DRASTIC ENHANCEMENT OF PROPENE YIELD FROM
1-HEXENE CATALYTIC CRACKING USING A SHAPE
INTENSIFIED MESO-SAPO-34 CATALYST

ZEESHAN NAWAZ*, JIE ZHU, FEI WEI

Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology (FLOTU), Department of Chemical Engineering, Tsinghua University, Beijing, 100084, China.
* Corresponding author: zeeshan@mails.tsinghua.edu.cn

Abstract

A shape intensified Meso-SAPO-34 catalyst was designed and used to improve the yield and selectivity of propene from 1-hexene cracking. The propene was produced with an optimal selectivity of 73.9 wt.% with high feed conversion 98.2 wt.% at 14 per hour WHSV. Robust exponential control of the stereochemistry was observed over the Meso-SAPO-34 shape selective catalyst’s cracking. The influence of the operating parameters on 1-hexene catalytic cracking, such as reaction temperature, time-on-stream effect on product distribution and conversion variations were systematically studied. The yield of propene and conversion rapidly increased with the reaction temperature, until 575°C. Shape intensification and topological integration of SAPO-34 increases the diffusion opportunities for feed, and this phenomenon was found to be responsible for drastic increase in 1-hexene conversion and propene yield. One other reason for this increase is the suppression of surface reactions (isomerization and hydride transfer) owing to better diffusion opportunities. About 55 wt.% propene yield and higher total olefins content was achieved over Meso-SAPO-34.

Keywords: Cracking, Propene, Shape intensification, Diffusion, Meso-SAPO-34.

1. Introduction

Propene is the principal raw material for production of important petrochemicals, such as polypropylene, acrylonitrile, propylene oxide, cumene, phenol, oxo-alcohols, alkylates blends, isopropyl alcohol, acrylic acid, isopropyl alcohol, polygas chemicals [1, 2]. The continuous increase in demand
of propene has lead to the development of new catalysts and on purpose propene producing processes.

Fluid catalytic cracking (FCC) products were containing higher olefins while it shows selectivity towards alkane and the processes were governed by hydrogen-transfer reactions. Moreover olefins yield from FCC is still limited due to its complexity and process severity. It is also known that increasing process severities, leads to maximize propene production in FCC units up to 7% [3].

The on-purpose propene technologies are currently being developed to obtain higher yields of propene from FCC units by upgrading low value refinery streams like C₄–C₆ olefins and their overall reaction kinetics is recently proposed by Huaqun et al. [4]. Recent developments in reactor’s integration, like millisecond catalytic cracking technology (MSCC), the down-flow reactor technology (Downer), deep catalytic cracking (DCC), two-stage riser FCC and the new catalytic cracking technologies for producing light olefins are on the verge of communication but no drastic improvement has been reported [5]. Catalyst intensification on the nano-scale was also currently being investigated, e.g. SAPO-34 in the fixed-bed catalytic cracking process “Propylur”, developed by Lurgi in 1996. In this process Lurgi claims to convert approximately 60 wt.% of C₄ and C₅ olefins to propene and ethene using steam cracker [6].

The catalytic enhancement of SAPO-34 zeolite catalysts is still not well understood and not available through open resources; but it does claim to demonstrate better performance in hexene catalytic cracking [5]. The effect of topology on SAPO-34 catalyst performance has been studied here to ascertain any possible propene production enhancements. In previous studies SAPO-34 was observed to be more effective for butene cracking and hexane [5, 7, 8].

In the work presented here, 1-hexene cracking over shape intensified catalyst Meso-SAPO-34 was studied and found that the shape selectivity not only increased the reaction rate but also improved the propene yield and feed conversion. Both SAPO-34 and Meso-SAPO-34 results were obtained under similar operating values and compared in order to explain superiority. The overall 1-hexene process was parametrically characterized to explored operational optimization.
2. Experimental

2.1. Preparation of Meso-SAPO-34 catalyst and characteristics

Conventional, solid, acidic, zeolite-based catalysts are widely used in the petrochemical industry for hydrocarbon conversion. In significant features of SAPO-34 catalyst, it has high catalytic activity for cracking reactions and low activity for hydrogen-transfer reactions. Characteristics of SAPO-34 including packing density (0.84 g/cm$^3$), the internal pore size (0.34 Å) and average diameter of the particles (~5µm) [9]. The shape intensified catalyst; Meso-SAPO-34 was designed by Zhu Jie et al. of Beijing Key Lab of Green Reaction Engineering & Technology (FLOTU), Tsinghua University, Beijing, China [10].

The kaolin (a source of aluminum and silicon), phosphorus, template and de-ionized water are mixed together and stirred to obtain uniform crystallization solution. The Al$\text{_2}$O$\text{_3}$: SiO$\text{_2}$: P$\text{_2}$O$\text{_5}$: H$\text{_2}$O molar ratio is 0 ~ 1.5:0 ~ 1.2:0.8 ~ 1.5:2 ~ 4:10 ~ 500. The silicon aluminum phosphate catalyst of slit shape i.e. Meso-SAPO-34 is available shortly after crystallization. The shape intensified Meso-SAPO-34 catalyst was characterized through X-ray diffraction (XRD). The Meso-SAPO-34 catalyst possesses an internal structure similar to cube shape SAPO-34, but with different quoin and topology. Although in many experimental studies SAPO-34 cracking ability has proven to be uniform among available cracking catalysts, the slit shaped topology of Meso-SAPO-34 offers a more robust design for exponential enhancement of activity by increasing pore diffusivity.

The structure of Meso-SAPO-34 is shown in Fig. 1 and its XRD pattern is shown in Fig. 2 [8]. The internal pore size, acidity, and XRD pattern of Meso-SAPO-34 is almost similar to SAPO-34 [8], except the outer shaping quo’s (see Fig. 1). Therefore characterization of Meso-SAPO-34 is useless but their cracking performance can only be justified on the experimental grounds. The single point surface area at $P/P_o$ is 0.2012: 540.3451, BET surface area 522.3917 and Langmuir surface area was 689.102.

![Fig. 1. SEM Image of the Outer Shaping Quo’s of Meso-SAPO-34 Catalyst.](image1)

![Fig. 2. XRD of Meso-SAPO-34.](image2)
2.2. Feed stock and products
All alkenes have the general formula $\text{C}_n\text{H}_{2n}$, so propene is CH$_3$-CH=CH$_2$ and molar mass of 42.08 g/mol [11]. Although the official IUPAC nomenclatures for saturated and unsaturated hydrocarbons are alkanes and alkenes, respectively by IUPAC, these compounds are also known as paraffin’s and olefins. Thus many acronyms and industrial concepts are also based on these common names e.g. “PIONA” (paraffin’s, i-paraffins, olefins, naphthenes, and aromatics) analysis and “olefinicity” (the relative amount of olefins within a certain product group) [12]. Here we refer to individual species according to IUPAC nomenclature; e.g. ethane, propene and use non-IUPAC nomenclature (olefins and paraffin’s) when addressing groups of hydrocarbons. Analytical grade 98 % pure 1-hexene (IUPAC name: hex-1-ene) of AlfaAesar (A. Johanson Matthey Company, UK) was used as a model FCC feed in current experimental investigations in a micro-reactor. All the values were calculated and presented in weight percentages.

2.3. Feed stock and products
The experimental setup was designed to analyze the robustness and exponential control of the Meso-SAPO-34 catalyst’s on a model FCC component 1-hexene cracking in a micro-reactor. After the cracking reaction the product gas was analyzed using on-line Gas Chromatography equipped with FID (Techcomp Holdings Ltd., Model GC-7890II). The used FID has a sensitivity of $M_t = 1 \times 10^{-11}$ g/s and was used at 200°C. The measured amount of Meso-SAPO-34 catalyst was mixed with 0.2 g of inert material. The rector pressure was maintained at 0.02 MPa and the feed loading rate was adjusted at 10 ml/min in all experiments in order to obtain the desired WHSV i.e 14 h$^{-1}$.

3. Results and Discussions
The activity of intensified topological SAPO-34 catalyst (Meso-SAPO-34) has been experimentally studied and found suitable for propene enhancement. As isomerization rate is much faster than cracking [13], but Slit-SAPO-34 better diffusion ability reduces the possibilities of surface reactions. Extensive experimentation has been carried out between the temperature range of 450-600°C at varying TOS and fixed WHSV, 14 h$^{-1}$.

Initially, the selectivity of propene increased, but then decreased at 500°C with a sudden increase in conversion. After 500°C, both selectivity and yield gradually increased with the increasing conversion of propane on TOS = 1 min. (see Fig. 3). At higher TOS (5 min.) the catalyst quickly deactivates above 575°C with a maximum 66.5% propene yield and 73.9% selectivity was obtained (see Fig. 4). The present conversion begins to decline after TOS = 4 min. and temperature 575°C with a sudden decrease in yield and selectivity (see Fig. 5).

1-hexene was first cracked over Lewis acid site and as the L/B ratio increased with the increase in temperature, conversion also increased [14]. It has long been reported that at higher temperatures and lower pressures, the adsorption of hydrocarbons decreases and monomolecular mechanism will enhanced; in fact dominating the dimeric cracking mechanism [12]. The cracking of olefins at FCC reaction conditions favors the formation of small olefins such as propene experimentally explained by...
Fig. 3. Effect of Temperature on 1-hexene Cracking at TOS = 1 min. in a Micro-reactor.

Fig. 4. Effect of Temperature on 1-hexene Cracking at TOS = 5 min. in a Micro-reactor.

Fig. 5. At Constant Temperature 575°C, TOS Influence on % Conversion, % Yields and % Selectivity of Propene.
Xaioping et al. [5]. It has also been demonstrated that the medium pore size zeolite catalyst, SAPO-34 has better cracking ability owing to its shape selectivity as reported by Tabak et al. [15, 8].

In current experimentation, however we observed that for the same catalyst pore size, changes in quo’s and topology can have a drastic effect in enhancing the desired product. This enhancement can be attributed to better diffusion abilities provide by Meso-SAPO-34. There is still controversy regarding the nature of acid sites action for sustained hydride transfer and it may prolong alkylation activities [16]. The decrease of the hydrogen transfer coefficient with the reaction temperature indicates that higher temperatures favor monomolecular cracking and enhancement of light olefin formation [17]. Comparison of Meso-SAPO-34 and SAPO-34 catalytic performance for 1-hexene cracking under identical conditions has been shown in Fig. 6, and similar results were shown in literature [8]. Significant difference in conversion can be seen while slightly higher propylene selectivity at higher conversion over Meso-SAPO-34 was observed. Detailed experimental results obtained at different temperatures and TOS were show in Table 1, except propene because it has been presented through graphs.

![Fig. 6. 1-Hexene Conversion over SAPO-34 and Meso-SAPO-34 at 550°C.](image)

The product distribution obtained at optimum cracking temperature of 575°C is shown in Fig. 7. Under fixed feed flow rate of 10 ml/min, increasing the TOS from 1-5 min. decreases the CTO to 25.1, 12.5, 8.4, 6.4 and 5.1 respectively. The % yield of propene and % selectivity increases with the increase in TOS up to 4 min and then becomes stagnant. The $C_3/C_2$ ratio also increases with time and temperature up to 575°C. In all the current experiments, at WHSV = 14 h$^{-1}$, no methane and $C_7$+ carbons were detected. Buchanan et al. [18] explained all possible cracking schemes after extensive experimentation; the dominant cracking reaction is C-type $\beta$-scission (see Scheme 1) while using Slit-SAPO-34 as a catalyst [18, 8].
Table 1. Percentage Yield of Total Olefins and Ethene with Percentage Conversion of Feed (in Temperatures Range of 450-600°C and TOS = 1 - 5 min., at WHSV = 14 h⁻¹).

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>TOS, min</th>
<th>% conversion of 1-hexene</th>
<th>% yield of total olefins</th>
<th>% yield of ethene</th>
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<tr>
<td>450</td>
<td>1</td>
<td>63.949</td>
<td>95.229</td>
<td>4.237</td>
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<td></td>
<td>2</td>
<td>47.187</td>
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<td>3</td>
<td>42.246</td>
<td>96.712</td>
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<td>4</td>
<td>38.989</td>
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<td>5</td>
<td>36.861</td>
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Fig. 7. At Temperature 575°C and WHSV 14 h⁻¹, TOS and CTO Influence on Product Distribution.

Scheme 1. Carbenium Ion Formation in 1-hexene Cracking, C-type β-Scission Mode [8].
At the same reaction conditions the balance between mono-molecular and bimolecular mechanisms will depend on the characteristics of the catalyst. The medium pore size of Meso-SAPO-34 will favors the monomolecular mechanism. Since the bimolecular reaction intermediates cannot be formed during the course of cracking. The conversion of 1-hexene and yield of propene shows a rapid increase with the increase in reaction temperature and decreases with reference to the catalyst-to-oil ratio. However, at lower catalyst-to-oil ratios the hydrogen-transfer reactions were negligibly low. The optimum operating conditions are therefore moderate residence time for high yields of propene combined with (i) lower yields of dry gas and (ii) a lower apparent hydrogen-transfer coefficient. One of the interesting findings of our current experimentations is the initially high yield and selectivity of propene, which decreased rapidly up to 80% by increasing TOS at all temperatures (Fig. 8). Therefore, optimum TOS and catalyst deactivation integration provides a significant guidance towards severity of the operating parameters with the Meso-SAPO-34 catalyst.

Fig. 8. Influence of Temperature on % Yield of Propane during 1-hexene cracking over Meso-SAPO-34.

Meso-SAPO-34 catalyst exhibits high activity and can reduce the production of by-products such as methane and coke. It should be noted that the ethene and butane are the second prominent products which promotes a significant impact in overall % yield of total olefins. Meso-SAPO-34 catalyst has a significant advantage as the higher desired product yield and gives less coke formation than SAPO-34.

4. Conclusion

The influence of primary operating parameters such as reaction temperature, catalyst-to-oil ratio and residence time on product distribution and conversion was systematically studied. Because of very high conversion rates, even at high WHSV, therefore lower CTO is needed during cracking. The Meso-SAPO-34 catalyst promotes C-type β-scission and significantly retards HT-surface reactions.

Increasing catalyst-to-oil ratio can enhance 1-hexene cracking rate and improves the yield of propene even at higher temperatures to some extent. While increase in catalyst-to-oil ratio will leads towards secondary reactions and decrease the desired product yield and selectivity. The percentage selectivity of
propene and conversion showed a rapid increase with increasing reaction temperature up to 575°C. But further increase in propene selectivity was at the cost of lower feed conversion along with the increase of by-products were observed and found unsuitable. This drastic increase in propene yield was attributed to an enhanced opportunity for diffusion owing to the change in existing SAPO-34 catalyst intensification.

The results suggest that at the optimum operating parameters investigated were 575°C and TOS = 1 min. at WHSV = 14 h⁻¹, the conversion of 1-hexene achieved was approximately 98.2 wt.%. The optimum propene selectivity was observed to be 73.9 wt.% at 575°C and at TOS = 5 min, propene yield reached a maximum 66.5 wt.% At optimum conditions, the yield of total olefins was 97.9 wt.%.

This new generation Meso-SAPO-34 catalyst with improved quo’s and topology provides a significant increase in propene yield and may emerge as a significant milestone in commercial catalyst design and development for the enhancement of propene via petroleum based route.

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References


