

CONTRIBUTION OF Fe AND PROTONIC SITES IN CALCINED AND STEAMED ZSM-5 ZEOLITES TO OXIDATION OF BENZENE WITH N₂O TO PHENOL AND SELECTIVE CATALYTIC REDUCTION OF NO WITH PROPANE TO NITROGEN

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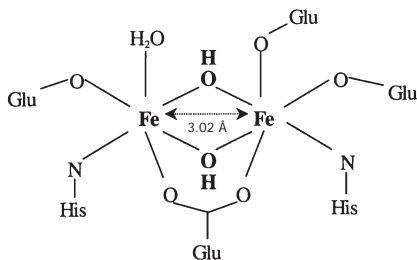
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NH₄-(Fe)ZSM-5 zeolites with concentrations of Fe ranging from 30 to 2000 ppm, introduced into zeolites during their synthesis, either calcined in dry oxygen at 720 K or steamed at 870 K in oxygen stream with 30% water vapor, were investigated in benzene oxidation with N₂O to phenol and selective catalytic reduction of NO_x to nitrogen. The concentration of Brønsted and Lewis sites was determined by quantitative analysis of IR spectra of adsorbed d₃-acetonitrile. The changes in Fe ion coordination were monitored by ESR spectra of Fe(III) ions. The Fe ions have been shown to control the activity of zeolites in the above reactions, while the Al-related acid sites play only a minor role. The steamed zeolites compared to calcined ones exhibited substantially higher activity in oxidation of benzene with N₂O to phenol, while the reduction of NO_x to nitrogen was considerably suppressed. The steaming resulted in a dramatic decrease in concentration of Brønsted sites, low concentration of Lewis sites and relocalization of Fe ions into cationic sites exhibiting distorted tetrahedral coordination (ESR signals at *g* = 6.0 and 5.6). It has been concluded that specific Fe sites are required for benzene oxidation to phenol without participation of Brønsted sites, while with the complex SCR-NO_x reaction both Fe cationic sites and protonic sites are involved in the catalytic process. Fe sites contribute to oxidation of NO to NO₂ and protonic sites control reduction of NO₂ to molecular nitrogen.

Keywords: Benzene; Oxidations; Nitrous oxide; Heterogeneous catalysis; SCR-NO_x; Iron; Fe-zeolites; Steamed zeolites; ESR spectroscopy.

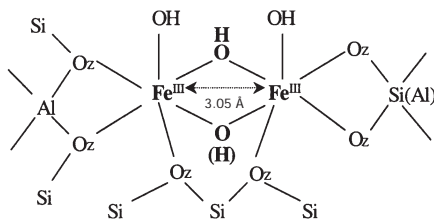
Fe sites in high silica zeolites of ZSM-5, ferrierite and beta structures have attracted a lot of attention due to their activity in oxidation of benzene to phenol with N₂O^{1,2} and selective catalytic reduction of NO_x with alkanes (SCR-NO_x) even in the presence of high concentration of water vapor, such existing in exhaust gases of combustion processes³⁻⁷. For both these quite different reactions with respect to their nature, a similar structure of Fe ac-

tive sites was suggested. Dinuclear Fe species in ZSM-5 have been proposed by Panov *et al.*^{8,9} to be the active sites in benzene oxidation with N_2O to phenol, based on the Moessbauer spectra of Fe(III) and Fe(II) species and analogy with the structure of Fe methane monooxygenase¹⁰.



Such species were suggested to be formed by removal of Fe isomorphously substituted in the silicate framework into extraframework positions under calcinations at high temperature.

Similar structure of Fe species in ZSM-5 zeolites, prepared by a solid-state exchange of $FeCl_2$ with H-ZSM-5, has been revealed by Prins *et al.*¹¹ and Sachtler *et al.*¹² using EXAFS technique. The Fe-Fe atom distance was estimated to be following:



Such prepared Fe-ZSM-5 zeolites exhibited high and stable activity in SCR- NO_x with isobutane to molecular nitrogen even at high concentration of water vapor³ and the dinuclear Fe complexes have been indicated as the active sites^{3,13,14}.

The present study analyzes the behavior of variously treated H-zeolites with low concentrations of Fe (from traces to 2000 ppm Fe) and compares their activity in oxidation of benzene with N_2O to phenol and in SCR- NO_x to bring a piece of understanding of the structure of Fe active sites in these redox reactions.

EXPERIMENTAL

Zeolites

Three samples of NH_4 -ZSM-5 zeolites containing different concentrations of iron (samples 1–3, Table I) introduced into zeolites during their syntheses were investigated in their H-form, obtained by their calcination in oxygen, and in their steamed form (S-form) resulting from steaming of NH_4 -zeolites.

NH_4 -ZSM-5 zeolites with iron concentrations 30 (sample 1) and 2000 (sample 3) ppm Fe were prepared in laboratory. Sample 2 containing 180 ppm Fe was a commercial sample, kindly provided in the Na-form by the Institute of Oil and Hydrocarbon Gases (Slovnaft, Slovakia). Samples 1 and 2 contained Fe as impurity, while during the synthesis of sample 3 iron was added to the synthesis gel. A special caution was paid to preparation of a zeolite containing a very low concentration (30 ppm) of iron. A solution of Al nitrate (Fluka) in deionized water was added to the mixture of tetraethyl orthosilicate (Fluka) and ethanol (laboratory grade). For preparation of sample 3 (2000 ppm Fe), an appropriate amount of Fe nitrate was added to the aluminium source. The mixture was stirred for 90 min, and then a solution of tetrapropylammonium hydroxide in water (20%; Fluka) was added; the resulting mixture was stirred for 90 min. The obtained gel was transferred into a Teflon-lined autoclave and crystallized under rotary conditions at 450 K for 72 h. Afterwards the mixture was centrifuged to separate the solids. The zeolite was thoroughly washed, dried and calcined in a stream of dry oxygen at 770 K for 6 h to remove the template. The NH_4 -forms of zeolite samples (1–3) were prepared by repeated (3 \times) ion exchange of the calcined materials with 0.5 M NH_4NO_3 at room temperature. XRD analysis indicated a highly crystalline ZSM-5 structure for all the NH_4 -zeolites.

TABLE I

Chemical composition of zeolites and concentration of Al-related Brönsted and Lewis sites (on dry basis)

No.	Fe, ppm	Si/Al	Treatment ^a	Brönsted sites ^b mmol g ⁻¹	Lewis sites ^b mmol g ⁻¹
1	30	28	C at 750 K	0.40	0.09
1a	30	28	HT at 870 K	0.08	0.06
2	180	14	C at 750 K	0.89	0.08
2a	180	14	HT at 870 K	0.08	0.09
3	2000	28	C at 750 K	n.d.	n.d.
3a	2000	28	HT at 870 K	n.d.	n.d.

^a C, calcination in dry oxygen stream at 750 K; HT, hydrothermal treatment in oxygen stream containing 30% water vapor. ^b Determined by quantitative analysis of FTIR spectra of adsorbed d_3 -acetonitrile on dehydrated zeolites.

In order to obtain steamed zeolites, a part of NH_4 -zeolites was treated in a stream of oxygen containing 30% of steam at 870 K for 3 h. The resulting steamed zeolite samples (S-zeolites), originating from samples 1–3, were denoted as 1a, 2a and 3a.

Elemental analysis of zeolite samples was performed by X-ray fluorescence spectroscopy and conductively coupled plasma emission spectrometry. Chemical composition of zeolites is given in Table I.

FTIR Spectroscopy

The IR spectra of zeolites in the region of OH and $\text{C}\equiv\text{N}$ vibrations of adsorbed d_3 -acetonitrile were recorded on a Nicolet Magna 550 FTIR spectrometer with a low-temperature MCT-B detector. Samples in the form of self-supporting wafers with a thickness of about 5 mg cm^{-2} were placed in a six-position sample holder in a vacuum cell with NaCl windows and connected to a dosing system for adsorption of d_3 -acetonitrile.

To determine the concentration of strongly acidic Brønsted and Lewis sites, the zeolites were dehydrated (and deammoniated) at 720 K and 10^{-3} Pa for 4 h. This procedure was followed by adsorption of d_3 -acetonitrile (Aldrich; 1.2 kPa) at room temperature with subsequent desorption carried out at the same temperature for 30 min under evacuation; for details, see ref.¹⁵

The spectra of adsorbed d_3 -acetonitrile were recorded at ambient temperature with resolution of 2 cm^{-1} by collecting 200 scans for a single spectrum. The spectra were normalized on a sample thickness of 5.5 mg cm^{-2} by using the integrated area of the zeolite skeletal bands in the region between 1750 and 2100 cm^{-1} . The spectra of adsorbed d_3 -acetonitrile were analyzed in the region between 2360 and 2220 cm^{-1} and the bands were deconvoluted into Gaussian profiles using a procedure given elsewhere¹⁵. A band at 2297 cm^{-1} was ascribed to the interaction of Brønsted sites (both Si–OH–Al and Si–OH–Fe) with the $\text{C}\equiv\text{N}$ group of acetonitrile, while the bands at 2325 and 2315 cm^{-1} corresponded to the interaction of $\text{C}\equiv\text{N}$ groups with Lewis sites (two types of Al–Lewis sites at 2325 and 2315 cm^{-1} were detected). The following extinction coefficients, determined elsewhere¹⁵, were used: for Brønsted sites $\epsilon_{\text{B}} = 2.05 \text{ cm } \mu\text{mol}^{-1}$ and for Al–Lewis sites $\epsilon_{\text{L}} = 3.62 \text{ cm } \mu\text{mol}^{-1}$ (the latter one regardless of the Lewis site type). If Fe–Lewis sites were present in zeolites, the interaction of these sites with $\text{C}\equiv\text{N}$ group of d_3 -acetonitrile resulted in a band at 2300 cm^{-1} (see ref.¹⁶). This band strongly overlapped the band of $\text{C}\equiv\text{N}$ group adsorbed on Brønsted sites (2297 – 2298 cm^{-1}). Therefore, determination of the concentration of Brønsted and Fe–Lewis sites, if simultaneously present, was not possible.

ESR Spectroscopy

ESR spectra of Fe(III) ions were monitored in the X-band region ($\approx 9.2 \text{ GHz}$) on an ESR spectrometer ERS-220, Germany. Spectra were recorded at room temperature in the region 30–500 mT. As an internal standard, Mn(II) ions in solid matrix were used. Before the measurements the samples were pretreated in a stream of dry oxygen at 750 K for 2 h, cooled to room temperature, evacuated at 10^{-2} Pa for 30 min and transferred under vacuum into a quartz cell and sealed.

Oxidation of Benzene with N₂O

Oxidation of benzene to phenol was carried out in a flow catalytic set-up in a fixed-bed through-flow microreactor with 0.5 g of catalyst. The reactant mixture consisting of 20 vol.% N₂O, 20 vol.% benzene and N₂ as a balancing gas was kept constant at a total flow rate of 60 ml min⁻¹. Corresponding weight hour space velocity (WHSV) based on benzene was 5.0 h⁻¹. Prior to the reaction the catalyst was activated in a stream of oxygen at 750 K for 1.5 h and then in a nitrogen stream at the reaction temperature, *i.e.* 620 K, for 30 min. The analysis of the reaction mixture was performed using an on-line gas chromatograph Hewlett Packard 5890 II series (model G1540A) with FID detector and 75 m low-polar DB-VRX fused silica column. The column provided separation of benzene, phenol, benzoquinone and dihydroxybenzenes. The catalyst activity was expressed as the rate of phenol formation (in mmol g⁻¹ h⁻¹). The conversions of benzene were typically lower than 30% at selectivity to phenol above 95%. Benzoquinone and dihydroxybenzenes were found only in trace concentrations.

Selective Catalytic Reduction of NO_x with Propane

SCR-NO_x with propane (or oxidation of NO to NO₂) was carried out in a glass through-flow microreactor, typically with 400 mg of the catalyst. Reactant mixtures consisting of 1000 ppm NO, 0 or 1000 ppm C₃H₈, 2.5% O₂, 0 or 10% H₂O and He as a balancing gas were continuously fed at a total flow 100 ml min⁻¹. The corresponding gas hour space velocity (GHSV) value was 7500 h⁻¹.

The catalyst was activated in oxygen stream at 720 K for 1 h. Then the reactor was cooled down to the lowest reaction temperature, typically 470 K, and connected with a stream of the reaction mixture. The steady state of the reaction with constant product composition at a given temperature was usually reached within 40–60 min. Then the temperature of the catalyst was increased in 50 K steps up to 720 K.

Concentrations of NO and NO₂ in the inlet and outlet of the reactor were continuously monitored by a NO/NO_x chemiluminescence analyzer (VAMET-CZ). Concentrations of C₁–C₃ hydrocarbons, sum of C₄⁺ hydrocarbons, CO₂, CO and N₂O were provided by an on-line gas chromatograph Hewlett Packard 6090. Two gaseous samples were simultaneously injected. In one branch, columns of Poraplot Q (30 m × 0.53 mm) and Molecular sieve 5A (30 m × 0.53 mm, *d_f* = 25 μm) were used for separation of CO₂, CO and N₂O (TCD detector). A by-pass of Molecular sieve 5A column was used for analysis of CO₂. In the second branch, FID detector monitored C₁–C₃ hydrocarbons separated on a non-polar HP-5 column (30 m × 0.32 mm with 0.25 μm thickness of active phase).

The total conversion of NO and C₃H₈ was defined as

$$x_i, \% = \frac{c_i^0 - c_i}{c_i^0} 100, \quad (1)$$

where *c_i⁰* is the concentration of the reactant (NO or C₃H₈) before and *c_i* is the concentration of the reactant after the reaction.

Yields of N₂, NO₂ and N₂O or CH₄, C₂H₆, C₂H₄ and C₃H₆ were defined as

$$y_j, \% = \frac{v_j c_j}{v_m c_m^0} 100, \quad (2)$$

where c_j is the concentration of N_2 , NO_2 , N_2O , CH_4 , C_2H_6 , C_2H_4 or C_3H_8 in the reactor outlet and v_j is the number of C or N atoms in the corresponding molecule, c_m^0 is the concentration of NO or C_3H_8 in the reactor inlet and v_m is the number of C or N atoms in the corresponding molecule.

RESULTS

Different treatment of zeolites, *i.e.* calcination in a stream of dry oxygen (H-zeolites) and hydrothermal treatment in an oxygen stream containing water vapor (S-zeolites) resulted in the changes of both the concentration of protonic acid sites, Al-Lewis sites and the location and structure of Fe sites.

Acid Sites

Calcination of zeolites in a dry oxygen stream led to formation of zeolites with highly prevailing concentration of Brönsted sites and very low concentration of Al-Lewis sites. With the exception of sample 3, the concentrations of these sites were determined by quantitative analysis of characteristic spectra in the $C\equiv N$ mode of adsorbed d_3 -acetonitrile (Table I and Fig. 1). While the concentration of Brönsted sites in steamed zeolites was dramatically suppressed, the concentration of Al-Lewis sites was not substantially changed. With sample 3 containing relatively high concentration of Fe (2000 ppm), d_3 -acetonitrile was adsorbed also on Fe cations. However, as the frequency of $C\equiv N$ vibration of adsorbed d_3 -acetonitrile on

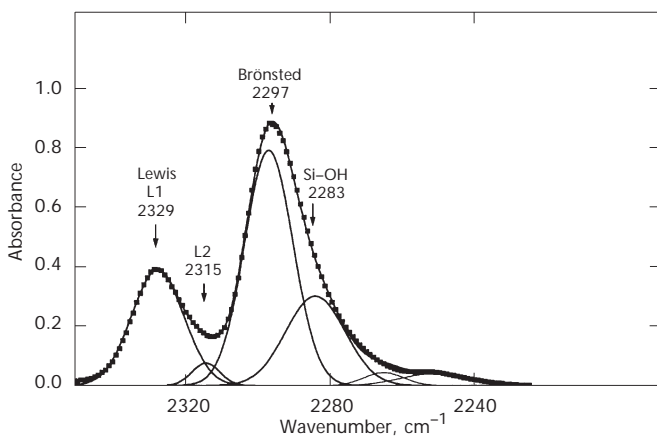


FIG. 1

FTIR spectra of H-zeolite after d_3 -acetonitrile adsorption and followed evacuation at room temperature in the region of $C\equiv N$ group vibration. Illustration of the band deconvolution

Fe sites was very close to that on Brönsted sites (2300 vs 2297–2298 cm^{-1}), we were not able to determine the concentration of Brönsted and Fe-Lewis sites for the sample 3.

Fe Species

The Fe species were introduced into zeolites during their syntheses. Therefore, it can be expected, especially at higher concentrations, that the Fe ions are located at framework sites, in addition to the other positions. Sample 1 dehydrated in oxygen, containing only trace concentration of iron, exhibited only a broad ESR signal with maximum at about $g = 2.3$ and $\Delta H = 1300$ G (Fig. 2). Therefore, the presence predominantly of Fe oxide-like species was assumed^{17,18}. With increasing concentration of Fe the ESR spectra indicated increasing intensity of a new signal at $g = 4.3$, $\Delta H = 50$ G in samples 2 and 3, while the intensity of a broad signal at $g = 2.3$ reflected the presence of Fe oxide-like species in the synthesized zeolite. The signal at $g = 4.3$ is ascribed^{18–20} to tetrahedrally coordinated Fe either in the framework or at the cationic sites. In addition to this signal, sample 3 exhibited low intensity signals at $g = 5.6$ and 6.0. The latter signals were ascribed to isolated Fe(III) ions in distorted tetrahedral environment likely at cationic sites^{21,22}.

After zeolite steaming at 870 K (samples 1a–3a) and subsequent dehydration in oxygen at 720 K, the concentration of Brönsted sites dramatically decreased (Table I) and the intensities particularly of the ESR signals at $g =$

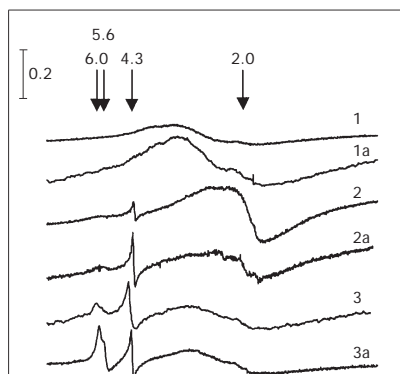


FIG. 2

X-Band ESR spectra of NH_4 -ZSM-5 zeolites with different Fe concentrations (in ppm): 30 (1), 180 (2) and 2000 (3) and treated under various conditions (calcined in dry oxygen stream, 1–3; hydrothermally treated in oxygen stream containing water vapor, 1a–3a

5.6 and 6.0 were substantially increased; concentration of Fe in sample 1 was too low to detect these signals. Steaming of zeolites also increased the intensity of the signal at $g = 4.3$ for sample 2, but with sample 3 the steaming resulted only in an increased intensity of the signals at 5.6 and 6.0. With steamed zeolites the signal at $g = 4.3$ might represent either Fe in extraframework cationic site or tetrahedrally coordinated Fe in extraframework Al–O type clusters formed by the removal of aluminium from the framework sites²³.

Oxidation of Benzene with N_2O to Phenol

Figure 3a and 3b show the performance of H-zeolite samples 1–3 and steamed S-zeolites (samples 1a–3a) in oxidation of benzene to phenol depending on time-on-stream (TOS) at 620 K. A high initial activity of all zeolite catalysts decreased with TOS of the experiments due to coke formation. Complete regeneration of the catalysts was achieved by their calcination under oxygen stream at 720 K. This indicates that no structural collapse of the zeolite or no changes in the character and concentration of active sites of zeolites took place during the reaction and the following regeneration.

Figure 3 also shows an increasing zeolite activity in benzene oxidation to phenol with increasing Fe concentration for both calcined and steamed zeolites. However, the steamed zeolites were much more active than the

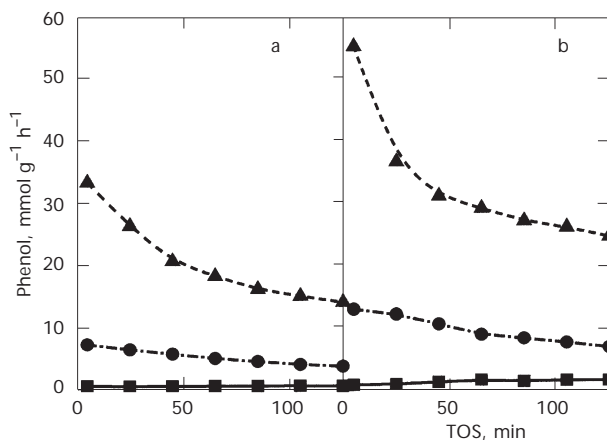


FIG. 3

Dependence of the rate of phenol formation on TOS at 350 °C on NH_4 -ZSM-5 with 30 (■), 180 (●) and 2000 (▲) ppm Fe: a calcined in a dry oxygen stream at 750 K (1–3), b treated in oxygen stream containing 30% of water vapor at 870 K for 3 h (1a–3a)

corresponding calcined H-zeolites (*cf.* samples 1–3 vs 1a–3a, respectively). It is also seen that the higher concentration of protonic sites of the zeolite with Si/Al ratio of 14 (sample 2) compared to that with Si/Al 28 (sample 1) did not manifest itself in the higher hydroxylation activity. Similarly, calcined H-zeolites containing higher concentration of Brønsted sites compared to the steamed S-zeolites did not exhibit higher activity. These findings are in line with our previous conclusion that the protonic as well as Al-Lewis sites are not the active sites for benzene oxidation to phenol and that the concentration of active Fe species controls the reaction²⁴.

Selective Catalytic Reduction of NO_x with Propane. Oxidation of NO to NO₂

Figures 4a and 4b show the dependence of C₃H₈ conversion and N₂, CO₂ and CO yields in SCR-NO_x with propane on temperature for zeolites containing different concentrations of Fe and calcined in oxygen (Fig. 4a) or treated hydrothermally (Fig. 4b). No N₂O was observed in the products and only very low yields of NO₂ (below 3%) and lower hydrocarbons as methane, ethane, ethene and propene (below 2%) were found.

The N₂ yield increased exponentially with increasing temperature, reached a maximum and decreased at higher temperature, while the C₃H₈ conversion increased with increasing temperature up to 100%. The presence of a maximum in the N₂ yield depending on temperature might be associated with low concentration of NO₂ (formed by oxidation of NO) at high temperature due to the NO–NO₂ equilibrium or insufficient concentration of the hydrocarbon available for the SCR-NO_x reaction, if consumed by its oxidation with molecular oxygen to carbon oxides.

The SCR-NO_x activity of zeolites increased (N₂ yield increases and is shifted to lower temperatures) with increasing Fe concentration for both H- and S-forms of zeolites. The increase in N₂ yield with increasing Fe concentration was accompanied by an increase in C₃H₈ conversion and an increase in selectivity to CO₂ (in contrast to CO). With steamed zeolites, compared to the calcined ones, lower N₂ yields were found for individual zeolites. Similarly, the steamed zeolites (samples 1 and 2) exhibited a lower C₃H₈ conversion with the exception of the steamed zeolite 3a, on which the conversion of C₃H₈ was comparable to that of sample 3 (see Fig. 4). Zeolite steaming also resulted in a decrease in relative selectivity of CO₂ to CO in SCR-NO_x.

Figure 5 presents conversion of NO to NO₂ by molecular oxygen and NO to nitrogen in SCR-NO depending on temperature for H- (sample 3) and S-zeolite (sample 3a). In contrast to the zeolite SCR-NO activity, expressed

in N_2 yield, which was much lower for S-zeolites compared to H-zeolites, the values of conversion of NO to NO_2 were very close for such differently treated zeolites.

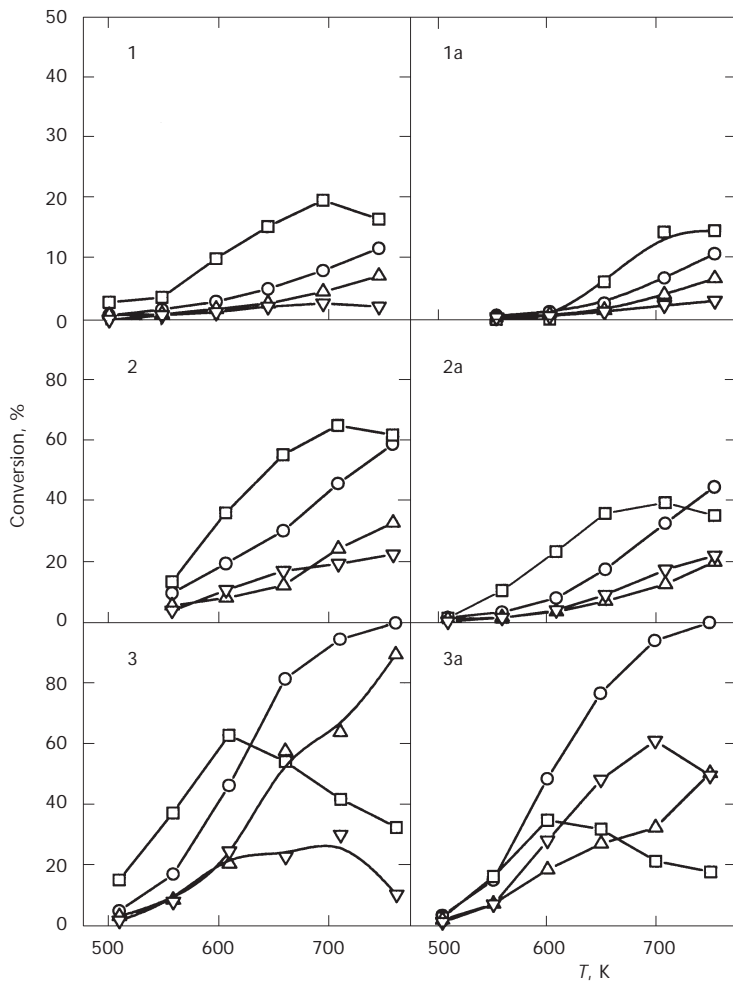


FIG. 4

Dependence of C_3H_8 conversion (\circ), and N_2 (\square), CO_2 (\triangle) and CO (∇) yields in C_3H_8 -SCR of NO on temperature over NH_4 -ZSM-5 zeolites with different Fe concentrations (30–2000 ppm), calcined in dry oxygen stream at 750 K (1–3) and treated in oxygen stream containing 30% of water vapor at 870 K for 3 h (1a–3a)

DISCUSSION

Although there are suggestions in the literature on the redox activity of protonic and Al-Lewis sites^{25,26}, a necessary presence and decisive role of Fe for the redox activity of H-zeolites have been proven in connection with the reactions of NO-NO₂ oxidation^{27,28}, SCR-NO_x with propane^{27,28} and oxidation of benzene with N₂O to phenol²⁴. Also the present study supports this conclusion. It has been shown that the activity of zeolites in both the latter reactions increased with increasing content of Fe apparently regardless of the state of Fe (Figs 3 and 4). H-ZSM-5 with very low Fe concentration (30 ppm) was practically inactive in the benzene oxidation to phenol and SCR-NO_x, but already a relatively low level of Fe concentration

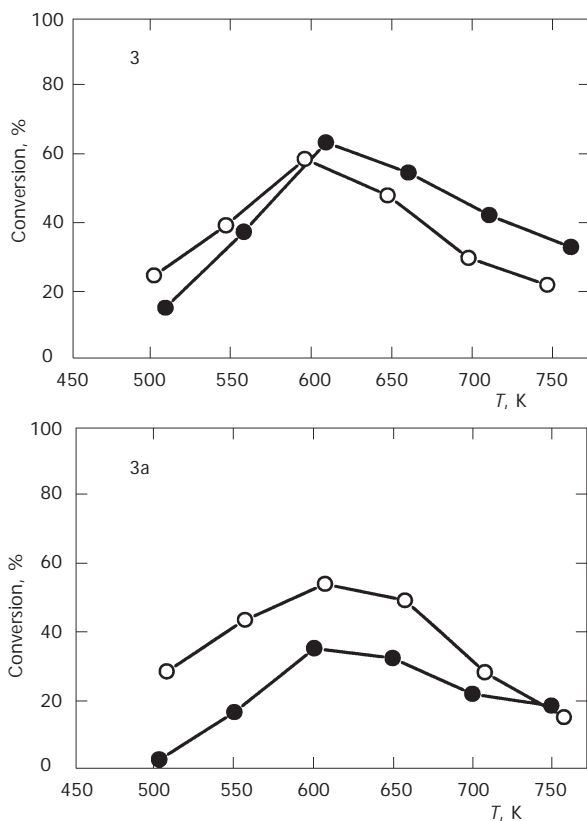


FIG. 5

Dependence of N₂ yield (●) in SCR-NO_x with propane and NO oxidation (○) on temperature over NH₄-ZSM-5 zeolite with 2000 ppm, calcined in dry oxygen stream at 750 K (3) and treated in oxygen stream containing 30% of water vapor at 870 K for 3 h (3a)

(180 ppm), as present in a commercial sample, was sufficient for a significant zeolite redox activity. In agreement with this finding, the higher concentration of Brønsted sites in zeolite sample 1 compared to sample 2 did not cause a higher activity of the former sample. Thus the concentration, location and state of Fe control both the investigated reactions.

The zeolites contained iron at several sites as follows from ESR spectra (see Fig. 2). All zeolites exhibited some Fe in the form of oxide-like species as evidenced from a broad ESR signal at $g = 2.3$. It can be expected that such Fe oxide-like species do not exhibit activity in selective benzene oxidation to phenol and SCR- NO_x reaction, as Fe oxides supported on silica do not possess such selective functions.

If Fe is added to the synthesis gel, it is incorporated mostly at the framework forming sites. Such Fe tetrahedrally coordinated in the silicate framework is reflected in the signal at $g = 4.3$. But also other Fe cations, not located in the framework, can exhibit tetrahedrally coordination. This concerns Fe ions at cationic sites as well as those located in some alumina or silica-alumina clusters present in channels of steamed zeolites.

It is to be mentioned that the Fe bonding at the framework sites is relatively weak. Under zeolite dehydration/deammoniation, the Fe–O bonds are strongly weakened and Fe ions are removed from the framework to extra-framework sites, where they are balanced by a negative framework charge. With more severe calcinations²⁴ or hydrothermal treatment more Fe cations are moved to these cationic sites, as reflected by an increase in intensity of ESR signals at $g = 4.3$, and $g = 5.6$ and 6.0 , indicating the presence of tetrahedrally coordinated and distorted tetrahedrally coordinated Fe species, respectively.

In benzene oxidation to phenol with N_2O , the activity of all H-ZSM-5 zeolites with different Fe concentrations was substantially enhanced by zeolite hydrothermal treatment at 870 K (Fig. 3). This indicates that Fe ions in cationic sites, particularly with distorted tetrahedral coordination, increasing in concentration by zeolites steaming are responsible for the activity in benzene oxidation to phenol. As these ions are detected by the ESR spectra we suggest that they might likely be associated with the single Fe ions. As the activity of steamed zeolites, containing very low concentration of protonic and Al-Lewis sites, was higher in comparison with calcined zeolites with high concentration of Brønsted sites we suggest that the protonic sites did not contribute to the oxidation of benzene to phenol.

In contrast, the activity of steamed S-zeolites in SCR of NO_x to molecular nitrogen was substantially depressed (samples 1a–3a) compared to the cal-

cined H-zeolites (Fig. 4). However, the SCR-NO_x reaction is a complex process, in which several reactions participate in and, therefore, the effect of zeolite steaming on the individual reactions should be considered. Generally, the mechanism of SCR-NO_x with hydrocarbons in the simplest scheme consists of oxidation of NO with molecular oxygen to NO₂, which is in a subsequent step reduced by a hydrocarbon to molecular nitrogen. Simultaneously, a hydrocarbon can be oxidized by molecular oxygen, which is present in excess in the reactant stream. A similar effect of zeolite steaming on SCR-NO_x to nitrogen was reflected, but less pronounced, in a slight decrease in propane conversion, accompanied by substantially increased selectivity to CO at the expense of CO₂. On the other hand, the conversion of NO to NO₂ did not significantly differ for calcined H-zeolites and steamed S-zeolites (see Fig. 5).

The lower activity of steamed zeolites compared to H-zeolites in SCR-NO_x, reflected in a lower conversion of NO to nitrogen, a lower conversion of propane and higher selectivity to CO, indicates different character of Fe active sites in benzene oxidation with N₂O and in SCR-NO_x. However, different concentration of protonic sites in H- and S-form of zeolites (Table I) should be also considered in connection with the SCR-NO_x zeolite activity. It has been shown that the reduction of NO₂ to nitrogen is catalyzed by protonic sites²⁸ without participation of Fe ions. Therefore, a decrease in concentration of protonic sites with steamed zeolites might be also a reason for a lower activity of these zeolites in the overall SCR-NO_x process compared to calcined zeolites.

It can be concluded that the zeolite steaming in comparison with its calcination leads to a substantial increase in zeolite hydroxylation activity in benzene oxidation to phenol, while the activity in the overall SCR-NO_x process to nitrogen is suppressed. A considerable reorganization of the zeolite structure due to zeolite steaming, involving relocalization of Fe ions into cationic sites, exhibiting mostly distorted tetrahedral coordination, and destruction of a vast amount of Brönsted sites, if correlated with the catalytic results implies that (i) the oxidation of benzene to phenol is controlled by the specific structure of Fe at cationic sites without substantial contribution of protonic sites, while (ii) the overall SCR-NO_x process, besides the active Fe sites (necessary for oxidation of NO to NO₂ and paraffin activation), is also controlled by protonic sites, the presence of which contributes to the reduction of NO₂ to nitrogen.

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