

HEXENE CATALYTIC CRACKING OVER 30% SAPO-34 CATALYST FOR PROPYLENE MAXIMIZATION: INFLUENCE OF REACTION CONDITIONS AND REACTION PATHWAY EXPLORATION

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Abstract - Higher olefins are produced as a by product in a number of refinery processes and are one of the potential raw materials to produce propylene. In the present study, FCC model feed compound was considered to explore the olefin cracking features and options to enhance propylene using 30% SAPO-34 zeolite as catalyst in a micro-reactor. The superior selectivity of propylene (73 wt%) and higher total olefin selectivity was obtained over 30% SAPO-34 catalyst than over Y or ZSM-5 zeolite catalysts. The thermodynamical constraints were found to be relatively less serious in the case of 1-hexene conversion. Most of the 1-hexene follows a direct cracking pathway to give two propylene molecules, due to weak acid sites and better diffusion opportunities. The higher temperature and short residence time could also suppress the hydrogen transfer reactions. From OPE (olefins performance envelop) the products were classified as primary, secondary, or both. Iso-hexene (2-methyl-2-pentene) cracking was also analyzed in order to justify a shape selective effect of the SAPO-34 catalyst. A detailed integrated reaction network together with an associated mechanism was proposed and discussed in detail for their fundamental importance in understanding the olefin cracking processes over SAPO-34.

Keywords: Catalytic cracking; Shape selectivity; Conversion; Propylene selectivity; 30% SAPO-34.

INTRODUCTION

Propylene is a basic organic chemical raw material, mainly used in the production of polypropylene, acrylonitrile, propylene oxide, and other well-known petro-chemical products. The continuously increasing demand for propylene has exceeded ethylene demand in recent years (Nawaz et al., 2009). According to the U.S. Chemical Market Association (CMAI) statistics, it is forecasted that the propylene demand is increasing at the rate of

about 5% annually (Ladwig et al., 2000). In overall production scenario, about 70% of propylene is produced by steam crackers and 28% is from the FCC processes (Xiang and Tian, 2005). Moreover, independent of the catalyst and reactor choices, in the existing FCC process the one-way yield of propylene is not more than 30 percent (Nawaz et al. 2009). Therefore, in recent years, on-purpose propylene production technologies were considered to be the better option in order to meet the growing propylene demand (Nawaz et al., 2006 and 2009).

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Among on-purpose technologies, higher olefin to lower olefin conversion is the most economical and viable route to produce propylene (Nawaz et al., 2009).

The olefin cracking reactions over zeolite have been studied extensively and explained in terms of a carbenium ion mechanism (Jacobs, 1977). Most of the commercially available catalysts fail to exhibit shape selective phenomena for propylene and their acidic strength did not meet the reaction requirements. The concept of shape-selective catalytic cracking is mainly reflected in two ways (Smit and Maesen, 2008), first in the shape-selective molecular sieve that improves conversion of raw materials and second in the increase in desired product selectivity. Therefore, the catalyst, having selective pores, does not allow the higher hydrocarbon to form, which is highly desirable for olefin cracking. This is the simplest concept of shape selectivity, yet our mechanistic understanding remains limited regarding the phenomenological behavior during the course of cracking reaction.

Previously, Y-zeolite and ZSM-5 zeolite catalysts were examined as cracking catalysts in a micro-reactor, pilot plant and full scale models (Tang et al., 2005). These zeolite materials are crystalline and contain micro-pores of different sizes. Y-zeolite is too acidic and promotes both cracking and hydrogen transfer reactions violently (Buchanan et al., 1996). On the other hand, ZSM-5 zeolite has the macromolecular shape-selective effect, while light hydrocarbon does not follow shape-selectivity (Buchanan et al., 1996). The strong Brønsted acid sites of ZSM-5 promote surface reactions and somehow take part in further propylene cracking. However, a silico-aluminophosphate molecular sieve (SAPO-34) has a small pore size and weak acidity (Lok et al., 1984). Molecular sieve modification and the use of various additives can improve the product quality and selectivity. SAPO-34 is composed of central oxygen having an elliptical cage and the three-dimensional structure of silicon channel aluminum phosphate, structural code CHA (Jacobs, 1977; Marchese et al., 1999; Lok et al., 1984; Such and Pang, 2004). The orifice diameter is 0.43 nm and the cage diameter 0.67×1.0 nm (Dent and Smith, 1958).

In this paper, we not only experimentally justify the superior olefin cracking ability of 30% SAPO-34 catalyst for propylene enhancement, but emphasize the explanation of the shape selectivity behavior in comparison with Y-zeolite and ZSM-5. A cracking reaction network was proposed on the basis of a β -scission carbenium ion mechanism. Previously,

much attention has been given to improve operating conditions, integration of reactors and their assemblies. However, no discussion has been found in the open available literature about selective hexene catalytic cracking over SAPO-34 and how to control cracking at the molecular level to enhance the desired product selectivity.

EXPERIMENTAL

The Y-zeolite (Y-type faujasite) with a Si/Al ratio of 2.5 and ZSM-5 zeolite with a Si/Al ratio of 25 was provided by Nankai Catalyst Company, Tianjin, China. The 30% SAPO-34 catalyst was prepared as a mixture of pure SAPO-34 zeolite, kaolin and silicon solution with a weight ratio of 30%, 40% and 30%, respectively. At first, SAPO-34 catalyst was prepared by sequential mixture of Al_2O_3 : P_2O_5 : SiO_2 : TEA: H_2O = 1: 1: 0.5: 2: 100 (molar ratios), then stirred, aged at room temperature for 24 h, autoclaved at 200°C for 24 h, filtered, dried and finally crystallized at 550°C. In order to increase the attrition resistance of SAPO-34 to meet commercial requirements of fluidization catalysts, 30% SAPO-34 was prepared. As SAPO-34 has Si based acid sites and structure, kaolin and silicon solution were used as binder, without affecting internal pore structure and acidity. The presence of kaolin modifies its outer quo's (outer shape and/or structure), which is really useful to enhance diffusion opportunities. BET surface area, SEM and XRD characterization tests were conducted to confirm textural stability of the SAPO-34 catalyst.

In this experimental study, 98% pure 1-hexene was used as a feed to investigate the catalytic activity of prepared SAPO-34 catalyst. Analytical grade 98% pure 1-hexene (IUPAC name: hex-1-ene) and 2-methyl-2-pentene of *Alfa Aesar* (A Johanson Matthey Company, UK) were used as raw materials for the current experimental investigation in a micro-reactor. The product distribution obtained from the continuous flow fixed bed quartz reactor (6 mm in diameter, 100 mm in length) with a controlled temperature setup was analyzed by online gas chromatography (with a 50-m PLOT Al_2O_3 capillary column and a FID detector). A number of experimental conditions, like temperature, 350-650°C; WHSV from 0.5-8 h^{-1} and TOS between 1.5-9 min; were applied to explore catalyst shape selectivity and optimum conditions for increasing existing propylene selectivity. The calculated values are given in weight percentages.

RESULTS AND DISCUSSION

Catalyst Characterization

The SEM image of 30% SAPO-34 is shown in Figure 1. The small slits can be seen in the side picture of the SEM image; these are due to the presence of kaolin. The XRD spectrum of 30% SAPO-34 ensured that there is no significant change in structural topology, as shown in Figure 2. SAPO-34 zeolite frameworks and crystal shape depend upon AlO_4^- , PO_4^+ , SiO_4 composition and its appropriate elemental mixing ratio. SAPO-34 has Si based acid sites and structure, while both Y and ZSM-5 have Al based acid sites and structures (Buchanan et al, 1996). The comparison of these

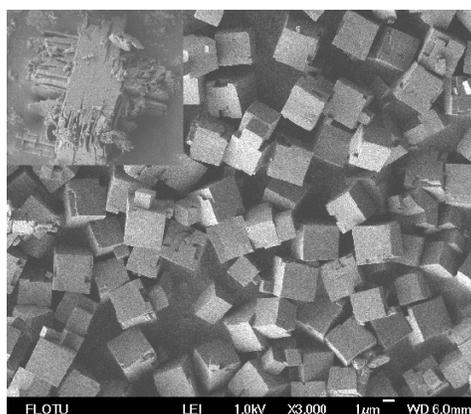


Figure 1: SEM image of the 30% SAPO-34 catalyst

zeolite catalyst characterization results is tabulated in Table 1. The larger surface area of the catalyst helps to retard coke formation and weak acidity helps to reduce surface reactions that lead to coke precursors (Tang et al., 2005).

Effect of Thermal Cracking

At first, the pyrolysis (thermal cracking) of hexene (both n-hexene and iso-hexene) at 500°C and 0.12 MPa was experimentally investigated. Under the above mentioned operating conditions, the conversion rate was negligibly low, being 1.12 and 1.94 wt% for 1-hexene and 2-methyl-2-pentene, respectively. Therefore, in the current study the impact of pyrolysis has been neglected.

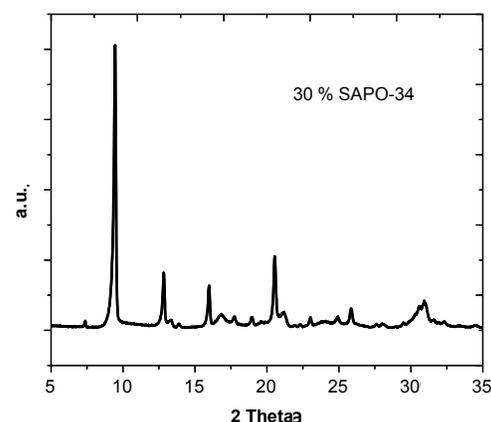


Figure 2: XRD spectrum of the 30% SAPO-34 catalyst

Table 1: Basic characterization data of different zeolite catalysts

Catalyst	BET Surface Area (m^2/g)	Pore size (nm)	Acidity (Buchanan et al., 1996)
Y-zeolite	616.3	0.69-0.74	Highly acidic
ZSM-5 zeolite	349.8	0.51-0.58	Acidic
SAPO-34 zeolite	440.1	0.34-0.43	Weak acidic

Shape-Selective Effect of SAPO-34

The performance of Y, ZSM-5 and 30% SAPO-34 zeolite catalysts was analyzed and it was observed that the cracking was only enhanced due to the shape selectivity (Smit and Maesen, 2008) and suitable acidity. 2-methyl-2-pentene (iso-hexene) with its large dynamic diameter is not able to enter into the 30% SAPO-34 catalyst pores (internal channels). Therefore, SAPO-34 shows lower conversion in comparison with Y and ZSM-5 zeolite catalyst, as shown in Table 2. Owing to this inherent problem, most of the iso-hexene stayed over the catalyst surface and promotes isomerization and hydrogen transfer reactions. The large pore size of Y and

ZSM-5 allowed iso-hexene to undergo cracking with higher conversion rate, but failed to exhibit shape selectivity phenomena for propylene. Detailed experimental results are shown in Table 2.

Using Y-zeolite as catalyst, the total olefins selectivity obtained was also relatively low. On the other hand, using SAPO-34 as a catalyst, iso-hexene cracking results showed superior propylene selectivity, i.e., 72.8%, with higher total olefins selectivity. Iso-hexene was considered as feed just to explain the shape selectivity effect of different catalysts. Because the isomerization rate is faster than cracking, exceptional control of stereochemistry during the olefins cracking reaction is needed, as provided by the SAPO-34.

Table 2: Iso-hexene (2-methyl-2-pentene) cracking over different types of zeolite catalysts (Temperature 500°C, Pressure 0.12 MPa, WHSV 2 h⁻¹ and TOS 1.5 min)

Catalyst	Y-zeolite	ZSM-5	SAPO-34
Conversion of feed, wt%	98.23	98.26	42.35
The apparent reaction rate coefficient k, s ⁻¹	10.1	10.0	1.9
Propylene yield, wt%	19.57	45.78	30.82
Total olefins selectivity, wt%	24.97	81.78	92.88
Propylene selectivity, wt%	19.92	46.59	72.79

However, during olefin conversion to lower olefins, it is undesirable that even a small amount of olefins be converted to paraffins. The problem of lower conversion is solvable, but to reprocess paraffins to olefins is too difficult. The catalysts of higher conversion and lower desired product selectivity were not recommendable. SAPO-34 has a better catalytic performance in converting higher olefins to lower olefins than Y and ZSM-5 zeolites.

Impact of Raw Material

In the present experimental study, n-hexene (1-hexene) and iso-hexene (2-methyl-2-pentene) were used as feed to analyze catalytic activity in the sense of conversion and desired product selectivity, but no distinction was made of other products. Hexene has seventeen isomers, shown in Table 3, with their thermodynamic equilibrium composition in the cracking reaction. Because of the presence of the double bond, olefin isomerization is very quick and thermodynamic equilibrium immediately reached, which affects the overall performance of the reaction.

Although the hexene configuration has less effect on propylene selectivity, the conversion rates over SAPO-34 declined from 47.24% to 42.35% upon using n-hexene and iso-hexene as feed, respectively. n-Hexene easily diffuses into the channels of SAPO-34, while iso-hexene isomers could not. Moreover, reaction in the internal channels and diffusion

opportunities directly affected the conversion rate of 1-hexene in terms of concentration. In iso-hexene cracking, the isomerization rate is far greater than the decomposition rate and affects product distribution. It has been reported in the literature that, with the increase in the carbon chain, the isomerization rate was unchanged (Abbot and Wojciechowski, 1985), while the cracking rate increased rapidly (Kissin et al., 2001). Therefore, by using SAPO-34 as a cracking catalyst for 1-hexene, we prevent that the feed undergoes isomerization and HT reactions, with ultimately enhanced propylene selectivity.

Temperature Effect on Cracking

The effect of temperature on the 1-hexene catalytic cracking reaction over 30% SAPO-34 zeolite was investigated over the range of temperatures between 350 - 650°C and results are shown in Figures 3 and 4. It is obvious that, with the increase in temperature, the conversion rises. At 350°C, the conversion was 19.5% and the main products were butene, pentene and propylene. While at 500°C, the conversion of raw material reached 46.7 % with the propylene selectivity of 72.2 %. The further increase in temperature up to 650°C resulted in higher conversion, i.e., 84.25%, at the expense of lower propylene selectivity. Optimum propylene selectivity was noted around 550°C, where the total olefin selectivity is also high (see Figures 3).

Table 3: Hexene isomers and their balanced percentage composition at 500°C

Hexene Isomers	Balanced composition, %	Hexene Isomers	Balanced composition, %
1 - hexene	1.01	3,3 - dimethyl -1 - butene	0.08
2,3 - dimethyl -1 - butene	11.61	trans-3 - hexene	2.20
2,3 - dimethyl -2 - butene	18.15	4 - methyl -1 - pentene	0.64
2 - ethyl -1 - butene	5.35	cis -2 - hexene	3.10
2 - methyl -1 - pentene	8.63	cis -3 - hexene	1.42
2 - methyl -2 - pentene	21.41	cis -4 - methyl-2 - pentene	4.43
3 - methyl -1 - pentene	2.30	trans-2 - hexene	4.46
cis -3 - methyl-2 - pentene	4.15	4 - methyl -2 - pentene	5.99
trans -3 - methyl-2 - pentene	5.07		
n-hexene			12.19
iso-hexene			87.81

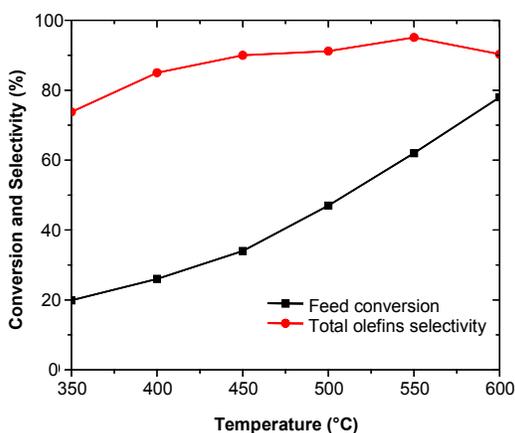


Figure 3: Effect of temperature on the conversion and total olefins selectivity

The decrease in the hydrogen transfer reaction results in decrease in final paraffin content and the total olefin content increased, as shown in Scheme I. The slight shift in acidity and pore blockage may disturb the whole scheme. 1-Hexene cracking mainly follows two pathways. At lower temperature, 1-hexene converts to propylene via indirect cracking and butene, pentene, propylene were quite selective as shown in Figure 4. With the increase in temperature, the direct cracking becomes dominant (1-hexene split into two propylenes). Further increase in temperature enhanced the cracking rate and propylene produced by both routes. On the other hand, a free radical mechanism increases coke and/or may crack propylene further.

Weight Hourly Space Velocity (WHSV) Impact

1-Hexene was investigated as FCC model feed compound over 30% SAPO-34 zeolite to obtain optimum desired product selectivity in the range of WHSV from 0.5 - 8 hr⁻¹ as shown in Figure 5 and 6. Owing to the short residence time with the improvement in space velocity, the conversion of raw material declined. With the increase of space velocity, the total olefins selectivity remains almost constant

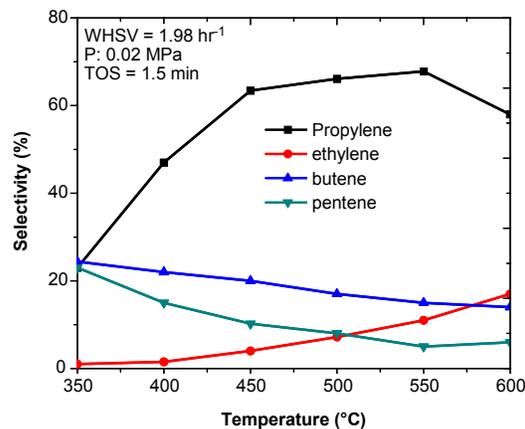
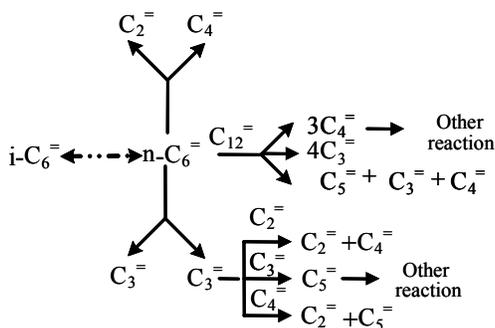


Figure 4: Temperature impact on the selectivity

because of limited hydrogen transfer reactions and/or secondary reaction. At 500°C and lower WHSV, 1-hexene has enough time to interact with the catalyst, therefore it favors secondary reactions. The increase in WHSV favors the uni-molecular direct cracking reaction, reflecting the small catalyst contact due to the decrease in the catalyst to oil ratio.

Influence of Time-on-Stream (TOS)

TOS response towards desired product selectivity, total olefins selectivity and conversion of 1-hexene catalytic cracking over 30% SAPO-34 zeolite catalyst was experimentally investigated between 1.5 - 9 min and the results are shown in Figures 7 and 8. With the extension of time-on-stream, the conversion of raw material dropped from 46.74 % initially at 1.5 min to 31.22 % at 9 min. A slight increase in total olefins selectivity was noted. This reaction behavior was mainly due to gradual catalyst deactivation (due to a decrease in surface acidity). Therefore, hydrogen transfer activity decreases and total olefin content increases. Figure 8 clearly demonstrated that, with the extension of TOS, propylene, ethylene, butene and pentene selectivity changes slightly.



Scheme I: 1-hexene cracking reaction network

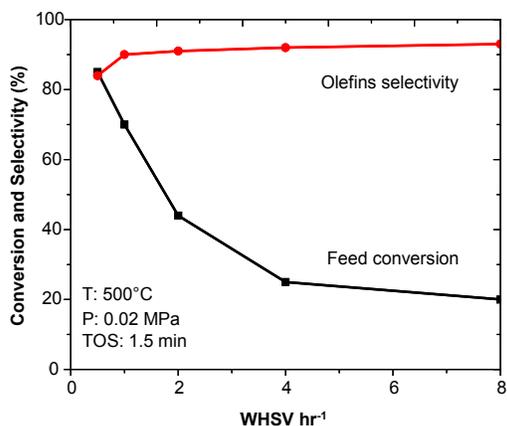


Figure 5: Space velocity impact on total olefins selectivity

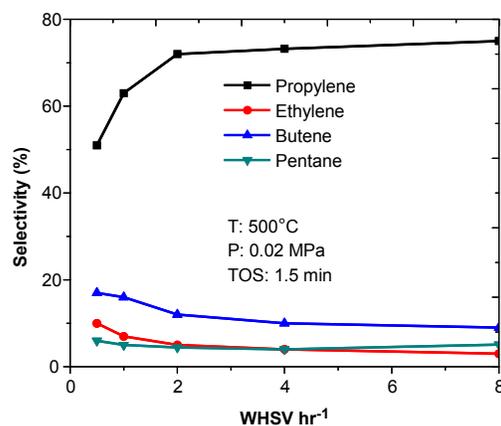


Figure 6: Space velocity impact on product selective

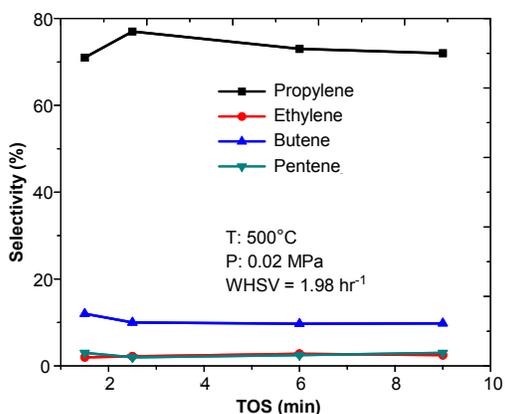


Figure 7: TOS impact on products selectivity

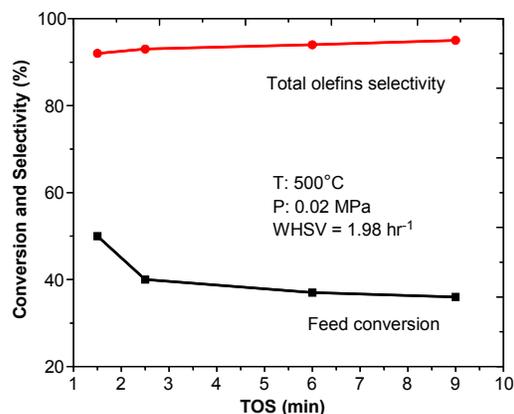


Figure 8: TOS effect on the conversion rate and the total olefins selectivity

1-Hexene Cracking Reactions

1-Hexene cracked over 30% SAPO-34 shape-selective zeolite catalyst via direct cracking, hydrogen transfer, heterogeneous and polymerization reactions etc. From the OPE (olefins performance envelop) curves of cracking reactions, the impact on desired product distribution with conversion was analyzed, as shown in Figure 9. 1-Hexene was generally cracked into two propylene molecules via direct cracking with co-production of ethylene, butane, pentane. The appreciable trend of a continuous increase in propylene yield with conversion was obtained over SAPO-34. The reaction was explained by a β -scission carbenium ion mechanism and possible routes are shown in Scheme II (Buchanan et al., 1996 and Huaqun et al., 2008). The chance of polymerization has been ruled out, as no C_7 and higher hydrocarbons were

obtained under the designated operating conditions using 30% SAPO-34.

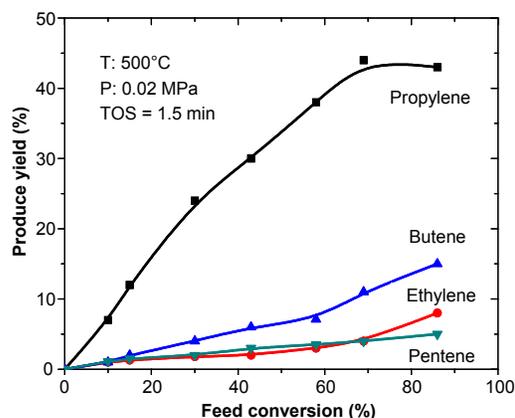
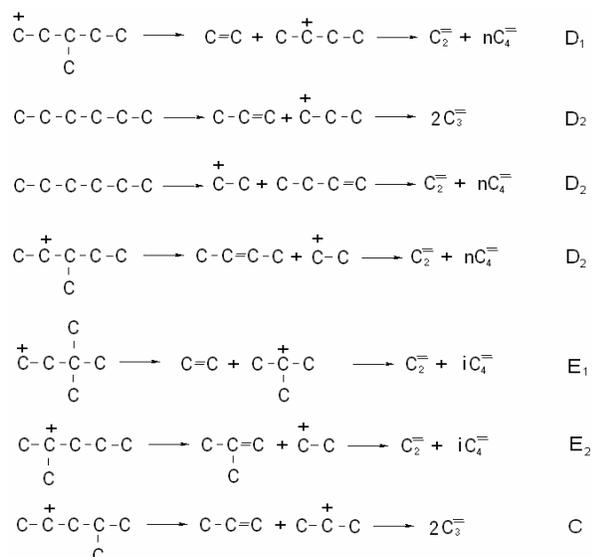


Figure 9: 1-hexene cracking process OPE at 500°C



Scheme II: 1-hexene carbenium ion models of β -scission (Buchanan et al., 1996)

The alkane OPE indicates that methane, ethane, propane, butane and pentane are stable secondary products. Figure 10 indicates that paraffins increased with the conversion rate due to hydrogen transfer reaction activation. Carbon and hydrogen have different transfer rates depending upon the differences in concentration of carbon-response rate (Lukyanov et al., 1994). Secondary products were derived from primary products in a similar manner. This early response of the system with increasing conversion generates hexane and propane.

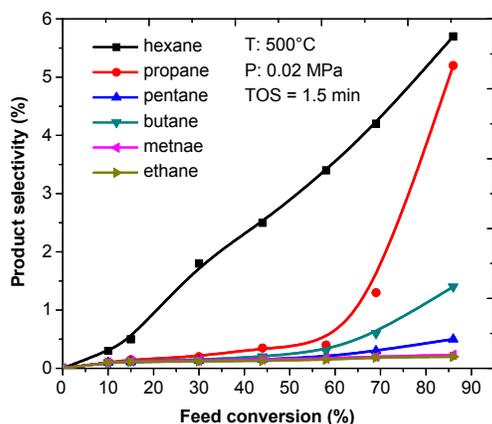
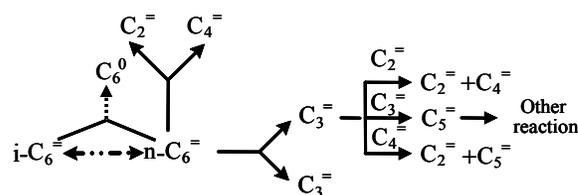


Figure 10: 1-hexene catalytic cracking process OPE for alkanes

There is no major dispute about the mechanism of alkene cracking over solid acidic catalysts. Overall, the active centers in these reactions are

protic acidic centers on the catalyst surface and these reactive species are known as carbenium ions. The product distribution of 1-hexene cracking over 30% SAPO-34 at 500°C was focused to describe its reaction pathway on the basis of the above discussion and shown in Scheme III. In direct cracking, the carbon chain broke in the center to give two propylene molecules, while only a small amount of 1-hexene cracking proceeds via two-way reactions. The response time of raw material to secondary reactions after cracking generates the corresponding paraffins.



Scheme III: 1-hexene cracking reaction pathway over 30% SAPO-34 catalyst

CONCLUSION

The shape selective opportunity provided by SAPO-34 catalyst was experimentally verified using 1-hexene (n-hexene) and 2-methyl-2-pentene (isohexene) as feed, under identical conditions. The small pore size gives the shape selective effect for propylene, and weak acidity of 30% SAPO-34 controls light olefins stereochemistry in a more robust way. The shape selectivity of SAPO-34 catalyst increased both propylene yield and selectivity to 48% and 75%, respectively, from 31% and 36% over a ZSM-5 zeolite catalyst. 1-Hexene could diffuse into the inner pore of the 30% SAPO-34 and cracking proceeds via a β -scission carbenium ion mechanism. An increase in temperature shifted the 1-hexene cracking mechanism from indirect to direct propylene formation pathways. With the further increase in temperature, ethylene yield was enhanced and push propylene to participate further in the secondary reactions. Therefore, propylene selectivity declined after reaching a maximum 75% at 550°C. At higher WHSV and TOS, propylene selectivity shows a continuous positive increment at the cost of lower conversion. Some 1-hexene converted into paraffins by hydrogen transfer reactions over 30% SAPO-34 catalyst, but higher WHSV's and short resident times mitigated the hydrogen transfer reactions and enhanced propylene yield and selectivity.

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