



Title	EFFECT OF WATER TREATMENT ON THE CATALYTIC PROPERTIES OF DECATIONATED ZEOLITE
Author(s)	EL-SHOBAKY, G. A.; SELIM, M. M.; EZZO, E. M.
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 26(3), 163-170
Issue Date	1979-02
Doc URL	http://hdl.handle.net/2115/25052
Type	bulletin (article)
File Information	26(3)_P163-170.pdf



[Instructions for use](#)

EFFECT OF WATER TREATMENT ON THE CATALYTIC PROPERTIES OF DECATIONATED ZEOLITE

By

G. A. EL-SHOBAKY*, M. M. SELIM*
and E. M. EZZO**

(Received August 10, 1978; in revised form October 23, 1978)

Abstract

The effect of water on the catalytic activity for cumene cracking at 320°C was studied using the micro-reactor. The addition of water was found, generally, to decrease the catalytic activity. The deactivation effect was more pronounced in case of the addition of water at room temperature followed by thermal treatment in a current of air at 450°C. The least degree of deactivation was observed in the catalyst treated with water at the reaction temperature 320°C and without any thermal treatment, due to the presence of condensation products on the surface. The results obtained were discussed in terms of decomposition of zeolite during water treatment.

The X-ray investigation showed that water treatment of zeolite affected its crystallinity, a marked modification of the zeolite's structure was achieved when treated with water at room temperature and activated in air at 450°C. A moderate decrease in the crystallinity was observed when the treatment and reaction were done at 320°C in helium stream without regeneration.

§ 1. Introduction

It is well known that the catalytic activity of zeolites depends mainly on the water content.¹⁻⁵⁾ As zeolite contains, generally, about 30% of its weight water, its activity is affected by the temperature and time of thermal activation. On the basis of the data of spectroscopic investigations⁶⁾ it has been reported that the promotion effect of water was directly related to the appearance of structural hydroxyl groups, increasing thus the concentration of acid centres. The prior thermal treatment⁷⁻⁹⁾ of zeolites was found to affect much the quantity and distribution as well as the stability of these structural hydroxyl groups.

* Laboratory of Surface Chemistry and Catalysis, National Research Centre, Dokki, Cairo, Egypt.

** Chemistry Department, College of Girls, Ain Shams University, Cairo, Egypt.

G. A. EL-SHOBAKY, M. M. SELIM and E. M. EZZO

The addition of a small quantity of water to zeolites was found to increase their catalytic activity for reactions which proceed via carboniumion mechanism, such as cracking and alkylation¹⁻⁴⁾ and decrease in case of other reactions⁵⁾.

It has been reported recently using NMR technique¹⁰⁾ that treating zeolites with water, although it increased the concentration of structural hydroxyl group, led to decomposition of the catalyst. It is therefore interesting to study the effect of water on the catalytic properties of zeolite.

In this investigation the effect of water on the catalytic properties of zeolite in cumene cracking was studied using micropulse technique.

§ 2. Experimental

(2-1) Catalyst used

NaY-zeolite SK-40 supplied by Lind Company, from which the deca-tionated zeolite was prepared by exchanging the sodium ion with ammonium from ammonium chloride solution for a period of 20 minutes at room temperature. The exchanged zeolite was then washed with distilled water till the absence of chloride ions and dried at 100°C, 65% of sodium ions were substituted with NH_4^+ ions. The catalyst was activated by heating at 450°C in a current of dry air for 2~3 hrs then in a current of helium gas, for one hour before the catalytic measurements were carried out.

(2-2) Catalytic measurements

Cumene was injected into the reactor in pulses of 1×10^{-3} mℓ (0.718×10^{-5} mole) at a flow of 50 mℓ helium per min. The system consisted of an electrically heated silica tube reactor of 30 cm length and 0.5 cm int. diam. The temperature was regulated and controlled within $\pm 0.5^\circ\text{C}$ via chromal alumel thermocouple and potentiometer. The catalytic reactor contained 20 mg of the catalyst diluted with 1 mℓ of quartz fragments of 2~3 mm. The products from the reactor were passed through a chromatographic column of 80 cm length and 0.4 cm int. diam. pyrex glass tube packed with porapak T and cilite 545 with 15% glycerine, and thermostated at 90°C. After separation, the individual components were detected by passing the stream through a thermostating catarometer and recorded via a 5 mV potentiometer.

§ 3. Results and Discussion

If we consider that the deca-tionated zeolite contains Brönsted acid centres and the addition of water may increase the number of these centres,^{1,11)}

Effect of H₂O on the Catalytic Properties of Decationated Zeolite

it is expected that the catalytic activity of a water treated zeolite in the cumene cracking reaction should be increased. Taking into consideration that the catalytic activity of zeolite depends mainly on the structure, an evidence of structure stability can be tested by studying the effect of water treatment on the catalytic activity of zeolite in the cumene cracking reaction.

(3-1) The effect of water on the catalytic activity of zeolite in cumene cracking :

(3-1-1) Successive addition of water at the reaction temperature 320°C without regeneration of the catalyst.

Using the pulse technique method, the cracking of cumene was followed up. Cumene was added in small doses of 1.0×10^{-3} ml at the constant temperature of 320°C and rate of helium 50 ml/min, each injection of cumene was followed by water injection 2×10^{-3} ml. The water injection was carried out after the cracking products were completely given off (after 20 min.). About 13 successive injections of cumene/water were carried out and the % conversion in each case was calculated. The obtained results concerning the % conversion as function of number of cumene/water injections are represented by Fig. 1a. It can be seen from this figure that % conversion decreases from 83 gradually reaching almost a constant value 50 after 10 pulses. Further addition of water was found to have no effect on the % conversion.

(3-1-2) Effect of prior regeneration on % conversion

In the following set of experiments the reaction was carried out at 320°C. Before and after the water injection the catalyst was heated at 450°C in a current of helium for about 30 min. The injection of water was carried out at 450°C. The obtained results are graphically represented in Fig. 1b. It is seen that the % conversion decreases suddenly from 83% to 20% after 4 injections of water only. Any further water injection exerted no influence.

(3-1-3) The effect of regeneration by air at 450°C on the water treated catalyst.

The addition of water (5×10^{-3} mol/g catalyst) was carried out at room temperature, and the zeolite was subjected to thermal treatment in air at 450°C for 30 min before and after the addition of water. The obtained results concerning the % conversion as function of water pulses are graphically represented in Fig. 1c. It is seen from this figure that the catalytic activity suffers a sudden decrease from 83% to 10% after the admission of 4 pulses of water only. Increasing the amount of water was not accompanied by any significant decreases in % conversion.

G. A. EL-SHOBAKY, M. M. SELIM and E. M. EZZO

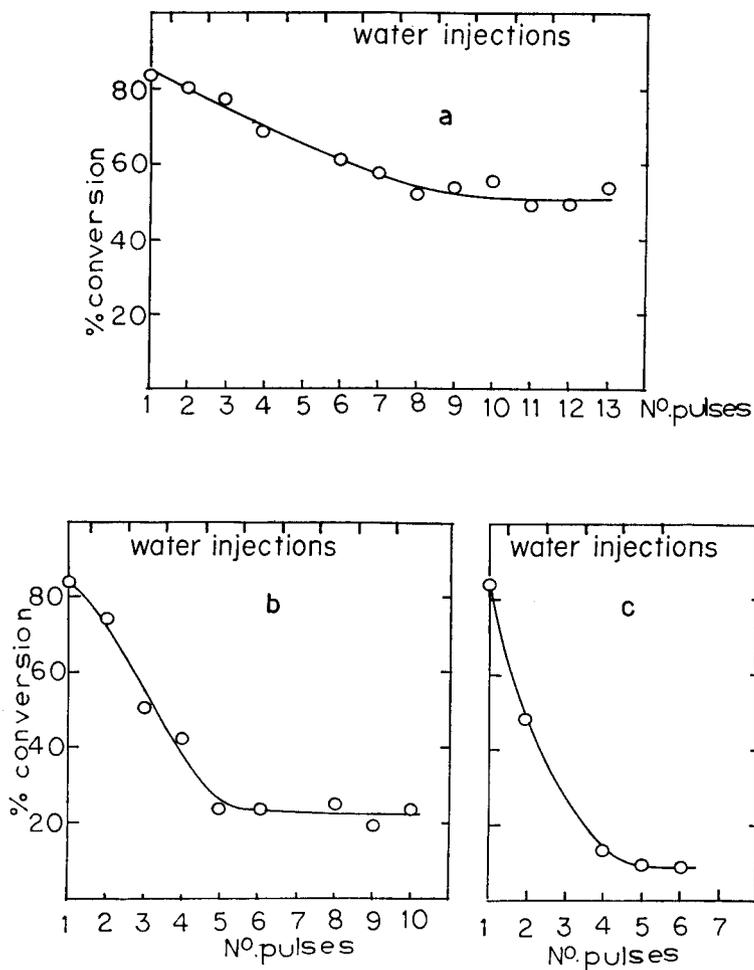


Fig. 1. % conversion as function of number of cumene pulses for catalysts treated with water,

- Catalyst treated with water at reaction temperature 320°C without regeneration.
- Catalyst treated with water at 450°C and then heated in helium atmosphere at 450°C.
- Catalyst treated with water at room temperature followed by heating in air at 450°C.

Contrary to the published results¹²⁾ showing a promotion effect of water on the catalytic activity of zeolites with respect to some reactions proceeding via carbonium ion mechanism, the obtained results showed clearly an opposite effect of water for cumene cracking which proceeds also via the carbonium

Effect of H₂O on the Catalytic properties of Decationated Zeolite

ion mechanism. However, the inhibition effect exerted by water treatment differs according to the experimental conditions, namely mode and temperature of activation. The maximum deactivation effect was observed when the catalyst was treated with water at room temperature and activated in air at 450°C. The minimum degree of deactivation was found when the zeolite sample was treated by water at 320°C (reaction temperature) in helium stream without regeneration. In the first case it seems that the presence of air (O₂) during the activation process at 450°C enhanced much the process of deactivation. As a result of energetic oxidation (removal) of condensation products, this will be discussed later on. It is well known that both silica and alumina have extremely small catalytic activity for cumene cracking. The observed decrease in catalytic activity of zeolite by water treatment may thus be taken as an evidence for structure collapse of the catalyst. These results point to the inhibition effect of water on catalytic properties of zeolite as a result of structure modification.

The results represented in Fig. 1a showing the minimum inhibition effect by water treatment may be explained as follows: through the cumene cracking reaction some condensation products may cover a fraction of the zeolite surface. These surface compounds may oppose the water molecules entrance to the catalyst surface, where they exist, preventing thus this fraction of the surface to undergo structure modification. Moreover such condensation products may be regarded as active complexes for the reaction^{13, 14, 15, 17}. So the limited degree of deactivation showed a limited extent of structure modification by water and the gradual formation of condensation products covering progressively the surface of undecomposed zeolite (the active form). It is to be concluded that the condensation products are, in such case, responsible for the steady state activity of water-treated zeolite. These results which indicate the partial decomposition of zeolite confirm the polymolecular mechanism proposed by Rudenko¹⁶ according to which several surface catalytic reactions proceed via condensation complexes. The results of Fig. 2b, intermediate degree of deactivation by water, indicate also an intermediate extent of structure modification. The thermal treatment with helium at high temperature (450°C) removes the condensation products from the surface giving suitable chance for water molecules to attack the zeolite surface leading to further modification of the zeolite structure. In this case, heating of the catalyst in a current of helium was not sufficient to remove all the condensation products formed on the surface, like in the case of heating in air (*c.f.*, Fig. 1b, c).

The results obtained from x-ray investigation showed that the crystal-

linity of zeolite was affected clearly when zeolite was treated with water at room temperature and activated in air at 450°C (Fig. 2, HY-2). The crystalline form of zeolite was transferred or changed into an amorphous phase and consequently the catalytic activity decreased considerably.

Figure 2 (HY-3) shows that zeolite upon successive addition of water at 320°C in helium stream retained its crystallinity to certain extent. So the catalytic activity of zeolite remained almost constant inspite of the further

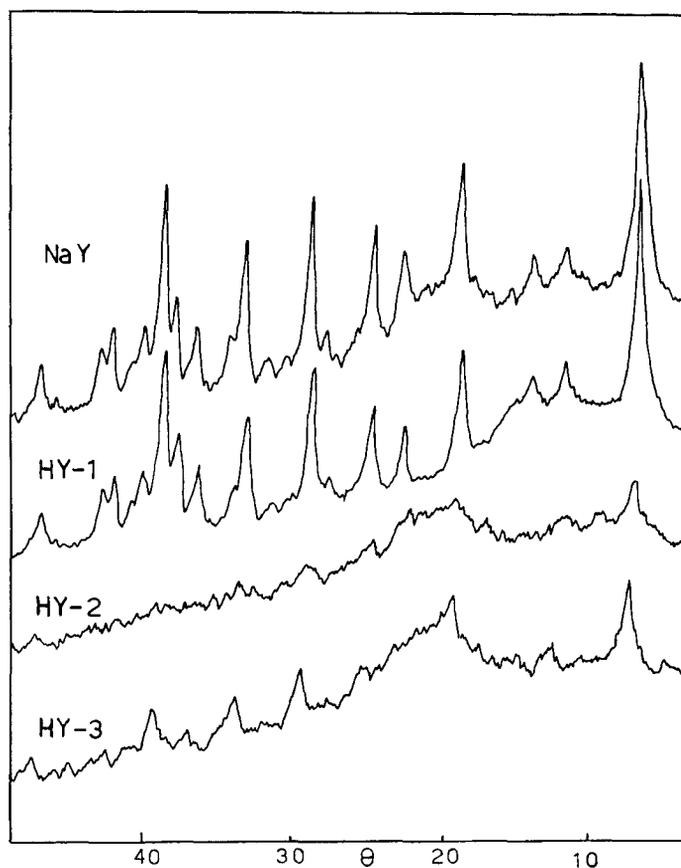


Fig. 2. X-ray diffraction pattern of NaY and HY-zeolites

NaY- The original sodium zeolite.

HY-1- Decationated zeolite without any treatment.

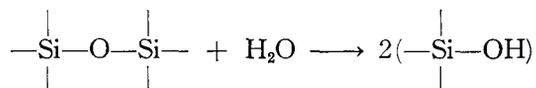
HY-2- After carrying out cumene cracking reaction at 320°C, regeneration at 450°C by air before and after the addition of water, which carried out at room temperature.

HY-3- After successive addition of cumene and water in helium flow at 320°C.

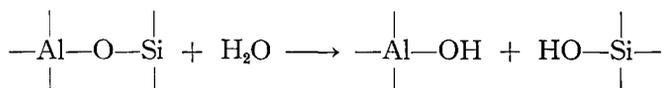
Effect of H₂O on the Catalytic Properties of Decationated Zeolite

addition of water. In other words the coverage of zeolite's surface with the condensation products prevented the water molecules to cause a further attack of its surface decreasing slightly its crystallinity (*c.f.* Fig. 2 HY-3).

It has been shown by one of the authors¹⁰ using NMR technique, that the water content of zeolite affected its decomposition at 400°C according to the following mechanism :



or



Such mechanism is accompanied by an increase in the concentration of the OH groups, although the catalytic activity was found to decrease much as previously mentioned. It is to be concluded that a relationship between the concentration of OH groups on a given solid and its catalytic activity is not observed in our case.

§ 4. Conclusions

From the results obtained in this investigation the following conclusions could be derived :

1) Treating decationated zeolite with water was found to influence much its catalytic properties. Such influence however depends upon the amount of water, mode and temperature of activation.

2) Addition of water (25×10^{-3} mol/g catalyst at room temperature followed by thermal treatment in air at 450°C was found to decrease considerably the catalytic activity (% conversion decreased from 83% to 10%).

3) The addition of the same amount of water without carrying out any thermal treatment of the catalyst decreased its catalytic activity but to less extent due to the presence of condensation products which catalyze cumene cracking and prevent, to a certain extent, the decomposition of the zeolite.

4) X-ray diffraction pattern showed a direct relationship between the degree of crystallinity and the catalytic property of zeolite treated with water depending on the way of treatment.

5) No direct relationship between the catalytic activity of the zeolite and the concentration of OH group was observed in our case.

G. A. EL-SHOBAKY, M. M. SELIM and E. M. EZZO

References

- 1) P. B. Venuto, L. A. Hamilton and P. S. Landis, *J. Catalysis*, **5**, 484 (1966).
- 2) Ho Shi Toang, B. V. Romanovskii and K. V. Topchieva, *Dokl. Akad. Nauk USSR*, **168**, 1114 (1966).
- 3) J. Morita and H. Matsumoto, *J. Chem. Soc. Japan Industr. Chem. Sec.*, **70**, 1363 (1967).
- 4) K. V. Tochiewa, B. V. Romonovskii, L. I. Piguzova, Ho Shi Toang and E. V. Bezre., *Osmovy predvideniya Kataliticheskovo deistviya*, Vol. 2, Moscow, "Nauka", 1970, p.144.
- 5) Z. V. Gryaznova, K. A. Baskunjan and I. A. Mel'nichenko, *Kinetika i Kataliz*, **12**, 1471 (1971).
- 6) J. W. Ward, *J. Catalysis*, **11**, 238 (1968).
- 7) P. E. Eberly, *J. Phys. Chem.*, **72**, 1042 (1968).
- 8) J. Turkevich and J. Onon, *2nd Intern. Conf. on Zeolites, Washington, 1970, prepr.*, p. 239.
- 9) J. W. Ward, *J. Catalysis*, **10**, 34 (1968).
- 10) M. M. Selim, S. P. Habuda and Z. V. Gryaznova, *J. Surface Technology*, **7**, 3, 195 (1978).
- 11) J. B. Wytterhoeven, L. G. Christner and W. K. Hall, *J. Phys. Chem.*, **69**, 2117 (1965).
- 12) G. V. Gvakhariya, V. I. Kvlividze, V. F. Kiselev, M. B. Pylova and G. V. Tsitsishvili, *Dokl. Akad. Nauk USSR*, **188**, 379 (1969).
- 13) A. P. Rudenko, M. F. Rodicheva, D. E. Bodrina and A. A. Balandin, *Vestn. Moscow State University*, **4**, 99 (1966).
- 14) M. M. Selim and A. P. Rudenko, *Vestn. Moscow State University Ser. Chem.*, **3**, 350 (1974).
- 15) M. M. Selim, *Vestn. Moscow State University Ser. Chem.*, **5**, 605 (1974).
- 16) A. P. Rudenko, *The Theory of self progress of opened catalytic systems* (Moscow State University, 1969).
- 17) P. A. Jacobs, H. E. Leeman and J. B. Uytterhoeven, *J. Catalysis*, **33**(1), 17 (1974).