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The Effect of Binders on the Morphology and Performance of HZY/HZM-5 Zeolite Catalysts in Cracking *n*-heptane to Light Olefins

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Light olefins (ethylene and propylene) are essential building blocks of the chemical industry. Fluid catalytic cracking and steam cracking are the key technologies to produce light olefins. However, these technologies can no longer satisfy the current demand for light olefins. Previous studies have found the catalyst formulation (ZY, ZSM-5, and binder) increased production with the most outstanding results using the catalytic cracking process. This study reports catalyst formulations with different loading of ZSM-5 (5%,10%, and 20%). The performance of catalysts were tested in the catalytic cracking of n-heptane as a model compound of light naphtha for the production of light olefins at 500 ºC and atmospherical pressure. The results of the tests showed high performance in terms of increased light olefins yield (24 - 64%) and improved C2 and C3 selectivity (35 %) over ZY/ZM/K/B(20:20:30:30) and ZY/ZM/K(20:20:60) with alkene/alkane= ~1.33 and reduction into the amount of undesired C1-C5 alkanes (3%). Therefore, adding ZSM-5 (20%) to catalyst formulation enhances the activity and shape selectivity of the catalytic cracking process onto the catalyst.

1. Introduction

The global petrochemical market showed an increase with a compound annual growth rate (CAGR) of 5.1 % for 2021-2030. The estimated market size of global petrochemical by 2023 will approach approximately USD 729 billion (Tanimu, et, al., 2022). Light olefins are essential building materials; they produce many different derivatives used in our daily lives, such as packaging, solvents, synthetic fibres, construction, and coating (Gholami et al., 2021). The primary processes to produce light olefins are thermal cracking (TC) and the use of steam cracking (SC) of hydrocarbons from fossil fuels, such as, naphtha and biomass (Nasser et al., 2021). The thermal cracking of naphtha requires operating temperatures above 800 ºC, about 250 ºC higher than the operating temperature in the fluidised catalytic cracking (FCC) (Chen, et, al., 2020). This conventional TC process was the primary technology for producing light olefins for more than half a century. However, a few drawbacks make the process less economical in terms of production, for example, the multiple steps needed to separate the products (C2= and C3=), and less desired, because of a negative impact on the environment due to the high CO2 emissions. The vast demand for light olefins to manufacture polymers, for example, raises the need for improved or innovative technologies to increase efficiency and selectivity. The FCC is key to the chemical community's interest in developing new and improved catalytic technologies for the selective conversion of naphtha (e.g., typically iso/n- alkanes in the C5 – C10 range) into essential raw materials for the chemical industry (Gholami et al., 2021). The catalytic cracking process can produce more light olefins and carbon deposition is restrained compared to TC at the operating temperature is typically 520 – 540 ºC. Very recently, n-heptane (n-C7) has been used as a model compound for heavy naphtha (typically C_7 – C_{10} hydrocarbons) cracking. **T**he application of selective zeolite catalysts to the cracking of hydrocarbon molecules can be seen from the similarity of the catalyst pore dimensions (e.g. HZSM-5**,** 0.55 x 0.51 nm) compared to the molecular dimensions of light hydrocarbons (such as C_2 – C_4) (Velthoen et al., 2020)(Figure 1). ZSM-5 can

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produce light olefins due to their unique properties. Its pore structure, which contains channels and cages of varying sizes, allows for the shape selectivity of reactant molecules and facilitates the formation of desired products. Additionally, the high thermal stability of ZSM-5 allows it to withstand the high temperatures required for catalytic cracking reactions, making it an effective catalyst for producing light olefins**.**

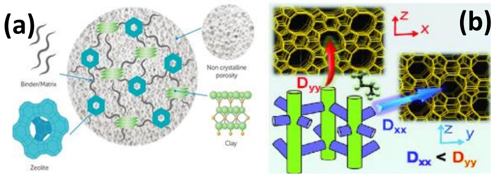

Figure 1:Components in FCC catalyst (a) and aspects of ZSM-5 structure (b) (Levasil® CA, 2023).

Catalytic cracking is one of the most effective approaches for improving light olefins' conversion, selectivity, and product distribution. The catalyst composition is generally made by mixing a binder and a zeolite in varying proportions to enhance stability, activity and resistance to coking. Many studies have been conducted to improve the catalytic properties of zeolite-Y catalysts to increase light olefins production yields. However, the majority of this work focuses on adding additives (ZSM-5) and binder (Kaolin and bentonite) variables used during the modification processes for zeolite structures (Velthoen et al., 2020). The main focus of this research is to increase ligh olefins production by synthesizing a similar catalyst formulation to the FCC and examining the effect of binders (bentonite and kaolin) in combination with two commercial zeolites.

2. Materials and Methods

The model compound, n-heptane (n-C_7), obtained from Sigma-Aldrich (99.99%) was used. Two commercial zeolites (supplied by Zeolyst) with Si/Al ratios of 6 and 11.5, respectively, namely zeolite Y and HZSM-5, were utilized in the experiment. In addition, binders such as bentonite and kaolin, purchased from Sigma-Aldrich, were incorporated to help prepare catalyst mixtures and to dilute the catalyst formulations. The catalyst preparation for the samples was via slurry preparation. Zeolites and binders mixed with water (2 mL of water per gram of zeolite) to form the mixture and stirred for 10 min. At this point, the produced slurry was formed and fed to the hand extruder. Then, extrudates are left to dry at room temperature and thereafter calcined (2 ºC/min) at 550 ºC for 5 h in static air. After the calcination, all catalysts were pressed at 7.5 tonnes/cm^2 using a press and die. The pressed catalyst disc was then gently ground and sieved using a mortar and pestle and a sieved to 250 – 400 µm, The requisite amount of pelleted catalyst (600 mg) was then packed into the stainless reactor (fixed-bed) tube sandwiched between two plugs of glass wool. The catalyst formation and composition of the samples prepared for this study are presented in Table 1. The catalytic cracking was carried out in a stainless steel reactor tube (ID = 9 mm and OD = 14 mm) at 550 ºC with N_2 as a carrier gas (70 ml/min). The cracking activity of the prepared catalysts was tested using n-heptane and characterisation measurements (BET, XRD, FTIR, TGA and TPD) were carried out for all catalysts.

Table 1: Catalyst used in this study and compositions

#	**CATALYST FORMULATION**	**ZY (6) (wt%)**	**ZSM-5 (11.5) (wt%)**	**Clay (K) (wt.%)**	**Bentonite (B) (wt%)**
1	ZY (100%) (CBV 712)	100	0	0	0
2	ZSM-5(100%) (CBV 2314)	0	100	0	0
3	ZY/ZSM-5 (95/5)	95	5	0	0
4	ZY/ZSM-5 (90/10)	90	10	0	0
5	ZY/ZSM-5 (80/20)	80	20	0	0
6	ZY/ZSM-5/K(35/5/60)	35	5	60	0
7	ZY/ZSM-5/K (30/10/60)	30	10	60	0
8	ZY/ZSM-5/K (20/20/60)	20	20	60	0
9	ZY/ZSM-5/K/B (35/5/30/30)	35	5	30	30
10	ZY/ZSM-5/K/B (30/10/30/30)	30	10	30	30
11	ZY/ZSM-5/K/B (20/20/30/30)	20	20	30	30

2.1 Gas analysis and catalysts performance

Prior to the catalytic run, the catalysts were activated in-situ in flowing air by heating to 550 ºC and then switched to flowing N_2 both at 50 ml/min (supplied by the BOC Linde group). The system was purged with N_2 (70 *ml/*min) at atmospheric pressure for one hour prior to commencing a catalytic test. The n-heptane was carried to reactor (ID = 9 mm and OD = 14 mm) using N_2 which passed through three bubblers in series (saturator) in a chiller at -2 ºC. in Figure 2. The catalysts under test were heated to the required reaction temperature (550 ºC) at 10 ºC /min, and the reactions were carried out typically for 4 hours at atmospheric pressure with a weight / molar flow rate of 224 g.h/mol. Gas samples were taken every hour, and the flow rate (ml/min) through the reactor was measured several times throughout each hour of reaction to confirm no leaks in system. The gas products were analysed using a Varian 3800 GC-FID fitted with a 50 m x 5 mm x 0.32 µm. PLOT Al_2O_3 KCl capillary column supplied by Restek (model number 19762) and products were identified and quantified using a standard gas mixture of 1% mol. C_1-C_5 (BOC Linde Group) to calculate appropriate response factors and check no change in detector responses.The results were calculated as both mole % and weight % , the latter presented here. For the calculation of light olefin, the conversion, yield, and selectivity were based on the peak areas concerning the total area of the peaks in the hydrocarbon mixture. The peak area was calculated based on a GC chromatogram. After identifying unknown the hydrocarbon mixture using the following equations:

$$n - heptane\ conversion\ (wt.\%) = \frac{n{-}heptane_{in} - heptane_{out}}{heptane_{in}} \times 100\% \qquad 1$$

$$C_xH_y selectivity\ (wt.\%) = \frac{C_xH_y}{n{-}heptane_{in} - heptane_{out}} \times 100\% \qquad 2$$

$$Yield\ (wt.\%) = (C_xH_y selectivity\ (wt.\%) \times n - heptane\ conversion\ (wt.\%) \qquad 3$$

Where n-C_7 conversion is the conversion of n-C_7 in the experiment (wt. %) at time of stream, *$C_xH_y$selecti*vity (wt.%) is the selectivity of the desired product, and Yield (wt. %) of light oilfens.

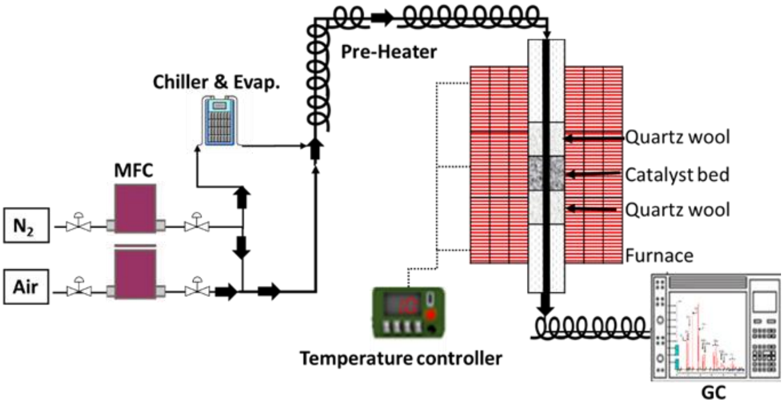

Figure 2:Scheme of the reactor system showing precatalyst drying using air and stages of n-heptane cracking

3. Results and Discussion

3.1 BET and SEM results

The BET surface area and pore-sized distribution analysis of catalysts are presented in ,
Table 2. As expected the surface area of mixed ZY/ ZSM-5 catalysts decreased from 578 to 465 m^2/g losing approx. 20% of its surface area. That was because of adding ZSM-5. Furthermore, after adding binder and ZSM-5, the BET surface area of ZY/ZSM/K catalysts decreased dramatically due to adding binders losing approx. 50 % of its surface area and can be explained by the addition of more mesoporous (binder) molecules to the catalyst formulation.

3.2 Catalyst evaluation

The catalytic cracking on formulated catalysts had an n-C_7 conversion rate of over 85%, with the highest conversion rate (95 wt.%) achieved using the ZY/ZSM/K/B (20:20:30:30) catalyst, which contained 20 wt.% of ZSM-5. Adding a binder to the catalyst mixture increased the yield of light olefins and slowed deactivation,

Table 2: Result of BET analysis for catalysts resulting in yields between 24-64 wt.% for ZY/ZSM/K/B (20:20:30:30) and ZY/ZSM/K (20:20:60). Light olefin production was mainly due to hydrogen transfer via carbenium ion and C–C cracking through the β-scission mechanism during cracking. The ZY/ZSM/K/B (20:20:30:30) catalyst exhibited an 8% decrease in the total alkanes yield (C_1-C_5) over time on stream. The mild acidity of the catalyst improved its performance by reducing the production of lower alkanes (C_1-C_5) and increasing the yield of light olefins. In summary, the study found that adding ZSM-5 to the catalyst formulation could enhance its performance and lead to a higher yield of light olefins. Additionally, using a binder in the mixture could help slow down the catalyst deactivation.

Catalysts	S_{BET} (m²/g)	S_{micro} (m²/g)	$S_{external}$ (m²/g)	V_{total} (cm³/g)	V_{micro} (cm³/g)	V_{meso} (cm³/g)
ZY (CBV 712)	340	265	75	0.23	0.14	0.09
ZSM-5 (CBV 2314)	491	363	128	0.21	0.19	0.02
ZY/ZSM-5 (95/5)	578	458	120	0.29	0.24	0.05
ZY/ZSM5 (90/10)	572	447	125	0.29	0.23	0.06
ZY/ZSM5 (80/20)	465	375	90	0.23	0.20	0.03
ZY/ZSM5/K (35/5/60)	190	144	46	0.09	0.07	0.02
ZY/ZSM5/K (30/10/60)	221	166	55	0.11	0.09	0.02
ZY/ZSM/5K (20/20/60)	238	180	57	0.12	0.09	0.03
ZY/ZSM5/K/B(20/20/30/30)	180	47	133	0.15	0.07	0.08

**ZY/ZSM5/K/B(35/5/30/30) and ZY/ZSM5/K/B(30/10/30/30) awaiting analysis*

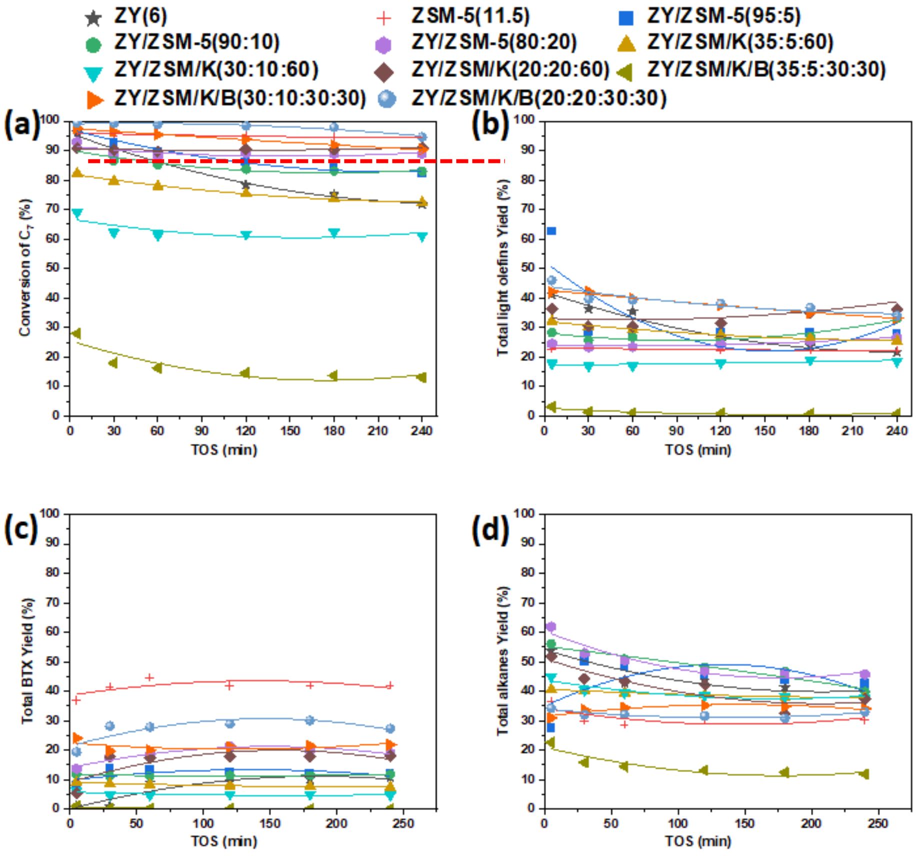

Figure 3: (a) n-heptane conversion,(b) total light olefins yield, (C) total BTX, and total alkanes

3.3 Cracking Mechanism Ratio (CMR)

The cracking of n-C_7 undergoes two different pathways either via a monomolecular mechanism or biomolecular using CMR. CMR is the ratio of $(C_1 + \sum C_2)/iC_4$ where C_1, $\sum C_2$, and iC_4 denote the selectivities to methane, total C_2 hydrocarbons, and isobutane, respectively (Figure 4a). For CMR of alkanes when using more than four carbon atoms', it becomes difficult to determine the type of cracking mechanism (protolytic and β-scission) that results in the final product distribution. The CMR value of n-C_7 over the majority of catalysts tested stabilised with the time of the stream (Figure 4a). Based on the experimental conditions used, a high CMR value reflects that the monomolecular contributed to a "protolytic" cracking mechanism, while a low CMR value reflects a bimolecular hydride transfer leading to a β-scission cracking mechanism (C-C or H-C) for n-C_7. As might be expected, the pore size of ZSM-5 introduces a shape selectivity effect that will control the relative amounts of protoytic and β-scission mechanism. The ethylene/propylene (C_2=/C_3=) ratio indicates the selectivity of the cracking conditions to produce $C_2^=$ (Figure 4b) where there is a general increased in light olefins production and more importantly increased the amount of $C_2^=$ produced.

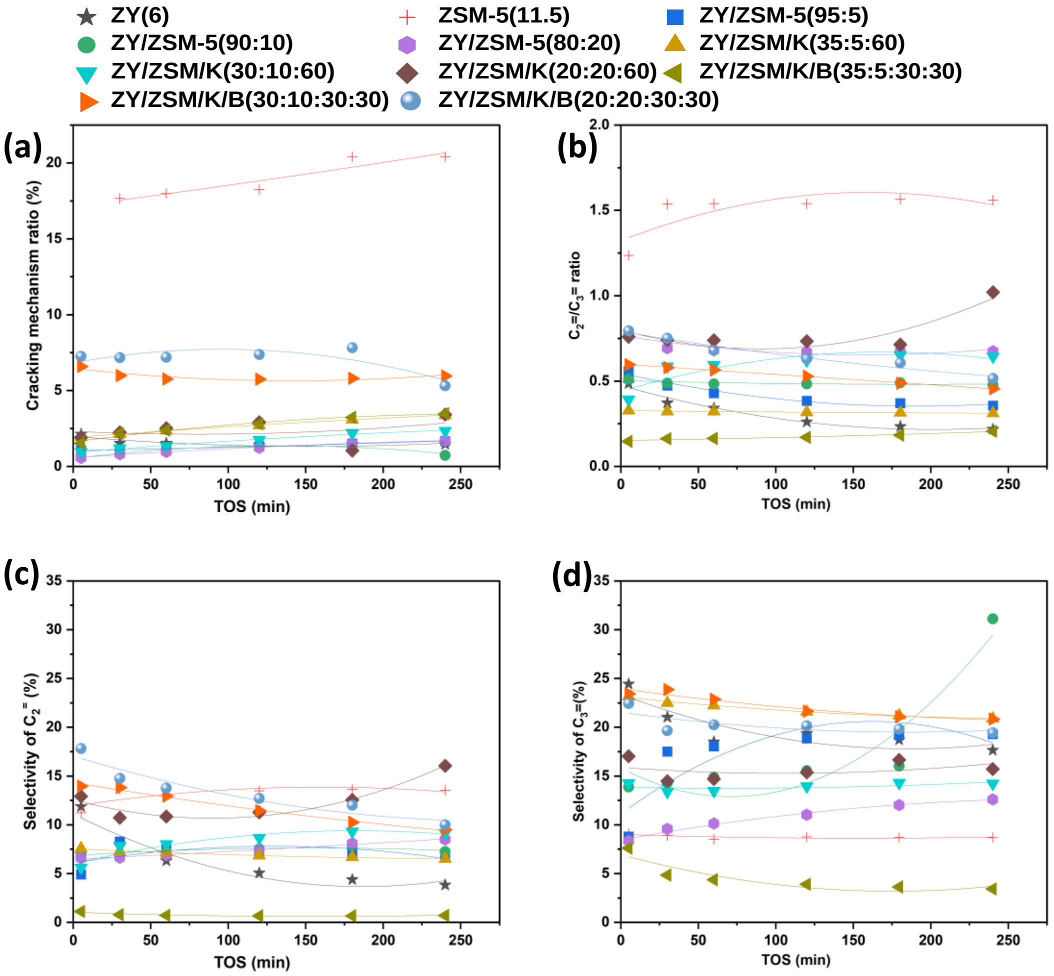

Figure 4: (a) cracking mechanism ratio, (b) C_2=/C_3= ratio, and (c and d) Selectivity of C_2= and C_3=

4. Conclusions

In summary, this study aimed to enhance the conversion and selective production of light olefins (C_2= and C_3=) via catalytic cracking of n-C_7 using a fixed-bed reactor under mild conditions (550 ºC and atmospheric pressure). The results demonstrated that the ZY/ZSM5/K/B (20:20:30:30) and ZY/ZSM5K (20:20:60) catalysts were highly effective in significantly increasing the production of light olefins at this temperature. These catalysts were identified as the best performers in terms of producing light olefins. Moreover, the addition of ZSM-5 (20%) to the catalyst formulation was found to be responsible for the formation and shape selectivity of light olefins.

The study is still ongoing, and future work will focus on varying the reactant contact time (W/F) and exploring additives such as mesoporous supports.

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