IJCPE
Iraqi Journal of Chemical and Petroleum Engineering

Iraqi Journal of Chemical and Petroleum Engineering
Vol.15 No.4 (December 2014) 9-14
ISSN: 1997-4884

University of Baghdad
College of Engineering

Naphtha desulfurization by prepare Cu-Ni-zeolite adsorbent

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Abstract

For desulfurization of naphtha, NaY zeolite was prepared from Dewekhala kaolin clay (Al-Anbar region). For the prepared zeolite adsorbent, x-ray diffraction, sodium content, silica to alumina ratio, surface area, bulk density and crushing strength were determined. From the x-ray diffraction of the prepared NaY zeolite and by a comparison with the standard NaY zeolite, it was found that the prepared adsorbent in this work has approximately the same crystal structure as the standard. Adsorption process was done in a laboratory unit at 25 $^{\circ}$C and 4.1 h^{-1} LHSV. The experimental results show that the promoted adsorbent gives higher percentage of sulfur removal (82.15%) after 10 minute and reaching 40.15% after 120 minute. The adsorption capacity is equal 0.167 mmole "S"/ g after 10 minute while it reached up to 0.77 and 0.98 mmole "S"/g at 50 and 120 minute, respectively.

Keywords: zeolite NaY, naphtha, desulfurization.

Introduction

The presence of sulfur compounds in petroleum fractions is highly undesirable since they result in corrosion, environmental problems and reduction performance of engines. Removal of sulfur compounds from naphtha solutions has been investigated by using adsorption methods. Y-type zeolite with loading metal, activated carbon, zeolite 5A, and zeolite 13X were used for this purpose [1]. **Kikkinides and et al**. (1995) studied the removal of H_2S from pre-dried natural gas contains 1000 ppm H_2S and 5% CO_2 by using zeolite 5A. The purified adsorption product contains 0.5 -1 ppm H_2S [2]. **Herna´ndez-Maldonado and Yang** (2004) studied the desulfurization of diesel, gasoline, and jet fuels by sorbents obtained by ion exchanging faujasite type zeolites with Cu^{+}, Ni^{2+} or Zn^{2+} cations using different techniques, including liquid phase ion exchange, and vapor phase ion exchange . They found that the adsorption amount in the vapor phase decreases at 300°C, rather than 450 °C, and they found that the adsorption capacity in liquid phase for Cu-Y decreases with decreasing the temperature from 450 °C to 350 °C with ultra high purity helium and decrease more by using dry air [3]. **et al. and Fradet,**. (2004) studied adsorption process for natural gas treatment by zeolite and activated charcoal adsorbents. They found that tetra hydro thiophene adsorption capacity is about ten times higher for

zeolite than for activated charcoal [4]. **Nanoti and Dasgupta** (2011) studied the effect of changing in parameter for the prepared zeolite on desulfurization process for naphtha. They changed the type of active components (Cu-Ni-Y, Zn-Y, Cu-Mn-Y, Cu-Me-Y) on the adsorbent, and the number of metal in each sample. They found that the sulfur capacity reduced from 500 mg/g in naphtha at 45 °C to 55 mg 'S' /g for Cu-Mn-Y and Zn-Y, and reduced to 60 mg 'S'/g for Cu-Ni-Y, so they concluded that the adsorption capacities of ion exchange Y-zeolite system gives the best results in terms of exhibiting adsorption capacities (greater than 55 mg/g) [5].
This work deals with the preparation of NaY zeolite promoted with Cu-Ni and using it in desulfurization of naphtha

Experimental Work Materials

Feed Stock

Naphtha with boiling range 30-180 °C was supplied from AL-Dura refinery; and used as a feedstock for desulfurization, the properties of naphtha are given in table 1.

Table 1: Naphtha properties

Specific gravity@ 15.6 °C/15.6 °C	0.678
Reid vapor pressur @ 37.8°C ,(kg/cm^2)	14.09
Initial boiling point , °C	31.0
End boiling point , °C	210
Sulfur content , ppmw	650
Aromatic , Volume %	0.89
Olefin , Volume %	0.03
Naphthenes , Volume %	4.20
N-Paraffins , Volume %	51.78
Iso- Paraffins , Volume %	43.1
RON clear	50

Kaolin Clay

The kaolin clay was supplied from State Company of Geological Surveying and Mining, it available locally in Al - Dewekhala Quarry in Al – Enbar region. This kaolin was used as a raw material for the adsorbent preparation. The chemical analysis of kaolin given in Table 2.

Catalyst Preparation of NaY Zeolite

Kaolin was sieved to a particle size ≤ 75µm. The kaolin with particles of ≤ 75µm was mixed with 40% sodium hydroxide solution using kaolin / NaOH = 1/1.5 and fused at 850°C for 3 hours. 50 g of fused kaolin and 63 g of sodium silicate were added to 500 ml of deionized water under constant stirring at 50°C for 1 hour by electrical magnetic stirrer . The slurry of previous step with pH 13.3 was placed in 1000 ml glass jar and subjected to ageing at 50°C for 24 hr in a programmable electrical furnace. The product was crystallized at 100 °C for 48 hr in a programable electrical furnace. The crystalline mass was filtrated using Buckner funnel with the aid of a vacuum pump and washed with deionized water until arriving pH to 11.7. The washed crystalline was dried at 100 °C for 16 hours by using programable electrical furnace. The chemical analysis of NaY was done by wet chemical analysis and achieved in State Company of Geological Surveying and Mining, as given in table (2).

Table 2: Chemical analysis of kaolin and NaY

Component, wt%	Kaolin	NaY
SiO_2	49.64	41.50
Fe_2O_3	1.72	1.09
Al_2O_3	34.05	20.85
CaO	1.10	1.10
L.O.I.	12.28	20.30
Na_2O	0.46	13.46
Others	0.75	1.7
Total	100.00	100.00

Preparation of promoted Zeolite Catalyst

Promoted zeolite was obtained by ion exchanging process of prepared NaY zeolite with copper nitrate solution,

followed by nickel chloride solution. 100 g of NaY zeolite was mixed with 283 ml of saturated aqueous solution of 0.5 M $Cu(NO_3)_2$ at a room temperature for 48 hours, followed by washing with de-ionized water . The resultant from previous step mixed with 346.7 ml of saturated solution of 0.5 M of $NiCl.6H_2O$ at a room temperature for 48 hours, followed by washing with de-ionized water and drying at about 90 $^{\circ}C$ for 24 hours. During the ion exchange, PH was kept at 6 to avoid hydrolysis of nickel species in solution. The prepared dried promoted adsorbent contains 3.62 wt% of Na_2O, 3.80 wt% of Ni and 5.34 wt% of Cu.

Fixed Bed Adsorption Experiments

The desulfurization adsorption experiments were carried out in a laboratory fixed bed unit. The unit includes: dosing pump, absorber and separating flask. The adsorber loaded with the 50 cm^3 of adsorbent from the top of the adsorber. The experiment started with a constant LHSV 4.1 h^{-1}, and the samples were taken after each 10 minute. The last sample was taken after 120 minute. Figures 1 shows the Schematic diagram of the adsorption unit.

1- Dosing pump and volumetric flow rate.
2- Adsorber.
3- Separation flask.

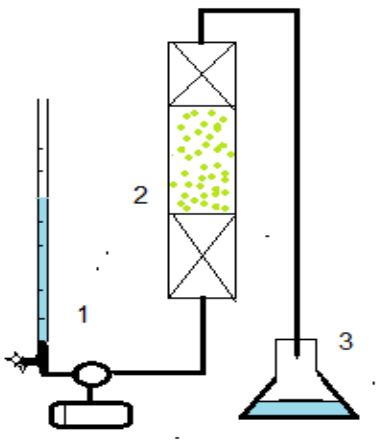

Fig. 1 Schematic diagram of the adsorption unit

Test Methods

The sulfur content for treated naphtha was done in AL-Dura refinery by using Antek instrument 9000N-S (USA) according to ASTM D 5453.

Sodium contentand and silica to alumina of prepared NaY determined by wet chemical analysis in at State Company for Geological Survey and Mining.

X– Ray diffraction analysis was done in the Research Center of Chemistry and Petrochemical – Ministry of Science and Technology.

surface area of adsorbent was determined using BET method by Thermo Finnegan type , apparatus located at Petroleum Development and Research Center , Ministry of Oil.

Bulk density is determined in the Petroleum Research and Development Center by a bulk density device Autotap-Quantchrom/US. Crushing strength of the zeolite granules was obtained by using the testing device (CRUSH BK – CRUSH STRENGTH from MA materials technologies, USA).

Results and Discussion

The comparison between the lattice spacing obtained by x-ray diffreaction shows that the prepared NaY zeolite is approximately comparable with the standard. Table 3 shows the comparison between lattice spacing of prepared NaY zeolite with standard synthesis faujasite, while figure 2 shows X-ray diffraction pattern of prepared zeolite. The value of relative crystallinities determined by equation 1 was 140%.

$$\text{relative crystallinity NaY} = \frac{Sx}{Sr} X\ 100 \quad \ldots (1)$$

This result is agreed with published by N. Ali [6].

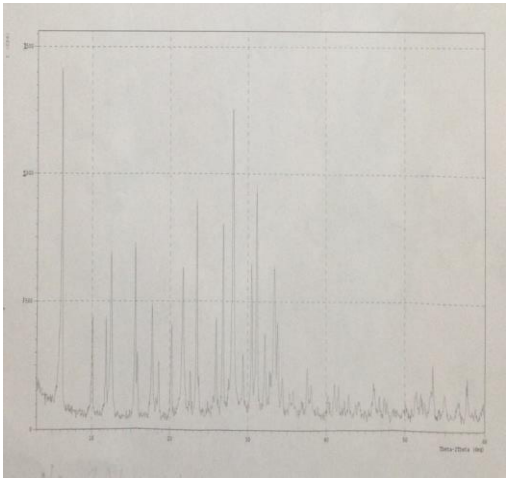

Fig. 2: X– Ray diffraction Spectrum for the prepared NaY zeolite

Table 3: Comparison of lattice spacing, between prepared Catalyst and standard synthesis faujasite –Na

Prepared catalyst		Standard synthesis faujasiteNa	
Angle (2Theta) deg.	d, spacing(Å)	Angle (2Theta) deg.	d, spacing(Å)
12.51	7.06	12.59	7.02
18.57	4.77	18.65	4.36
21.70	4.09	21.80	4.07
26.85	3.78	26.64	3.30
28.14	3.31	28.27	3.15
29.41	3.16	29.27	3.01
30.5	2.92	30.64	2.76
32.20	2.77	32.04	2.70
33.42	2.67	33.56	2.66
35.79	2.50	35.90	2.53
37.88	2.37	37.72	2.4
40.20	2.24	40.3	2.23

The prepared adsorbent was modified by exchanging sodium ion with copper ion and nickel ion using copper nitrate and nickel chloride solution, respectively. Na_2O content of prepared NaY zeolite before and after ion-exchange were 13.46 and 3.62 wt%, respectively, this means that the percent exchange was 73.1 %. This result is in agreement with the result published by *Reza* and Jones et al [7, 8].

The surface area of prepared adsorbent was measured by nitrogen physical adsorption at liquid nitrogen temperature using the BET (Brunauer, Emmett, and Teller) method, and it equals to 210 m^2/gm, while the bulk density is equal to 0.599 gm/cm^3 and the crushing strength is 0.203 N/mm. The most preferred surface area of adsorbent with gamma alumina support is higher than 100 (m^2/gm) [9]. A high surface area is obvious due to the micro porosity of prepared powdered zeolite [10]. An increase in surface area generally increases the adsorbent capacity. The result of surface area agreed with Olguin [11], Yaseen Muhammad, Chunxi Li [12], The results of bulk density is agreed with Kareem Nassrullah, who prepared zeolite 5A with the bulk density of 0.597 gm/cm^3 [13].

Figure 3 shows the breakthrough curve of naphtha adsorption at 25 °C and atmospheric pressure. This figure shows that the value of the effluent total sulfur concentration (ppm) per the total sulfur concentration in the feed (ppm) [C/Co] increases with increasing duration time reaching 0.59 after 120 minute. Figure 4 shows the effect of adsorption duration time on sulfur removal of naphtha at 25 °C and atmospheric pressure. This figure shows that the promoted adsorbent gives higher percentage of sulfur removal (82.15%) after 10 minute then the sulfur removal becomes lower and lower until reaching 40.15% after 120 minute. This result is not far from those obtained by Herna´ndez-Maldonado and Yang [3]. The dynamic adsorption capacity of promoted NaY is calculated from summation of accumulative adsorption after a given time by equation 2.

$$qi = \frac{Co - Ci}{M} * \frac{1}{m.wt} * Q * t \qquad \ldots (2)$$

Where,

q_i =The quantity of the sulfur adsorbed per unit mass of NaY zeolite adsorbent

at any given time, milimole adsorbate/gram adsorbent.
C_o =Initial concentration of adsorbate (S), miligrams/mililiter.
C_i= Effluent concentration of adsorbate at a given time, milligrams/mililiter.
m.wt = Molecular weight of sulfur, milligram/milimole
M= Mass of adsorbent, grams.
Q= Volumetric flow rate, mililiter/minute.
t = Time of sampling, minutes.
The adsorption capacity is equal 0.167 mmole "S"/ g after 10 minute while it reach up to 0.77 and 0.98 mmole "S"/ g after 50 and 120 minute, respectively. These results are in agreement with data published by Welters and Vorbeck [14] , Ma and Velu [15] and Anshu and Dasgupta [5].

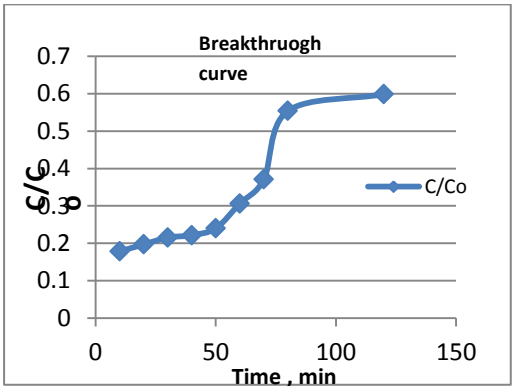

Fig. 3: Breakthrough curve of naphtha adsorption with duration time

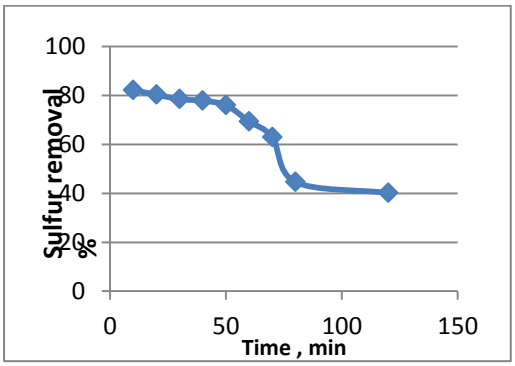

Fig. 4: The effect of adsorption duration time on sulfur removal of naphtha

Conclusions

The comparison of x-ray diffraction pattern of prepared NaY zeolite and the standard zeolite shows a good agreement with relative crystallinity of 140%. From the adsorption process at a room temperature and LHSV 4.1 h^{-1}, promoted NaY adsorbent givers higher sulfur removal for naphtha after 10 min then it decreases with time.

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