

The Effect of Promoters on the Activity of Prepared Zeolite Catalyst in FCC Process

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Abstract

Faujasite type NaY zeolite catalyst was prepared from locally available kaolin, then the prepared NaY zeolite have been modified by exchanging of sodium ion with ammonium to produce NH_4Y zeolite. NH_4Y zeolite was converted to HY zeolite by ion exchanging with oxalic acid. Zinc and nickel promoters have been added to the prepared HY zeolite catalyst, and the effect of these promoters on the catalytic activity of the prepared HY catalyst was studied in fluid catalytic cracking process using light gas oil as a feedstock. The experimental results show that the promoted catalyst gives higher gas oil conversion and gasoline yield than HY zeolite catalyst at the same reaction temperature and WHSV. It was also found that the promoted catalyst gives gasoline with lesser olefin content and higher aromatics compared with the gasoline produced by HY catalyst.

Keyword: FCC catalyst promoters, zeolite preparation, zeolite promoters

Introduction

Fluid catalytic cracking (FCC) is the most important conversion process used in petroleum refineries. It is widely used to convert the high-boiling, high-molecular weight hydrocarbon fractions of crude oils to more valuable gasoline, olefinic gases and other products [1]. The most popular catalyst used in petroleum refineries is zeolite. Most zeolites used commercially are synthetically produced. Zeolite Y is the most important catalytic zeolite, and is generally synthesized in the Na form. Most of the catalysis of interest is acid catalysis, which requires replacing the Na cations by protons, converting the sieve into the H-form [2]. Zeolite catalyst can be activated by addition of promoters, Promoter is a substance

added to a solid catalyst to improve its performance in a chemical reaction. Some promoters interact with active components of catalysts and thereby alter their chemical effect on the catalyzed substance [3]. Rare earth mixtures is used in fluid cracking catalysts made for the petroleum refining industry. Gong et al [4] studied the effect of addition of zinc and Galium promoters to HZSM-5 zeolite catalyst on its activity using vacuum gas oil as a feedstock for catalytic cracking, A modified zeolite was prepared by impregnation of zinc and Galium nitrates separately. The cracking reaction conditions were: reaction temperature 510°C and catalyst/ oil ratio was 6.5 - 6.7 g/g and residence time of reaction 2.5 - 3.5 minutes, these conditions gives

conversion between 50 – 56.33 weight% and gasoline octane number from 89.5 to 94. Trigueirp et al [5] studied the influence of the introduction of different rare earth cations, including the light (La, Ce, Nd, Sm, Gd) and heavy elements (Tb, Dy, Ho, Er, Tm), on the thermal stability of NaY zeolite catalyst. The result of this study showed that all the studied elements have the ability of the increasing thermal stability of NaY type zeolite.

The main objective of this work is preparation of cracking catalyst from locally kaolin clay and study the effect of impregnated of Zinc and Nickel promoters on the catalyst activity using gas oil as a feedstock.

Experimental Work Feedstock

Light gas oil with boiling range of 190 to 340 °C was supplied from AL-Dura refinery; it was used as a feedstock for fluid catalytic cracking experiments. The properties of gas oil is shown in table 1.

Table 1, Gas oil properties

API gravity, °API	38.4
Viscosity at 98.8°C, mm ² /s	21.96
Molecular weight g/mole	210
ASTM distillation	
IBP, °C	190
5% volume distilled, °C	208
50% volume distilled, °C	282
70% volume distilled, °C	302
E.P, °C	340

Catalyst Preparation

Preparation of NaY Zeolite Catalyst

Kaolin was mixed with 40% weight percent sodium hydroxide solution using kaolin / NaOH = 1/1.5 g/g and fused at 850°C for 3 h. 50 g of fused kaolin and 63 g of sodium silicate were placed in 500 ml of deionized water under constant stirring at 50°C for 1 hour, then the slurry with pH 13.3 was placed in a glass jar and subjected to

ageing at 50°C for 24 h. The produced slurry was crystallized at 100 °C for 48 h. The crystalline mass repeatedly washed with water until pH arriving to 11.7, then the crystalline mass was dried at 100 °C for 16 h.

Preparation of HY Zeolite Catalyst

100 g of NaY zeolite was mixed with 600 ml of saturated aqueous solution of 1 M NH₄NO₃ at 80 °C for 4 h, followed by filtration and washing with deionized water and drying at 100 °C for 6 h. The resultant catalyst from this step is called NH₄Y zeolite. NH₄Y zeolite was treated with oxalic acid to produce HY zeolite. 40 g of NH₄Y zeolite was mixed with 800 ml of 0.5 N oxalic acid at room temperature for 8 h, then the slurry was filtered and washed with deionized water and dried in an oven at 100 °C for 6 h. The dried zeolite was calcined at 550 °C for 5 hours. Table 2 shows the chemical analysis of prepared HY zeolite catalyst.

Table 2, Chemical analysis of prepared HY catalyst

Component	Weight %
SiO ₂	62.78
Al ₂ O ₃	19.83
Fe ₂ O ₃	1.68
K ₂ O	0.63
Na ₂ O	0.134
CaO	0.89
L.O.I	5.57

Preparation of Promoted Zeolite Catalyst

100 g of HY zeolite catalyst was mixed with 226 ml of 0.15 M Zn(NO₃)₂ aqueous solution, then the resultant product was slurried by rapidly stirring at 40°C for 2 h.

The resulting slurry was filtered, and the resulting filter cake was dried at 110 °C for 2 h, then calcined at 550 °C for 3 h. The resulting catalyst was impregnated with 44 ml of 0.6 M Ni(NO₃)₂.2H₂O aqueous solution at 40

°C for 2 h, followed filtration , drying at 110 °C for 2 h, then calcination at 550 °C for 3 h.

Fluid Catalytic Cracking Experiments

FCC experiments were carried out in a laboratory fluidized bed unit. Figure1 shows the schematic flow diagram of the unit. The unit includes: dosing pump, reactor, condensation system, separation flask, gas collector and power supply box.

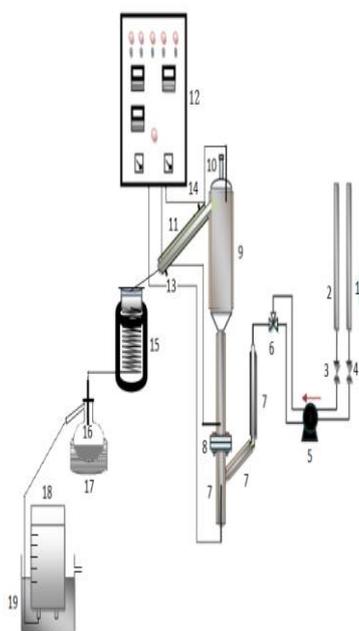


Fig. 1, Schematic flow diagram of the fluidized catalytic unit

(1) Burette gas oil feeding; (2) Burette water feeding; (3) Valve1; (4) Valve2 (5) Dosing pump (6) Three way valve (7) Preheated section (8) Distributor (9) Fluidized bed reaction section; (10) Catalyst charge inlet (11) condenser (12) Control panel; (13) Chilled water in; (14) Chilled water out; (15) Internal tube ice water bath (16) Separation and collection flask (17) Ice water bath (18) Gas collector (19) Water tank.

Distillation Unit

Distillation of FCC liquid product was achieved in laboratory distillation unit, Separation of gasoline fraction from the heavier cracking liquid

products was achieved at this unit shown in figure 2.

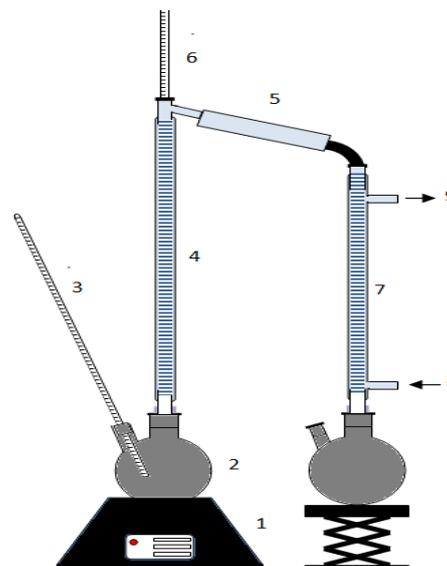


Fig. 2, The Schematic diagram of the laboratory distillation unit

(1) Mental heater (2) Distillation flask (3) Thermometer (4) Distillation column (5) Glass connection (6) Thermometer (7) Condenser (8) Chilled water out (9) Chilled water in.

Conversion

Conversion may be defined as the volume or weight percent of feedstock converted to gasoline and other lighter products and coke, however, conversion is typically calculated by subtracting the volume percent or weight percent of liquid products heavier than gasoline from fresh feed and dividing by the volume or weight of fresh feed.

$$\text{Conversion\%} = \frac{\text{Feed} - (\text{cycle stock})}{\text{Feed}} \times 100 \dots (1)$$

Cycle stock is the portion of catalytic-cracker effluent not converted to gasoline, gases and coke, generally it is the material boiling above 430°F (220°C) [6].

Test Methods

X – Ray Diffraction

X-ray diffraction analysis was done in the State Company of Geological

Survey and Mining by using Maxima XRD-7000 diffractometer.

Sodium Content

The sodium content of prepared faujasite type NaY zeolite before and after ion exchange with ammonium ion was determined by flame photometer Galen Kamp in at State Company for Geological Survey and Mineral. Sodium is commonly reported as the weight percent of sodium oxide (Na_2O).

Silica and Alumina

The percent of silica and alumina in prepared zeolite catalyst before and after dealumination was achieved in State Company of Geological and Mineral.

Surface Area and Pore Volume

Determination of prepared catalyst surface area was found by BET method.

PONA Analysis

PONA analysis is the analysis of hydrocarbon mixtures by separation and quantization of fractions according to the carbon number or type of hydrocarbon. PONA is an acronym for Paraffins, Olefins, Naphthenes and Aromatics. PONA analysis by capillary gas chromatography utilizes a non-polar chemically bonded capillary column with a high theoretical plate number to separate constituent hydrocarbons into as many peaks as possible. PONA analysis features quantitation of olefins at sub-percentage levels, quantitation of individual components in addition to type identification, and calculation of mean density and mean molecular weight.

Results and Discussion

Characterization of Prepared Catalyst

X-ray Diffraction Pattern

X-ray diffraction pattern was determined for prepared NaY zeolite and compared with the standard NaY zeolite. The comparison between the lattice spacing between the prepared and the standard NaY zeolite show that the prepared NaY zeolite is approximately comparable with the standard as shown in figure 3.

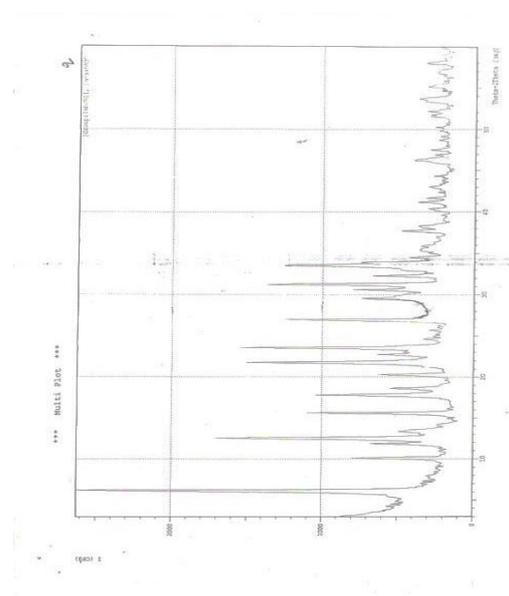


Fig. 3, X – Ray diffraction Spectrum for the prepared NaY zeolite

Sodium Content

Na_2O content of prepared NaY zeolite was analyzed and it was 12.5 wt%, while HY zeolite contains only 1.34 wt%, that means the percent exchange was 89.2 %. This result is in agreement with the result published by Reza and Jones et al. [7]. They recorded that a typical NaY zeolite contains approximately 13 wt% Na_2O .

Surface Area and Pore Volume

The surface area of prepared catalyst was measured by BET method and it was equal to $148.73\text{m}^2/\text{g}$, and this value was in the range of FCC catalyst

surface area of 125 to 192 m²/g [8], while the Pore volume was equal to 0.254 cm³/g.

Effect of Promoters on the Catalyst Activity

The effect of zinc and nickel promoters on the activity of the prepared catalyst (HY zeolite) was studied at WHSV = 10 h⁻¹ and different reaction temperatures (470 - 530°C). Figures 4 and 5 show the effect of promoters on gas oil conversion and the yield of gasoline at different reaction temperatures, respectively. These figures show that promoted catalyst, in general gives higher conversion and gasoline yield than HY catalyst at constant temperature and WHSV.

The chemical composition of the catalytic cracking gasoline was analyzed using PONA analysis. Table 3 shows the comparison between the chemical composition of cracked gasoline fraction that produced by HY and promoted HY zeolite catalysts.

Table 3, Comparison between the chemical compositions of cracked gasoline fraction

Chemical Composition of cracked gasoline (vol. %)	Gasoline produced using HY zeolite catalyst	Gasoline produced using promoted zeolite catalyst
Paraffins	24.06	24.29
Olefins	30.14	12.3
Naphthenes	9.2	9.31
Aromatics	36.6	54.1

It can be seen from this table that the olefin content in the produced gasoline was decreased remarkably by addition of promoters to the cracking catalyst, and the aromatic content was increased, that means addition of promoters increased catalyst activity

and increased gasoline research octane number (RON).

Baker and Whittington [9] measured the chemical composition and research octane number of cracked gasoline produced from different feedstocks and found that the RON depended mainly on the aromatic content as shown in figure 6.

Octane number (RON) of the produced gasoline from this work was calculated from the equation of figure 6 (Aromatics = 2.436RON - 191.9), and it was equal to 93.8 for the produced gasoline using HY zeolite catalyst, while the promoted catalyst gives gasoline with octane number above 100.

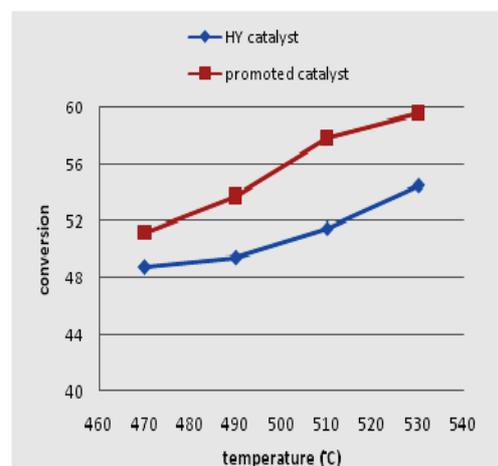


Fig. 4, Effect of promoters on gas oil conversion at WHSV of 10 h⁻¹ and different reaction temperatures

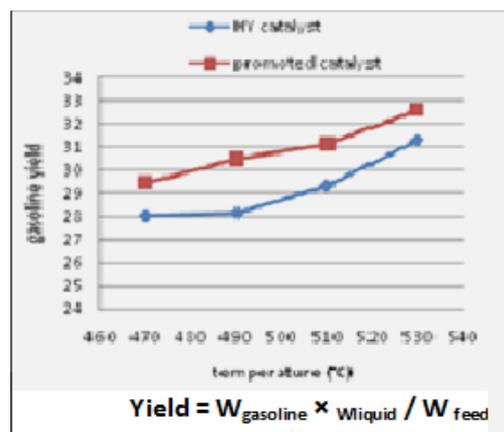


Fig. 5, Effect of promoters on gasoline yield at WHSV = 10 h⁻¹ and different reaction temperatures

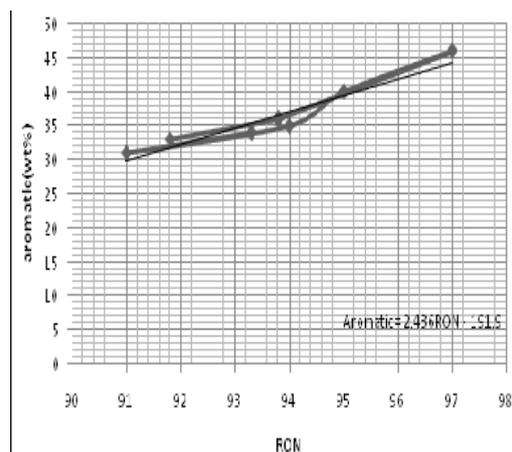


Fig. 6 Relation between RON and aromatic content for cracked gasoline

Conclusions

Addition of Zn and Ni promoters to the prepared HY zeolite catalyst reduces olefin content and increases aromatics in the produced gasoline.

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