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DOI:

[DOI:10.3303/CET1543144](https://doi.org/10.3303/CET1543144)

[Link to publication record in Manchester Research Explorer](#)

Citation for published version (APA):

Garforth, A., & Alnaimi, E. (2015). The Effect of Zeolite Structure and Acidity on Maximizing Propylene Production from an FCC Unit. In S. P. Pierucci, & J. J. Klemeš (Eds.), *12th International Conference on Chemical and Process Engineering* (Vol. 43, pp. 859-864). (CHEMICAL ENGINEERING TRANSACTIONS - VOL.43). AIDIC. <https://doi.org/DOI:10.3303/CET1543144>

Published in:

12th International Conference on Chemical and Process Engineering

Citing this paper

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The Effect of Zeolite Structure and Pore Systems on Maximizing Propylene Production in FCC Unit

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The effect of zeolite topologies and key operating parameters such as temperature and residence time on the cracking of n-heptane was investigated. Zeolite Beta, nano ZSM-5, regular ZSM-5, Ferrierite and mixtures were tested in a fixed bed reactor under atmospheric pressure. The behaviour of these catalysts in terms of products distribution especially propylene yield is discussed utilizing different parameters such as olefins/paraffins ratio, i-C₄/n-C₄, and i-C₄/total C₄. Nano ZSM-5 and the mixture of Beta and ZSM-5 showed their potential to be used as FCC additives with high propylene yield and conversion. Further work exploring the effect of zeolite crystal size, acidity and acid strength by modification of catalyst structure and surface topology is being conducted.

1. Introduction

Propylene is a major industrial chemical intermediate that serves as one of the building blocks for an array of chemical and plastic products such as polypropylene, acrylonitrile, propylene oxide, and acrylic acid. The demand of petrochemical feedstock propylene is expected to grow at an annual rate of 4 – 6 wt. %. Propylene is typically produced by direct processes such as propane dehydrogenation and metathesis as well as a by-product in processes such as steam catalytic cracking (SCC), fluid catalytic cracking (FCC), coking and visbreaking unit. The majority of propylene production, equivalent to 68 – 70 %, occurs in the SCC unit as a by-product of ethylene under a strict ratio between 0.4 – 0.6 (propylene/ethylene) to maintain its economical feasibility. A further 10 – 20 % of the total propylene is produced in refineries, where FCC is responsible for 97 % of that amount. The remainder is attributed to on purpose processes (Aitani, 2006). Therefore, improvements in current processes for propylene selectivity or alternative routes have to be undertaken to meet the world demand of propylene.

Fluid catalytic cracking possesses the capability to increase the production of propylene due to the fact that the process could handle a variety of feedstocks such as naphtha, vacuum gas oil and vacuum residue. The research around maximizing propylene yield from an FCC unit has followed different paths such as process development, base catalyst modification, and catalyst additive enhancement or replacement (Farshi, et al., 2011).

In order to maximize propylene yield in an FCC unit without major modifications to that unit, the catalytic system needs to be improved. The typical role of an FCC catalyst is to convert long chain hydrocarbons, mainly vacuum gas oil, to shorter chain and more valuable hydrocarbons such as gasoline and diesel while minimizing dry gas yield which is the result of over cracking. However, currently, refiners are shifting their product palette to maximize propylene yield due to its increased market value. Therefore, several research studies have looked at modifying the base of the formulated e-Cat (equilibrium catalyst), ultrastable Y-type zeolite (USY), by the addition of amorphous silica-alumina (Hosseinpour, et al., 2009) to be a more active catalyst that doesn't promote hydrogen transfer reaction which plays a significant role in olefin hydrogenation (Triantafyllidis, et al., 1999). Other researchers, compared the characteristics and the performance of the typical e-Cat additive, ZSM-5, to that of MCM-68 (Inagaki, et al., 2010), Beta (Corma, et al., 1996), and MCM-22 (Corma and Martinez-Triguero, 1997) more acidic catalysts in order to increase the cracking activity of the

additive. Corma, et al. (2000) showed that propylene yield of an FCC unit could be improved by adding more ZSM-5 catalyst to the FCC formulation; however, the overall conversion would drop. For example, at high addition of ZSM-5 (75 wt. %), the conversion of gas oil dropped 19.1 wt. % which is almost 5 times greater than the loss of conversion obtained at lower level of ZSM-5 (25 wt. %) (Adewuyi, et al., 1995). Corma, et al. (2002) looked at compensating the loss of cracking activity due to the increased addition of ZSM-5 by increasing the acidity of USY using rare earth metals. However, high addition of rare earths promoted hydrogen transfer reaction which resulted in a decrease in the total olefin yield. Therefore, in order to achieve high feed conversion and high propylene selectivity while minimizing side products, a balance between the zeolite structure and availability of acid sites and their strength has to be optimized (Triantafyllidi, et al., 2004). The role of zeolite structure focusing on Beta, Ferrierite and ZSM-5 catalysts as FCC additives for enhancing propylene yield is reported here. The catalytic performance of these additives were evaluated in a fixed-bed reactor unit using the cracking of n-heptane as a model system.

2. Experimental

2.1 Catalysts

The catalysts under study were zeolite Beta with tridirectional 12-MR channels, Ferrierite with bidirectional 10 × 8 MRP, and (nano – regular) ZSM-5 with bidirectional 10 MRP (Table 1.)

Table 1: Characteristics of zeolites tested

Catalyst	SiO ₂ /Al ₂ O ₃	Crystal size (nm)	Dimensions	Source
Ferrierite	20	n.a	10×8MR (2-D)	ZEOLYST
Regular ZSM-5	36	2000	10-MR (2-D)	ZEOLYST
Nano ZSM-5	26	300	10-MR (2-D)	ACS Material
Beta	25	200	12-MR (3-D)	ZEOLYST

2.2 Catalytic Performance Evaluation

The catalyst powder was pressed, crushed and sieved to give 170-260 µm pellets and packed into a stainless steel tube (530 mm × 4 mm. i.d.). The catalysts were heated to 823 K and kept at that temperature for 16 h under air flow (100 mL min⁻¹). Then, the air was switched to pure nitrogen (50 mL min⁻¹) for 2 h prior to introducing the feed and the reactor cooled to the appropriate temperature in a three-zone furnace (Carbolite). The catalytic cracking performance of zeolite Beta, Ferrierite, regular ZSM-5, nano ZSM-5, and the mixture of Beta and ZSM-5 were evaluated in a fixed bed reactor at atmospheric pressure and reaction temperatures between 723 – 773 K. A flowing stream of nitrogen passed through a series of glass bubblers filled with n-heptane (Aldrich, Purity>99.99 %) maintained at - 2 ± 0.01 °C to control the feed concentration. The mixture of carrier gas and feed vapour went to the reaction system through an electrically heated pipe (90 °C, ± 5 °C) to prevent condensation. The ratio of catalyst weight to total flow rate (W/F) was varied from 38 to 92 g_{cat} h mol⁻¹. All products were analyzed by gas chromatography (GC) in a Varian 3800 GC equipped with a 50 m × 0.32 mm i.d. PLOT Al₂O₃/KCl capillary column fitted to a flame ionization detector (FID).

3. Results and Discussion

The cracking mechanism of n-heptane is a complex reaction network, however, cracking mainly occurs via two routes ; firstly, monomolecular cracking where the cracking takes place at the Brønsted acid site breaking C-C or C-H bond to produce paraffin or olefin respectively; secondly, bimolecular cracking which requires two adjacent acid sites (Corma, et al., 1996). Bimolecular cracking is not ideal for maximizing olefin yield production as it promotes the hydrogen transfer reaction where the rate of olefin hydrogenation is higher than the rate of paraffin dehydrogenation (Aitani, et al., 2000;). As can be seen in Figure 1 (a), differing zeolites gave a wide range of conversion (5 – 99 mol %), however, the yield of propylene was predominantly between 27 – 34 mol %. Ferrierite showed a narrow range of conversion between 20-40 mol %. Although beta exhibited a wide range of conversion (5 – 60 mol %), it was prone to deactivation. ZSM-5 and nano ZSM-5 showed much higher activity typically greater than 90 mol %. Interestingly it was noted that the addition of zeolite Beta to regular ZSM-5 not only improved its propylene yield, but also improved its catalytic cracking activity by around 5 mol %. The nano ZSM-5 showed high level of conversion and achieved high propylene yield showing its potential as FCC additive.

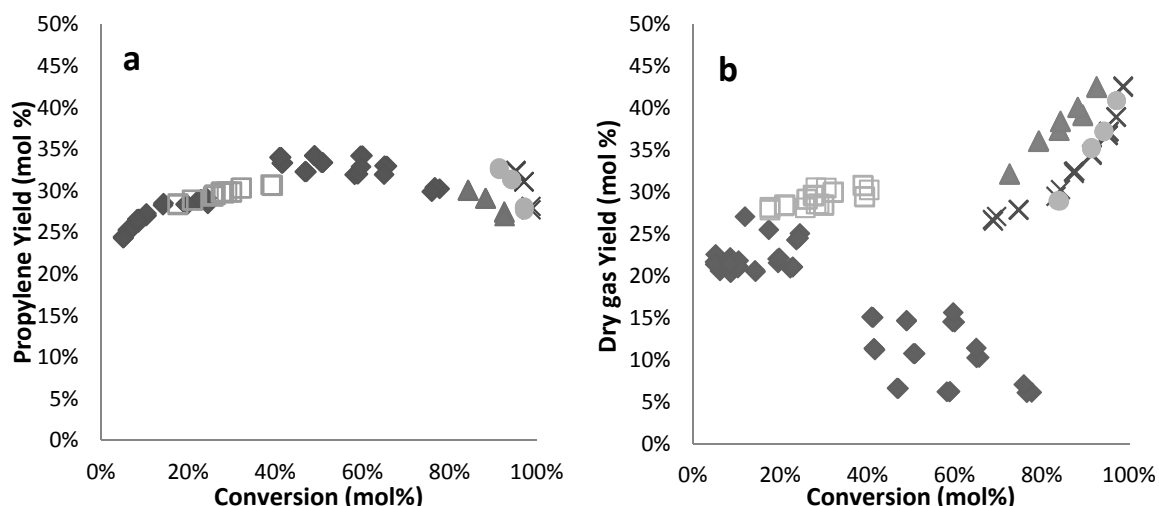


Figure 1: a) Propylene yield obtained over tested catalysts at different conversions of *n*-heptane; b) Dry gas yield ($C_1 + C_2$) over tested catalysts as a function of the conversion of *n*-heptane where

◆ Beta □ Ferrierite ▲ ZSM-5 (R) × ZSM-5 (N) ● Beta + ZSM-5 (R)

One of the drawbacks of using Ferrierite and ZSM-5 was the increase in dry gas yield (Figure 1 b) from typically 10 – 20 mol % in zeolite Beta to between 30 – 43 mol % with ZSM-5. This is mainly due to their higher catalytic cracking activity which caused over cracking of primary products, hence, the decrease in propylene yield and the increase in dry gas yield with conversion. Zeolite Beta successfully enhanced propylene yield while maintaining low dry gas yield, however, its catalytic cracking activity was significantly lower than that of ZSM-5 which suggests that in order to consider zeolite Beta as FCC additive, its cracking activity should be increased while maintaining the high propylene yield. Additive mixture of ZSM-5 and Beta were targeted bringing together the higher conversion with good propylene yield.

3.1 Effect of temperature on propylene selectivity

Propylene yield increased with increasing temperature for all tested zeolite catalysts with the exception of Ferrierite and nano ZSM-5 where the propylene yield slightly decreased (Figure 2). These findings agree with reported literature where it was noticed that the yield of light olefins increased with increasing temperature (Aitani, et al., 2000). At high temperature, the dehydrogenation reaction of paraffins is more favourable than the hydrogenation reaction of olefins, hence, the increment in propylene yield. The highest propylene yield (34 mol %) was obtained over zeolite Beta followed by other catalysts in this order Beta + regular ZSM-5; nano ZSM-5; regular ZSM-5; and finally Ferrierite and Beta which had undergone deactivation but had stabilised conversion. It is also worth noting the synergistic effect of mixing Beta and regular ZSM-5 on the propylene yield selectivity with increased propylene yield and increased catalyst stability. Unfortunately, there was a pronounced increase of 11 mol % in the dry gas yield.

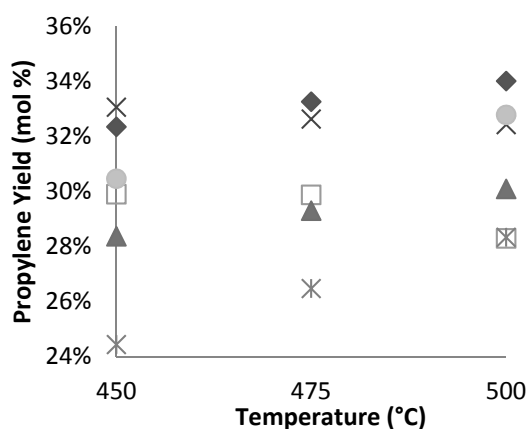


Figure 2: Propylene yield over tested catalysts at different temperatures; D-beta is deactivated stable Beta.

◆ Beta □ Ferrierite ▲ ZSM-5 (R) × ZSM-5 (N) × D-Beta ● Beta + ZSM-5 (R)

3.2 Effect of residence time on propylene selectivity

Increased contact time resulted in overall conversion increased (Figure 3 **Errore. L'origine riferimento non è stata trovata.** d). Comparison of the small pore zeolites, Ferrierite and ZSM-5, revealed two different behaviours. As expected with ZSM-5, higher flow rate increased the yield of propylene as the decreased residence time reduced secondary cracking. The biggest yield change was noticed over the mixture of Beta and regular ZSM-5, as well as nano ZSM-5 with an increase of around 5 mol %. Interestingly, the more restricted Ferrierite showed an increase in the yield of propylene with contact time (Figure 3 a). This suggests that increasing the flow rate of n-heptane improved the propylene yield by minimizing the effect of mass transfer film around the catalyst pores allowing the feed to be in contact with additional active sites, hence, increasing the effectiveness. On the other hand, comparison of the larger fresh with the “stabilized” deactivated Beta highlighted a drop in the propylene yield on deactivation but that the overall (Figure 3 b). propylene yield in both catalysts remained constant over the range of W/F studied. Finally, the comparison of all three Beta containing catalysts (**Errore. L'origine riferimento non è stata trovata.** c) showed the effect of ZSM-5 as shorter contact times increased propylene yield.

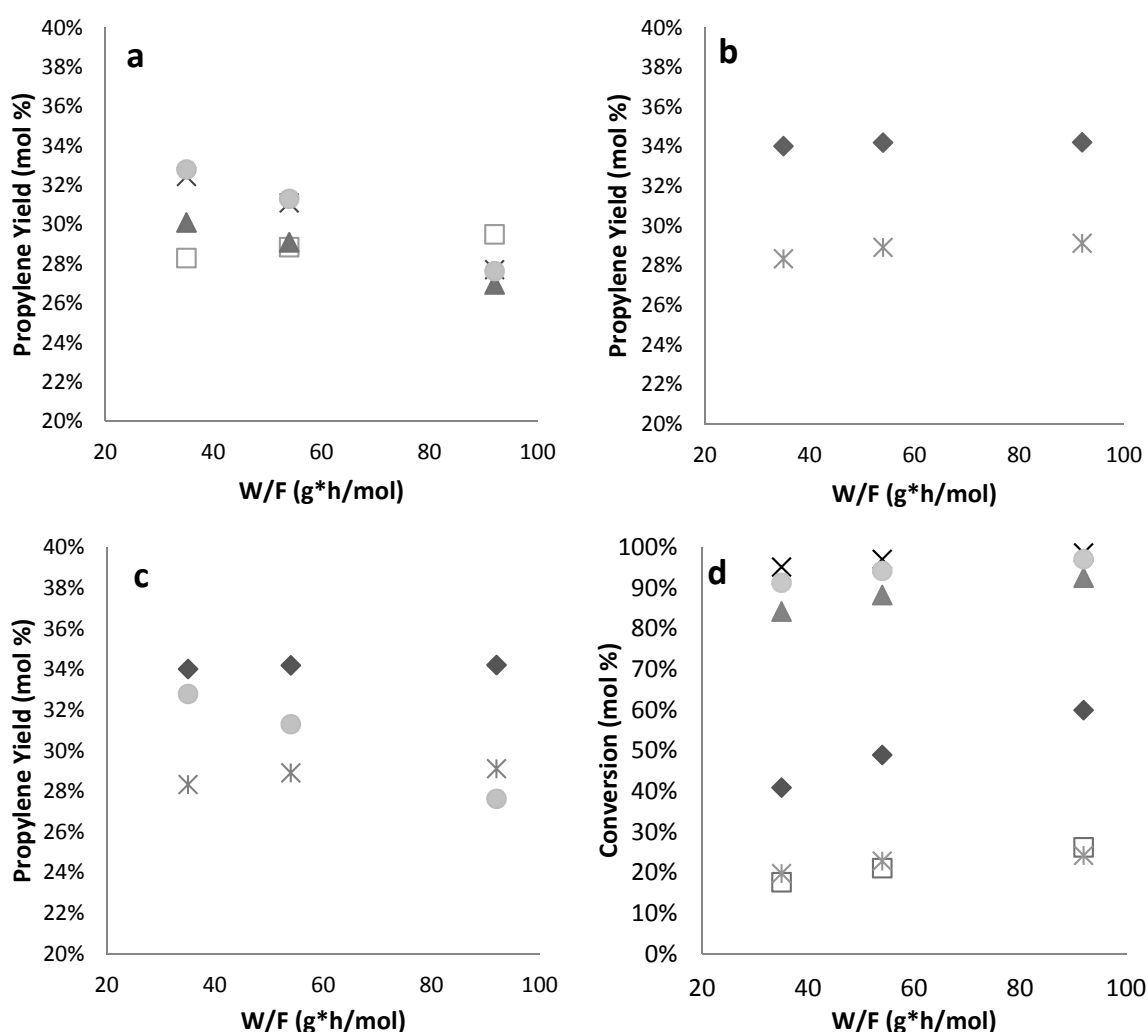


Figure 3: Propylene yield obtained over tested catalysts at different residence times a) effect of residence time on the small pore zeolite; b) on large pore beta; c) on ZSM-5 and the mixture; d) effect on the conversion of n-heptane where ◆ Beta □ Ferrierite ▲ ZSM-5 (R) × ZSM-5 (N) ⊗ D-Beta ● Beta + ZSM-5 (R)

3.3 Effect of catalyst structure

Hydrogen transfer reaction is the reaction responsible for hydrogenating olefin products formed in primary cracking. The structure of the catalysts plays an important role in promoting or suppressing this reaction since it is space demanding (Meier and Olson, 1992). The tendency of a catalyst to promote hydrogen transfer reaction could be measured by introducing a parameter that captures the overall yield of olefins with respect to paraffins, namely the olefins/paraffins ratio (o/p) (De Jong, 1986). The obtained ratios of o/p over all catalysts decreased with increasing conversion level as high activity favoured hydrogen transfer reaction and hydride reaction. Therefore, in order to compare the effect of different zeolite structures on the product selectivity, conversion of n-heptane should be similar in all cases. At conversion higher than 80 mol % comparison of fresh Beta and ZSM-5 catalysts revealed that the largest o/p ratio was in the order of nano ZSM-5 > mixture of Beta and ZSM-5 > regular ZSM-5 > Beta. However, as Beta deactivated over time the resulting o/p ratio (at X= 40-60 mol %) increased similar to that of ZSM-5 catalysts (at X >= 80 mol %).

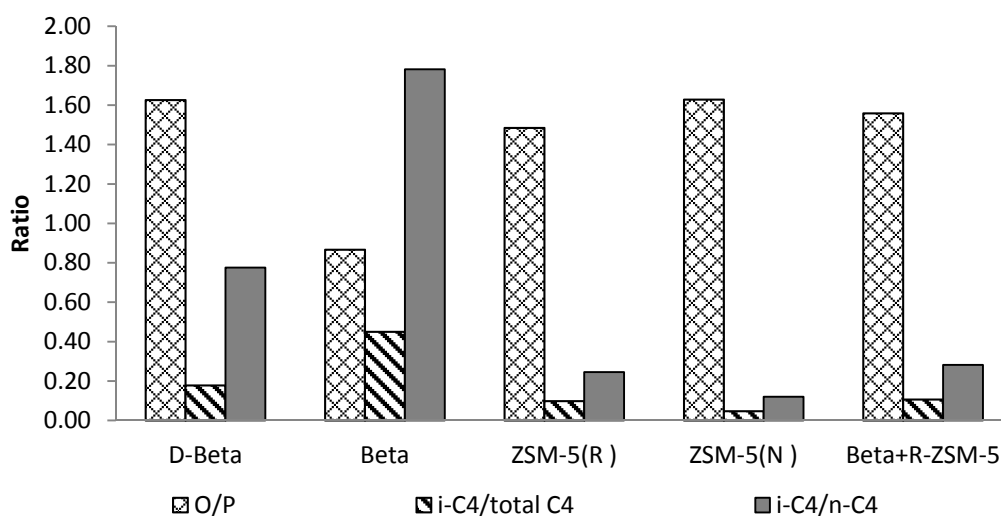


Figure 4: Key cracking parameters of tested catalysts at conversion = 78 mol %, except for D-Beta where conversion = 41 mol %

The results presented here support those from literature that zeolite Beta promotes hydrogen transfer more than ZSM-5 and Ferrierite (Corma, et al., 1996). These results showed that over zeolite Beta the olefins yield was very dependent on conversion level. i.e. cracking activity. The o/p ratio was doubled when the fresh Beta was deactivated. However, the selectivity toward propylene was higher over the fresh catalyst. Another useful indication of the extent of secondary reaction is to consider the i-C₄/n-C₄ ratio. Bimolecular cracking becomes dominant in catalysts with high selectivity toward hydrogen transfer. The i-C₄/n-C₄ ratios were in this order Beta > D-Beta > Beta + regular ZSM-5 > regular ZSM-5 > nano ZSM-5. For 10-MR zeolites the ratios of i-C₄/n-C₄ were low for both (regular and nano) ZSM-5 which can be attributed to the steric limitation of ZSM-5 channels and cavities for the occurrence of butane isomerization. As the crystal size of the ZSM-5 was reduced by a factor of 10, there is a change in the ratio of external /internal surface and also a significant reduction in overall pore path length. The change in external/internal surface might have been expected to increase cracking and hence more dry gas yield at any given conversion. However, this was not the case with the nano ZSM-5 producing 10 % less C₁+C₂ at the same conversion. In addition, the i-C₄/n-C₄ ratio dropped by 50 % for the nano ZSM-5 with the overall selectivity toward propylene 5 mol % higher compared to that of regular ZSM-5.

4. Conclusions

This is a thorough study of four zeolite structures and admixtures for n-heptane cracking. The effect of zeolite structures along with some key operating conditions such as temperature and residence time on the cracking of n-heptane were explored in order to maximize propylene yield. The reaction temperature had a positive effect on propylene yield over all tested catalysts; however, the degree of change varies. Inversely the residence time has a negative effect on 10-MR zeolites and no effect on the 12-MR. The highest propylene yield at the highest conversion was achieved over 10-MR nano ZSM-5. Despite the high yield of propylene,

dry gas yield was significantly higher than that obtained over Beta which shows room for improvement of nano ZSM-5 to make it a good choice as an FCC additive. Further research is underway investigating post synthesis modification focussing on the effect on propylene yield of acidity and external surface area.

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