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ESR STUDY OF CATION EXCHANGED FORMS OF TYPE Y-ZEOLITE

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Abstract

The ESR absorption spectra at room temp. and reduced pressure of 10^{-2} Torr of six forms of type Y-zeolite, NaY, NaNiY (1), NaScY (2), NaScY (3), NaZrY (D), NaZrY (5) were investigated before and after treatment with different organic reagents. These zeolites were also exposed to γ -irradiation at 77°K with and without cumene.

It was found that at room temperature and under reduced pressure of 10^{-2} Torr, these samples showed no electron spin resonance (ESR) signals. The introduction by injection of microamounts of reagents to the scandium and zirconium forms led to the appearance of a single narrow line in the ESR spectrum, its intensity depends on the nature of reagent. On the other hand, these reagents gave no signal with the NaY and NaNiY (1). After γ -irradiation at 77°K, NaY and NaNiY (1) gave an intense single line from an electron-centre. In the case of the scandium and zirconium forms, besides the intense line, a second broad unresolved one appeared, which may be related to the hole centres. The introduction of cumene on the zeolite followed by γ -irradiation showed different ESR behaviour. For NaY and NaNiY (1), besides a single line from electron-centres, another sharp signal with a five line hyperfine structure was also observed. In the case of the zirconium forms, the latter signal decreased with the appearance of a weak broad line from the hole centres. In the case of the catalytically active scandium forms, only a line from electron-centres and a less intense broad one from the hole centres were detected.

Introduction

The catalytic activity of zeolites is clearly influenced by the exchange of cations. In cracking, alkylation, and dehydration, it increases with increasing the replacement of sodium ions by multivalent ones.^D If care is taken to avoid iron contamination, the sodium A, X, and Y-zeolites show no electron

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spin resonance signals even after extent dehydration²⁾ Replacement of sodium ions by other ones such as Cu^{2+} ³⁾ or Mg^{2+} ⁴⁾ showed that the crystalline field in zeolite can be determined by examining the electron spin parameters of the multivalent ion signal. On the other hand, an attempt was made to study crystal field interaction between the adsorbed O_2^- ions and some group III-cation-exchange Y-type zeolites including AIHY, ScY and LaY-zeolites.⁵⁾

Many investigators showed that the properties of zeolites, in particular their catalytic properties, may be connected with the surface defects, which particularly appear in ESR-spectra as electron or hole centres.^{6,7)}

In this report, the changes of ESR-spectra of different cation exchanged zeolites were studied at 77°K with and without adsorption of organic compounds, before and after γ -irradiation, to investigate the nature of surface centres and their influence on the catalytic activity.

Experimental

The NaY, NaScY (2) and NaScY (3) zeolites with a silica to alumina ratio of 5 and NaNiY (1), NaZrY (D) and NaZrY (5) zeolites with a ratio 4.1 were studied. Some data on these zeolites are listed in Table 1. The method of preparation of these samples, their X-ray data and the catalytic properties in cracking hydrocarbons, dehydration of alcohols, isomerization of olefins and other reactions were previously reported.⁸⁻¹⁰⁾ ESR-measurements were carried out with an ESR-spectrometer operated at 9.8 GHz. Samples of the same weight in the ESR tubes (4 mm o. d.) were activated in vacuum at 450°C for 4 hrs, the tubes were sealed with tightfitting rubber spectrum caps and then neatliquid samples to be studied were injected through the septums. The adsorption of reagents (toluene, cumene, n-octane, benzene hexafluoride and ethanol) was carried out at room temperature. The adsorption time is

TABLE 1. Some properties of the zeolites under investigation

No.	Zeolite	% exchange of sodium ions.	silica to alumina ratio	method of preparation
1	NaY	0	5	—
2	NaNiY (1)	22	4.1	ion-exchange
3	NaScY (2)	39	5	ion-exchange
4	NaScY (3)	55	5	ion-exchange
5	NaZrY (D)	35	4.1	solid solution
6	NaZrY (5)	55	4.1	ion-exchange

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one hour till the moment of ESR-measurement or γ -irradiation. The samples were exposed to γ -irradiation at 77°K using γ -source of ^{60}Co (dose=1.5 M Rad) and examined by ESR without warming.

Results

During the study of ESR spectra of fresh samples at temperatures between 77°K and 300°K no lines were found. The introduction of toluene, cumene, *n*-octane, benzene hexafluoride or ethanol to the activated scandium or zirconium zeolites, led to the appearance in the ESR-spectrum a single narrow line with $g=2.002$ and $\Delta H \sim 8-10$ G. The intensity of the line (not exceeding 10^{17} spin/cm³) and the small value of ΔH , were considerably dependent on the forms of zeolites and the reagents introduced. For the more catalytically active form of the zeolites, the most intense electron-centre was observed. In the case of cumene adsorption, the intensity of electron-centres on NaScY (3) was 1.5 times greater than that on NaScY (2), and to a certain extent, this increase is connected with the increase in the degree of exchange of sodium ions by scandium ions. For Zr-forms, the intensity of the line was lower than that of scandium, and for NaZrY (D) the signal was more intense than that of NaZrY (5), as shown in Fig. 1. In the case of NaY and NaNiY (1), no lines in the ESR-spectrum were obtained by the introduction of cumene or toluene. The behavior of one and the same zeolite against different reagents is also interest, the ESR spectra for cumene, toluene and *n*-octane are nearly the same, for benzene hexafluoride the intensity is less than the mentioned above reagents. But for ethanol a very small intensity was observed. This may be attributed to the fact that the zeolite dehydrates ethanol with the separation of water which causes the decrease in the intensity of ESR signal, *i. e.*, masking. For the NaScY (3) sample, after the introduction of toluene and heating from 20° to 240°C, the decrease in line intensity up to its complete disappearance was noticed, and this behaviour is indicative of a desorption process.

In order to study the nature of zeolite

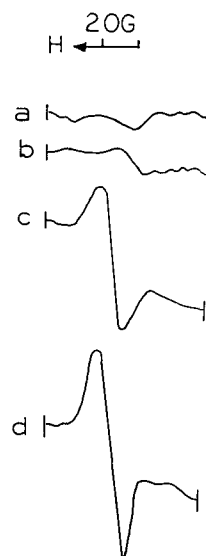


Fig. 1. ESR-spectra of catalytically active forms of zeolites with adsorbed cumene ($T=300^\circ\text{K}$)

a—NaZrY (5), b—NaZrY (D), c—NaScY (2) and d—NaScY (3).

surface centres, the ESR-spectra of the zeolites were investigated after irradiation at 77°K and the ESR measurements were made also at 77°K.

In ESR-spectra of the NaY and NaNiY (1) samples, an intense (10^{18} spin/cm³) single line from an electron-centre appeared, with $g=2.002$ and $\Delta H \approx 9$ G. From the obtained parameters, this line is contributed to the radiated electron-centres, which may arise at the moment of capturing electron on the defective silicon-oxygen tetrahedron.

In the case of the scandium and zirconium forms, not only an intense line from electron-centres (10^{18} spin/cm³), but also a characteristic broad unresolved line with $g=2.002$ and $\Delta H \approx 40$ G were observed, (Fig. 2). The broad line, based on its parameters, may be related to a hole centre, *i. e.*, a type of hole captured on an oxygen ion. It was also observed that there is an increase in line intensity of hole centre with increase in catalytic activity from zirconium to scandium forms *e. g.*, in cracking reaction.

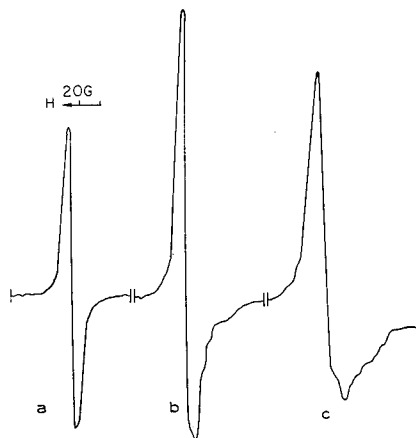


Fig. 2. ESR-spectra of γ -irradiated at 77°K samples
a—NaNiY (1), b—NaZrY (D) and c—NaScY (3).

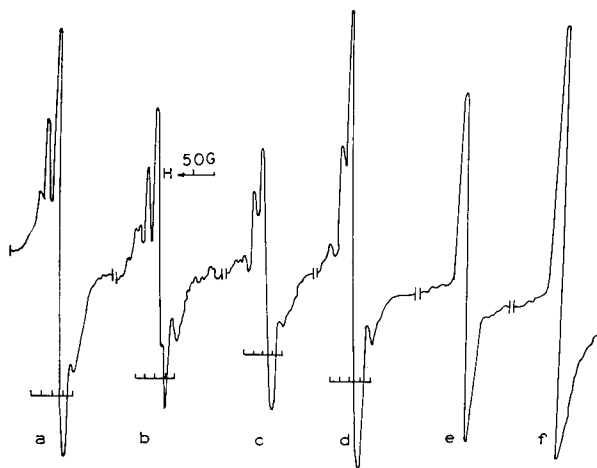


Fig. 3. ESR-spectra of γ -irradiated zeolites at 77°K after adsorption of cumene
a—NaY, b—NaNiY (1), c—NaZrY (5), d—NaZrY (D),
e—NaScY (2) and f—NaScY (3).

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The ESR-spectra of the γ -irradiated zeolites containing cumene also possessed a regular variation as can be seen from Fig. 3.

A). For NaY and NaNiY (1), besides a single line from an electron-centre, a sharp intense signal was observed, with a five-line (or more) hyperfine structure with a splitting constant of 25 G, and g -factor of 2.002 (the number of spins is $< 10^{18}$ spin/cm³).

B). In the case of zirconium forms, the intensity of the five-line system decreased with respect to the intensity of electron-centre and a weak broad line representing the hole centre appeared. On the other hand, the scandium forms gave only an intense line from electron-centre and a less intensive broad line from the hole centre.

Discussion

The ESR data obtained from the activated and γ -irradiated zeolites show that the state of surface defects change regularly depending on the composition of the investigated zeolites.

1. NaY and NaNiY (1) forms of zeolites.

The ESR-spectra of activated and γ -irradiated samples showed only an intense line from electron centres ($g=2.002$). The surface defects for these centres apparently cause the formation of only centres of localized paramagnetic states with the capture of an electron (defective silicon-oxygen tetrahedrons). The corresponding hole centre, which lost the electron, can be represented by delocalized paramagnetic state, which cannot be detected in the spectrum due to the great width of the line.

2. NaZrY and NaScY forms of zeolites.

The samples were activated and γ -irradiated before the ESR-spectra is taken. The spectra revealed an intense line from electron centres ($g=2.002$) and a line from hole centres ($g=2.020$). Analogous to the previous results on inactive zeolites, the electron centres can be regarded as electrons which are captured by defective silicon-oxygen tetrahedrons. The formation of the localized hole centres of the type O^- may be connected with the non-isovalent exchange of sodium ions by scandium or zirconium ions. Only as a results of the latter exchange can the appearance of defective oxygen positions of aluminium or silicon of the oxygen anion groups be expected. This may be transferred into the paramagnetic O^- species.

In the light of the above discussion, the rest of the experimental facts can be understood. The ESR-spectra of the irradiated zeolites, to which cumene was introduced, possess a regular change. So, for the samples NaY

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and NaNiY(1) having significant adsorptive properties, it is a characteristic that a line from electron-centres, and a signal of five component system appears with a splitting of 25 G from the radical-product as a result of radiolysis. On the other hand, in the case of the zirconium forms with less adsorptive capacity, the hyperfine system decreases in intensity with respect to the line from electron-centres. However, for the highly active scandium forms which possess the least adsorptive capacity the hyperfine system does not appear.

In connection with the above, the reagent molecules in zeolites are effectively adsorbed by the "surface defective centres". In general, the intensity of the spectra decreases in comparison with the intensity obtained in the previous experiment. It is of interest to notice a weak broad line ($g=2.020$) from hole centres, in the spectrum of NaScY and NaZrY forms. This line may be related to the small part of the observed localized states of the hole centres, which appeared to be "unconnected" with reagent molecules.

It is naturally to suppose that upon introduction of certain reagent to NaScY or NaZrY form, the adsorbed molecules combine with scandium or zirconium ions in the structural cavities of zeolite forming a coordination complexes. The result of this combination is that some structural displacements of oxygen-groups close to the ions of scandium or zirconium will be subjected to an additional disturbance, which, in certain cases, is sufficient to be an active donors of electrons.

On the bases of the results obtained, we may suppose that in the process of catalysis, the coordinated complexes which are able to form "combined states" with the reagent molecules can effect the catalytic activity depending on the type of reaction.

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