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High Selectivity Production of Propylene from *n*-Butene: Thermodynamic and Experimental Study Using a Shape Selective Zeolite Catalyst

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Abstract Propylene production by *n*-butene catalytic cracking was studied. Thermodynamic analysis and experimental results showed that a shape-selective catalyst, SAPO-34, with a small pore diameter and weak external acidic sites, can increase the propylene yield and selectivity to 48% and 66%, respectively, from the values of 31% and 36% over a ZSM-5 zeolite by inhibiting the formation of isobutene and other hydrocarbons whose dynamic diameters are larger than isobutene. The optimal temperature for the maximum equilibrium yield of propylene decreases from 600 to 550 °C. The effect of temperature, weight hourly space velocity and time-on-stream in the *n*-butene cracking process were also studied.

Keywords *n*-Butene · Catalytic cracking · Propylene · Shape-selective

1 Introduction

Due to the wide application of polypropylene-based products, there is a strongly increasing demand for propylene worldwide. The market demand of propylene is expected to be 84 × 10^6 ton by 2010 and the annual growth rate of propylene capacity is estimated to be almost 5% in average [1, 2]. Currently, propylene is mainly produced by steam cracking (61%) and fluid catalytic cracking (FCC) in refineries (34%). It is expected that these traditional methods will be unable to produce enough propylene to satisfy the increasing market demand, and some new methods using other raw materials as the feed are being developed, which include the dehydrogenation of propane [3], conversion of methanol or dimethyl ether to propylene [4], metathesis of ethylene and 2-butene [5], and butene cracking [6–11]. Among these methods, the process of butene cracking has attracted much more attention, because of the large and stable supply of butene from FCC and stream cracking processes.

Previous results indicated that the yield of propylene in the butene cracking process was limited by thermodynamic equilibrium [12, 13]. However, these calculations considered butene as one species, while experimental results showed that all four isomers of butene were present in the system. Moreover, their concentrations with ZSM-5 or Y zeolite as catalyst agreed well with the thermodynamic equilibrium distribution [14]. Thus, to be more accurate, a thermodynamic calculation should include all four butene isomers as distinct species.

UOP has reported the use SAPO-34 instead of ZSM-5 or Y zeolite as catalyst to crack *n*-butene to propylene in a fixed bed and obtained a feed conversion of 75% and propylene selectivity of 35% at 580 °C [11]. And Zhu et al. [15] introduced that the higher propylene yield of 43% could be achieved on SAPO-34 zeolite and they owed briefly the higher propylene yield to the shape-selectivity of SAPO-34 zeolite. In this work, we included all the butene isomers in the thermodynamic calculation as distinct species, analyzed the relationship between the equilibrium yield and molecular size of each component, and proposed that it was the shape-selectivity of the catalyst which inhibited the formation of isobutene and other hydrocarbons whose dynamic diameters are larger than isobutene, and consequently significantly increased the yield and selectivity of propylene. The effect of

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temperature, weight hourly space velocity (WHSV) and time-on-stream (TOS) in the butene cracking process with SAPO-34 as the catalyst were also experimentally studied.

2 Experimental

2.1 Synthesis of Zeolite and Catalyst Preparation

The SAPO-34 zeolite was prepared using the method reported by Brent et al. [16]. Chemical reagents included phosphoric acid (H_3PO_4, 85 wt%), triethylamine (TEA, 99 wt%), pseudo boehmite ($AlO(OH)_xH_2O$), and silicon sol (40 wt%) with the following chemical composition: Al_2O_3:P_2O_5:SiO_2:TEA:H_2O = 1:1:0.5:2:30 (mol). The cation in SAPO-34 is hydrogen ion. And special surface area of SAPO-34 zeolite is about 500 m^2/g, the pore volume is 0.24 cm^3/g. The XRD spectrum of the synthesized SAPO-34 shown in Fig. 1 contained peaks at about 9.4, 12.8, 17.5, 20.4, 30.5, which is similar to the diffraction of peaks reported previously [17]. The SAPO-34 catalyst we used was a mixture of pure SAPO-34 zeolite, Kaolin and silicon sol with a weight ratio of 30%, 40% and 30%, respectively.

The ZSM-5 catalyst was a mixture of HZSM-5 zeolite, Kaolin and silicon sol with a weight ratio of 30, 40 and 30%, respectively. HZSM-5 zeolite with SiO_2/Al_2O_3 mole ratio of 50 was purchased from NanKai Catalyst Company. The special surface area of HZSM-5 zeolite is about 350 m^2/g, the pore volume is 0.20 cm^3/g.

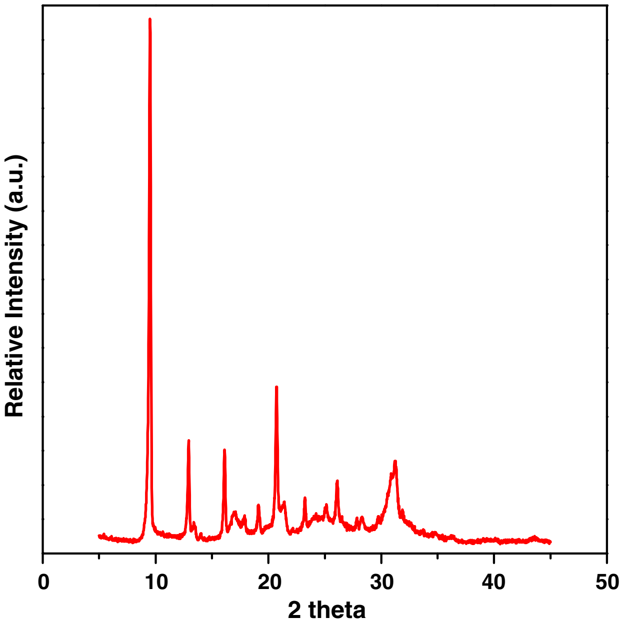

Fig. 1 XRD pattern of synthesized SAPO-34 zeolite

The Kaolin was bought from Sinoma-kaolin Company, whose particle size was about 10 μm. The silicon sol contains SiO_2 with concentration of 40 wt% and the sol particle size is between 10 and 20 nm.

2.2 Catalytic Experiments

Catalytic cracking of 1-butene over the different catalysts was carried out in a continuous flow quartz reactor (6 mm in diameter, 100 mm in length) with a thermocouple in the center of the catalyst. 1-butene had the purity of above 99.5% and was diluted by N_2 in the mole ratio of 2:8. An amount of catalyst was put into the reactor and was activated at 500 °C for 0.5 h under a nitrogen flow (20 mL/min) before a reaction run. Then the feed was introduced into the reactor at the desired WHSV (1–3.3 h^{-1}), temperature (450–650 °C), and TOS (1–5 min). The products were analyzed by online gas chromatography (HP4890D, with a 50-m PLOT Al_2O_3 capillary column and a FID detector). The conversion of the feed, the yield and selectivity of the products are all in terms of the weight percentage.

n-Butene could be 1-butene, *cis*-2-butene, *trans*-2-butene or the mixture of them. Since the reaction rate of double-bond isomerization of 1-butene is much faster than that of the skeletal isomerization [26]. We treat 1-butene, *cis*-2-butene, *trans*-2-butene (*n*-butene) as the feed gas and isobutene as the product when the yield and selectivity of the products were calculated, though the feed is just 1-butene.

3 Results and Discussion

3.1 Thermodynamic Calculation of Butene Cracking

From the literature results [8–10, 13], for a thermodynamic analysis of butene cracking, it can simplify to consider that only $C_2^=$, $C_3^=$, and $C_4^=$ species are present. With Y or ZSM-5 zeolite as the catalyst, the rate of butene isomerization is very fast and the concentrations of the four isomers of butene are always close to the thermodynamic equilibrium concentrations [14]. Thus, regardless of what kind of butene isomer is as stocks, all four isomers of butene exist in the system. The thermodynamic calculation of butene cracking was carried out by the method of minimum Gibbs free energy [18–20] and the calculation results are shown in Fig. 2. The trends are in agreement with experimental results [21] and other thermodynamic calculations [13]. However, considering that the four isomers of butene were existed instead of including only 1-butene, the equilibrium composition of propylene in this work is different from that of Zhu et al. [13].

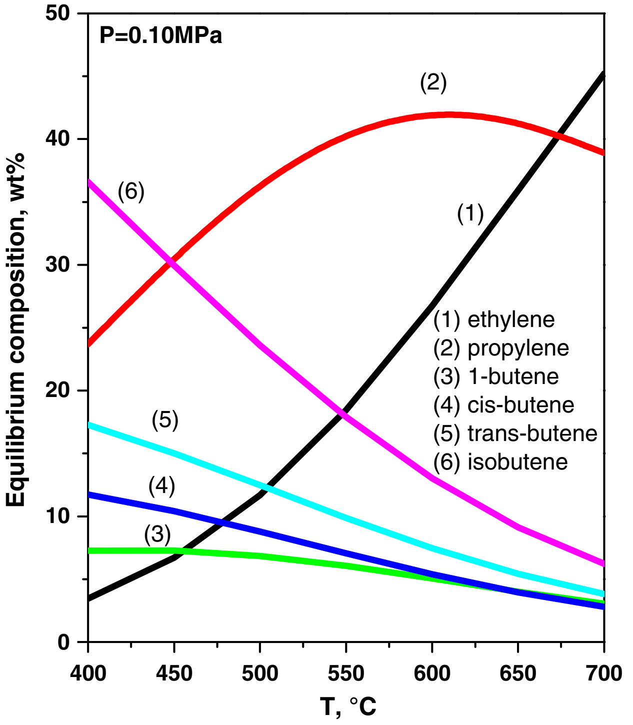

Fig. 2 Influence of temperature on the equilibrium product compositions

The equilibrium concentration of each component at 500 °C and 0.1 MPa is shown in Table 1. The dominant product is propylene whose concentration is 36.57 wt%. These compositions can be compared with the industrial ProPylur process products developed by Lurgi Company where the composition of propylene in the system was about 33–37 wt% at the operation condition of 500 °C, 0.1–0.2 MPa, WHSV 1–3 h^{-1} and ZSM-5 zeolite as catalyst. This is quite close to the equilibrium composition of propylene in Table 1. Apparently, the yield of the propylene in the butene cracking process almost reaches the equilibrium yield.

We also compare the compositions of gas species with molecular dynamic diameter in Table 1 [22]. Since its Gibbs free energy is less, the equilibrium yield of isobutene is higher than that of 1-butene, *cis*-2-butene, *trans*-2-butene and ethylene, and only lower than the equilibrium yield of propylene. The diameters of 1-butene, *trans*-2-butene and *cis*-2-butene are nearly the same and close to that of propylene, while isobutene has a larger diameter. When the catalyst is ZSM-5 with a pore size of 0.53 × 0.56 nm, all the components above can diffuse into the pores. Thus, it has no shape-selective limitation on the formation of propylene and the four isomers of butene.

3.2 The Influence of a Shape-selective Catalyst

On the other hand, the above comparison between the molecular dynamic diameter and equilibrium concentration of the components suggests that if there is no isobutene in the system, a higher selectivity of propylene can be expected. Thus, the use of a shape-selective catalyst with proper external surface acid strength and acid density to limit *n*-butene isomerization on the surface, and proper pore diameter to inhibit the formation of isobutene and other hydrocarbons whose dynamic diameters are larger than isobutene in the inner pores can be expected to be advantageous. By this method, it may be possible to tailor the hydrocarbon components that can be present in this system, change the equilibrium composition of the hydrocarbon species in this system, and thus, increase the yield of propylene. A thermodynamics calculation that uses a different composition of species from those in section 3.1, that is, C_2-, C_3-, and all C_4- species except isobutene are present in the system, is shown in Fig. 3. The system pressure is 0.1 MPa, and the feed mole ratio of 1-butene to N_2 is 2:8.

As shown in Fig. 3, the equilibrium compositions of ethylene and propylene increase, and this is the effect of a shape-selective zeolite which can inhibit the formation of isobutene. Furthermore, the optimal temperature for the yield of propylene also decreases from 600 to 550 °C. The calculation indicated the feasibility of using a shape-selective catalyst to increase the yield of propylene, which encouraged us to seek a catalyst to meet the above requirements.

The pore diameters of ZSM-5 and SAPO-34 zeolite are 0.53 × 0.56 nm [23] and 0.43 nm [24], respectively. When products are formed in the inner pores of a zeolite, only species with a dynamic diameter smaller than the pore diameter (of the zeolite) plus 0.1 nm can be produced by the corresponding zeolite [25]. This explains why ZSM-5 has no selectivity to isobutene (diameter 0.56 nm). In comparison, SAPO-34 with a smaller pore size (0.43 nm) should inhibit the formation of isobutene, while having no limitation on the other products.

From Table 2, it can be seen that the above conjecture on shape selectivity is supported by the experimental

Table 1 Equilibrium composition of the components and their corresponding dynamic diameters

Components	Ethylene	Propylene	1-butene	*cis*-2-butene	*trans*-2-butene	Isobutene
Equilibrium composition wt% (500 °C, 0.1 MPa)	11.57	36.57	6.85	8.80	12.48	23.62
Dynamic diameter/nm	0.43	0.50	0.51	0.51	0.51	0.56

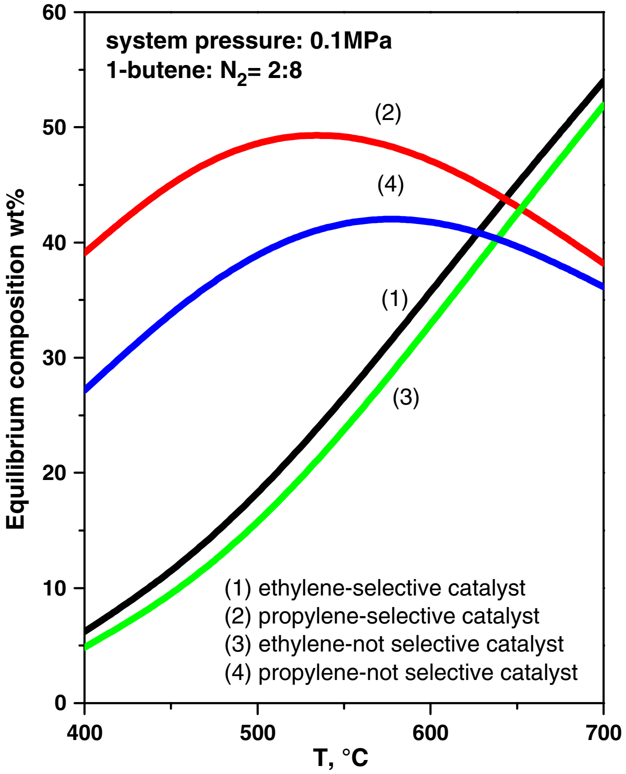

Fig. 3 Comparison of the catalyst effect on equilibrium composition of ethylene and propylene

results. The concentrations of the four butene isomers almost reach the equilibrium values catalyzed by ZSM-5. However, using SAPO-34 as the catalyst, the concentrations of the four butene isomers are far from the thermodynamic equilibrium values. Specifically, the value of isobutene is much lower than the equilibrium value. This result confirms that the formation of isobutene from *n*-butene can be almost completely inhibited by using SAPO-34 as the catalyst. US Patent 6,049,017[11] indicated that the conversion of a linear butene catalyzed by SAPO-34 was about 60–70%, while the conversion of isobutene was less than 15%. Those quite different conversions can also be explained by the shape selectivity of SAPO-34 for *n*-butene and iso-butene.

Table 2 Distribution of the four butene isomers from 1-butene cracking over different catalysts (500 °C, 0.1 MPa, 1.4 h^{-1}, 1-butene:N_2 = 2:8, TOS: 1 min)

	Equilibrium composition wt%	Composition with ZSM-5 wt%	Composition with SAPO-34 wt%
1-butene	13.23	16.65	27.93
Isobutene	45.65	42.66	5.91
trans-2-butene	24.11	23.53	37.33
cis-2-butene	17.00	17.15	28.90

The feed conversion with ZSM-5 as catalyst is 86.74 wt%, and with SAPO-34, 72.32 wt%

Furthermore, we compared the selectivity and yield of ethylene and propylene produced using ZSM-5 and SAPO-34 as the catalyst, respectively. Since the isomerization of 1-butene, *cis*-2-butene and *trans*-2-butene are much faster than the skeletal isomerization, their concentrations reach equilibrium quickly [26]. Therefore, we can treat the three *n*-butenes as the feed gas and isobutene as the product. The conversion of butene and the selectivity and yield of the different products are shown in Table 3.

As shown in Table 3, there is a dramatic increase in the selectivity of propylene from 36% (ZSM-5 catalyst) to 66% (SAPO-34 catalyst). Meanwhile, the yield of propylene also increases from 31% to 48%. The experimental results confirm that SAPO-34 zeolite is effective in increasing the yield and selectivity of propylene by inhibiting the formation of isobutene.

3.3 The Effect of the Operation Condition

The effect of the operation conditions, temperature, WHSV and TOS on the feed conversion, product yield and selectivity were studied during the 1-butene catalytic cracking process with the SAPO-34 as catalyst. The experimental results are shown in Figs. 4, 5 and 6.

From Fig. 4a, it can be seen that the butene conversion increases with temperature rising. The selectivity and yield of propylene have the optimal value in the temperature range between 450 and 650 °C which are in agreement with the values obtained from the thermodynamic calculation. It should also be noted that the yield of propylene in the experiment is approximately the equilibrium yield of propylene, as shown in Fig. 4a. From Fig. 4b, with the temperature increases, the selectivity of methane, ethane and the ethylene also increase for the reason that those products are usually considered as the products of the thermal creaking and with the temperature increase, the reaction rate of thermal creaking rises. The propane and the butane are the products of hydrogen transfer reaction which is exothermic reaction, and therefore their selectivity declines with the increasing of the temperature. And the selectivity of C_{5+} drops as the temperature rises for the cracking rate will increase and C_{5+} will crack into other small olefins further.

Table 3 Influence of the catalyst on the product selectivity and yield (500 °C, 0.1 MPa, 1.4 h^{-1}, 1-butene:N_2 = 2:8, TOS: 1 min)

Zeolite	Product selectivity wt%		Product yield wt%	
	Ethylene	Propylene	Ethylene	Propylene
ZSM-5	14.56	35.61	12.63	30.89
SAPO-34	13.15	66.33	9.51	47.98

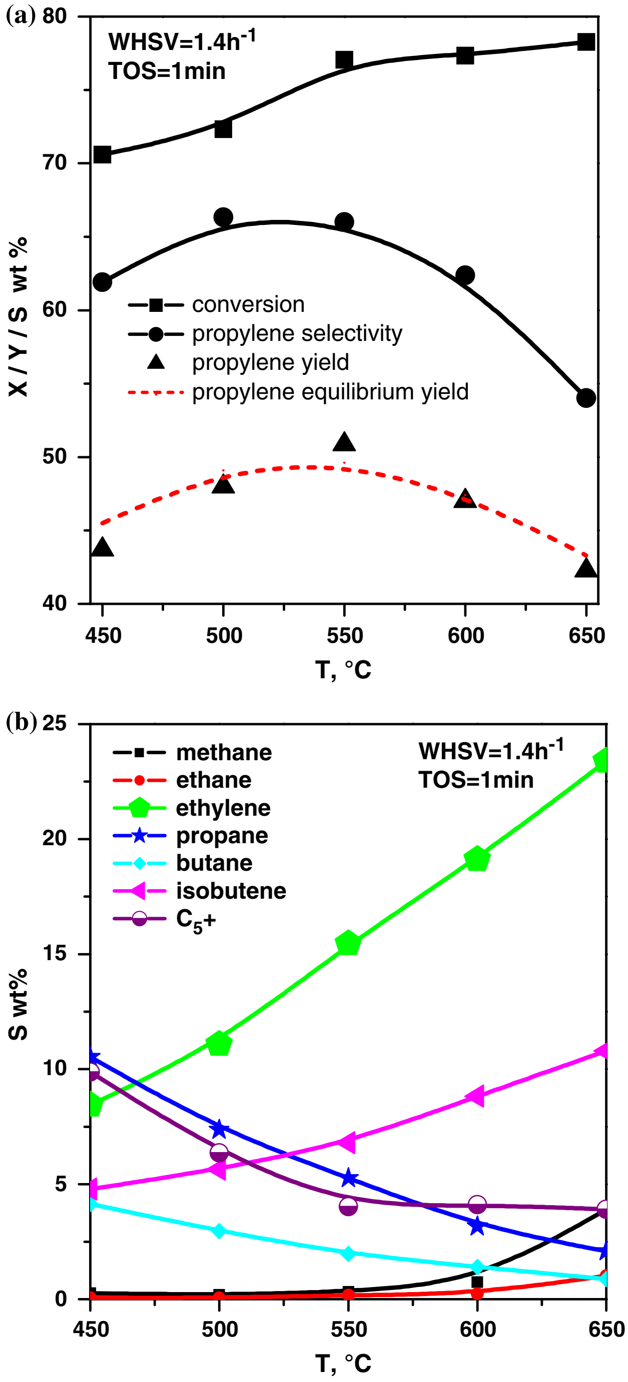

Fig. 4 (**a**) Effect of temperature on the feed conversion, propylene yield and selectivity (**b**) Effect of temperature on the selectivity of products

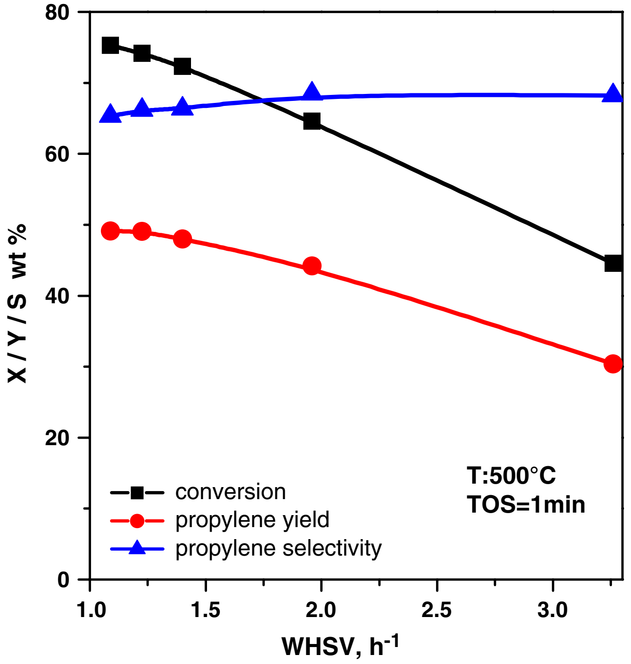

Fig. 5 Effect of WHSV on the feed conversion, propylene yield and selectivity

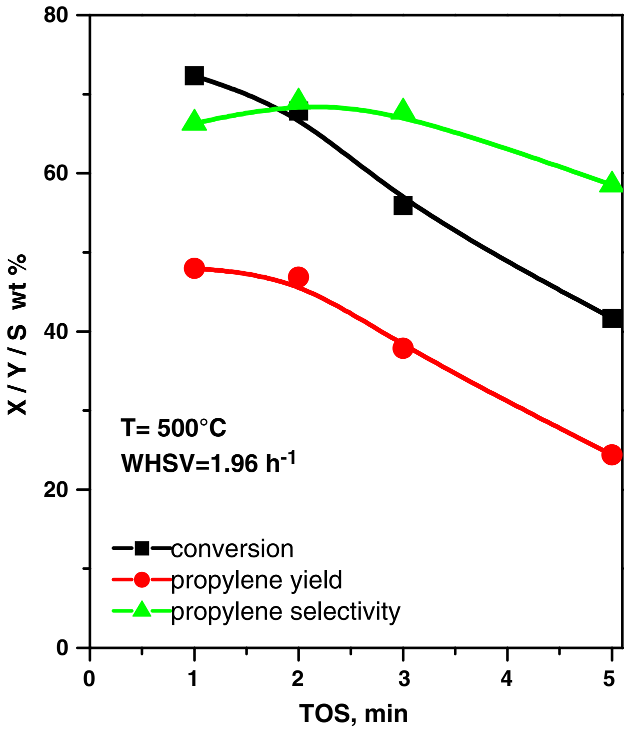

Fig. 6 Effect of TOS on the feed conversion, propylene yield and selectivity

From Fig. 5, it can be seen that as the WHSV increases, the residence time of the feed, the feed conversion and the propylene yield decreases. The selectivity of propylene increases with increasing WHSV because the side reaction, hydrogen transfer, is limited due to the short residence time.

As the TOS increases, the activity of the catalyst declines. As shown in Fig. 6, the feed conversion and propylene yield decreases rapidly and this indicates that the proper reactor form for this process should be a fluidized bed. The selectivity of propylene first increases slightly for that with the increasing of TOS, the acidity of the catalyst decreases and the hydrogen transfer reaction are restrained. The reason for the subsequent decrease of the propylene selectivity can be explained by the reported reaction pathway of butene [9]. With activity decreasing of the catalyst, there is less cracking of the pentene produced by the dimerization of butene, and pentene selectivity increases from 3.14% to 14%. This leads to the decrease of the propylene selectivity.

4 Conclusions

A thermodynamic calculation and experimental result shows that the yield and selectivity of propylene is greatly increased by the use of a shape selective catalyst, SAPO-34, compared with the use of ZSM-5 as catalyst. The reason is that SAPO-34 can limit the production of isobutene and other hydrocarbons whose dynamic diameters are larger than isobutene due to its small pore diameter and weak external surface acid sites. The yield of propylene has an optimal value in the temperature range between 450 and 650 °C and decreases with WHSV and TOS increase. Due to the rapid deactivation of SAPO-34 with extended TOS, the proper reactor for this process should be a fluidized bed.

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