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CRACKING ACTIVITY OF PREPARED Y-ZEOLITE CATALYST USING CUMENE ON FLUIDIZED BED REACTOR

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ABSTRACT

The catalytic activity of faujasite type NaY catalysts prepared from local clay (kaolin) with different Si/Al ratio was studied using cumene cracking as a model for catalytic cracking process in the temperature range of 450-525° C, weight hourly space velocity (WHSV) of 5-20 h^1, particle size $\leq 75 \mu m$ and atmospheric pressure. The catalytic activity was investigated using experimental laboratory plant scale of fluidized bed reactor.

It was found that the cumene conversion increases with increasing temperature and decreasing WHSV. At 525° C and WHSV 5 h^{-1}, the conversion was 42.36 and 35.43 mol% for catalyst with 3.54 Si/Al ratio and Catalyst with 5.75 Si/Al ratio, respectively, while at 450° C and at the same WHSV, the conversion was decreased to 29.15 and 21.86 mol% respectively, and the catalyst of 5.75 Si/Al ratio gave the higher cumene activity than the catalyst with 3.54 Si/Al ratio.

Keywords: Fluid catalytic cracking; cumene cracking; benzene production

INTRODUCATION

Catalytic cracking breaks complex hydrocarbons into simpler molecules in order to increase the quality and quantity of lighter, more desirable products and decrease the amount of petroleum residua. This process rearranges the molecular structure of hydrocarbon compounds to convert heavy hydrocarbon feedstock into lighter fractions such as LPG, gasoline, kerosene heating oil, and petrochemical feedstock [1].

Zeolites are the alumina silicate members of the family of micro porous solids known as ‘’molecular sieve‘’ because zeolite has the capacity to selective adsorption of molecules based on their size. There are 40 types of natural zeolites that have been found, in addition, the number of synthetic zeolite has increased to more than 150[2].

Plank and Nace [3] studied the cumene cracking and coke formation over silica -alumina at 800-1000 F and 2-6 h^{-1} LHSV in fixed bed reactor and found that when temperature increases the conversion of cumene increases, and decreases as LHSV increases.

Peter et al. [4] studied dealkylation of cumene over zeolite Y in hydrogen form pretreated at temperatures between 500 and 800° C and they found that the main products were benzene and propylene and they calculated the conversion data from the concentration of benzene in the product.

Corma and Wojciechowski [5] studied the kinetics of cumene cracking over an HY zeolite catalyst at atmospheric pressure and at temperatures of 360, 430, and 500° C. The rate constant for dealkylation as well as the decay parameters have thus been determined. These parameters are compared with those obtained using a LaY catalyst, and the observed differences are discussed in terms of the nature and number of Bronsted sites in the two catalysts. These conclude that the nature of the active sites is identical in the two catalysts, but that HY has a greater number of active sites per unit weight.

Albert Gomezplata, and W. W. Shuster [6] studied the effect of uniformity of fluidization on the catalytic cracking of cumene, with a silica alumina catalyst, in a 3 in.-diameter reactor operated at 527° C. Superficial gas velocities were varied from 0.06 to 0.24 ft./sec. for bed heights of 1.5, 3, 5, and 8 in. The percentage conversion in a fluidized bed was found to be lower than in a fixed bed .It was noted that the first few inches of bed are very effective in bringing in contact the continuous and discontinuous phase, and therefore most of the conversion due to the interaction of the two phases takes place here.

Corma and Wojciechowski [7] studied the initial selectivities for primary products in the catalytic cracking of cumene on HY and LaY zeolite catalysts in an integral fixed bed glass tubular reactor. It was observed that the reac-tion products and their characteristics behavior have been found to be the same for both LaY and HY zeolites at 360, 430, and 500° C which are due to the similarity in the nature of the active sites in both catalysts. The obtained selectivity for benzene ranged from 0.16 to 0.94 and from 0.65 to 0.94 mol % over HY and LaY zeolites, respectively.

The aim of the present work is study the performance of prepared catalysts from kaolin of Al-Dewekhala Quarry, Al- Enbar region using cumene as a feedstock for fluid catalytic reaction.

EXPERIMENTAL

Feedstock

Cumene (isopropyl benzene) supplied by BDH with 98% purity and boiling point of 423 K was used as a raw material for fluidized catalytic cracking activity test.

Kaolin clay

Kaolin clay available in Al-Dewekhala Quarry in Al- Enbar region was used as raw material for catalyst preparation. Table 1 shows the chemical analysis of this material.

Table 1 Chemical analysis of kaolin

Component	Weight %
SiO_2	53.2
Al_2O_3	32.13
Fe_2O_3	1.41
Na_2O	0.35
MgO	0.21
CaO	0.13
TiO_2	0.41
L.O.I	12.00

L.O.I = Loss on Ignition

Catalyst preparation

Preparation Of Catalyst With 3.542 Si/Al ratio:

Mixture of 300 g sodium hydroxide with 200 g kaolin was prepared and heating at 900° C for 4 hr, after that, this mixture added to 400 g of sodium silicate dispersed in 450 ml of deionized water under constant stirring for 2 hr to product the slurry with pH =12.6. This product was aged at 60° C for 25 hr. The temperature increases to 110° C for 60 h for Crystallization process. The crystalline mass is then washed with deionized water until a pH =11. The results powder was dried at 100° C for 20 hr, after that the produced catalyst was milled into a fine powder, and sieved to a particle size ≤ 75 µm.

Preparation of Catalyst with 5.758Si/Al ratio:

100 g of prepared Catalyst With 3.542 Si/Al ratio was stirred with 1 liter of 2 N hydrochloric acid solution, for 3 hrs at 80° C.

The stirring was done at the same apparatus. The product was carefully washed with large quantities of deionized water to free of all chloride ions, and dried at 110° C for 5 h. The dried zeolite was calcined for 5 h at 550° C. The prepared catalyst then subjected to chem.-ical analysis for SiO_2/Al_2O_3 ratio determination [8].

FCC experiment

The FCC experiments were carried out at temperature range 450 to 525°C, WHSV ra-nge 5 to 25 h^{-1},catalyst practical size ≤75µm, and atmospheric pressure. Figure 1 represents the schematic flow diagram of the fluidized catalytic cracking system.

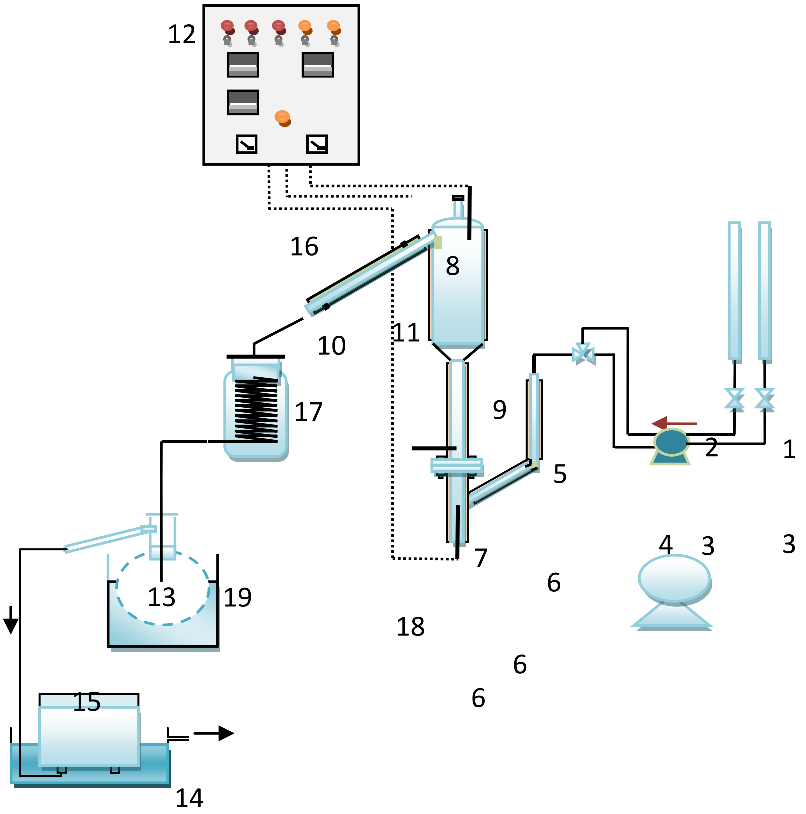

Fig. 1 Schematic flow diagram of the fluidized catalytic cracking system*: (1) Burette cumene feeding; (2) Burette water feeding; (3) Valve; (4) Dosing pump; (5) Three way valve; (6) Preheated section; (7) Fluidized bed reaction section; (8) Catalyst charge inlet;(9) Reactor separation section; (10) Chilled water in; (11) Chilled water out; (12) Control panel; (13) Separation and collection flask ; (14) Water tank ; (15) Gas collection ; (16) Double pipe heat exchanger ; (17) Internal tube ice water bath ; (18) Distributor (19) Ice water bath .*

Analytical Method

Reaction products composition was determined by gas chromatographic analysis (Packed 438A located in Ibn Sina State Company).
The chromatograph used has a flame ionization detector and column type cpsil - 5CB with an inside diameter of 0.25 mm and length 50 m. The oven temperature of the gas chromatography is programmed at inlet temperature 75° C and raised to 110° C at rate 50 C/min. Injection temperature was 250° C. The carrier gas used for chromate-graphic analysis was pure helium.

RESULTS AND DISCUSSIONS

X-Ray Diffraction

X-Ray diffraction was used to study the crystalline and framework structure of zeolites.
Figure 2 represent the x-ray diffraction pattern of the prepared with 3.54 Si/Al ratio catalyst. This pattern was compared with x-ray data of standard Y-zeolite (figure 3)[9]. Table 2 shows that the lattice spacing of prepared catalyst sample gave similar lattice spacing of standard synthesis faujasite-Na. This means that the prepared catalyst has approximately the same crystal structure as the standard type Y-zeolite.

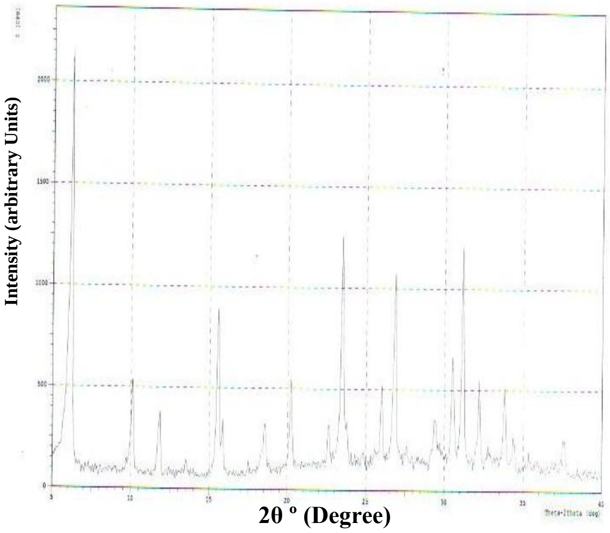

Figure 2 X-Ray diffraction Spectrum for the prepared catalyst.

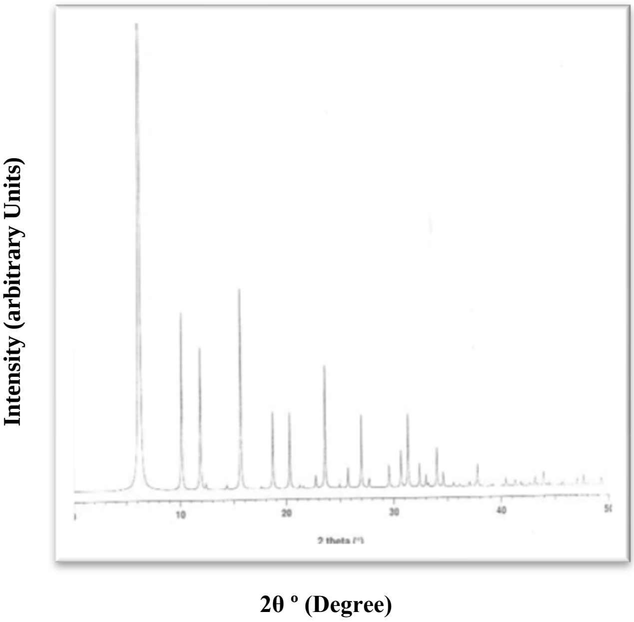

Figure 3 X -Ray diffraction Spectrum for the standard zeolite Y [9].

Table 2 Comparison of lattice spacing, between prepared Catalyst and standard synthesis faujasite -Na

prepared catalyst		standard synthesis faujasite -Na [10]	
Angle (2Theta) deg.	d,spacing (Å)	Angle(2Theta)deg.	d,spacing (Å)
12.536	7.055	12.47	7.09
20.386	4.352	19.80	4.48
21.703	4.0914	21.76	4.08
26.847	3.318	26.74	3.33
28.127	3.1699	28.21	3.16
29.444	3.031	29.55	3.02
31.151	2.868	30.94	2.88
32.396	2.761	32.26	2.77
33.414	2.679	33.49	2.67
35.864	2.5018	35.95	2.49
38.135	2.357	38.16	2.35
38.485	2.33	39.27	2.29

Effect of superficial gas velocity on cumene conversion

The effect of the ratio of superficial gas velocity to minimum fluidization velocity (u_o/u_{mf}) on the cumene conversion was investigated in the range of 2 - 6. Experiments were performed at different weights of prepared NaY catalyst to vary the u_o/u_{mf} ratio at constant weight hour space velocity. The experimental conditions of these tests are WHSV of 10 h^{-1}, reaction temperature of 500° C. Figure 4 show the effect of u_o/u_{mf} ratio on the conversion. It is seen that the cumene conversion is affected by the inlet gas velocity, when the u_o/u_{mf} ratio increases the cumene conversion also increase up to u_o/u_{mf} five times, after that the conver-sion slightly decreases. Therefore the value of u_o/u_{mf} equal five will be selected for the study. This result was agree with ***Karim*** [11] the experimental conditions of these tests are WHSV of 10 hr^{-1}, reaction temperature of 480 ^oC, and atmospheric pressure.

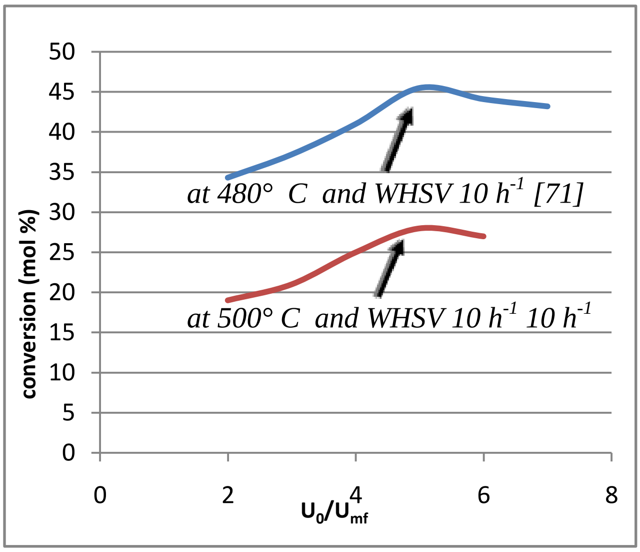

Fig. 4 Effect of u_o/u_{mf} ratio on the cumene.

Effect of Temperature

Figure 5 and 6 shows the effect of temperature on cumene conversion for Catalyst with 3.54 Si/Al ratio and Catalyst with 5.75 Si/Al ratio respectively. At 525° C and WHSV 5 h^{-1} , the conversions are 34.22 and 41.97 mol% for catalyst with 3.54 Si/Al ratio and catalyst with 5.75 Si/Al ratio respectively, while at 450° C using the same WHSV the Conversion reach 22.37 and 28.64 mol% respectively. As shown in these figures, the cumene conversion increases with increasing the temperature. This is may be attributed to the increase of active sites that can be used for reaction when the temperature increases and accelerates the intermolecular motion which enhances the rate of reaction. These observa-tions are well agreed with the results reported by Karim et al.[11], Donalad and Wojciechowski [12], Wollaston et al.[13],

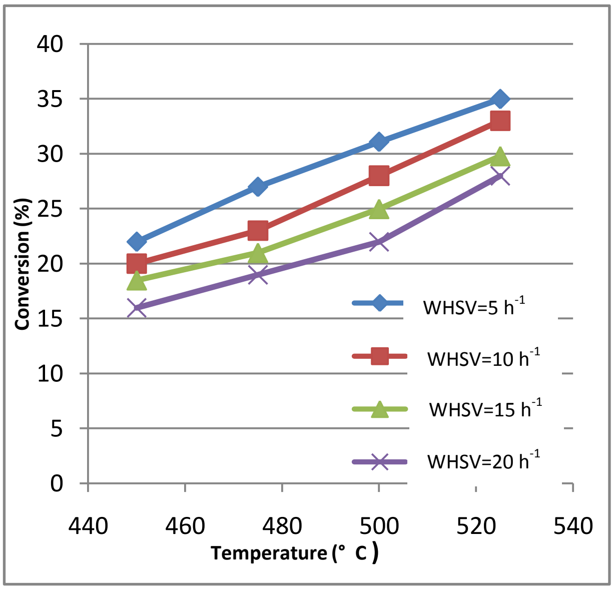

Fig. 5 Effect of temperature on conversion at different WHSV for Catalyst with 3.54 Si/Al ratio.

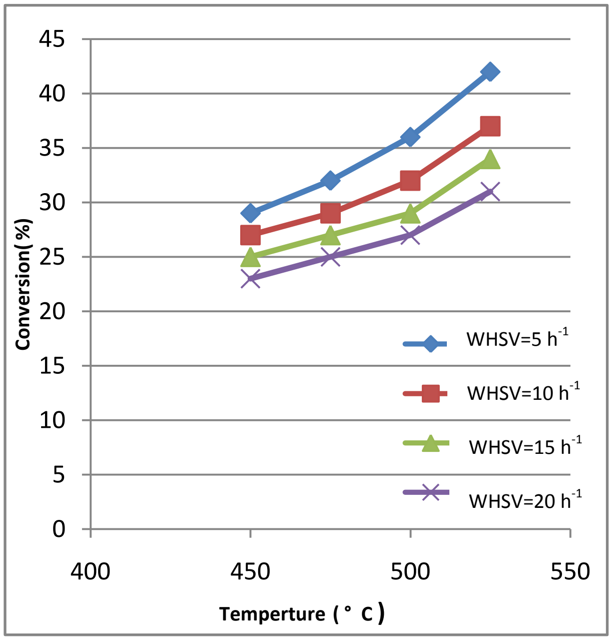

Fig. 6 Effect of temperature on conversion at differ-ent WHSV for Catalyst with 5.75 Si/Al

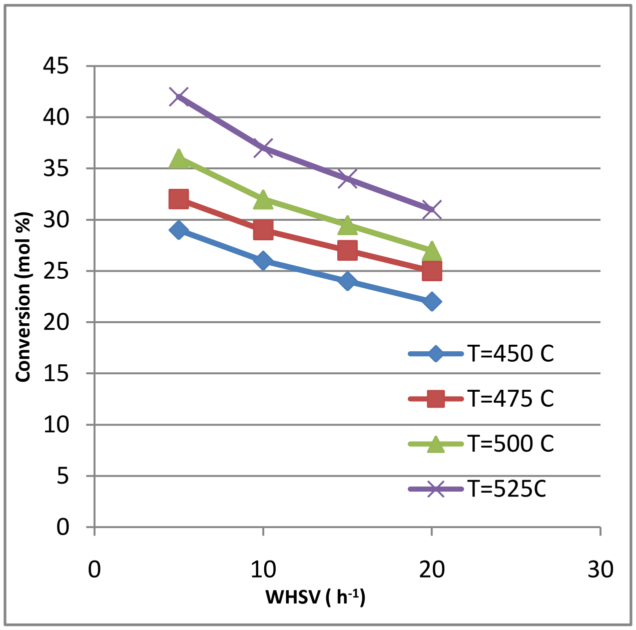

Fig. 7 Effect of WHSV on cumene conversion at different temperatures catalyst with Si/Al 3.542

Effect of WHSV

Figure 7 and 8 shows the effect of WHSV on cumene conversion for Catalyst with Si/Al 3.542 ratio and Catalyst with Si/Al 5.75 ratio respectively. At 525° C and WHSV 5 h^{-1} , the conversions are 29.4 and 35.1 mol% for catalyst with Si/Al 3.542 ratio and catalyst with Si/Al 5.75 ratio respectively while at 450° C using the same WHSV the conversion reach 22.3 and 32.6 mol% respectively.

These figures show that, the cumene conversion increase with decreasing of WHSV at constant temperature. This means that decreasing in the WHSV offers a plenty of contact time for cumene with catalysts. These observation are well agreed with the results reported by Plank and Nace [3], Wollaston et al.[13], Samar et al.[14].

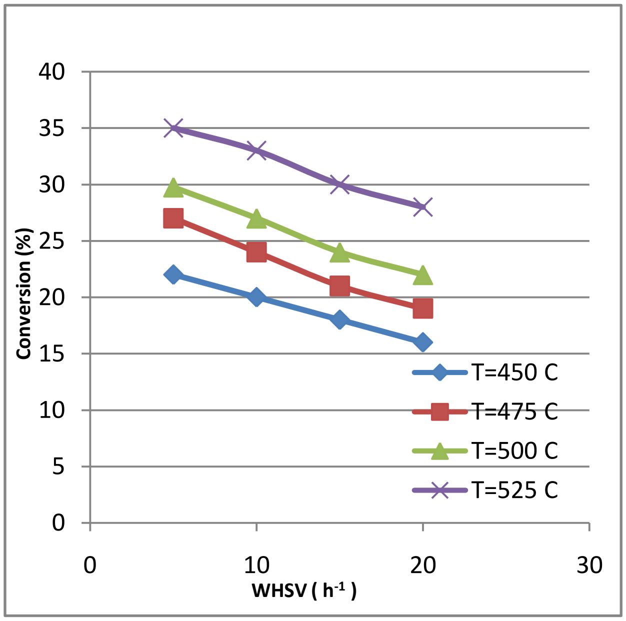

Fig. 8 Effect of WHSV on cumene conversion at different temperatures catalyst with Si/Al 5.758.

Comparison between the Performance of Catalyst X and Y Zeolite Prepared From Iraqi Kaolin.

The performance of Y-zeolite prepared from Iraqi clay (Al - Dewekhala) according to this steady was compared with X-zeolite prepared by other author [14] from the same clay and using cumene as a model for cracking reaction.

The ratio of silica to alumina ratio for prepared Y-zeolite 3.54 and 5.75 while 2.8 X-zeolite for prepared.

Figure 9 shows the effect of space time (1/WHSV) on the conversion obtained for the two mentioned catalyst at 500° C. This figure clearly indicates that the Y-zeolite prepared in this steady gave higher conversion at the same space time. For example the conversion obtained from Y-zeolite 3.54 and 5.758 Si/Al, while X-zeolite with 2.8 Si/Al at space time 0.4 h-1 are 40, 48 and 18 mol% respectively.

This is may be due to the high Si/Al ratio of Y-zeolite. This observation well agrees with previous investigation reported by Break et al. [16].

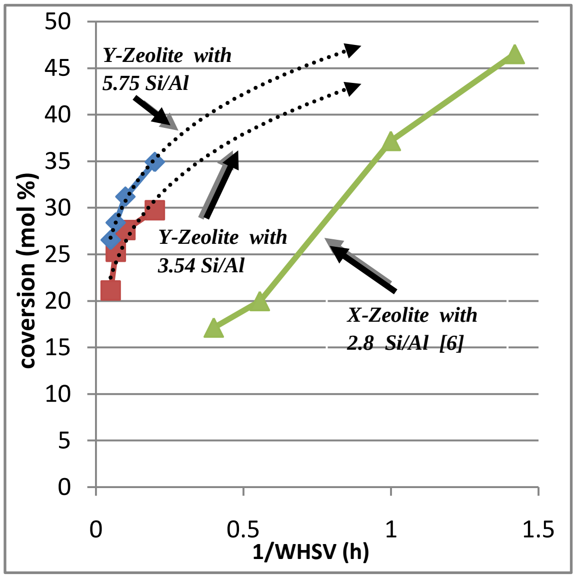

Fig.9 The effect of conversion and 1/WHSV for prepared catalysts at 500 ° C.

CONCLUSIONS

1- The comparison of the X-ray diffraction prepared NaY zeolite catalyst with that of standard shows that the prepared catalyst is approximately Y-zeolite.
2- Cumene conversion and benzene yield increase with temperature increasing from 450° C to 525° C and decrease with WHSV increasing from 5-10 h^{-1} for both catalysts.
3- The catalyst of 5.75 Si/Al ratios gave higher cumene conversion than the catalyst with 3.54 Si/Al ratio.
4- The experimental results indicate that the effect of WHSV higher than the effect of temperature on the cumene conversion within the process variable
5- Y-Zeolite gave higher conversion than X-zeolite at the same operating condition and using the same clay for preparation.

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الخلاصة

تم دراسة الفعالية الحفازية للعامل المساعد المحضر من الكاؤلين المحلي وبنسب مختلفة من السليكا الى الالومينا باستخدام الكيومين كموديل للتكسير الحفازي المائع باستحدام درجات حرارية بين 450-525 درجة سليزية وسرعة فراغية بين 5-20 سا$^{-1}$ وحجم جزيئات اصغر او يساوي75مايكرومتر في وحدة تجريبية وباستخدام مفاعل ذو الطبقة المميعة.

وجد ان نسبة التحول للكيومين وكذلك نسبة تكوين البنزين تزداد بارتفاع درجات الحرارة ونقصان السرعة الفراغية حيث كانت نسبة التحول عند درجة حرارة 525^{o} C وسرعة فراغية 5 سا$^{-1}$ 35.43% و 42.3% للعامل المساعد ذونسبة السليكا الى الالومينا 3.542 و 5.758 على التوالي عند درجة الحرارة 450^{o} C وبنفس السرعة الفراغية لوحظ نسبة التحول قد انخفض الى 29.15 و 21.86% للعاملين على التوالي