPO-11 in the composite and the mechanical mixture was estimated from a plot of the XRD peak intensity of SAPO-11 ($2\theta = 23.3^\circ$) versus weight fraction of SAPO-11. The plot was obtained by correlating the relationship of the XRD peak intensity of SAPO-11 ($2\theta = 23.3^\circ$) with the known SAPO-11 weight fraction in the mixture of SAPO-11 with Beta prepared by the mechanical blending method.

2.2. Preparation of catalysts

Dilute nitric acid was added into a mixture of the molecular sieve and Al₂O₃ with mass ratio 9, which was extruded to the carrier. The catalysts of 0.5 wt% Pt-loaded zeolite carriers were prepared by the wet impregnation method with H₂PtCl₆ solutions for the metal precursor. The catalysts were dried at 120 °C and then calcined at 450 °C for 4 h.

2.3. Characterization

Powder XRD patterns were collected using a Bruker AXS-D8 powder X-ray diffractometer with Cu K α radiation (0.154 nm) at 30 kV and 10 mA in the scan range 5° to 50°. SEM was performed with a Quanta 400F scanning electron microscope (FEI, Eindhoven, The Netherlands). The morphology and chemical composition of the composite were determined by TEM (Tecnai™ G² F30, FEI) combined with EDS. N₂ adsorption-desorption was measured on a Micromeritics ASAP 2420. Prior to the measurements, the sample (about 200 mg) was outgassed under vacuum at 350 °C for 8 h. The surface area was calculated according to the Brunauer-Emmett-Teller (BET) method and the volume of pores was obtained by *t*-plot analysis. The ²⁹Si, ²⁷Al, and ³¹P MAS NMR spectra were recorded on a Bruker AvanceIII™ 600 spectrometer with frequencies of 119.2, 156.4, and 242.9 MHz, respectively. The ²⁹Si MAS NMR spectra were acquired using a 7-mm probe with a rotor spinning rate of 5 kHz. The ²⁷Al MAS NMR and ³¹P MAS NMR spectra were measured using a 4-mm probe with a spinning speed of 13 kHz. The Py-IR spectra were recorded with a Bruker Ver-

tex 70 FTIR spectrometer. The catalyst samples were ground into a fine powder and pressed into self-supported discs with ZnSe windows. The sample discs were heated to 400 °C and kept for 3 h under vacuum. He flow saturated with pyridine was then introduced into the IR cell at room temperature until adsorption saturation of the samples. The Py-IR spectra were recorded at 150 and 300 °C.

2.4. Catalytic test

The catalytic performance of the samples in the hydroisomerization reaction was tested in a continuous down-flow fixed-bed reactor. The catalysts were reduced *in situ* in a flow of H₂ at 400 °C for 4 h prior to the reaction. The reaction conditions were as follows: *n*-dodecane with liquid hourly space velocity (LHSV) 2.0, H₂/*n*-dodecane molar ratio 2, pressure 2.0 MPa, temperature 240–360 °C. The liquid products were collected after condensation and analyzed by a gas chromatograph (Agilent 6890N) equipped with OV-101 capillary column. The gas-phase product analysis was carried out on-line with a gas chromatograph (Agilent 6890N) equipped with HP-Mole-Sieve5A (30 m × 0.53 mm) and HP-Plot Al₂O₃ (30 m × 0.53 mm). The material balance calculation shows that >95% of the feed was recovered as product.

We used the related physical quantities defined as follows.

The conversion of *n*-dodecane:

$$\text{Conversion (\%)} = \frac{(n\text{-dodecane})_{\text{feed}} - (n\text{-dodecane})_{\text{effluent}}}{(n\text{-dodecane})_{\text{feed}}} \times 100$$

The percentage yield of a particular product fraction *i*:

$$\text{Yield (\%)} = \frac{(i)_{\text{effluent}}}{(n\text{-dodecane})_{\text{feed}}} \times 100$$

Here, $(n\text{-dodecane})_{\text{feed}}$ and $(n\text{-dodecane})_{\text{effluent}}$ are the mass concentrations of dodecane in the feed and effluent, respectively, and $(i)_{\text{effluent}}$ is the mass concentration of product *i* in the effluent.

3. Results and discussion

3.1. Characterization

3.1.1. XRD

Figure 1 shows the XRD patterns of SAPO-11, Beta, SAPO-11/Beta, and SAPO-11 + Beta. The XRD pattern of SAPO-11/Beta shows all the diffraction peaks of both SAPO-11 and Beta without any other diffraction peaks. This indicates that SAPO-11/Beta could be synthesized by the hydrothermal method. The weak diffraction peak at 7.5° in the SAPO-11/Beta pattern indicates that the Beta content was low. The contents of SAPO-11 in SAPO-11/Beta and SAPO-11 + Beta are shown in Table 1.

3.1.2. N₂ adsorption-desorption

Figure 2 shows the N₂ adsorption-desorption isotherms of SAPO-11, Beta, SAPO-11/Beta, and SAPO-11 + Beta. Monolayer adsorption occurred on all the samples at low pressure, so the isotherms had shapes that are characteristic of microporous networks [26]. The adsorption-desorption isotherms of

Fig. 1. XRD patterns of the samples. (1) Beta; (2) SAPO-11/Beta; (3) SAPO-11+Beta; (4) SAPO-11.

Table 1
Textural properties of the samples.

Sample	SAPO-11 (wt%)	$A_{\text{BET}}/(\text{m}^2/\text{g})$			$V_{\text{BET}}/(\text{cm}^3/\text{g})$
		Micropore	External	Total	
SAPO-11/Beta	85	180.4	50.5	230.9	0.089
SAPO-11+Beta	85	204.9	43.5	248.4	0.101
Beta	—	257.3	118.3	375.6	0.130
SAPO-11	—	169.7	39.1	208.8	0.035

SAPO-11 + Beta and SAPO-11/Beta were between the isotherms of SAPO-11 and Beta, indicating that both were a mixture of SAPO-11 and Beta. Furthermore, the SAPO-11/Beta isotherm was different to the SAPO-11 + Beta isotherm. This indicates that the combination mode of SAPO-11 and Beta in SAPO-11/Beta was different to that in SAPO-11 + Beta.

From Table 1, the BET areas (A_{BET}) of SAPO-11 + Beta and SAPO-11/Beta were between those of SAPO-11 and Beta. SAPO-11/Beta had a lower surface area than SAPO-11 + Beta. In addition, the microporous BET area of SAPO-11 (144.2 m²/0.85 g) plus that of Beta (38.6 m²/0.15 g) was equal to 182.8 m²/g, which is close to that of SAPO-11/Beta (180.4 m²/g). There-

Fig. 2. N₂ adsorption-desorption isotherms of the samples. (1) Beta; (2) SAPO-11 + Beta; (3) SAPO-11/Beta; (4) SAPO-11.

fore, the channels of Beta in SAPO-11/Beta were not blocked after the addition of SAPO-11 during the synthesis of SAPO-11/Beta.

3.1.3. SEM and TEM-EDS

Figure 3 shows the SEM images of Beta, SAPO-11, SAPO-11/Beta, and SAPO-11 + Beta. There is an obvious difference in the morphology and particle size of the samples. The particle size of Beta ranged from 0.4 to 0.5 μm . SAPO-11 was composed of uniform cubic particles with particle size of *ca* 4 μm . The image of SAPO-11 + Beta showed a mixture of spherical Beta and cubic SAPO-11 particles. However, the micrograph of SAPO-11/Beta showed pseudo-spherical aggregates accumulated with columnar crystals without single SAPO-11 or Beta particles, and the particle size was *ca.* 5 μm . It has been suggested that SAPO-11 may grow around the undissolved Beta zeolite, forming a SAPO-11 (shell)/Beta (core) structure [27]. These results indicate that Beta and SAPO-11 were combined more tightly in SAPO-11/Beta than in SAPO-11 + Beta. Furthermore, more external surface area was formed owing to the increased interspaces between the SAPO-11 and Beta particles in SAPO-11/Beta [28], which was confirmed by the BET results.

The TEM-EDS analysis results of SAPO-11/Beta are shown in Fig. 4 and Table 2. From Fig. 4(a), the micrograph of SAPO-11/Beta showed rectangularly packed pseudo-spherical aggregates. This can be seen more clearly in the micrograph of Fig. 4(b). Table 2 shows the chemical composition of SAPO-11/Beta from EDS. For the outside (shell) of SAPO-11/Beta (1#), the contents of Si, Al, and P were approximately the same as SAPO-11. The $n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3)$ ratio of SAPO-11/Beta was more than double that of SAPO-11. These results confirmed that SAPO-11/Beta was made up of SAPO-11 (shell) and Beta (core).

3.1.4. Solid-state MAS NMR

Figure 5 and Table 3 show the ^{29}Si MAS NMR results of the

Fig. 3. SEM images of the samples. (a) Beta; (b) SAPO-11; (c) SAPO-11/Beta; (d) SAPO-11 + Beta.

Fig. 4. TEM images of SAPO-11/Beta.

Table 2

Chemical composition of the samples (TEM-EDS).

Sample	$n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3)$	$n(\text{P}_2\text{O}_5)/n(\text{Al}_2\text{O}_3)$
SAPO-11/Beta	0.35	0.99
Beta	28.5	—
SAPO-11	0.10	1.05
1#	0.09	1.07

solid samples. In the ^{29}Si MAS NMR spectra, the resonance peaks at -86 and -91 were assigned to the $\text{Si}(\text{OSi})$ environment of SAPO, and the resonance peaks at -97 , -102 , -107 , and $-110/-116$ corresponded to the $\text{Si}(\text{1Si})$, $\text{Si}(\text{2Si})$, $\text{Si}(\text{3Si})$, and $\text{Si}(\text{4Si})$ environments, respectively [29–32]. From the ^{29}Si MAS NMR spectra of the different samples, the Si chemical environments of SAPO-11/Beta were different with those of SAPO-11 + Beta. The low silicon content of SAPO-11 led to the weak resonance peaks of $\text{Si}(n\text{Al})$ ($n = 1-3$), so SAPO-11 + Beta and Beta have similar ^{29}Si MAS NMR spectra. The ^{29}Si MAS NMR spectrum of SAPO-11/Beta showed a broad band in the range -115

Fig. 5. ^{29}Si and ^{27}Al MAS NMR spectra of the samples. (1) Beta; (2) SAPO-11 + Beta; (3) SAPO-11/Beta; (4) SAPO-11.

Table 3Deconvolution of the ^{29}Si MAS NMR spectra of the samples.

Sample	Si(0Si) -86/-90	Si(1Si) -96	Si(2Si) -102	Si(3Si) -107	Si(4Si) -110/-116
Beta	0	0	16.6	20.5	62.9
SAPO-11	37.7	13.4	16.5	13.2	19.2
SAPO-11 + Beta	5.9	3.9	10.2	11.2	68.8
SAPO-11/Beta	18.7	17.1	15	14.1	35.1

to -86. Compared with SAPO-11 + Beta, SAPO-11/Beta had more Si species of Si(*n*Al) (*n* = 1–3). From the ^{27}Al MAS NMR spectra, SAPO-11/Beta and SAPO-11 + Beta showed two signals at 37.5 and 54.5, which originated from the resonances of tetrahedral aluminum in the framework of SAPO-11 and Beta, respectively [23]. Generally, the chemical shifts of tetrahedral aluminum in microporous aluminophosphate materials are about 40 [33]. The three peaks in the ^{27}Al MAS NMR spectrum of SAPO-11/Beta indicate that the Al atoms have complex coordination environments, which is possibly because of the presence of defect structures in the framework of SAPO-11 with Beta. Moreover, the broad signal at -14 was attributed to the presence of extra-framework aluminum. In addition, the content of extra-framework aluminum in SAPO-11/Beta was clearly more than in SAPO-11 + Beta.

Figure 6 shows that the ^{31}P MAS NMR spectra of SAPO-11, SAPO-11 + Beta, and SAPO-11/Beta. SAPO-11 and SAPO-11 + Beta have two signals at -30.7, which originate from the resonance of tetrahedral phosphorous in the framework [34]. SAPO-11/Beta not only showed the signal at -30.1, but also showed a new signal at -22.5 owing to the presence of extra-framework aluminophosphate [23,35].

3.1.5. Acidity characterization

The acidity of Pt-Beta, Pt-SAPO-11, Pt-SAPO-11/Beta and Pt-SAPO-11 + Beta was investigated by Py-IR. The density and distribution of acid sites were estimated according to the areas of the corresponding IR bands. The results are summarized in Table 4. The weak acid sites, strong acid sites, total acid sites, and the density of B acid sites decreased in the order Pt-Beta > Pt-SAPO-11 + Beta > Pt-SAPO-11/Beta > Pt-SAPO-11. $(\text{B} + \text{L})_{150}/(\text{B} + \text{L})_{300}$ was used to characterize the distribution of weak and strong acid sites. From the $(\text{B} + \text{L})_{150}/(\text{B} + \text{L})_{300}$ values (Table 4), the four catalysts have more weak acid sites than strong acid sites. The order of $(\text{B} + \text{L})_{150}/(\text{B} + \text{L})_{300}$ was as follows: Pt-SAPO-11/Beta > Pt-SAPO-11 > Pt-SAPO-11 + Beta > Pt-Beta. Pt-SAPO-11/Beta had the highest $\text{B}_{150}/\text{L}_{150}$, $\text{B}_{300}/\text{L}_{300}$, and $\text{B}_{\text{total}}/\text{L}_{\text{total}}$ values of the investigated samples, indicating that the catalyst of the composite molecular sieve had the

Fig. 6. ^{31}P MAS NMR spectra of the samples. (1) SAPO-11; (2) SAPO-11 + Beta; (3) SAPO-11/Beta.

highest distribution of B acid sites.

The presence of defect structures in the framework and the formation of extra-framework aluminophosphate demonstrated that the SAPO-11 and Beta frameworks combined by chemical bonds in SAPO-11/Beta. Thus, Pt-SAPO-11/Beta had a different density and distribution of acid sites to Pt-SAPO-11 + Beta. The B/L ratio of Pt-SAPO-11/Beta was higher than the B/L ratios of the other catalysts. Pt-SAPO-11/Beta had a different acidity from the other catalysts. This confirmed that the framework of SAPO-11 and Beta was combined by chemical bonds in SAPO-11/Beta.

3.2. Hydroisomerization performance of the catalysts

Figure 7 shows the conversion of *n*-dodecane over Pt-Beta, Pt-SAPO-11, Pt-SAPO-11 + Beta, and Pt-SAPO-11B catalysts. The conversion of *n*-dodecane measured over the different catalysts decreased in the order Pt-Beta > Pt-SAPO-11 + Beta > Pt-SAPO-11/Beta > Pt-SAPO-11. This order is the same as that of the total amount of acid [14,36].

The yield of isomers over the four catalysts is shown in Fig. 8. Pt-SAPO-11/Beta had the highest isomer yield. Pt-SAPO-11 + Beta had an intermediate isomer yield to the yields of the pure zeolite catalysts.

Höchtel et al. [37] concluded that loading of 0.5 wt% Pt in a bifunctional catalyst could meet the requirement for the hydrogenation-dehydrogenation function. In the isomerization reaction, when the hydrogenating function is highly active, the catalytic performance depends on the B acid sites [8,38]. The isomer yield increased with increasing B/L ratio, in agreement with the results of Py-IR, indicating that the distribution of B

Table 4

Acidity properties of samples determined by Py-IR characterization.

Sample	Acidity ($\mu\text{mol Py/g}$)						Distribution of acid sites			
	150 °C		300 °C		Total					
	L	B	L	B	L	B	$(\text{B} + \text{L})_{150}/(\text{B} + \text{L})_{300}$	$\text{B}_{150}/\text{L}_{150}$	$\text{B}_{300}/\text{L}_{300}$	$\text{B}_{\text{total}}/\text{L}_{\text{total}}$
Pt-Beta	141.4	90.7	107	64	248.4	154.7	1.36	0.64	0.60	0.62
Pt-SAPO-11	15.9	21.8	11.3	14.9	27.2	36.7	1.44	1.37	1.32	1.35
Pt-SAPO-11/Beta	39.7	54.7	19.7	33.9	59.4	88.6	1.76	1.38	1.72	1.49
Pt-SAPO-11 + Beta	48	43.7	26.4	37.9	74.3	81.7	1.43	0.91	1.44	1.10

Fig. 7. Hydroisomerization of *n*-dodecane as a function of temperature over the different catalysts.

Fig. 8. Yield of the isomers against conversion of *n*-dodecane.

acid sites over the bifunctional catalyst had a great influence on the hydroisomerization performance of *n*-dodecane. The Pt-SAPO-11/Beta catalyst, which had the highest number of B acid sites and B/L ratio, gave the highest isomer yield in the hydroisomerization of *n*-dodecane. Compared with Pt-SAPO-11/Beta, Pt-SAPO-11 + Beta had higher conversion of *n*-dodecane at the same reaction temperature owing to the larger total number of acid sites. However, the isomers were easily cracked into small molecules on the strong acid sites of Pt-SAPO-11 + Beta (300 °C), and thus the yield of isomers decreased.

Claude et al. [39] investigated long-chain alkane hydroisomerization over Pt/HZMS-22. The results indicated that short alkanes such as decane and undecane were mainly converted by pore mouth mechanisms, while for dodecane and larger alkanes the contribution of key-lock mechanisms increases with increasing carbon number. In addition, pore mouth mechanisms favored branching at the end position over medium pore zeolite catalysts. As shown from Figure 5, the hydroisomerization reaction of *n*-dodecane was mainly by pore mouth mechanisms over Pt-SAPO-11. Pt-SAPO-11 + Beta and Pt-SAPO-11/Beta gave quite different distributions of mono-

Table 5

Distribution of monobranched isomers obtained by the isomerization of dodecane.

Monobranched isomers	Distribution (wt%)			
	Pt-Beta	Pt-SAPO-11	Pt-SAPO-11/Beta	Pt-SAPO-11 + Beta
2-methyl undecane	15.38	31.34	1.96	2.29
3-methyl undecane	24.07	21.94	22.56	23.09
4-methyl undecane	20.96	16.69	17.00	20.73
5-methyl undecane	37.90	28.65	21.14	19.72
6-methyl undecane	1.69	1.39	37.35	34.17

Reaction conditions: $T = 270\text{ }^{\circ}\text{C}$, $P = 2.0\text{ MPa}$, $\text{LHSV} = 2.0\text{ h}^{-1}$.

branched isomers to the pure zeolite catalysts. Isomers with branching at the C₂ position were rarely detected over the binary carrier catalysts, which favored C₅ and C₆ isomers in monobranched isomers. Thus, the hydroisomerization reaction of *n*-dodecane was mainly by the key-lock mechanism over the binary carrier catalysts.

The relationship between the yield of multibranched isododecanes and dodecane conversion is shown in Figure 9. The yields of multibranched isomers over the binary carrier catalysts were higher than those over the pure zeolite catalysts. This indicates that synergism of Beta and SAPO-11 existed in bifunctional conversion of *n*-dodecane over the composite or mechanical mixture catalyst. The hydroisomerization reaction of *n*-dodecane was mainly by the key-lock mechanism over the binary carrier catalysts. The alkanes were adsorbed on the surface of the catalyst, and then the two ends of the hydrocarbon chain penetrated into a different pore opening, resulting in the formation of more multibranched isomers. Furthermore, the yield of multibranched isomers over Pt-SAPO-11/Beta was higher than that over Pt-SAPO-11 + Beta. The core-shell structure of SAPO-11/Beta differs from the independent structures of SAPO-11 and Beta in SAPO-11 + Beta. Compared with SAPO-11 + Beta, the smaller spacing of SAPO-11 and Beta in SAPO-11/Beta was more favorable for conversion by the key-lock mechanism and migration of the multibranched isomers. On the other hand, Pt-SAPO-11 + Beta has many strong acid sites (300 °C), which result in the multibranched interme-

Fig. 9. Yield of the multibranched isomers against conversion of *n*-dodecane.

diates cracking into small molecules. However, owing to the combination of SAPO-11 and Beta with chemical bonds, the composite molecular sieve had an appropriate number of B acid sites and acid distribution. Thus, a higher multibranched isomer yield was obtained over Pt-SAPO-11/Beta.

4. Conclusions

The SAPO-11/Beta composite molecular sieve was synthesized by the hydrothermal method using zeolite Beta as the silica source. The close combination of the Beta and SAPO-11 forms resulted in many Si species of $\text{Si}(n\text{Al})$ ($n = 1-3$) and extra-framework aluminum atoms, which led to the composite molecular sieve having more weak acid and B acid sites. Compared with the single and mechanically mixed molecular sieve catalysts, *n*-dodecane hydroisomerization over the Pt-SAPO-11/Beta catalyst gave the highest yield of multibranched isomers. The yield of multibranched isomers reached a maximum value of 34% at 89% conversion on Pt-SAPO-11/Beta.

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Graphical Abstract

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Investigation of synthesis and hydroisomerization performance of SAPO-11/Beta composite molecular sieve

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The SAPO-11 (shell)/Beta (core) composite molecular sieve was synthesized using zeolite Beta as the silica source and seed. The Pt-SAPO-11/Beta catalyst gave a higher multibranched isomer yield for the *n*-dodecane hydroisomerization than the mechanically mixed and separate zeolites.

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SAPO-11/Beta复合分子筛的合成及其异构化性能研究

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摘要: 以Beta分子筛为硅源通过水热合成法合成了SAPO-11/Beta复合分子筛, 采用X射线衍射、N₂物理吸附脱附、扫描电镜、透射电镜-能谱分析、固体核磁及吡啶红外等方法对单分子筛、复合分子筛和机械混合分子筛的物化性质进行了表征。以正十二烷为模型化合物, 在固定床反应器上考察了铂负载型分子筛催化剂的异构化性能。结果表明, 复合分子筛的物理化学性质明显不同于单分子筛和机械混合分子筛, 其呈现核壳结构, SAPO-11和Beta间存在化学作用, 使得复合分子筛具有适宜的B酸分布。在正十二烷异构化反应中, 复合分子筛催化剂的异构化性能优于单分子筛催化剂和机械混合分子筛催化剂, 多支链异构体收率高。

关键词: SAPO-11; Beta分子筛; 复合分子筛; 核壳结构; 协同作用; 临氢异构化反应; 多支链异构体

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1. 前言

将直链烷烃异构化可提高汽油馏分的辛烷值、降低柴油馏分的凝点和改善含蜡产品的低温性能。特别是随着近年来煤间接液化F-T合成技术在我国实现大规模产业化, 对其产品异构降凝可生产高品质柴油。目前, 异构化反应大多使用分子筛催化剂。Beta^[1], MOR^[2], SAPO-11, SAPO-41和ZSM-22^[3]分子筛催化剂在烷烃异构化反应中表现出高的活性和异构选择性。为了进一步改善催化剂异构化性能, 双载体催化剂的研究越来越受到诸多学者的关注^[4-9]。Parton等^[10]采用不同的机械方法制备了一系列Pt负载的ZSM-22和Y双载体催化剂, 对ZSM-22和Y分子筛在正癸烷异构反应中协同作用进行了研究, 并提出了协同作用机理。孙霞等^[11]用模型化合物正十六烷对Beta + SAPO-11机械混合分子筛的异构化性能进行了研究, 表明由酸性相近的SAPO-11和Beta分子筛组成的机械混合分子筛催化剂有利于多支链异构体的形成。通常机械混合分子筛由于各分子筛间距较

大, 相互间作用不明显。而化学法合成的复合分子筛除具有多种分子筛的结构特征外^[12], 分子筛间的强相互作用使得复合分子筛具有合理分布的酸性、良好的择形催化性能和水热稳定性, 因此复合分子筛在异构工艺中具有潜在的应用价值^[13]。Liu等^[5]将水热合成的复合分子筛(β -MCM-41)和机械混合分子筛(β + MCM-41)用于正庚烷异构反应研究。相比于Pt/H β , 两种双载体催化剂均表现出更高的异构选择性, 并且复合分子筛催化剂的异构选择性明显优于机械混合分子筛催化剂。

目前, 关于复合分子筛在长链烷烃异构化性能的研究较少。由于不同碳数的正构烷烃在催化剂上的扩散和反应机理存在较大差异, 因此, 复合分子筛的物理化学性质对直链烷烃的异构化性能具有较大的影响。Beta分子筛是一种高硅铝比的大孔硅铝分子筛, 在轻质烷烃异构化反应中表现出良好的异构性能^[14,15]。SAPO-11分子筛具有温和的酸性和适宜的孔道结构, 在柴油馏分的异构降凝中比其他分子筛具有更明显的优势^[16-21], 将两者复合有望在烷烃的异构化反应获得高的催化性能。

Wang 等^[22]采用预制晶种法合成了球形的 Beta (core)/SAPO-11 (shell)复合分子筛。Zhang 等^[23]在弱碱性条件合成了镶嵌结构的 SAPO-11/Beta 复合分子筛。本文以 Beta 为硅源在弱酸性条件合成了 SAPO-11/Beta 核壳结构的复合分子筛,并与机械混合分子筛 SAPO-11 + Beta 进行对比。通过 X-射线衍射、N₂吸附-脱附、扫描电镜、透视电镜-能谱分析、固体核磁和吡啶吸附红外光谱等手段对 SAPO-11/Beta 复合分子筛的物理化学性质进行表征,并以正十二烷为模型化合物对其异构性能进行研究。

2. 实验部分

2.1. 分子筛的合成

复合分子筛采用水热法进行合成。在 25 g Beta 分子筛粉末(南开大学催化剂厂, $n(\text{SiO}_2/\text{Al}_2\text{O}_3) = 20$)中加入 40 g 蒸馏水,调节 pH = 8.0,室温搅拌 0.5 h;将拟薄水铝石(70 wt%, 中国铝业)和正磷酸(85 wt%, 国药集团)与蒸馏水混合,搅拌 10 min;将上述两份浆液混合均匀,再加入二正丙胺与二异丙胺(两者的质量比为 1:1, 国药集团)混合模板剂,继续搅拌 0.5 h 后,调节 pH = 6.0,倒入 2 L 晶化釜中密封,200 °C 晶化 24 h;晶化完成后,经洗涤,120 °C 干燥过夜,550 °C 焙烧 15 h 脱除模板剂得复合分子筛,记为 SAPO-11/Beta。

将 Beta 分子筛(南开大学催化剂厂, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 20$)和 SAPO-11 分子筛按质量比 3:17 混合均匀制得机械混合分子筛(记为 SAPO-11 + Beta)。SAPO-11 分子筛按文献[24,25]中的水热法合成。将拟薄水铝石、磷酸和蒸馏水混合,搅拌 10 min,再依次加入硅溶胶和混合模板剂,强烈搅拌 0.5 h 混合均匀,调节 pH = 6.0,将凝胶到入晶化釜中密封,其晶化条件和后处理与 SAPO-11/Beta 相同。

SAPO-11 + Beta 和 SAPO-11/Beta 中 SAPO-11 的含量由 XRD 谱图中 SAPO-11 衍射峰 $2\theta = 23.3^\circ$ 峰强度与 SAPO-11 含量的标准曲线来确定。标准曲线由一系列已知 SAPO-11 含量的机械混合分子筛的 XRD 中 SAPO-11 衍射峰 $2\theta = 23.3^\circ$ 峰强度所获得。

2.2. 催化剂的制备

将分子筛与氧化铝以质量比 9:1 混合,加入一定量稀硝酸,挤条成型,制成催化剂载体。以 H_2PtCl_6 溶液为金属前驱体,采用湿式浸渍法负载 0.5 wt% Pt,经 120 °C 烘干,450 °C 焙烧 4 h 后制得分子筛催化剂。

2.3. 催化剂的表征

XRD 数据采用装有 Cu 靶 K_α 射线光源(0.154 nm)的 Bruker AXS-D8 型 X 射线衍射仪进行采集。实验条件:

管电压 30 kV, 电流 10 mA, 扫描步长 0.02°, 扫描范围 5°–50°。SEM 为 FEI 公司的 Quanta 400F 场发射扫描电子显微镜。样品的形貌和组成采用备有 EDS 的 Tecnai™ G² F30 型透视电镜进行表征。氮气的物理吸附实验在 Micromeritics ASAP 2420 型物理吸附仪上测定,样品(大约 0.22 g)在 350 °C 真空处理 8 h。样品的比表面积和孔容分别由 BET 方法和 t -plot 方法获得。MAS NMR 在 Bruker 公司的 Avance III™ 600 型核磁共振波谱仪上完成,²⁹Si MAS NMR 采用 7 mm 探头测定,²⁹Si 的共振频率为 119.2 MHz, 转速为 5 kHz。²⁷Al MAS NMR 和 ³¹P MAS NMR 均采用 4 mm 探头测定, 转速为 13 kHz, 共振频率分别为 156.4 和 242.9 MHz。在 Vertex 70 型红外光谱仪(Bruker 公司)上测定吡啶吸附的 FT-IR。先将样品磨成细粉,然后压制自撑片置于 Harrick 公司的原位高温漫反射池(ZnSe 窗片)中密封,升温至 400 °C 保持 3 h 抽真空。然后在室温下向原位池中通入吡啶蒸气至吸附饱和,开始升温,分别在 150 和 300 °C 真空脱附 1 h,并测量 FT-IR 谱。

2.4. 催化剂性能评价

催化剂异构性能的评价在连续流动固定床装置上完成。在反应之前,5 ml 催化剂在氢气气氛中 400 °C 还原 4 h。反应条件: LHSV = 2.0 h⁻¹, $n(\text{H}_2)/n(n\text{-C}_{12}) = 600$, $p = 2.0$ MPa, $t = 240\text{--}360$ °C。液体产物经冷凝后收集,由 Agilent 6890N 型气相色谱分析,色谱柱为 OV-101 毛细管柱, FID 检测器。气相产物经 Agilent 6890N 型气相色谱仪在线分析,其色谱柱为 HP-MoleSieve 5A (30 m × 0.53 mm) 和 HP-Plot Al₂O₃ (30 m × 0.53 mm),并分别连接 TCD 和 FID 检测器。各催化剂的异构反应的物料平衡均达到 95% 以上。本文所用到的相关物理量定义如下。

正十二烷的转化率:

$$\text{Conversion (\%)} = \frac{(n\text{-dodecane})_{\text{feed}} - (n\text{-dodecane})_{\text{effluent}}}{(n\text{-dodecane})_{\text{feed}}} \times 100$$

产物 i 组分的收率:

$$\text{Yield (\%)} = \frac{(i)_{\text{effluent}}}{(n\text{-dodecane})_{\text{feed}}} \times 100$$

其中, $(n\text{-dodecane})_{\text{feed}}$ 和 $(n\text{-dodecane})_{\text{effluent}}$ 分别表示原料和产物中正十二烷的质量浓度。 $(i)_{\text{effluent}}$ 为产物中 i 组分的质量浓度。

3. 结果与讨论

3.1. 催化剂的表征

3.1.1. XRD 结果

图 1 为 Beta, SAPO-11/Beta, SAPO-11 + Beta 和 SAPO-11 的 XRD 谱。由图可见,复合分子筛中出现了 SAPO-11 和 Beta 分子筛的特征衍射峰,没有其他杂峰出

现,表明SAPO-11/Beta分子筛可以很好的通过水热法合成。2 θ = 7.5°是Beta分子筛的特征衍射峰,复合分子筛中7.5°处衍射峰的峰强度较弱,表明复合分子筛中Beta分子筛含量较低。复合分子筛和机械混合分子筛中SAPO-11质量百分含量见表1。

3.1.2. N₂物理吸附结果

图2为Beta, SAPO-11 + Beta, SAPO-11/Beta和SAPO-11的N₂等温吸脱附曲线。在低压时,所有样品均发生单层吸附,曲线呈现平台,此为典型的微孔特征^[26]。机械混合分子筛SAPO-11 + Beta和复合分子筛SAPO-11/Beta的吸脱附曲线位于单分子筛SAPO-11与Beta的吸脱附曲线之间,表明两者是SAPO-11和Beta两种样品的混合物,但两者存在较大差异,由此可知复合分子筛中Beta和SAPO-11的结合方式不同于机械混合分子筛。

由表1可见,SAPO-11 + Beta和SAPO-11/Beta的比表面积均介于SAPO-11和Beta分子筛之间,机械混合分子筛的比表面积大于复合分子筛。并且SAPO-11的微孔比表面积(144.2 m²/0.85 g)加上Beta的微孔比表面积(38.6 m²/0.15 g)等于182.8 m²/g,此值与复合分子筛SAPO-11/Beta的微孔比表面积(180.4 m²/g)接近,表明在复合分子筛的合成过程中Beta分子筛的孔道没有被新生成的SAPO-11分子筛所堵塞。

3.1.3. SEM和TEM-EDS结果

图3为Beta, SAPO-11, SAPO-11/Beta和SAPO-11 + Beta的SEM图。各分子筛样品的形貌及晶粒大小都存在明显的差别。Beta分子筛的粒径大约为0.4~0.5 μ m。SAPO-11呈现出规则的立方体形貌,粒径大小分布均匀,约为4 μ m。机械混合分子筛SAPO-11 + Beta为SAPO-11和Beta简单的混合。复合分子筛SAPO-11/Beta的形貌为柱状颗粒堆积的类球形聚集体,粒径大约5 μ m,没有单独生长的Beta和SAPO-11分子筛存在。由此可推测SAPO-11可能是围绕未溶解的Beta分子筛周围生长的,形成了以SAPO-11包裹Beta的核壳结构^[27]。相比于机械混合分子筛,复合分子筛中SAPO-11和Beta分子筛结合得更紧密,同时,复合分子筛SAPO-11和Beta分子筛的晶间空隙结构可形成更多的外比表面积^[28],这在BET结果中也得到证实。

SAPO-11/Beta复合分子筛的TEM-EDS分析结果见图4和表2。由图4(a)可见,SAPO-11/Beta为长方形材料致密堆积包裹成类球形颗粒。通过球形聚集体散落下的小聚集体(图4(b))可以更清晰看到柱状材料的致密镶嵌。实验中对SAPO-11/Beta进行了EDS能谱分析,结果见表

2。复合分子筛SAPO-11/Beta的外层(1#)硅、磷和铝的分布与SAPO-11分子筛的类似,并且其硅铝比不到复合分子筛的一半,可以证实复合分子筛是由SAPO-11分子筛包裹Beta分子筛形成的核壳结构。

3.1.4. MAS NMR结果

²⁹Si MAS NMR的表征结果见图5和表3。在²⁹Si MAS NMR谱图中,−86和−91处的谱峰可归属于SAPO区的Si(0Si)物种,−97, −102, −107, −110/−116处的谱峰分别归属于Si(1Si), Si(2Si), Si(3Si)和Si(4Si)物种^[29–32]。从图5中各分子筛的²⁹Si MAS NMR可以看出,复合分子筛SAPO-11/Beta与机械混合分子筛SAPO-11 + Beta中硅所处的化学环境存在一定差异。SAPO-11 + Beta的²⁹Si MAS NMR谱图与Beta分子筛的谱图相似,这是由于SAPO-11分子筛中硅含量低,导致谱图中Si(nAl)(n = 1–3)的谱峰较弱。复合分子筛SAPO-11/Beta在化学位移−86到−115间有强弱不等的多重峰。与SAPO-11 + Beta相比,SAPO-11/Beta中具有较多的Si(nAl)(n = 1–3)配位结构的硅。由²⁷Al MAS NMR谱图可见,SAPO-11/Beta和SAPO-11 + Beta在37.5和54.5附近出现谱峰,分别归属于SAPO-11和Beta分子筛的骨架四配位铝^[23]。有文献报导,微孔磷酸铝材料的四配位铝物种在40附近出现共振峰^[33]。复合分子筛在40附近出现三个肩峰,说明分子筛中铝配位环境复杂,这可能是由于SAPO-11和Beta骨架相互作用形成的晶格缺陷所致。同时,SAPO-11/Beta和SAPO-11 + Beta在−14处出现一个宽包峰,可归属于非骨架六配位铝。此外,复合分子筛中非骨架的铝物种明显多于机械混合分子筛。

图6为SAPO-11, SAPO-11/Beta和SAPO-11 + Beta的³¹P MAS NMR谱。由图可见,SAPO-11和SAPO-11 + Beta在−30.7处均出现骨架四配位磷物种的共振峰^[34]。复合分子筛不仅在−30.1处出现一个尖峰,并且在−22.5处出现一个小包峰,后者可归属于非骨架的磷酸铝相中的磷物种^[23,35]。

3.1.5. 分子筛酸性结果

通过Py-IR对Pt-Beta, Pt-SAPO-11, Pt-SAPO-11 + Beta和Pt-SAPO-11/Beta催化剂的酸性进行了表征。由IR谱图振动峰面积可得到催化剂的酸密度和酸分布,结果见表4。可以看出,四种催化剂的单位质量总酸量和B酸量顺序为: Pt-Beta > Pt-SAPO-11 + Beta > Pt-SAPO-11/Beta > Pt-SAPO-11。(B + L)₁₅₀/(B + L)₃₀₀的比值被用于表征催化剂的强酸和弱酸的分布,可见,四种分子筛的表面均有较多的弱酸。四种催化剂中(B + L)₁₅₀/(B +

L)₃₀₀ 排列顺序为: Pt-SAPO-11/Beta > Pt-SAPO-11 > Pt-SAPO-11 + Beta > Pt-Beta. 同时, 从催化剂的酸分布结果可知, 在所有催化剂中, Pt-SAPO-11/Beta具有最高的B₁₅₀/L₁₅₀, B₃₀₀/L₃₀₀和B_{total}/L_{total}, 即复合分子筛催化剂具有较高的B酸分布.

SAPO-11/Beta复合分子筛出现骨架晶格缺陷位及骨架外磷酸铝, 表明复合分子筛中SAPO-11和Beta分子筛的骨架间存在化学作用. 从而导致Pt-SAPO-11/Beta与Pt-SAPO-11 + Beta的酸量和酸分布差异较大. SAPO-11/Beta复合分子筛具有较多Si(nAl)(n = 1–3)配位结构的硅, 因此复合分子筛催化剂表面B/L酸分布明显高于单分子筛和机械混合分子筛. 反之, 复合分子筛催化剂的酸性不同于单分子筛催化剂和机械混合分子筛催化剂, 也印证复合分子筛中SAPO-11和Beta分子筛间存在强相互作用.

3.2. 催化剂的异构化反应性能

图7为Pt-Beta, Pt-SAPO-11, Pt-SAPO-11 + Beta和Pt-SAPO-11/Beta催化剂对正十二烷的异构化性能. 由图可见, 各催化剂上正十二烷转化率大小顺序为: Pt-Beta > Pt-SAPO-11 + Beta > Pt-SAPO-11/Beta > Pt-SAPO-11, 这与它们的总酸量顺序一致^[14,36]. 四种催化剂上正十二烷异构体收率结果见图8. 由图可见, Pt-SAPO-11/Beta催化剂具有最高的异构体收率, Pt-SAPO-11 + Beta催化剂的异构体收率介于两种单分子筛催化剂之间.

Höchtl等^[39]研究表明, 0.5 wt%Pt负载型双功能催化剂具有足够的加氢-脱氢活性位. 在加脱氢活性位足够的催化剂上, 异构反应的控制步骤是烯烃异构体在分子筛载体B酸性中心上的异构反应, 催化剂的B酸中心数将影响反应异构活性^[8,38]. 结合Py-IR结果可见, 异构体收率随着B/L的增加而增加, 表明双功能型催化剂中B酸分布对正十二烷异构化性能有较大的影响. Pt-SAPO-11/Beta催化剂具有最高的B酸密度和B_{total}/L_{total}, 因此Pt-SAPO-11/Beta催化剂获得最高的异构体收率. 在双载体分子筛催化剂中, Pt-SAPO-11 + Beta具有更多的总酸量, 因此呈现出更高的催化活性, 但是Pt-SAPO-11 + Beta上较多的强酸位(300 °C)容易将异构产物进一步裂解为小分子, 从而使得异构产物收率较低.

Claude等^[39]对Pt/HZMS-22上长链烷烃的临氢异构化反应进行了研究. 结果表明, 碳数小于12的正构烷烃主要以孔口机理发生异构反应; 而对于碳数大于12的正

构烷烃, 锁钥机理成为重要的反应方式. 孔口机理有利于端甲基异构体在中孔分子筛催化剂上的生成. 由表5可知, 正十二烷在Pt-SAPO-11上主要以孔口机理发生反应. 双载体催化剂Pt-SAPO-11 + Beta和Pt-SAPO-11/Beta的单支链异构体分布明显不同于单分子筛催化剂, 前者的产物中端甲基异构体含量少, 5-甲基和6-甲基异构体在单支链异构体中所占比重较大, 因此正十二烷在双载体催化剂上的异构反应主要通过锁钥机理进行.

图9为不同转化率下Pt-Beta, Pt-SAPO-11, Pt-SAPO-11/Beta和Pt-SAPO-11 + Beta催化剂上多支链异构体收率. 两种双载体催化剂的多支链异构体收率均高于单分子筛催化剂, 表明复合或混合分子筛中Beta和SAPO-11在正十二烷的异构化反应中存在协同作用. 这是由于正十二烷在双载体催化剂上的异构反应主要通过锁钥机理进行, 即烷烃分子吸附在催化剂的表面, 其两端均可进入分子筛的孔口内发生异构化反应, 从而生成更多的多支链异构体. 同时还可以看出, 复合分子筛催化剂Pt-SAPO-11/Beta的多支链异构体明显高于Pt-SAPO-11 + Beta. 前者形成了以SAPO-11包裹Beta的核壳结构, 不同于SAPO-11 + Beta中SAPO-11与Beta的独立结构, 其SAPO-11与Beta结合更紧密, 锁钥机理发生的概率更大, 有利于生成更多的多支链中间体; 同时, SAPO-11与Beta分子筛间距小, 多支链异构体的迁移和扩散更容易, 减少了多支链中间体在酸性位上的停留时间, 抑制了裂解反应的发生. 另一方面, Pt-SAPO-11 + Beta中具有较多的强酸位(300 °C), 容易将多支链中间体进一步裂解为小分子. 复合分子筛中SAPO-11和Beta分子筛间存在强的相互作用, 具有适宜的B酸酸量和酸分布, 因此具有更高的多支链异构体收率.

4. 结论

以Beta为SAPO-11的硅源合成了SAPO-11/Beta复合分子筛. 复合分子筛中SAPO-11和Beta间结合紧密, 形成了较多的Si(nAl)(n = 1–3)配位结构的硅和骨架外磷酸铝, 使得复合分子筛具有较多的弱酸和B酸. 相比于单分子筛催化剂和机械混合分子筛催化剂, 复合分子筛催化剂Pt-SAPO-11/Beta在正十二烷异构化反应中获得最高的多支链异构体收率. 当正十二烷转化率为89%时, Pt-SAPO-11/Beta的正十二烷多支链异构体收率达到34%.

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