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Catalytic Performance of Molecular Sieves with Different Structures in 1-Butene Cracking

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Abstract: SAPO-18 with different contents of Si were synthesized and characterized by XRD, SEM and NH_3-TPD. Catalytic performance of H-ZSM-5(MFI), H-Beta(* BEA) and SAPO-18(AEI) as different types of molecular sieves have been investigated for of 1-butene cracking reaction in a fixed-bed microreactor. It was found that the acidity and structure of molecular sieves play key roles in the catalytic results of 1-butene catalytic cracking process. These results showed that the high acidity of catalysts improved the 1-butene conversion but led to the decrease of the selectivities of propylene owing to the side reactions (such as hydrogen transfer, aromatization) derived from additional acid sites. What is more, the pore dimension and channel structure determined the available selectivity of propene. SAPO-18-0. 8 with eight-ring pore and pear-shaped cage was achieved satisfactory propylene selectivity approach 59. 1% with 1-butene conversion was 60. 7% under the TOS of 20 min condition.

Key words: SAPO-18; 1-Butene; acidity; structure; propylene selectivity
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Light olefins, are very important feedstocks in modern petroleum and chemical industry. Especially propylene, for example, are exclusively important raw materials for propylene oxide, polypropene, acrylic acid and other derivatives[1]. Currently, the need of propylene is increasing continuously. However, the conventional technique to get propylene cannot fully satisfy the current demand. Some new methods using other raw materials as the feed are being developed, sach as the dehydrogenation of propylene, conversion of methanol or dimethyl ether to propylene, and butene cracking[2-4]. The technology for propylene production by 1-butene cracking are drawing our attention, because the numerous and stable supply of butene from FCC and stream cracking processes.

With the deepening reseach of C_4 olefin cracking prcess, more applications of this tecnique have developed, sach as Propylur, Superflex, MOI, OCC etc.[5-7] Currently, ZSM-5(MFI) is widely applied to production of propylene in the 1-butene catalytic cracking reaction[4,8]. The hydrogen transfer reaction and aromatization reaction on the ZSM-5 lead to the increase of alkanes and C_5^+ hydrocarbon, and decrease propylene yield, which is the most valuable production. So, finding a new and more effective catalyst for 1-butene catalytic cracking reaction becomes the focus of this thesis. It is noteworthy that eight-membered ring microporous SAPO-18 (AEI) and SAPO-34 (CHA) molecular sieves revealed satisfactory performance in methanol-to-olefins (MTO)[9-10]. Some researchers once used SAPO-34(CHA) as cracking catalyst have achieved the high propylene selectivity[11-12]. Our laboratory have synthesized co-crystalline SAPO-18/SAPO-34 molecular sieves, it is applied to the catalytic

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cracking of 1-butene. Experimental results show that the molecular sieve structure had a critical role in the process of 1-butene catalytic cracking[13]. SAPO-18 (AEI) and SAPO-34 (CHA) have similar structure, we do the further reasearch of SAPO-18 molecular sieves. In this work, SAPO-18 samples of different acidity were obtained. Meanwhile, 1-butene cracking was carried out using ZSM-5, Beta and SAPO-18 with defferent ratios of Si/Al_2 to research the effects of the pore demension and channel structure on the propylene selectivity and influence of acidity on the 1-butene cracking reaction.

1 Experimental

1.1 Catalyst preparation

Zeolites ZSM-5 and Beta were obtained from Beijing Institute of petrochemical. The Si/Al_2 ratios of ZSM-5 followed by 88, 104, 163 were denoted ZSM-5-1, ZSM-5-2, ZSM-5-3 and the Si/Al_2 ratios of Beta followed by 34, 55, 84 denoted Beta-1, Beta-2, Beta-3. In order to remove organic template, the ZSM-5 and Beta were calcined at 550 ℃ for 6 h under static atmosphere. Followed by ion exchange with a 0.8 mol/L ammonium nitrate solution at 70 ℃ for three times. After the ion exchange, the samples were washed with distilled water. The distilled water was dried by vacuum pump. All the above zeolites were calcined at 550 ℃ for 6 h again to obtain the H-zeolites.

SAPO-18 was synthesized following the method by Chen *et al.* [14]. Molecular sieve was prepared by hydrothermal synthesized from a mixture of colloidal silica and sodium aluminate, phosphate and distilled water. The initial mixture had the mole composition x SiO_2 : 0.80 Al_2O_3 : 0.90 P_2O_5 : 50 H_2O : 1.60 R (x = 0.8,0.6,0.4), and the R is N,N-diisopropylethylamine hydroxide as template, was sealed in a Taflon-lined stainless steel autoclave and crystallized at 160 ℃ under atmospheric pressure for 8 days without agitation. After cooling the room temperature, this product was recovered by centrifugation and washed with distilled water, and then dried overnight at room temperature, and finally calcined for 5 h at 550 ℃. The morphology of sample SAPO with x = 0.8,0.6,0.4 were denoted SAPO-18-0.8, SAPO-18-0.6, SAPO-18-0.4.

1.2 Catalyst characterization

The sample crystallinity and phase purity were checked by X-ray diffraction patterns (XRD, Cu-K_α radiation, operating at 40 kV and 30 mA, Shimadzu, XRD-6000). XRD data were collected for 2θ between 5° and 60°. The molecular sieves crystal morphology and crystal size were obtained by scanning electron microscopy (SEM, JSM-6380). Measurement of the catalysts acidity by means of NH_3 temperature programmed desorption (NH_3-TPD) was carried out in an Auto Chem 3000 system, using a Micromeritics ASAP 2020, and the acid properties could be calculated. Measurement of specific surface area by N_2 adsorption-desorption isotherms was measured on BeiShiDe 3H-2000PM1 analyzer at 77 K. The total remaining carbon was performed on a NETZSCH TG 209 F3 analyzer with the temperature-programmedrate of 20 ℃/min from 30 to 850 ℃ under oxygen flow.

1.3 Catalytic Activity Evaluation

Catalytic activity tests were performed under atmospheric pressure in a continuous fixed-bed reactor. Generally, 1.0 g sample was filled in a stainless steel fixed bed reactor, which was placed in a furnace. The catalyst was heated to 500 ℃ under flowing N_2(27.3 mL/min). Thereafter, the 1-butene(≥99%) WHSV = 3.5 h^{-1} was added in the reactor. The product distribution of samples collected at 3, 5, 10, 15 and 20 min was analyzed respectively by gas chromatography (GC-14) with a flame ionization detector (FID).

2 Result and Discussion

2.1 Characterization of molecular sieve SAPO-18

In the XRD patterns is presented in Fig. 1, the peaks at 21.3°, 25.7°, 27.8° showed typical powder diffraction patterns of AEI structure and matched with those reported previously[15]. The SEM image of SAPO-18-0.8 exhibit uniform and regular cubic crystals with an average particle size of 0.5 ~ 1 μm and present high crystallinity. These are patterns show that the intrinsic AEI structure of SAPO-18 is preserved and the relative crystallinity changed only slightly. Thus, the change of Si content in the gel mixture had no obvious impact on the crystal structure of SAPO-18.

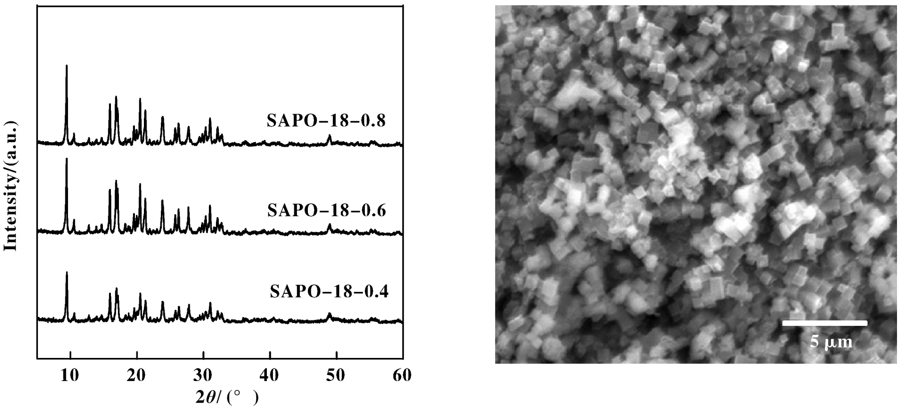


Fig. 1 XRD patterns for SAPO-18-0.8, SAPO-18-0.6, SAPO-18-0.4 and SEM image of SAPO-18-0.8

2.2 NH_3-TPD and BET analysis of different molecular sieves

Table 1 represent measurement results of NH_3-TPD. There are two NH_3-desorption peaks appearing at approximately 207 ~ 448 ℃ of all samples, which associate with weak and strong acid sites. However, there has been an obvious distinction between the acid strength and quantity . For example , T_{max} of ZSM-5, one of which is centered in 262, 267 and 287 ℃, while the other in 434, 442 and 448 ℃, corresponding to the weak acid sites and the strong acid sites, respectively. T_{max} of Beta weak acid sites centered in 258, 263, 270 ℃ and T_{max} of Beta strong acid sites in 412, 420 and 423 ℃. T_{max} of SAPO-18 centered in 207, 215, 220 and 396, 398, 405 ℃; corresponding to weak and strong acid sites, respectively. Hence, it is reasonable to say that the acidic strength of ZSM-5 is significantly higher than the others, while the SAPO-18 has the weakest acidic strength. On the other hand, the acidic quantity of ZSM-5 and Beta zeolites decreases with the increase of silica alumina ratio of zeolites. Beta has the highest amount of acidity (0.37 ~ 0.41 mmol/g), followed by ZSM-5 with the amount of acidity (0.23 ~ 0.36 mmol/g). Compared with above these zeolites, the silica content of silicoaluminophosphate molecular sieves is related to its acidic quantity

Table 1 Results of NH_3-TPD and BET of various molecular sieves

Sample	Ratios of Si/Al_2	T_{max} of weak acid site/℃	Weak acidity /(mmol · g^{-1})	T_{max} of strong acid site/℃	Strong acidity /(mmol · g^{-1})	Total acidity /(mmol · g^{-1})	Specific surface area/(m^2 · g^{-1})
Beta-1	34	270	0.31	423	0.10	0.41	654.7
Beta-2	55	263	0.29	420	0.10	0.39	668.7
Beta-3	84	258	0.30	412	0.09	0.37	636.2
ZSM-5-1	88	287	0.21	448	0.15	0.36	463.1
ZSM-5-2	104	267	0.15	442	0.10	0.25	450.2
ZSM-5-3	163	262	0.14	434	0.09	0.23	430.8
SAPO-18-0.8	0.03	220	0.17	405	0.09	0.26	298.2
SAPO-18-0.6	0.02	215	0.15	398	0.09	0.24	300.1
SAPO-18-0.4	0.01	207	0.11	396	0.09	0.20	318.8

intimately. Therefore, the SAPO-18 acidic quantity increases with the growth of silica content, while its amount of acidity (0.20 ~ 0.26 mmol/g) is the lowest among all samples.

2.3 Effect of acidity on 1-butene catalytic cracking reaction

Product distribution of 1-butene catalytic cracking over different molecular sieves is listed in Table 2. The main products are ethene and propene in 1-butene catalytic cracking reaction in SAPO-18. Methane, propane, butanes and C_5^+ hydrocarbons as byproducts are also formed due to the side reactions, sach as hydrogen transfer, dehydrogenation-aromatization and dealkylation reactions.

Table 2 Product distribution of 1-butene catalytic cracking over different molecular sieves

Catalysts	Conversion /%	product distribution/%					
		CH_4	C_2H_4	C_3H_6	C_3H_8	C_4H_{10}	C_{5+}
Beta-1	93.2	3.2	3.8	4.6	25.7	29.8	26.1
Beta-2	89.1	0.9	3.1	6.1	19.6	36.8	22.6
Beta-3	80.1	1.3	2.7	14.7	24.5	25.8	25.6
ZSM-5-1	97.7	6.4	12.8	3.5	33.8	5.5	35.7
ZSM-5-2	87.1	1.3	9.3	12.0	20.4	9.8	34.4
ZSM-5-3	86.1	1.4	8.0	12.9	21.1	9.2	33.5
SAPO-18-0.8	70.0	0.7	8.8	33.1	11.9	5.7	9.8
SAPO-18-0.6	66.7	1.1	8.4	32.5	11.6	4.6	8.5
SAPO-18-0.4	65.5	0.5	7.7	33.2	10.8	5.1	9.2

Reaction conditions: 1-butene WHSV = 3.5 h^{-1}; Reaction temperature = 500 ℃; TOS = 10 min

Beta-1, Beta-2, Beta-3 and ZSM-5-1, ZSM-5-2, ZSM-5-3 showed high conversion above 97% ~ 86%. As can be found in Table1 and Table 2, more acid sites and stronger acidic strength benefit to 1-butene conversion. Meanwhile, these can further produce a large amount of alkanes (e.g. propane and butane) from olefins (e.g. propylene and butene) by hydrogen transfer reaction on these zeolites. Lin and coworkers proved that high acidity led to a large amount of hydrogen transfer reaction in catalytic cracking reaction. The results are consistent with conclusion of the literatures[15]. SAPO-18 has features of lower acidity and weaker acidic strength, which cause the lower conversion than the Beta and ZSM-5 families zeolites. However, SAPO-18 showed higher propylene selectivity and decreased the hydrogen transfer reaction effectively, as shown in Table 2.

The conversion and propylene selectivity of different types of molecular sieves are listed in Table 3, which further support our opinion that 1-butene conversion increases with the increase of the acid strength and quantity, while propylene selectivity decreases in the series of ZSM-5 and Beta. For example, 1-butene conversion is following order: ZSM-5-1 > ZSM-5-2 ≈ ZSM-5-3, and the order of propylene selectivity is ZSM-5-1 < ZSM-5-2 ≈ ZSM-5-3. Beta shows similar results in the study. But the reaction results obtain from these samples of SAPO-18 are close to each other. We suggest that these results are probably related to the similar number of acid sites in SAPO-18 framework. We can find that reaction results on Beta and SAPO-18 change significantly with the increasing of TOS, because the hydrogen transfer reaction can be suppressed by decrease acid sites. In addition, the total amount of carbon deposition with different structure is following order: SAPO-18 ≈ Beta > ZSM-5.

Table 3 The catalytic performance comparison of different structures and acidity

TOS / Catalysts	3/min	5/min	10/min	15/min	20/min	Coke /% *
	Conversion/% / Propylene selectivity/%					
Beta-1	97.9/1.1	97.5/1.3	93.2/4.7	81.5/16.0	74.6/23.2	1.8
Beta-2	96.6/0.9	93.9/1.1	89.1/6.7	82.5/15.7	64.2/22.7/	1.7
Beta-3	88.6/8.2	85.5/12.1	80.1/18.4	61.8/24.6	56.5/29.8	1.9
ZSM-5-1	97.7/3.29	97.7/3.34	97.5/3.6	97.4/3.8	97.4/3.8	0.35
ZSM-5-2	87.3/13.7	88.1/12.7	87.1/13.8	87.9/13.9	87.4/14.3	0.26
ZSM-5-3	88.3/12.0	87.7/14.7	86.3/14.9	86.1/13.8	86.1/12.7	0.27
SAPO-18-0.8	85.1/13.7	80.3/28.8	70.0/47.3	65.0/55.7	60.7/59.1	2.1
SAPO-18-0.6	84.2/14.8	74.4/36.2	66.8/48.7	63.9/54.5	60.7/58.7	1.9
SAPO-18-0.4	83.4/16.6	76.6/29.4	65.5/50.7	60.2/56.3	52.4/59.9	1.9

Reaction conditions: 1-butene WHSV = 3.5 h^{-1}; Reaction temperature = 500 ℃

* The coke was tested by TG after a TOS of 20 min.

2.4 The influence of the structure of molecular sieves on the catalytic performance

Besides acidity, another important feature of molecular sieves is the ability to act as shape selectivity catalyst for reactant, products and intermediate product owing to their pore dimension and shape of channels. The change of propylene selectivity with 1-butene conversion is showed in Fig. 2. Most of data in Fig. 2 come from the Table 3 , in order to display shape selectivity catalysis of molecular sieves, the ZSM-5 catalytic cracking experiment has been added in the case of using 1-butene 82.5 h^{-1} WHSV as the feed and activation of the catalyst at 500 ℃ in order to obtain propylene selectivity under lower 1-butene conversion.

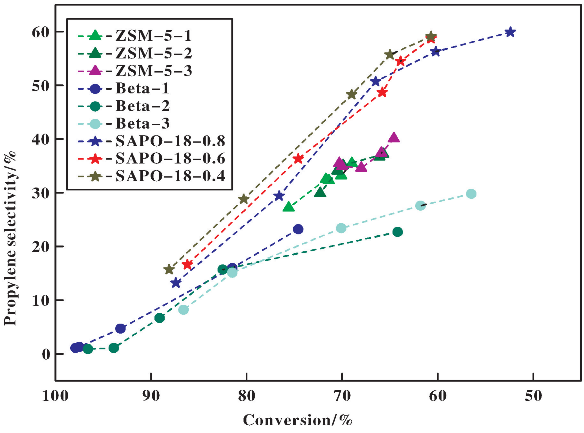
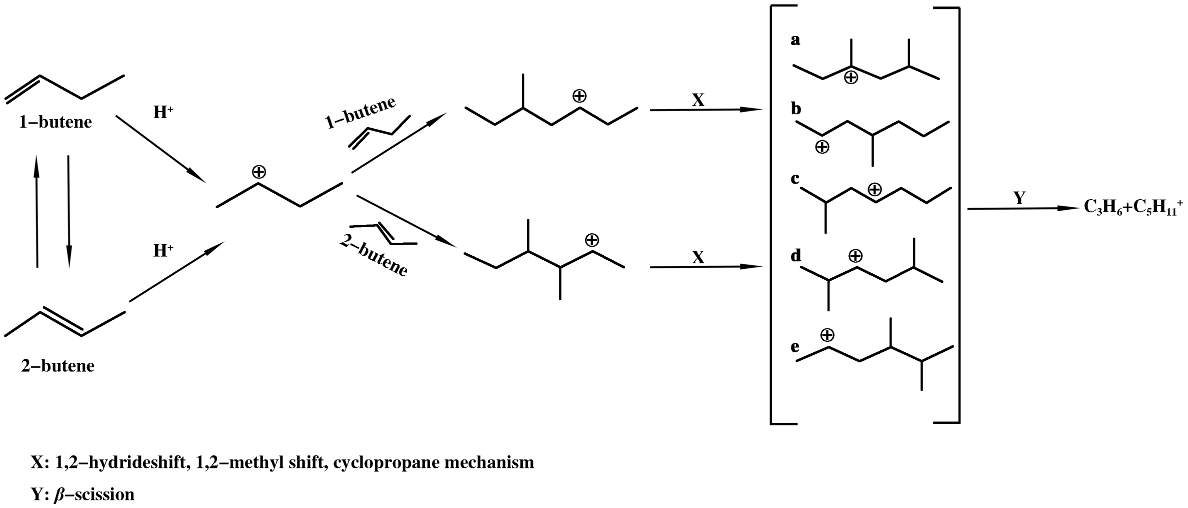


Fig. 2 Conversion and propylene selectivity on molecular sieves with different construction and acidity

Firstly, all three molecular sieves share a similar change trend, the propylene selectivity increases with the decrease of 1-butene conversion. This conclusion in accordance with what we discussed previously. Secondly, improving acid sites promote the 1-butene conversion, but also increase side reaction cause propylene selectivity is decreased. As far as the same structure of molecular sieves is concerned, it is evidently observe that change of propylene selectivity with 1-butene conversion limits within a specific area is shown in Fig. 2. The specific area has little change as different acidity of samples with the same framework. This means that the molecular sieves of channel structure paly significant role in propylene production by 1-butene catalytic cracking reaction. Under the same 1-butene conversion condition, the propylene selectivity gradually increases according to the order of Beta, ZSM-5, SAPO-18. For example, when the conversion reached 70.0% , propylene selectivity on Beta-1, ZSM-5-2, SAPO-18-0.8 was 23.2% , 34.1% , 47.3% respectively. Selectivity of propylene can even approach 59.1% under the condition of 60.7% 1-butene conversion on SAPO-18-0.8.

ZSM-5(MFI) framework contains two overlapping channel systems, which consists of straight channels running parallel to [010] direction having 10-ring of ca. 0.51 × 0.56 nm free diameter and sinusoidal channels running parallel to [100] directions having 10-ring openings of ca. 0.51 × 0.54 nm[16]. This structure, with a high connectivity and without cavities, favors the diffusion of the aromatics. So ZSM-5 has a large number of C_5^+ hydrocarbons in the product distribution and the fewest weight ratio of coke among all catalysts, as shown in Table 3. ZSM-5 exhibited desirable stability under the same reaction condition. The Beta(*BEA) has one-dimensional channel structure of <100> direction 0.66 × 0.67 nm and [001] direction 0.56 × 0.56 nm[17]. Though the Beta has larger pore dimensions with 12-ring windows than ZSM-5, it deactivate faster than ZSM-5 due to absence of multidimensional channel, and the coke result is also showed in Table 3.

The SAPO-18(AEI) framework structure consists of three-dimensional eight-ring channel with pore-openging dimensions of [010] direction 0.38 × 0.38 nm [110] direction 0.38 × 0.38 nm [001] direction 0.38 × 0.38 nm and pear-shaped cage with cage dimension of 1.27 × 1.16 nm[18]. Extensive research indicated that octyl carbocations could be produced by the dimerization of butenes, which is a crucial step of 1-butene catalytic cracking reaction[15,19-20]. In contrast to ZSM-5 and Beta, the SAPO-18 has better 1-butene catalytic cracking performance, because the SAPO-18 with pear-shaped cavity can provide more effective space for dimerization of butene and subsequent isomerization bring specific octyl carbocations to improve propylene selectivity, as listed in Scheme 1. SAPO-18 and SAPO-34 have similar cavity structure and the volume of cavity to match that of the specific octyl carbocations[18,21], which must be effective to provide access of octyl carbocations to the active sites in wall of cavity can occur the β-scission of specific octyl carbocations generate propylene. For example the β-scission of the octyl carbocations a, b, c, d, e by closely fitting the carbocation volume to that of the molecular sieve cavity. Therefore, the SAPO-18 has remarkable shape-selective feature of intermediate products. In addition, eight-ring pore of SAPO-18 can limit macromolecular product outside the cage to further improve propylene selectivity, but it also causes inactive easily. However, the used catalyst can be quickly regenerated by fluid-bed in industry to resolve the deactivation, SAPO-18 molecular sieve with high propylene selectivity has promising development prospect in 1-butene cracking.



Scheme 1 The formation of specific octyl carbocations for the production of C_3H_6 in SAPO-18 cavity

3 Conclusions

SAPO-18 with different contents of Si were successfully synthesized. The high acid amount improved the 1-butene conversion but led to the decrease of the selectivities of propylene owing to the side reactions (such as hydrogen transfer) derived from additional acid sites. What is more, the pore dimension and channel structure determined the available selectivity of propylene. The aromatization reaction which is easy to occur on overlapping 10-ring channel of ZSM-5 leads to the increase of C_5^+ hydrocarbons and the decrease of propylene selectivity. The pear-like cage of SAPO-18 with dimension of 1.27 × 1.16 nm will be more advantageous to for dimerization of 1-butene and β-scission of octyl carbocations to improve propylene selectivity. The SAPO-18 has remarkable shape-selective feature of intermediate products.

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不同结构的分子筛在 1-丁烯中催化裂解性能的研究

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摘要：我们合成了不同 Si 含量的 SAPO-18，并且利用了 XRD、SEM、NH_3-TPD 进行了表征分析. 利用微反固定床反应器评价了代表不同结构的 H-ZSM-5(MFI)、H-Beta(*BEA)、SAPO-18(AEI)系列分子筛的丁烯催化裂解性能. 实验结果表明分子筛的结构和酸性对反应结果都有明显影响，分子筛酸量的增加提高了 1-丁烯的转化率，但酸量过高会引发氢转移、芳构化副反应，从而降低丙烯的选择性；分子筛孔口大小、孔道结构决定了可以获得的最高丙烯选择性. 具有八元环孔口、笼形结构特点的 SAPO-18-0.8 在线时间 20 min 时 1-丁烯裂解中转化率为 60.7%，获得的丙烯选择性达到 59.1%.

关键词：SAPO-18；丁烯；酸性；结构；丙烯选择性