The role of iron species in Egyptian kaolin ore in the conversion of isopropanol over some zeolites prepared from the ore

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Abstract

The present study was directed to investigate the conversion of isopropanol over some kinds of zeolites such as A, P and X which originally prepared from Egyptian kaolin ore containing about 1.5% of iron species. The position of iron in either kaolin or different zeolites was investigated using ESR technique which showed that iron exists in zeolites in two main positions either in the framework position replacing Al found in tetrahedral position or in ion exchanging one. The presence of iron in the prepared zeolites showed higher selectivity for the dehydrogenation process with respect to the dehydration one. The role of each site of iron was discussed in the light of conversion results. Ion exchanging zeolite with calcium ions affects mainly the selectivity of zeolite. The effect of ion exchange was studied in both aspects for dehydrogenation and dehydration.
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1. Introduction

The incorporation of transition metals into the framework of zeolites was the subject of investigation of many researches in the past years due to the new catalytic activities of the modified materials. For example (iron which may exist in several types of zeolites as impurities [1,2]) has been introduced in a relatively large amounts into a number of zeolites [3,4].

To overcome the difficulty of the technique used for incorporation of iron into the framework structure or even into the cationic positions, it is a must of economic point of view to use raw materials which already contain iron in their structure such as kaolin clays which has been used for preparation of several kinds of zeolites [5–8].

ESR technique is considered to be very effective tool used for determination of the geometrical positions of iron in both kaolin ore and zeolites [9–11].

The study of the present investigation was directed to examine the catalytic activity of some zeolites prepared from Egyptian kaolin ore, using isopropanol conversion. Isopropanol is industrially used for production of acetone [12] via numerous metal oxide catalysts [12,13]. However, in case of using zeolite there are two different products, propene and acetone which resulted via dehydration and dehydrogenation process respectively. While dehydration is commonly attributed to acid centers, dehydrogenation process requires acid–base pair sites [12–14]. So that formation of acetone is directly attributed to the presence of iron species in zeolite structure [14]. The application of this research may be not only directed to use zeolite for production of acetone and/or propene but also for removal of isopropanol waste from water as cited in recent researches [15].

2. Experimental

2.1. Materials used

(a) Chemicals used throughout the preparation of zeolites and ion exchanging process were obtained from Merck Chemicals Company, Darmstadt, Germany, except that sodium silicate which is commercially sodium silicate ($Na_2Si_2O_5$, 43%).

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(b) Kaolin ore: the ore used in the present study were obtained from Kalabsha zone near Aswan, Upper Egypt. It has the following analysis, $SiO_2 = 45\%$, $Al_2O_3 = 35\%$, $TiO_2 = 3.5\%$, $Fe_2O_3 = 1.5\%$, $MgO = 0.1\%$, $CaO = 0.6\%$, $Na_2O = 0.3\%$, $K_2O = 0.05\%$, Ignition loss ~14%.

2.2. Method of preparation

Preheated kaolin at 550–900 °C is used as a source of silica and alumina. Additional source of silica is added order to increase the Si/Al ratio in case of Na-P and Na-X zeolites. Hydrothermal crystallization with NaOH at 70–110 °C for 2 h-7days crystallization time is done. The following table represents the composition of mixture for each zeolite prepared:

Zeolite	Reaction composition (moles/Al_2O_3)		
	Na_2O	SiO_2	H_2O
Na-A	3.03	2.18	149.34
Na-P	2.87	4.79	179.80
Na-X	6.43	5.4	184.48

2.3. Ion exchange process

Ion exchange process was carried out using 0.1 N $CaCl_2$ solution in three steps where 5 g of zeolite was stirred for about 1 h with 50 ml of $CaCl_2$ solution in each step. The zeolite between each step is dried at 80 °C. It is denoted to the zeolite from the first step by Ca-Z(I) and and to that produced from the third step by Ca-Z(III). Activation of each zeolite is carried out at 500 °C for 2 h before the catalytic test.

2.4. The catalytic measurements

The catalytic measurements were carried out using a micropulse technique. This method facilitates the working with microquantities of substances and catalysts and gives momental and quantitative information of the reaction proceeding.

The reactor was built from stainless steel tube (5 mm inner diameter and about 30 cm long) charged with 20 mg catalyst mechanically mixed with 1 cm³ silica fragments (>200 mesh size). The isopropnol was injected in micro quantities (($1–2) \times 10^{-3}$ ml) in the form of pulses to the catalyst, which was supported by a Pyrex wool plug midway through the reactor. The reaction products were transferred directly by the carrier gas (helium) at a flow of rate equals 60 ml min⁻¹ to a gas liquid chromatograph having a hot wire detector. A column of 2 m length and 4 mm inner diameter was used, where it is packed with diatomite loaded with 15% tricresylphosphate, which was suitable for the separation of hydrocarbons. The temperature of the column and detector was kept constant at 100 °C. A valuable advantage

of this method which is known with micropuls technique is that it can trace the first steps of the catalytic reaction, which cannot be obtained by the usual flow system.

2.5. X-ray diffraction

X-ray diffraction patterns were measured for the prepared zeolite using a Philips X-ray diffractometer (Goniometer PW 1050/25) Cu Kα radiation ($l = 1.5404$ Å). The X-ray tube was operated at 36 kV and 16 mA; the samples were packed into a plastic holder, no adhesive or binder was necessary. The spectra were scanned at a rate 2° min⁻¹ in 2θ.

2.6. The ESR measurements

The ESR spectra were recorded on a Brucker, ELEXSYS E-500 spectrometer, the spectrometer was operated at X-band frequency. The samples were hold in a silica tube and recorded at room temperature and no vacuum is employed. The conditions of measuring are unified for all samples in order to allow comparison among them and the parameters were as the following table:

Available parameters	
Averaged Scans	1
Resonator	shqwl_9914
Sampling Time [s]	0.04096
Field Mod. Amplitude	0.001
Field Mod. Frequency [Hzl	100000
Microwave Frequency [Hz]	9.81338e+09
Microwave Power [W]	0.00202637
Receiver Gain	60
Receiver Time Constant [s]	0.00512
Receiver Phase [°]	0.0
Receiver Harmonic	1
Receiver Offset [%FS]	0.0

3. Results and discussion

3.1. XRD of different zeolites

The prepared zeolites as well as their sodium and calcium exchanged forms were investigated by XRD (Figs. 1–3). Generally speaking one can say that the degree of crystallinity of zeolites is affected by the ion exchange process. Na-A and Na-X zeolites show remarkable stability towards ion exchange with calcium ions in comparison to Na-P which shows the least stability. This finding may be attributed to the lowest pore width of Na-P zeolite with respect to Na-A and Na-X zeolites. These findings must be taken into consideration while studying the catalytic process as we can see later.

3.2. Ion exchanging

The following table represents the ion exchange results for both Ca-Z(I)- and Ca-Z(III)-forms for each zeolite Table 1.
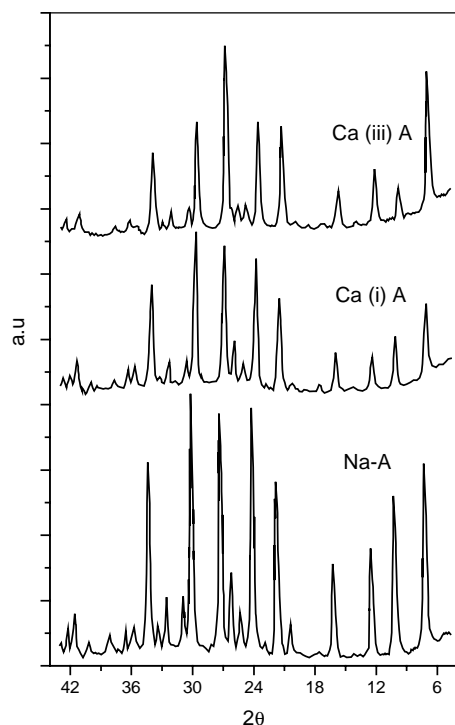
Fig. 1. XRD patterns of Na-A, Ca-(I)-A and Ca-(III)-A zeolites.

3.3. Electron spin resonance

Among the spectroscopic techniques ESR becomes on of the most sensitive techniques to study the iron species in
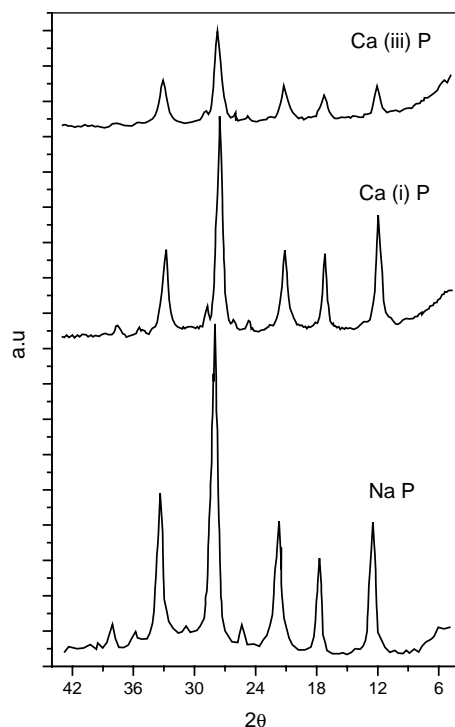

Fig. 2. XRD patterns of Na-P, Ca-(I)-P and Ca-Z(III)-P zeolites.
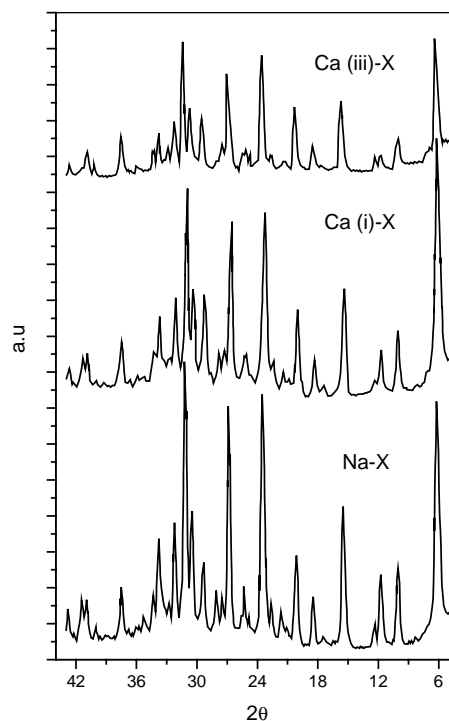

Fig. 3. XRD patterns of Na-A, Ca-(I)-X and Ca-(III)-X zeolites.

either kaolin or zeolite. Many studies were done to investigate the different species of iron in these compounds from these literatures one can conclude the following remarks.

3.3.1. For kaolin

In the case of kaolin there are two groups of signals which normally appears in such clays due to presence of iron [9,20]. The first group is lying around $g = 2.0$ and the second appears around $g = 4.3$.

The first group signal around $g = 2$ in kaolin is attributed usually to radiation induced defects (RID) in the clay with very sharp character. These signals are overlapped with the free Fe_2O_3 signal present in the clay [9] which appears as a broad signal also around $g = 2$.

The second group of signals lying around $g = 4.3$ are attributed to the iron substitute the Al in octahedral position which may replace the Al in more than one position as cited in literature [9].

According to the above argument one can explain the ESR spectra of Egyptian kaolin (Fig. 4) where the RID signals appears clearly around $g = 2$ with nearly no overlapping with the free Fe_2O_3 broad signals which indicate that

Table 1
Ion exchange percents of Ca-Z(I) and Ca-Z(III)-forms of prepared zeolites

Zeolite	Molecular formula	Ca-Z(I) (%exchange)	Ca-Z(III) (%exchange)
Na-A	$Na_{12}Al_{12}Si_{12}O_{48}\cdot37H_2O$	55.3	95
Na-P	$Na_6Al_6Si_{10.7}O_{33}\cdot12H_2O$	100	100
Na-X	$Na_{86}Al_{86}Si_{94.6}O_{361}\cdot228.5H_2O$	64.1	94

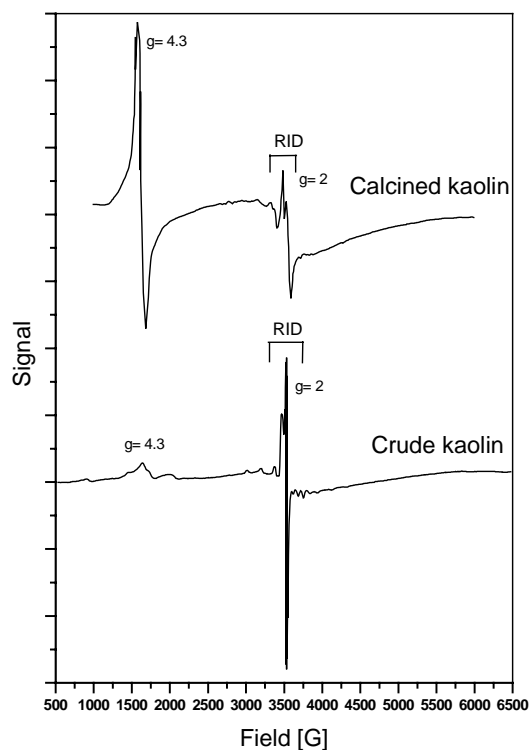Fig. 4. ESR spectra of kaolin ore and calcined kaolin.

Fig. 5. ESR spectra of Na- forms of A, P and X zeolites.

Fe_2O_3 species in this kaolin is very small. Moreover, the group of signals appeared around $g = 4.3$ enable us to differentiate between two types of iron, the first type of iron signal is corresponding to rhombically distorted sites and appears as a nearly isotropic signal centered at 1629 G [$g = 4.31$], whereas the second type corresponds to sites which possess more axial distortion consists of an anisotropic signals with resonance values located near 740 G [$g = 9.46$], 1424 G [$g = 7.89$], 1705.7 G [$g = 4.12$] and 2092.8 G [$g = 3.35$].

It is notably to mention that the first type of iron signal is more observed in disordered kaolin, while the second type signals are observed in the more ordered kaolin [9]. Based on the foregoing discussions one can explain the dramatic change in the signal at $g = 4.3$ in the case of calcinations of kaolin (Fig. 4).

3.3.2. For the zeolite

The ESR spectra of iron in zeolites were previously studied by many authors [10,17,21]. From these literatures one can drawn the following facts about the iron species present in the zeolite structure.

The ESR spectra of iron containing zeolites were found to be also consisted of two groups of signals. The first group located around $g = 4.3$ which is assigned to the presence of tetrahedral iron in the framework of the lattice of zeolite [11], while the other group located around $g = 2$ is assigned to non-framework hexacoordinated Fe^{3+} in cationic position [21,10].
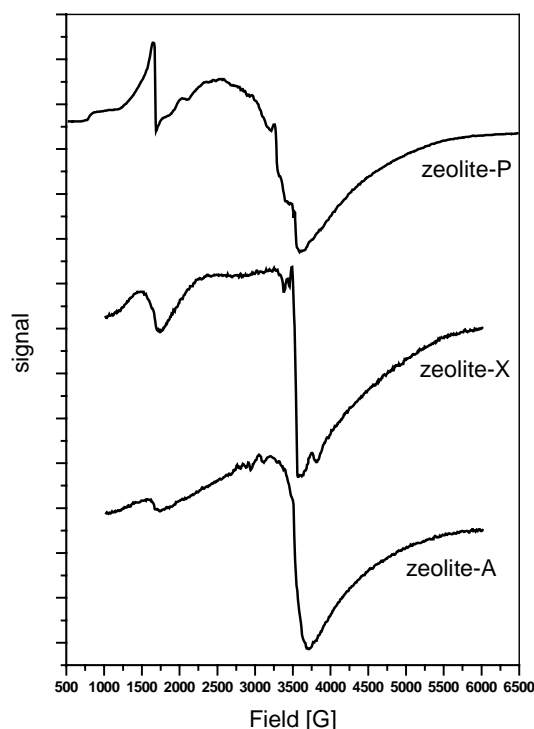
The intensity of signal located at $g = 4.3$ can be used either as a qualitative or quantitative determination for the amount of framework iron in both kaolin and zeolite [18,22].

Taking into consideration the above discussion one can observe in studying the zeolites under investigation that the intensity of the signal at $g = 4.3$ is decreased in the order Na-P > Na-X ≫ Na-A as seen from Fig. 5. This finding indicates that Na-P and Na-X zeolites contain a higher amount of the framework iron in comparison to Na-A zeolites. Indeed this means that most of iron in Na-A is in cationic position or at least in non framework positions.

It can be noticed easily from Figs. 6–8 that in case of Na-A and Na-X zeolites the intensity of the signal around $g = 2$ decreased by increasing the extent of ion exchange, which indicates clearly that the cationic iron in these zeolites is decreased by increasing the ion exchange process. However, in case of Na-P zeolite this peak are seemed to be nearly the same but a hyperfine splitting is observed as indicated in Fig. 9. This may be due to Mn^{2+} impurities originally comes from kaolin ore.

3.4. Conversion of isopropanol on different prepared zeolites

Figs. 10–15 represent the effect of temperature on the % conversion of isopropanol over A, P and X zeolites.

From these figures two products can be distinguished, acetone and propene resulting from dehydrogenation and dehydration processes respectively. Although the propene formation is cited to be formed on acid centers in zeolites,
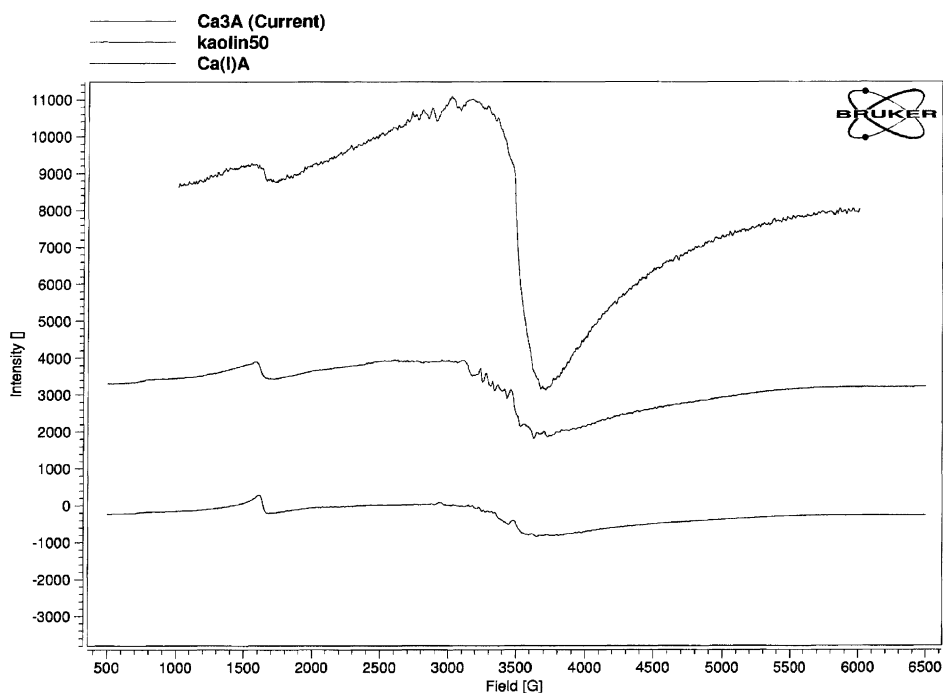
Fig. 6. ESR spectra Na-, Ca-Z(I)- and Ca-Z(III)-forms of zeolite A from above to down, respectively.
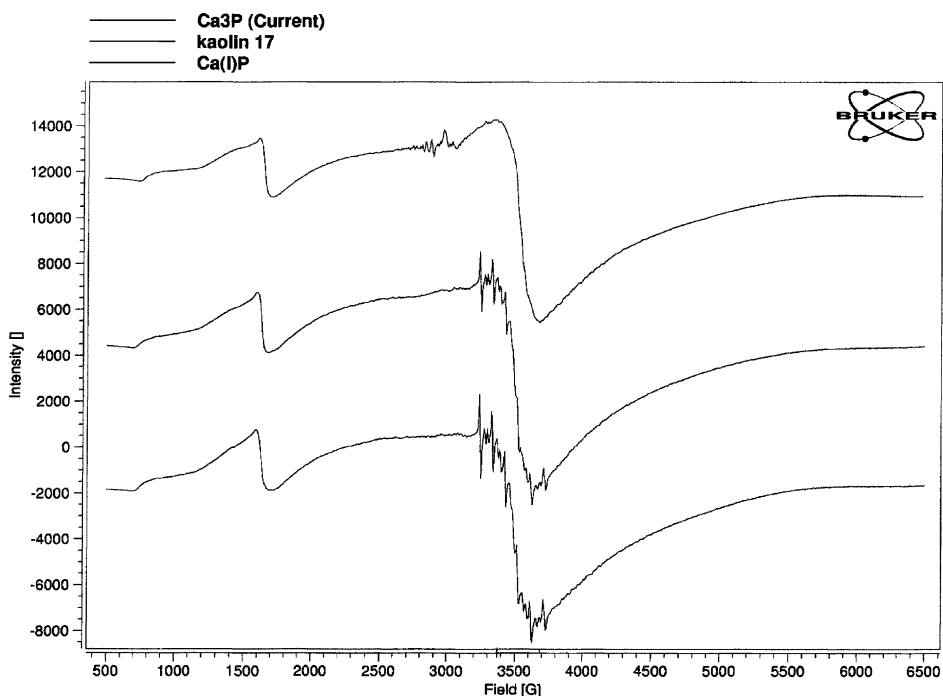

Fig. 7. ESR spectra Na-, Ca-Z(I)- and Ca-Z(III)-forms of zeolite P from above to down, respectively.

many authors reveal the formation of acetone due to the presence of iron impurities [14–16,19–21]. Moreover, Jacobs Peter and Uytterhoeven Jan [21] showed that ferric species in zeolite is existing in two forms, (1) cationic forms, which responsible for dehydrogenation at low temperature, and (2) iron particulates, which responsible for dehydrogenation at higher temperature.

Regarding to propene formation, it can be easily seen from Figs. 10, 12 and 14 that the maximum yield of propene on the sodium form of zeolites was found to be only 20–30%, which reflects the deficiency of acid centers in them. Although this maximum yield was reached at about 270 °C it remains constant till 500 °C. This can be explained by the fact that dehydration process is favored at elevated temperatures [19].
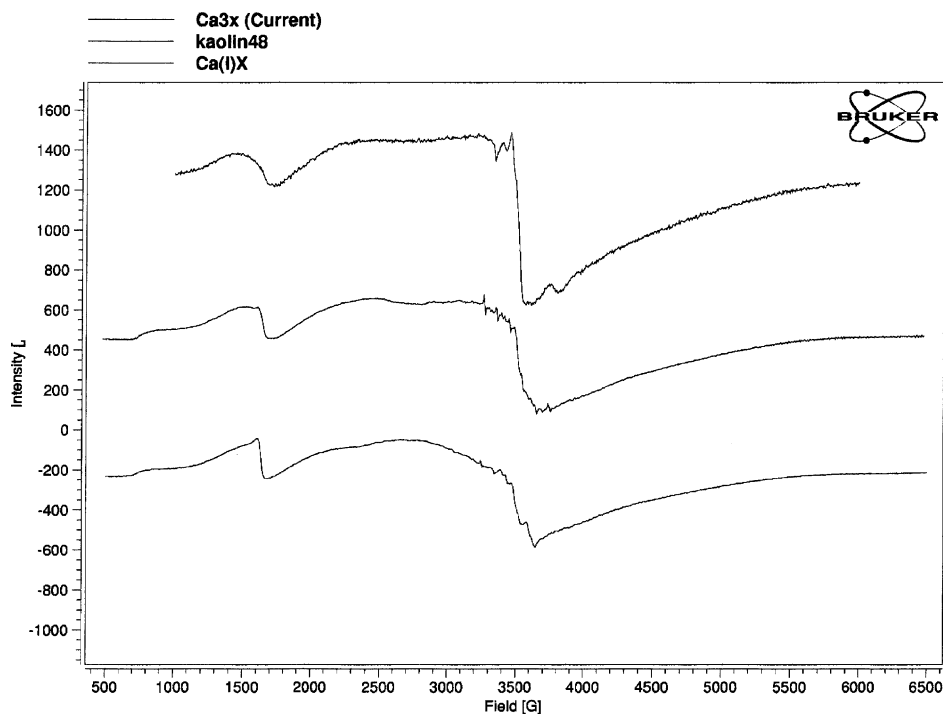
Fig. 8. ESR spectra Na-, Ca-Z(I)- and Ca-Z(III)-forms of zeolite X from above to down, respectively.
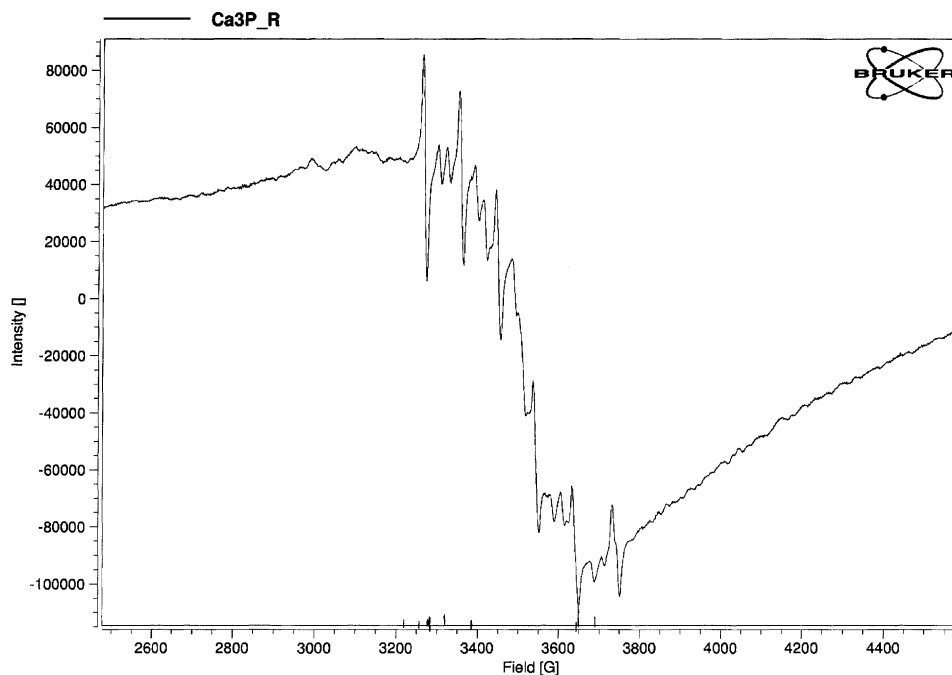

Fig. 9. ESR spectra Ca-Z(III)-form of zeolite P for a range of 2600–4400 G.

The ion exchange of Na ions by calcium ones increases the acid centers in zeolites. Furthermore this predicts the increase of propene yield by increasing the extent of ion exchange which can be easily seen in case of A and P zeolites where a linear relationship between the degree of ion exchange and the propene yield may be obtained. However, in case of X-zeolite a non linear increase in propene yield

is observed in Ca(III)-species (75%). Moreover the propene yield passes through a maximum at ~360 °C, after which a decrease in its yield is observed.

This can be explained on the fact that large fraction of S(I) site in Na-X zeolite must be filled first with bivalent cations before sodium ions at the potentially catalytically active site S(II) can be replaced. Thus, it can be seen from the reference
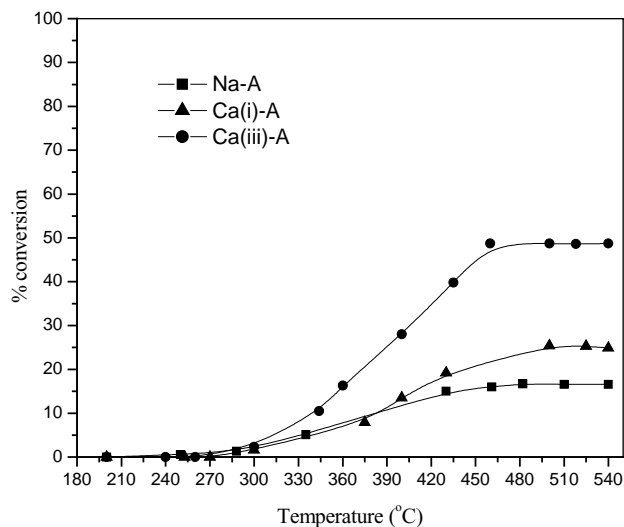
Fig. 10. Effect of calcium ion exchange on propene conversion over A-zeolite.

Fig. 12. Effect of calcium ion exchange on propene conversion over P-zeolite.

[22] where even at 65% ion exchange Na-Y zeolite only a fraction of Ca^{2+} occupy S(II) positions. As consequence, catalytic activity could increase more than linearly by excess ion exchange.

Moreover the decrease of propene yield at >360 °C can be explained on the basis of a competition between the acid sites (for propene) and iron particulate sites (for acetone), where the competition is found to be favoured for the acetone formation.

Regarding to acetone yield the following remarks can be noticed from Figs. 11, 13 and 15.

1. For Na form of zeolites (A, P and X) acetone starts to appear at relatively low temperature and reaches its maximum yield at 270–300 °C and then remains constant.
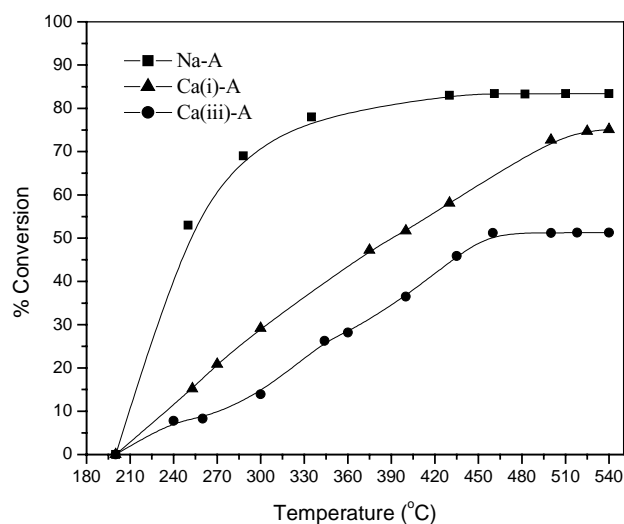2. As the degree of ion exchange increases the temperature at which acetone appears is shifted to higher temperature
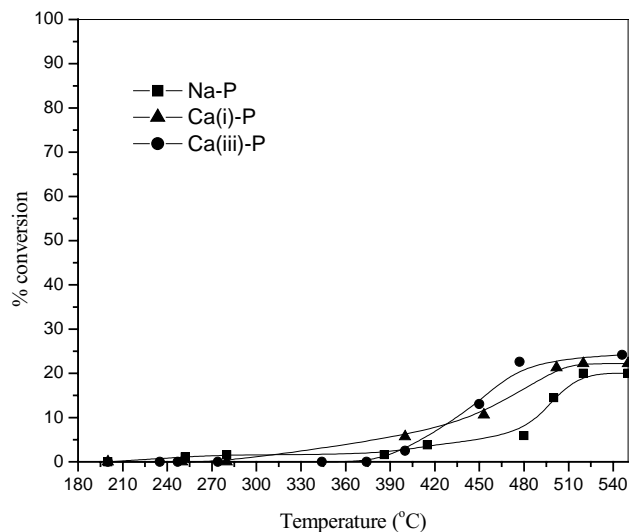
while the maximum yield obtained only at higher temperatures >500 °C.
3. The maximum yield is nearly the same for Na-Forms and the ion exchanged forms of different kinds of zeolites except for A zeolite where a remarkable decrease in the maximum yield of acetone is observed by increasing the degree of ion exchange.

The above observations can be explained in line with the previously mentioned facts that there are two types of Fe responsible for the formation of acetone, (1) cationic forms (for low temperatures) and (2) iron particulates (Fe_2O_3) (for high temperature). Consequently the lowering of the acetone yield in ion exchanged samples can be explained by assuming the decrease in cationic iron (as seen before from ESR spectra by decreasing in signal at $g = 2$ (Figs.

Fig. 11. Effect of calcium ion exchange on acetone conversion over A-zeolite.
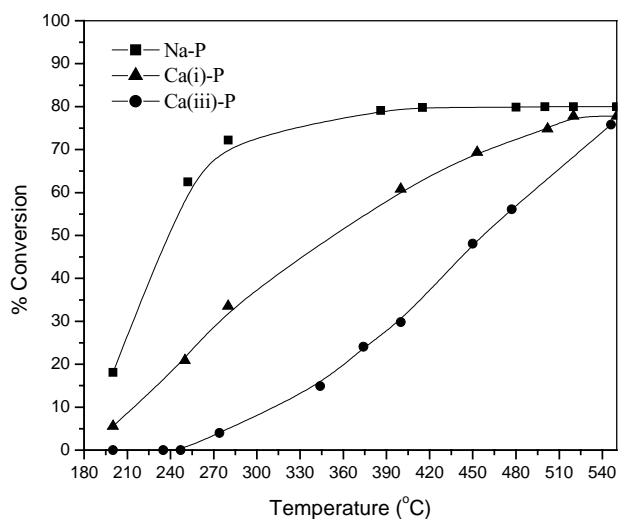

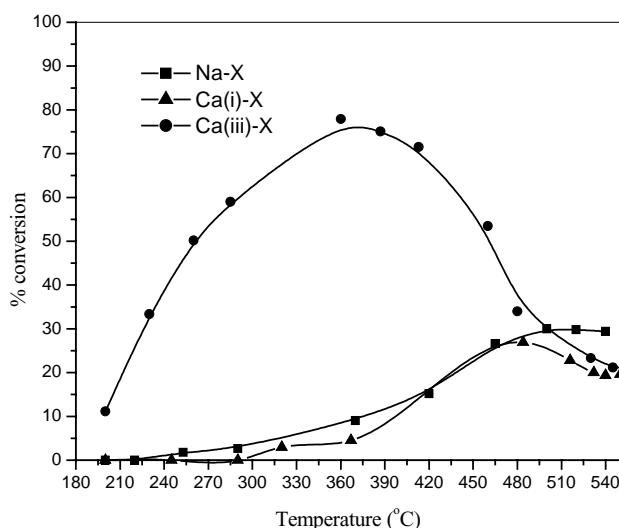Fig. 13. Effect of calcium ion exchange on acetone conversion over P-zeolite.

Fig. 14. Effect of calcium ion exchange on propene conversion over X-zeolite.

6–8). This can be much better explained regarding the higher concentration of calcium ions compared with that of Fe^{3+} ions. Thus this high concentration enables calcium to replace iron in cationic positions.

In addition to that we must take into consideration the type of each zeolite and its stability towards ion exchange.

Moreover, the iron particulates can be formed by two ways:

1. Oxidation of cationic iron at elevated temperatures.
2. Migration of framework iron.

Taking into consideration the previous ESR results which indicate that the framework iron is decreased in the order Na-P > Na-X ≫ Na-A, we can explain the results obtained
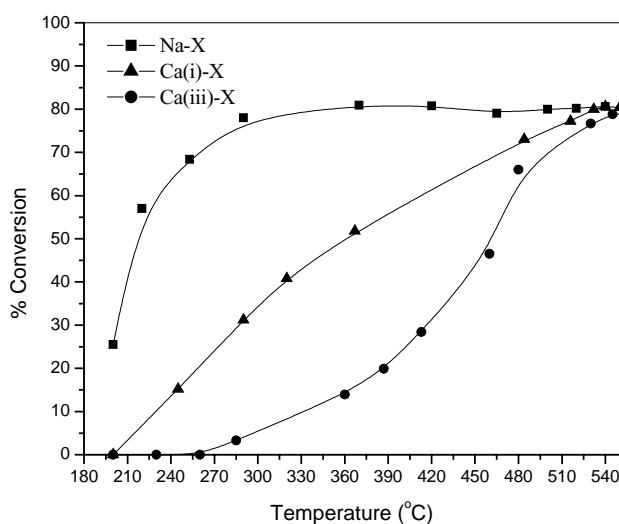

Fig. 15. Effect of calcium ion exchange on acetone conversion over X-zeolite.

as following: in case of A zeolite the iron particulates is mainly comes from cationic iron where the framework iron is very small. Consequently the maximum yield of acetone is supposed to be decreased by decreasing the cationic iron. This can be clearly seen in A-zeolite (Fig. 11). However, in case of X and P zeolites the main source of iron particulates will come from the migration of the framework iron so that the maximum yield would be expected to be not affected by ion exchange which is will seen in Figs. 13 and 15.

4. Conclusions

One can drawn the following conclusions from the above research:

1. Clay minerals such as kaolin may be act as a ready made incorporated iron to prepare zeolite.
2. The iron even in a very small amount can act as a very effective center in catalytic reactions.
3. Iron in zeolites can occupy either a framework positions or cationic positions.
4. Acetone can be yielded in a large amount from the conversion of isopropanol over zeolites prepared from Egyptian kaolin.
5. Selectivity of zeolite can be adjusted either to acetone or to propene by selection of an appropriate type of zeolite and adjusting both temperature and degree of ion exchange, where at higher degree of ion exchange with calcium propene was found to be favored.

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