

Synthesis and assessment of Y-Zeolite catalyst performance for direct olefin production from heavy feedstock; regulating salt content

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Abstract

Zeolites are crystalline aluminosilicates with open-framework structures and have been widely used in refinery processes. One of the significant utilisation processes is cracking heavy feedstocks into lighter fractions, which can be used as a feedstock for subsequent processes such as petrochemical applications. This work aimed to study the effect of the zeolite's different Si/Al ratios on heavy crude cracking under different salt content conditions. The feedstock used for this study is a heavy hydrocarbon fraction contains a large amount of metal and salt. Two synthesised prototype catalysts were prepared and characterised, mixed with the crudes in a 500 ml autoclave and left to react at different temperatures. The reaction's outlet gases were analysed directly in the connected Gas Chromatography (GC). The results showed a wide range of impacts on catalyst performance and a noticeable increase in C2 and C3 yield for the desalted crude. Moreover, a higher C3 was produced for both catalysts at 430-450 °C due to the catalyst's large pore.

Keywords: Zeolite, Desalted Crude, olefin, Cracking, refining

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Introduction

Historically, crude oil has always been associated more with the world's energy and transportation consumptions, with products such as gasoline, diesel fuel, jet fuel, fuel oil and heating oil (1, 2, 3). However, the new technological developments became more attractive to the chemical industry. Crude oil is becoming the focus of new refinery processes to produce chemicals and olefin, which consequently enhances the integration concept between refineries and petrochemical complexes. Before processing, crude oil in the refineries usually contains dirt and other suspended compounds (4, 5). Different metals in inorganic compounds in reservoir dirt and sand can produce catalyst poisoning in downstream processes such as catalytic cracking and hydro-treating. The poisoning is due to the possible adsorption at the catalyst surface (6, 7). Therefore, the objective of the oil cleaning process is to remove chloride salts and other minerals from the crude oil by water-washing over one or more cycles depending on the level of salt and other inorganics content in the crude.

The catalysts used in the refineries are typically complex in composition and structure, consisting of catalytically active phases, supports, and binders (8-11). The various components have a specific role in catalytic activities, such as textural properties, which provide heat and mass transfer to the catalytic sites and deliver acid-base sites within the catalyst. Thus, spontaneous activity at the catalyst surface due to salt or other components can directly reduce the catalyst activity and consequently process residence time and yield. Zeolite based catalysts are primarily used in refineries' cracking process; these zeolites can selectively convert large complex molecules into smaller molecules (12-15). They can be modified for their surface catalytic properties (acid-base) and poses binding characteristics with other oxides that allow them to use either alone or in combination as an oxide matrix. Generally, they are microporous solids (16-19). The accessibility

of zeolite pores becomes crucial in heavy crude or residue feedstock; thus, the larger pore may enhance feed diffusion and improve stability toward deactivation (20,21).

Desalting is a significant step required before processing the crude to any catalytic reaction to avoid any chemical interruption to the catalyst performance (22,23), which will lead to catalyst deactivation. Typically, the salts in the crude oil are dissolved as fine water droplets emulsified in the crude oil. Thus, preventing the salts from poisoning the catalyst in the catalytic hydroprocessing units, desalting crude becomes a significant step prior to the reaction process. Several desalting techniques for crude have been well established in the petroleum industry over the years, for many processes, monitoring of the salt content is needed for process control and cost reduction of a system (24-26). In addition, high chloride salts in crude oil affect corrosion rates and scale formation in refining units, which can also affect catalysts and equipment.

Finally, Hydrocracking is a process to hydrogenate and cleave the C-C bonds of hydrocarbons using hydrogen gas and a catalyst, thereby converting them into compounds of lower molecular weight (27-30). This work aims to understand the impact of crude salt content on zeolite based catalysts designed with large pore sizes for olefin production, mainly ethylene and propylene.

Materials and Testing

Catalysts: The proposed catalysts AlZ-25 and AlZ-75 were prepared in house of different components using dry physical mixing. The main components of support were alumina, zeolites, and pore extending binder (filler) PEG or carbon. The binder components provide the physical strength and integrity of the catalyst. The alumina is used in boehmite (Versal) as a binder or filler in a solid peptised with optimised nitric acid. The catalyst matrix, which contains neutral solid and usually large pore alumina, provides a large pore volume and macro-pore diameter to the catalyst.

Crude oil: In table 1 most essential properties of crude are reported

Testing: The crude and catalyst evaluating experiment was carried out over two steps as follows:

- i) **Desalting;** The collected crude sample from the local producer was filtered and desalted. The desalting procedure for heavy crude (20 litre feed tank) was as follow;
 - a. Preparing heavy crude and water in a 1:1 ratio in a barrel
 - b. Add 3 ml demulsifier and stir it for 1 hour.
 - c. The sample was left for 8 hours for stabilisation, and the water was drained.
 - d. Then again, fresh water was added, steps a to c were repeated five times, and the final product was collected.
- ii) **Batch Reactor;** the different crudes were tested in a batch reactor (500 ml capacity) under two catalyst types (AlZ-25 and AlZ-75). The catalysts were used in an extrudate form mixed with the feed (heavy oil) inside an autoclave. The temperature was varied, starting from 380 to 450 °C, where pressure was kept at a fixed value of 100 bar. The stirrer was adjusted at 150 rpm throughout the run. The produced gases from the reaction were analysed directly by the online gas chromatography (GC).

Results and discussion

1. Synthesised Catalysts: The catalysts were designed to contain large pores for heavy oil processing. The two prepared catalysts were examined for different characteristics, mainly

thermal stability and pore size. The AlZ-75 contains 25 wt% alumina and 75 wt% zeolites, which have higher acid sites but low textural properties, and the AlZ-25 contains 75wt% alumina and 25 wt% zeolites.

2. Catalyst Characterisation. The solid material of the prototype catalyst was characterised for its compositional analysis, thermal stability, surface and textural properties, and acid-base nature of catalysts. The catalyst's structural identification was analysed using FTIR and Raman analysis. Catalytic cracking breaks the larger, heavier, and more complex hydrocarbon molecules into simpler and lighter molecules to produce higher-value products. Zeolite catalysts have been the primary catalyst type used in refining in the last two decades.
- a. X-ray diffraction (XRD). It was performed to determine the bulk crystalline phases of the samples using a SIEMENS D-5000 X-ray diffractometer with CuK α ($\lambda = 1.54439 \text{ \AA}$). The spectra were scanned at a 2.4 min^{-1} in the range $2\theta = 20\text{--}80^\circ$. The prototype catalyst was compared for their phase analysis with FCC catalyst (commercial) using x-ray diffraction. These results are in figure 1. Later the prototype catalyst matched with the commercial catalyst, which has different preparation methods and compositions. Due to the vendor's instructions, other information will not be shared in this paper. This step aims to compare the prepared catalyst composition, which is close to the FCC catalyst, to ensure the suitability of the prepared catalyst for olefin production.

b. Thermogravimetric analysis (TGA) was done using a Linseis equipment temperature control from (10°C) RT up to 1100°C. The maximum decomposition temperature (T_{max}) was determined at a heating rate of 10°C/ min in an oxygen atmosphere at a 25 ml/min flow rate. TGA results in figure 2 confirm the decomposition as a function of temperature. Tests of the dehydration of fly ash zeolites carried out by the thermogravimetric method have suggested a possibility of changes and interaction between the zeolites and the binder used for the catalyst synthesis. Thus, the uncalcined catalyst (UC) characterised their thermal stability. The catalysts show a considerable loss from room temperature to 175 °C, corresponding to the loss of humidity and adsorbed material on the surface.

Furthermore, the prepared catalysts were subjected to pores and pore size distribution measuring using mercury (Hg) porosimetry. The support contains a bimodal type of pore-size distribution derived from the intrusion data, which are presented in figure 3. The AlZ-25 showed a lower average pore diameter and higher pore area in comparison with AlZ-75. Moreover, full texture properties of the prepared catalyst is described in table 2.

Table 2. Texture properties of Prepared Catalyst Support

3. Salted & Desalted Crude: Most chemical poisons are permanent and irreversibly absorbed into the active catalyst sites. Hence, processing feed is typically considered the most critical factor governing catalyst structure and performance, which can profoundly affect catalyst properties. Figure 3 shows the catalyst activity for both desalted and salted feeds, in figure 3-a and b show that both catalysts increased activity with the desalted feed with an apparent

increase for AlZ-75. This may be attributed to salt physically blocking multiple reaction sites or slowing the surface diffusion of adsorbed reactants. The high salt content inhibited the prepared catalyst by binding directly to an active site or disrupting the active site's local structure, leading to low AlZ activity and consequently low propylene and ethylene yield, as shown in figures 3-c and d. The crystalline structure of AlZ-25 tends to provide a more active site under the salted crude due to the high pore area available ($207.4 \text{ m}^2/\text{g}$).

Moreover, figure 4 results indicated that catalyst compositions have a relatively high impact at higher temperatures $430\text{-}450^\circ\text{C}$, reflecting the excellent stability of the synthesised catalysts at high temperatures.

Conclusion

This work investigated the impact of high salt content crude on zeolite catalyst activity during cracking, using two different feeds, and two types of zeolite based catalysts were used for this work. The characterisation tests showed the suitability of the prepared catalyst for olefin cracking in terms of thermal and chemical stability. Regardless of the alumina content in both AlZ-25 and AlZ-75 both catalysts showed better performance with the desalted crude using online GC analysis. Concerning the particular aspect of propylene and ethylene yield, the catalyst with a high average pore diameter showed better yield enhancement with the desalted crude. In general, desalting the crude before using olefin cracking catalyst is a very vital step which consequently gives the catalyst pore the suitable media to better crack and yield the desired product.

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Tables:

Table1, Crude oil and desalted crude properties

<i>Property</i>	<i>Unit</i>	<i>Crude</i>	<i>Desalted Crude</i>
Water content	wt%	2.00	1.90
Salt content	PTB	>150	15.4
API		11.57	11.35
Specific gravity		0.989	0.991
Density @ 15°C	gm/cc	0.988	1.000
@ 65°C	gm/cc	0.957	0.958
Asphaltene	wt%	4.94	6.37
*MCR	wt%	11.90	12.40
Sulfur content	wt%	5.27	4.84
Kinematic viscosity @ 40 °	mm ² /s	783	928

*Carbon residue

Table 2, texture properties of the prepared catalysts

Sample ID	Support Composition	Porosimetry			PA, m ² /g	APD, Å
		SSA, m ² /g	APD, Å	TPV, cc/g		
Al-Z-25	CBV-300 (25%) +Versal alumina (75%)	340.8	76	0.742	207.4	143
Al-Z-75	CBV-300 (75%) +Versal alumina (25%)	559.2	57	0.749	69.6	431

Specific Surface Area (SSA); Total Pore Volume (TPV); Average Pore Diameter (APD); Pore Area (PA); for all experiments = 25% and 75%; USY Zeolite (Zeolist, CBV300).

Figures legends:

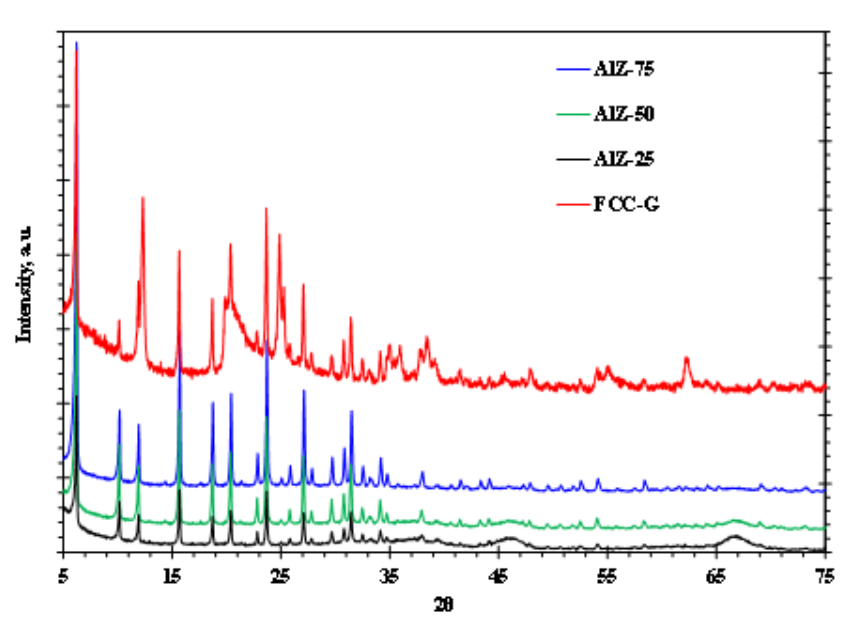


Figure. 1. Synthesised prototype catalysts and their phase identification using x-ray diffraction (XRD) technique (a comparison with the commercial FCC catalysts).

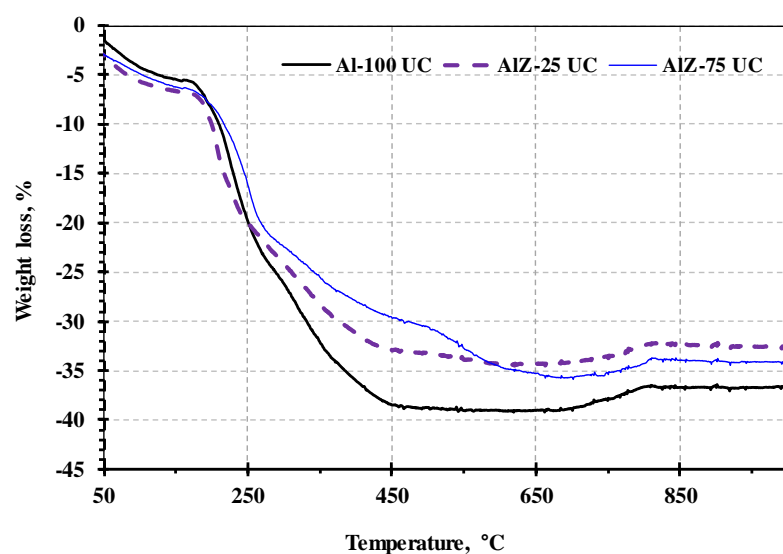


Figure 2. Thermogravimetric analysis of uncalcined catalysts in oxygen atmosphere (a)

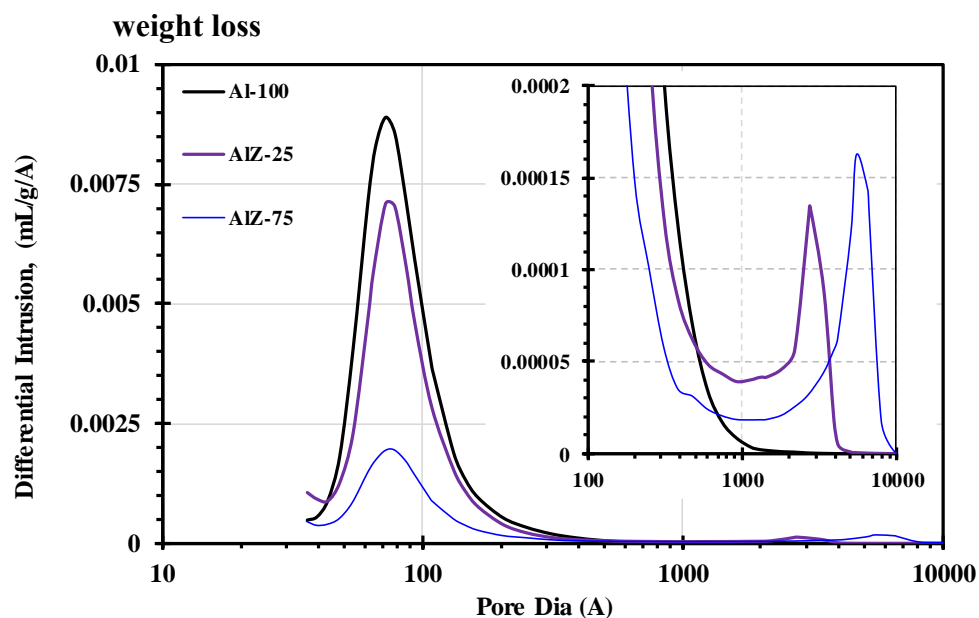


Figure 3. Variation of pore size distribution as a function of pore diameter.

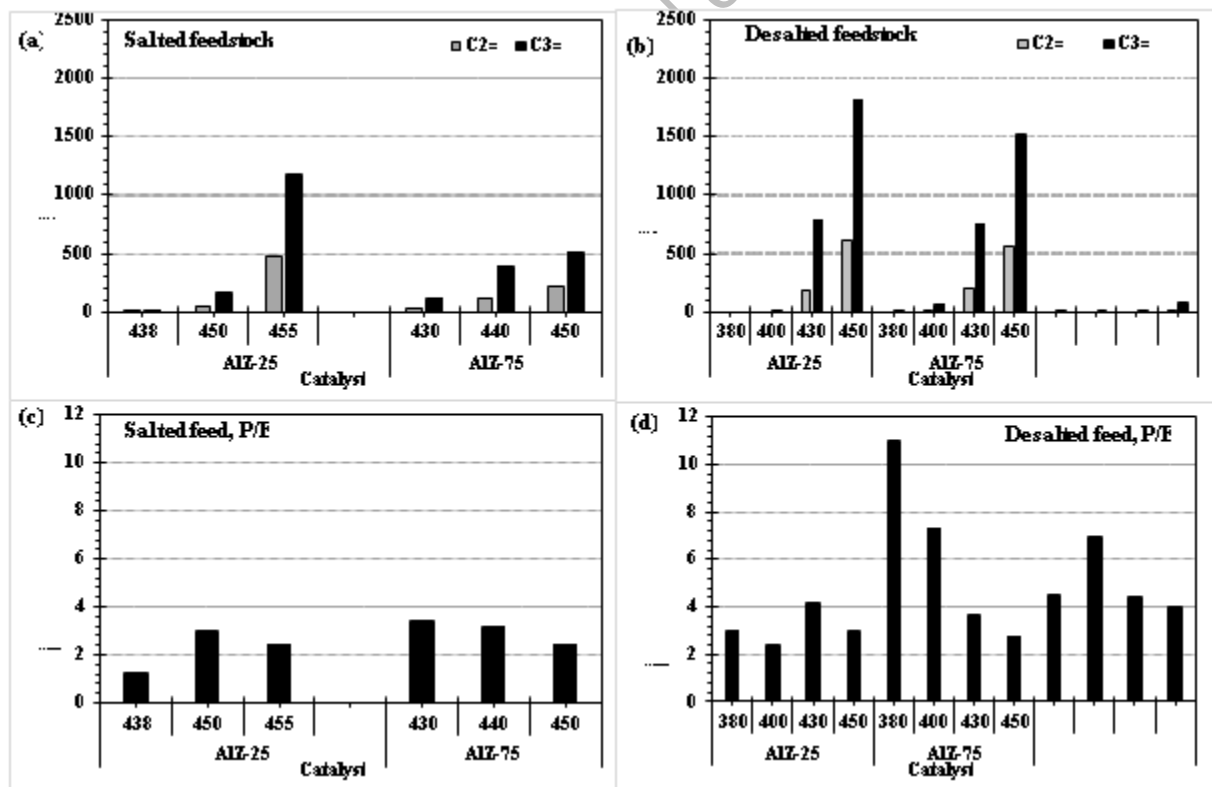


Figure 4. An effect of feed composition on olefin production [(a) salted feed, (b) desalted feed, (c) olefin ratio in salted feed, (d) olefin ratio in salted feed in a batch reactor.