

Effect of Dealumination of NH₄Y-zeolite on the Crystallinity, Thermal Stability and Catalytic Activity in Cumene Cracking

E.A. SULTAN AND M.M. SELIM*

Egyptian Petroleum Research Institute, Nasr City, Cairo, Egypt.
**National Research Centre, Dokki, Cairo, Egypt.*

(Received 30th February, 1988)

Summary: Different dealuminated Y-zeolite samples were prepared by the removal of aluminium atoms from NH₄ Y-zeolite using the conventional method with chelating agent EDTA. The DTA of different dealuminated samples was investigated. The X-ray diffraction spectra of the prepared samples were also studied. The catalytic activity of these zeolite samples was tested using the cumene cracking reaction in a microcatalytic system. The results obtained revealed that the zeolite samples are thermally stable. The degree of crystallinity was nearly the same as the original, except for samples with a degree of dealumination higher than 40%. In the cumene cracking study, the reaction was first order and the calculated energy of activation was 46-63 k J mol⁻¹. The increasing of dealumination percentage was accompanied by an increase in catalytic activity, passing through a maximum. The pretreatment at different calcination temperatures, 400-900°C, showed an optimum calcination temperature 550°C after which the catalysts showed maximum activities.

Introduction

The major application of zeolites in catalytic fields has been in the area of hydrocarbon cracking and hydrocracking processes which give the refiner added flexibility in oils which can be processed and products which can be made. However, zeolites have also been used as catalysts in a great number of other very important hydrocarbon reactions[1].

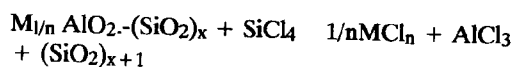
One of the standard test reactions for the characterization of cracking catalysts is the cracking (or dealkylation) of cumene. It is of the Friedel-Craft type, and is normally rationalized in terms of proton attack at an aromatic carbon atom with displacement of the side chain as a carbonium ion.

The cumene-cracking activity of a series of exchanged Y-zeolites has been described[2] and the relative activity found was La-Y > NH₄-Y > Ca-Y > Na-Y. The extent of conversion increased with

increasing cation exchange, and the major products below 773 K were benzene and propylene. Also examined was the effect of altering the SiO₂:Al₂O₃ ratio. With the Ca-Y zeolite, the cracking activity appeared to pass through maximum as the SiO₂:Al₂O₃ ratio was increased (the maximum occurring at about 4.6).

Topchieva et al.[3-7] have also examined the role of cations in Y-zeolites and the SiO₂:Al₂O₃ ratio in respect of cumene-cracking activity. They found that the thermal stability of the active centres was higher for zeolites with large SiO₂:Al₂O₃ ratios, and it was reported that dealumination increased the cracking activity. No simple direct relationship between aluminium content and catalytic activity was noted, but maximum activity corresponded to the situation when about 50% of the aluminium had been removed from the zeolite lattice.

Several methods have been applied to reduce the framework Al content; (A) Acid treatments; although zeolites such as mordenite are acid resistant, a simultaneous extraction of the framework aluminium is possible[8]. (B) Thermal treatment of NH_4 -exchanged zeolites; their decomposition under hydrothermal conditions is accompanied by the formation of cationic aluminium in the interstices[9]. The extraction of framework aluminium by steaming of H-mordenites[10] also falls in this category. (C) Al-extraction can also be achieved by more gentle treatments with chelating agents such as EDTA[11] or acetylacetone[12,13], or by chromium (III) salt solutions[14]. (D) Beyer and Belenkaya[15] use an entirely different method. Dehydrated Y-zeolites are reacted with SiCl_4 at temperatures between 730 K and 830 K whereby volatile AlCl_3 is formed. The reaction:



is essentially a substitution reaction. The salts formed can be washed out and highly crystalline faujasite-type zeolites were obtained with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 40 to 100. By all these methods (A through D) Al is removed from the lattice and a smaller unit cell is the result of this.

In this work, the effect of removal of structural aluminium in NH_4 Y-zeolite and the calcination temperature were studied in cumene cracking reaction using micropulse technique.

Experimental

Materials

Na Y-zeolite SK-40 supplied by the Lind Company USA, from which the decationated NH_4 Y-zeolite was prepared by exchanging the sodium ion with ammonium from ammonium chloride solution (2N). The process of exchange was repeated until the filtrate showed only trace amounts of sodium present. The removal of structural aluminium was made by the addition of ethylene diamine tetra acetic acid to the zeolite samples in boiling water through a period of 24 hr. After filtration the samples were washed and dried. The degree of dealumination was determined by gravimetric analysis. Table (1) shows the variation

of the number of aluminium ions per unit cell and the corresponding silica to alumina ratios for all dealuminated samples.

Table 1: The percentage dealumination, number of aluminium ions per unit cell and the silica to alumina ratios of the prepared zeolite samples.

Sample	% dealumination	No. of Al ³⁺ per unit cell	Silica to alumina ratio
1	00	56	4.60
2	20	45	5.42
3	30	39	6.56
4	33	37	6.85
5	40	34	7.65
6	43	32	8.05
7	50	28	9.18

Apparatus and Techniques

Thermal analysis: The differential thermal analyses of the prepared samples were carried out using a Du Pont 900 thermal analyzer with a differential scanning calorimeter cell. The rate of heating was 5°C min^{-1} .

X-ray diffraction; X-ray powder diffraction patterns were obtained at room temperature using a Philips X-ray diffractometer (Goniometer PW 1050/25) employing Ni-filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.5404 \text{ \AA}$). The X-ray tube was operated at 36 kV and 16 mA. Samples were packed into a plastic holder. No adhesive or binder was necessary. Spectra were scanned at a rate of 2°min^{-1} (in 2θ). The diffraction peaks with $d = 14.4, 5.68, 3.76$ and 2.85 \AA were used to detect the crystallinity of the zeolite under investigation.

Pulse microcatalytic system: The substance under investigation (cumene) was introduced in microquantities ($1-2 \cdot 10^{-3} \text{ cm}^3$) by the aid of a microsyringe, in the form of pulse, into a microreactor containing small amount of the catalyst (50 mg). The reaction products were transferred directly by the inert gas carrier (nitrogen) to a gas liquid chromatograph (Perkin Elmer 910), for separation and determination. A chromatographic column of 1.5m length and 4mm inner diameter

packed with 15% apison greas over diatomaceous earth was used at 90°C. The reaction products were detected with the aid of a flame ionization detector.

Results

Characteristics of Zeolites

The differential thermogram of NH₄-Y and the dealuminated zeolites, Fig. (1), shows two endothermic peaks of minima located between 250-300°C (strong peak) due to the release of physically sorbed water, and between 600-700°C (very weak peak) which are characteristic for the dehydration of the deammoniated zeolite. Two exothermic effect are also observed. The first exothermic peaks are located between 400 and 600°C. The other exothermic peaks are located in the temperature range 900-1050°C. These exothermic peaks may indicate the breakdown of the zeolite framework. Fig. (2) shows the effect of aluminium removal on the thermal stability of dealuminated zeolites.

Fig. (3) shows the X-ray diffraction patterns of the original Na-Y as well as the ammonium Y-zeolites and its dealuminated forms. This analysis revealed that these zeolites exhibit excellent crystallinity except the samples from which more than 40% of the framework aluminium is removed. For these zeolites the degree of crystallinity was less due to the structural collapse.

Cumene Conversion on Dealuminated Zeolites

It was found that Na Y-zeolite is inactive catalyst for hydrocarbon cracking reactions. The replacement of sodium ions by ammonium ions followed by heating at 550°C increased the activity

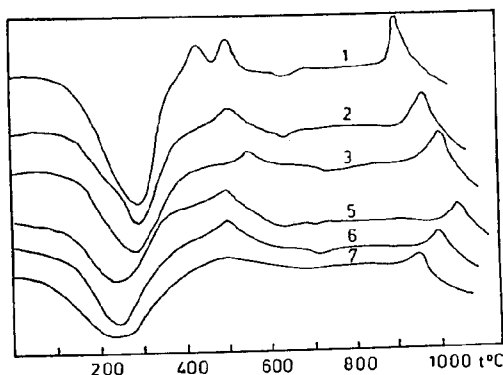


Fig. 1: DTA of NH₄ Y and dealuminated zeolites.

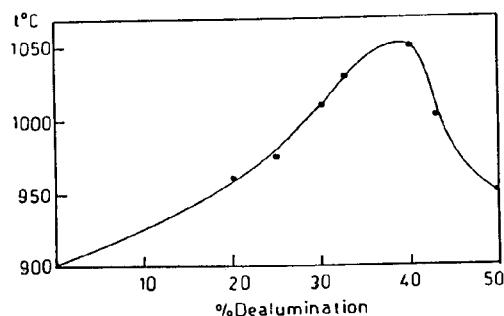


Fig. 2: Effect of aluminium removal on the thermal stability of dealuminated zeolites.

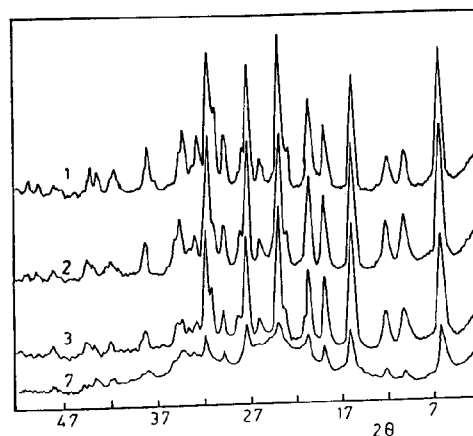


Fig. 3: XRD-patterns of Na Y, NH₄ Y and dealuminated zeolites.

towards many reactions[1,16-19]. Moreover, the increase of SiO₂:Al₂O₃ ratio by removal of aluminium may increase also the catalytic cracking properties of this zeolite. Therefore NH₄-zeolite was taken as a starting material for dealumination process in order to obtaine zeolites with different SiO₂:Al₂O₃ ratios.

The catalytic conversion of cumene in the pulse micro catalytic system was performed at constant reaction temperatures 300 and 380°C, on zeolites preheated at different calcination temperatures ranging from 400 to 900°C for 4 hr in a stream of air. The reaction of cumene cracking was carried out in gas flow of nitrogen at a rate of 30cm³ min⁻¹. A fresh catalyst sample was used for each run. Only propylene and benzene were observed as cracking products.

Fig. (4) illustrates the dependence of the catalytic activity of zeolite catalysts on the calcination temperatures in cumene cracking. It can be seen from this figure, that for all catalyst samples, the pretreatment temperature affect much their catalytic activity. This activity increased with increasing the calcination temperature, passing through a maximum at calcination temperature 550°C and then gradually decreased with increasing the temperature of pretreatment. All samples were found to possess the maximum catalytic activity after pretreatment of the catalysts at 550°C.

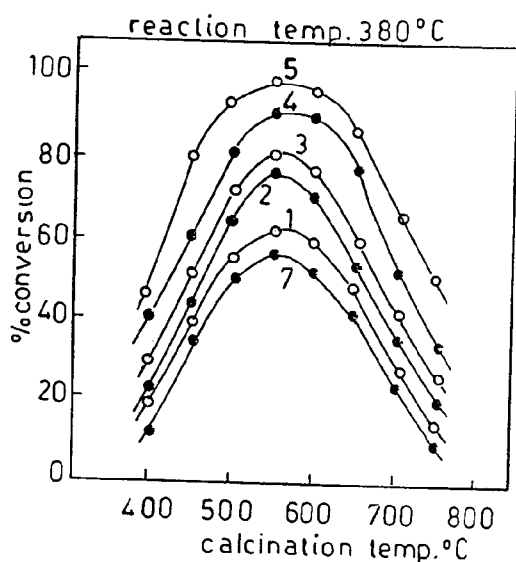


Fig. 4: Dependence of catalytic activity of zeolites in cumene cracking on the calcination temperature.

Another set of experiments dealing with the effect of flow rate on cumene conversion over zeolite samples was conducted at constant reaction temperature 340°C. The catalysts were precalcined at 550°C i.e. the optimum conditions for calcination. The nitrogen flow rate was varied from 30 to 100 cm³ min⁻¹. The data of this set of experiments are given in Table (2).

From this Table, it can be seen that the increase of flow rate of helium, i.e. decrease of contact time, was accompanied by a decrease in the cumene conversion. On the other hand, the increase in dealumination percentage of zeolite

Table 2: Effect of flow rate on cumene conversion at 340°C.

Flow rate cm ³ min ⁻¹	% conversion for sample						
	1	2	3	4	5	6	7
100	16	21	30	36	45	24	13
80	21	25	36	47	53	32	17
60	25	33	46	55	62	36	22
45	33	40	57	66	73	46	28
30	43	54	71	81	85	60	40

showed a detectable increase in the catalytic conversion of cumene. This activity passed through a maximum at sample 5 and then decreased.

For determination of the energy of activation of cumene cracking, the reaction was performed at different temperatures in a flow rate of 30 cm³ min⁻¹. The data were in the range 46-63 k J mol⁻¹, which agree with the previously obtained values[20].

Discussion

Characterization of Zeolites

X-ray diffraction analysis revealed that the original ammonium Y-zeolite and its dealuminated forms exhibit excellent crystallinity except the samples from which more than 40% of the framework aluminium is removed. For these zeolites a decrease in the degree of crystallinity is observed, indicating the breakdown of the framework and yielding an amorphous phase[21]. The differential thermal analysis showed two endothermic peaks with minima located at 250-300°C and 600-700°C. The first peak indicates the release of water content in zeolite[22,23], whereas the second related to the dehydration process. Two exothermic effects were also observed. The first peaks were located at 400- 600°C indicating the decomposition of ammonium group in zeolite. The other was located in the temperature range 900-1050°C. The increase of dealumination up to 40% shifts the maxima of the second exothermic peak to higher temperature i.e. increases the thermal stability[24]. The higher thermal stability may be attributed to the migration of Si atoms towards the sites left vacant by Al-removal and the formation of new

SiO₄ tetrahedra in the framework. Further increase in dealumination led to the decrease in the thermal stability of zeolite[21].

Cumene Conversion on Dealuminated Zeolites

The effect of flow rate of nitrogen on the cumene conversion was studied at constant reaction temperature 340°C and the flow rate was changed from 30 to 100 cm³ min⁻¹. The results were listed in Table (2) and graphically represented in Fig. (5). It can be seen from Table (2) and Fig. (5) that the increase of helium flow rate from 30 up to 100 cm³ min⁻¹, was accompanied by a decrease in the conversion of cumene.

In this set of experiments the flow rate was measured at room temperature and corrected to some standard temperature, usually 0°C, and mean column pressure, given a value:

$$F^{\circ} = (273 / T) F$$

where F = measured flow rate at room temperature; cm³ sec⁻¹.

T = room temperature; K.

and F[°] = corrected flow rate; cm³ sec⁻¹.

A test for first order reactions for cumene cracking over ammonium-zeolite and its dealuminate derivatives using the Bassett equation[25] is shown in Fig. (5). Thus plotting ln 1/(1-x) versus 1/F[°] indicates that cracking of cumene, in our

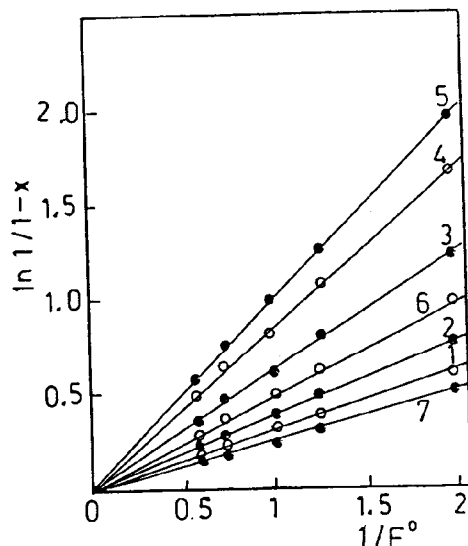


Fig. 5: Dependence of catalytic activity of zeolites on the flow rate of carrier gas.

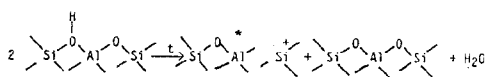
case, over different zeolite samples is a first order reaction.

The constancy of the calculated values of the activation energy (46-63 k. J mol⁻¹) indicates that the reaction of cumene cracking proceeds via the same mechanism and take place on active sites of the same nature but the change in the activity of zeolites depends on the number of these sites.

Studying the effect of thermal pretreatment of catalyst samples on cumene cracking is of paramount interest for determining the optimum conditions which correspond to maximum catalyst activity and selectivity.

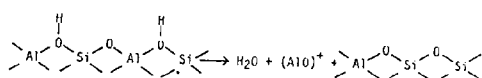
Fig. (4) shows the dependence of the catalytic activity of zeolite catalysts on the pretreatment temperatures. The optimum pretreatment temperature for all studied zeolites was found to be approximately 550°C. Only in catalysts having 30-40 aluminium atoms per unit cell, the conversion curves pass through a broad maximum. This can be attributed to the higher thermal stability of these zeolites as compared to the original NH₄ Y-zeolite.

It can be noticed also that the range of pretreatment temperature in which the optimum activity is achieved, is nearly identical to the range of temperature in which the catalyst showed a very weak endothermic peak (i.e. endothermically dehydrated to a minor extent). This indicates that the dehydration and thermal stabilization processes are associated with the activation of the zeolites. Thus the catalytic activity of zeolites increase with increasing pretreatment temperature up to a certain value, after which it decreases with further increase in pretreatment temperature. This decrease in activity can not be attributed to the thermal decomposition of the crystal structure of zeolite, since the latter does not occur below 900°C for H Y-zeolite and 1050°C to 1100°C for dealuminated zeolites having 34 to 40 aluminium atoms per unit cell. So, the decrease of catalytic activity with the increase of pretreatment temperature to a higher value than the optimum one may be due to the loss of structural water[26]. In such a process one molecule of water is eliminated from two hydroxyl groups to form an electron-pair acceptor, i.e. Bronsted acid sites are transformed into Lewis acid sites.



*(trigonal aluminium atoms.)

However, trigonal Al was not detected in dehydroxylated zeolites by X-ray fluorescence[27]. On this basis Kuehl proposed that upon dehydroxylation Al-oxo species are formed in exchangeable cation positions with restoration of the lattice:



The scheme has been confirmed chemically by Jacobs and Beyer[28] and physically by[29] Al-NMR[30,31]. Accordingly the number of Bronsted acid sites which are active for cumene cracking decreases. However, it can be noticed from Fig. (4) that comparatively to that of starting material, aluminium deficient zeolite catalysts (with 34 and 39 aluminium atoms per unit cell) still show a good catalytic activity giving about 20-30% cumene conversion after being thermally treated at 850°C in a stream of air. Catalyst with 28 aluminium atoms per unit cell showed the least thermal stability, crystallinity and the catalytic activity towards cumene conversion.

Yoshida et al.[24] concluded also that EDTA-extraction was accompanied by a partial loss in crystallinity. This process, however, was not accompanied by a destruction of the shape of the pseudomorphic particles. A measurement of the adsorption volume furthermore suggested that more than 66% of the large cavities remained even in nearly amorphous samples after dealumination.

References

1. P.B. Venuto and P.S. Landis, *Adv. Catal.* **18**, 259 (1968).
2. K. Tsutsumi and H. Takamashi, *Seisan-Kenkyu*, **21**, 455, 457 (1969).
3. K.V. Topchieva and Ho Chi Thuang, *Neftekhimiya* **10**, 525 (1970).
4. K.V. Topchieva and Ho Chi Thuang, *Dok. Akad. Nauk, SSSR.*, **193**, 641 (1970).
5. K.V. Topchieva and Ho Chi Thuang, *Kinetica i Kataliz*, **11**, 490, (1970).
6. K.V. Topchieva and E.N. Rosolovskaya, *Zhur, Fiz. Khim.*, **44**, 870 (1970).
7. K.V. Topchieva and Ho Chi Thuang, *Dok. Akad. Nauk SSSR.*, **198**, 141 (1971).
8. M.M. Dubinin, G.H. Federova, D.M. Plavnik, L.I. Piguzova and E.N. Prokofeva, *Izv. Akad. Nauk, SSSR., Ser. Khim.*, 2429 (1968).
9. C.T. Kerr, *J. Catal.*, **15**, 200 (1969).
10. K.H. Kuehl, in *Molecular Sieve Zeolites II*, J.R. Katzer, Ed., A.C.S. Washington, D.C., A.C.S. Symp. Ser. 40, 96 (1977).
11. G.T. Kerr, *J. Phys. Chem.*, **72**, 2594 (1968).
12. D. Barthomeuf and R. Beaumont, *C.R. Acad. Sci., Ser. C., Paris*, **269**, 1345 (1969).
13. R. Beaumont and D. Barthomeuf, *C.R. Acad. Sci., Ser. C., Paris* **272**, 363 (1971).
14. W.E. Garwood, J.J. Lucki, N.Y. Chen and J.C. Bailar, *Inorg. Chem.* **17**, 610 (1978).
15. H.K. Beyer and I. Belenykaya, in *Catalysis by Zeolites*, B. Imelik, C. Naccache, Y. Ben Taarit, J.C. Verdine, G. Coudurier and H. Praliaud, Eds., Elsevier, Amsterdam, *Studies in Surface Science and Catalysis*, **5**, 203 (1980).
16. P.A. Jacobs, H.E. Leeman, and J.B. Uytterhoeven, *J. Catal.* **33**, 17 (1974).
17. K. Tsatsumi and H. Takahashi, *J. Catal.* **24**, 1 (1972).
18. G.A. El-Shobaky, M.M. Selim and E.M. Ezzo, *J. Res. Inst. Catal. Hokkado Univ.* **26**, 163 (1978).
19. P.D. Hopkins, *J. Catal.* **12**, 325 (1968).
20. E.A. Sultan, M.A. Wassel and M.M. Selim, *Bull. N.R.C.*, **8**, 59 (1983).
21. A. Yoshida, H. Nakamoto, K. Okamishi, T. Tsuru and H. Takahashi, *Bull. Chem. Soc. Japan*, **55**, 581 (1982).
22. J.A. Rabo, C.L. Angell, P.H. Kasi, V. Shomaker, *Disc. Faraday Soc.*, **41**, 328 (1966).
23. Yu.S. Shadakov, I.D. Mikheikin, Kh.M. Minachev, *Izvest. Akad. Nauk SSSR., Ser. Khim.*, 523 (1969).
24. G.T. Kerr, A.W. Chester, D.H. Olson, *Acta Phys. Chim., NF* **24**, 169 (1978).
25. D.W. Bassett and H.W. Habgood, *J. Phys. Chem.* **64**, 769 (1960).
26. J.B. Uytterhoeven, L.G. Christner and W.K. Hall, *J. Phys. Chem.* **69**, 2117 (1965).

27. G.H. Kuehl, "Molecular Sieves", J.B. Uytterhoeven, Ed., Leuven University Press, Belgium, 1973, p.227.
28. P.A. Jacobs and H.K. Beyer, *J. Phys. Chem.*, **83**, 1174 (1979).
29. V. Gutmann, "The Donor-Acceptor Approach to Molecular Interactions", Plenum Press, New York, 1978, p.19.
30. D. Freude, T. Frohlich, M. Hunger, H. Pfeifer and G. Scheler, *Chem. Phys. Lett.* **98**, 263 (1983).
31. D. Freude, T. Frohlich, M. Hunger, H. Pfeifer and G. Scheler, *Zeolites* **3**, 171 (1983).