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Journal of Catalysis 219 (2003) 273–285

JOURNAL OF  
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# Active sites in HZSM-5 with low Fe content for the formation of surface oxygen by decomposing N<sub>2</sub>O: is every deposited oxygen active?

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Received 11 December 2002; revised 14 March 2003; accepted 29 April 2003

## Abstract

Surface-active centers were detected in HZSM-5 with a low content of iron (< 1000 ppm) activated by steaming and high-temperature calcination in inert atmospheres (up to 1323 K). These centers lead to the formation of surface oxygen (O)<sub>ad</sub> species from N<sub>2</sub>O and were characterized quantitatively by the transient response method. The total amount of active centers was proportional to the content of iron in the zeolites. Only a part of (O)<sub>ad</sub> deposited by decomposing N<sub>2</sub>O was active in CO oxidation at 523 K and appeared as sharp O<sub>2</sub> peaks at 666 K during the TPD measurements. A binuclear Fe center is suggested featuring a “diamond core” structure, similar to that of the monooxygenase enzyme, as an active center. The active O atoms were assigned to the paired terminal oxygen atoms each bonded to one Fe site (ferryl groups) in the diferric [Fe<sub>2</sub>O<sub>2</sub>H]<sup>+</sup> cluster. Oxygen pretreatment at 823 K decreases somewhat the total amount of active sites but does not affect the ratio of active/inactive oxygen. Zeolite presaturated by water vapor at 473–523 K generates (O)<sub>ad</sub> species from N<sub>2</sub>O completely inactive in the CO oxidation. Part of it appears as a broad peak at 940 K in the TPD profile. The total amount of the deposited oxygen corresponds to half of the stoichiometric amount of the surface Fe atoms and suggests that water blocks a half of the binuclear [Fe<sub>2</sub>O<sub>2</sub>H]<sup>+</sup> center, the remaining acting as a single Fe site.

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**Keywords:** Fe-containing HZSM-5;  $\alpha$ -Oxygen; Ferryl groups in zeolite; [Fe<sub>2</sub>O<sub>2</sub>] diamond core; Monooxygenase; N<sub>2</sub>O decomposition; Oxo-bridged species; Transient response method; Temperature-programmed desorption of oxygen

## 1. Introduction

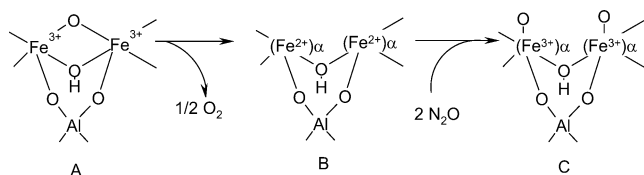
An efficient method for controlling zeolite activity/selectivity is modification of the zeolite by various metals. It is well known that the introduction of trivalent heteroatoms, like Al, Ga, B, or Fe into the crystalline framework of MFI-silicalites via isomorphous substitution of Si atoms, results in the formation of strong Brønsted sites affecting acid-catalyzed reactions. Thermal and hydrothermal treatment of H-zeolites induces the dehydroxylation and the migration of heteroatoms into extraframework positions. As a result, the Lewis acid sites appear and the zeolites possess both types of acid sites [1].

The nature of trivalent heteroatom influences the properties of the resulting zeolite. Contrary to Al-silicalite, Fe-containing zeolites show redox properties, since Fe can easily change its oxidation state (Fe<sup>2+</sup>, Fe<sup>3+</sup>, or Fe<sup>4+</sup>). Cata-

lytic function of isolated redox sites within zeolite cavities (or channels) may result in the material with specific redox properties [2]. One fascinating example is the N<sub>2</sub>O decomposition over Fe-containing ZSM-5. This process has been suggested to proceed via Fe<sup>2+</sup> transition to Fe<sup>3+</sup>, forming active oxygen species called by Panov and co-workers atomic “ $\alpha$ -oxygen” [3,4]. This oxygen can be transferred to benzene or methane forming selective oxidation products at temperatures as low as 243 K [4] similar to the enzymatic catalysis by methane monooxygenase (MMO) [5]. MMO is known to mediate the selective oxidation of hydrocarbons by molecular oxygen at ambient temperature and pressure [6–8]. Significant efforts have been made to develop an effective catalyst based on HZSM-5 zeolites for the direct oxidation of benzene to phenol by nitrous oxide (N<sub>2</sub>O). After catalyst optimization, selectivity to phenol close to 100% was achieved with a conversion up to 40%. However, the nature of active sites responsible for the  $\alpha$ -oxygen species formation (hereafter “ $\alpha$ -sites”) remains unclear. Some authors claim that Lewis acid sites of the extraframework aluminum [9,10] or gallium [11] are responsible for the ben-

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Scheme 1. Formation of  $\alpha$ -sites and active  $\alpha$ -oxygen [3].

zene to phenol transformation. Nevertheless, the fact that commercial zeolites used in these studies contained some amount of iron must be taken into account. Moreover, from the recent research results obtained by various groups, the active centers in benzene hydroxylation have been related to the presence of Fe species [4,12–14].

It has been understood that  $\alpha$ -sites are formed during zeolite activation by steam treatment followed by high-temperature calcination [3,13]. Breakage of the Fe–O–Si bonds takes place and leads to the formation of well-dispersed extraframework iron. Panov and co-workers [3] claim that active iron exists in the form of binuclear  $(\text{Fe}^{2+})_{\alpha}$  complexes, where each  $(\text{Fe}^{2+})_{\alpha}$  site would be able to generate  $\alpha$ -oxygen when reacting with  $\text{N}_2\text{O}$  (Scheme 1).

The binuclear complex **B** consists of a  $\mu$ -hydroxo group, but its role in the formation of active  $\alpha$ -oxygen has not been investigated. Nevertheless, the importance of Brønsted acid sites for the selective benzene transformation into phenol by  $\text{N}_2\text{O}$  has been reported in the literature [12,15]. Notté [12] claimed an importance of Brønsted acid sites in addition to the  $\alpha$ -sites primarily linked to iron. The latter study reports the relation among  $\alpha$ -sites, Brønsted acid sites, and catalyst performance in the phenol formation.

In our previous work [15] the detailed kinetics of benzene transformation into phenol by  $\text{N}_2\text{O}$  was studied. The kinetic results obtained suggest benzene and nitrous oxide molecules adsorbed on two distinct active sites and reacting by a Langmuir–Hinshelwood mechanism. The first would be an active  $\alpha$ -site and the second was suggested to be a Brønsted acid site responsible for the activation of benzene molecule. The surface reaction proceeds when these two sites are in close vicinity. The structure **B** (Scheme 1) could explain the importance of the OH group for the catalysis during the benzene transformation to phenol. Still the question remains: Is this  $\mu$ -proton important only for benzene activation during its transformation to phenol, or is this structure important for the formation of active oxygen ( $\text{O}_{\alpha}$ ) itself? Moreover, no experimental evidence, with the exception of Panov's group, is available on the question: Is every oxygen atom deposited on the surface from  $\text{N}_2\text{O}$ ,  $(\text{O})_{\text{ad}}$ , able to participate in oxidative reactions and can be considered as an active  $\alpha$ -oxygen?

The aim of our work is to contribute to the understanding of the nature of iron sites in the steamed HZSM-5, with a low content of isomorphous framework-substituted Fe and to develop a method for the quantitative determination of active sites in the zeolites under normal pressure and at the reaction temperature. The number of active sites is defined as the number of  $\text{N}_2\text{O}$  molecules that can be decomposed on

the zeolite surface:



Until now the concentration of active sites ( $\alpha$ -sites) has been measured in a static vacuum setup from the amount of the  $\text{N}_2$  released or the  $\text{N}_2\text{O}$  consumed, since these two amounts were found equal [3]. Herein we report the first application of a transient response method to quantitatively assess their concentration. Moreover, we aim to quantitatively clarify if every oxygen atom deposited on the surface  $(\text{O})_{\text{ad}}$  from  $\text{N}_2\text{O}$  has the same oxidative power.

## 2. Experimental

It is known that catalytic properties of Fe-containing MFI systems depend on the method of their preparation and activation. Two main preparation procedures have been reported to achieve a high dispersion of iron species inside the zeolite channels: (1) by Fe addition during hydrothermal synthesis followed by NaZSM-5 conversion to the H form [3,16] and (2) by the introduction of postsynthesis via ion exchange from an aqua solution or from the gas phase [17–19]. The first method gives isomorphous framework-substituted FeZSM-5, which is less sensitive to activation rendering stable *ex*-FeZSM-5 active in benzene hydroxylation. This method, from our point of view, is more adequate for the preparation of HZSM-5 with a low Fe content, since the parent zeolite consists of homogeneously distributed Fe atoms and was therefore employed in our study.

### 2.1. Catalyst preparation

The initial parent HZSM-5<sub>1000Fe</sub> with Si/Al ratio = 25 was kindly provided by Uetikon SA (Switzerland). The initial parent HZSM-5<sub>200Fe</sub> and HZSM-5<sub>70Fe</sub> zeolites with Si/Al ratio 36–42 (Table 1) were synthesized as reported elsewhere [20,21]. The synthesis solution was prepared by adding sodium aluminate (52.5 wt%  $\text{NaAlO}_2$ , Riedel–de Haën), sodium chloride (99.5 wt%, Fluka), and tetrapropylammonium hydroxide (20 wt% in water, Fluka), in deionized water at room temperature. Then, the tetraethyl orthosilicate (TEOS, 98%, Merck–Suchardt) was introduced under vigorous stirring. The molar ratio was as follows: TPA–OH:Si(OEt)<sub>4</sub>:NaCl:NaAlO<sub>2</sub>:H<sub>2</sub>O = 2.16:5.62:3.43:0.13:1000. Homogenization of the mixture were performed for 2–3 h. The gel was afterward poured in a 250-ml teflon-lined autoclave and the temperature was increased within 1 h up to 444 K. The synthesis took place for 2 days under autogenously regulated pressure. The crystalline material was filtered, washed with deionized water, and dried at 393 K. After calcination at 873 K in air for 5 h, the zeolite was converted into the H form using ammonia buffer and heated in nitrogen at 823 K for 5 h.

The main characteristics of the parent zeolites are summarized in Table 1. It is important to note that an iron source

Table 1  
Characteristics of parent HZSM-5 zeolites with low Fe content

Catalyst	Si/Al atomic ratio	Fe content ppm	Fe content (atoms $\times 10^{-18}$ /g)	SSA <sub>BET</sub> (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)
HZSM-5 <sub>1000Fe</sub> Uetikon SA	25	1000	10.7	335	0.32
HZSM-5 <sub>200Fe</sub> home-made	42	200	2.14	370	0.27
HZSM-5 <sub>70Fe</sub> home-made	36	70	0.75	340	0.21

intentionally was not added to the synthesis solution in order to obtain zeolite samples containing a “natural,” impurity level of Fe. Therefore, the HZSM-5<sub>200Fe</sub> was prepared with deionized water, and during the HZSM-5<sub>70Fe</sub> synthesis only bidistilled water was used.

For activation, all zeolites were pretreated by steam (310 mbar) in nitrogen at 823 K for 3 h. Before the measurements, the samples were calcined in flow of He for 1 h at 823 K. This pretreatment will be referred to from now on as “standard.”

## 2.2. Catalyst characterization

The analysis of chemical composition of the zeolites was carried out using atomic absorption spectroscopy (AAS) via a Shimadzu AA-6650 spectrometer with air–acetylene flame. For these measurements the samples were dissolved in hot aqua regia containing several drops of HF.

The specific surface areas (SSA) of the catalysts were measured using N<sub>2</sub> adsorption–desorption at 77 K via a Sorptomatic 1990 instrument (Carlo Erba). Before the measurements, the catalysts were heated in vacuum at 250 °C for 2 h. The SSA of the samples was calculated employing the BET method while the Dollimore/Heal method was applied for the calculation of pore volume.

X-ray diffraction (XRD) patterns of catalysts were obtained on a Siemens D500 diffractometer with Cu-K $\alpha$  monochromatic radiation ( $\lambda = 1.5406 \text{ \AA}$ ).

Infrared diffuse-reflectance spectroscopy (DRIFTS) studies were performed via a FT-NIR spectrometer (Perkin-Elmer 2000) with a TGS detector. The spectra of the samples were taken in Ar at 823 K after the pretreatment under the same conditions for 1 h in a high-temperature in situ cell (SpectraTech 0030-102). The spectra were obtained by averaging of 64 scans with a resolution of 4 cm<sup>-1</sup> with respect to KBr powder.

## 2.3. Transient response, reactivity, and temperature-programmed desorption studies

The determination of the concentration of active sites, reactivity, and temperature-programmed (TPD) studies were performed in a Micromeritics AutoChem 2910 analyzer provided with a quartz plug-flow reactor. A ThermoStar 200 (Pfeiffer Vacuum) mass spectrometer was used to control the composition of the gas phase. It was calibrated using gaseous mixtures of known compositions. The intensity of the fol-

lowing peaks was measured simultaneously: 4, 18, 28, 30, 32, 40, 44, and 46 *m/e*.

The amount of a catalyst placed into the reactor was 1.04–1.09 g. The catalysts were pretreated in He (> 99.999%, 50 ml (STP)/min) at different temperatures 823–1323 K for 1 h and then cooled in He to the temperature of the transient response experiment (473–653 K). The latter was performed by a quick switch of the He flow to the flow of gaseous mixture: 2 vol% N<sub>2</sub>O/2 vol% Ar/96 vol% He at a flow rate 20 ml (STP)/min. Argon served as an inert tracer.

Effect of oxygen pretreatment was also studied after pretreatment of the catalyst at 1323 K in He and cooling to 823 K in He where a 10 vol% O<sub>2</sub> mixture in He was introduced for 1 h. Then the reactor was cooled in He to the temperature of the transient response experiment.

Nitrous oxide reacts with the catalyst resulting in the formation of gaseous nitrogen and oxygen bound by the catalyst [reaction (1)]. The amount of active sites was calculated by integration of the nitrogen peak area. The amount of nitrogen formed at 523 and 603 K was the same, indicating a complete occupation of active sites by oxygen. Formation of molecular oxygen was observed only at higher temperatures.

To study an effect of water on the amount of active sites, water was pulsed to the catalyst using a 0.5- $\mu$ l syringe via a special injector after the pretreatment of the catalyst (HZSM-5<sub>200Fe</sub> and HZSM-5<sub>1000Fe</sub>) and cooling to 473–523 K. Saturation of the sample with water vapor was controlled by the mass spectrometer. After a 15-min purge by He the N<sub>2</sub>O interaction was performed for 5 min.

Reactivity of adsorbed oxygen was characterized by CO interaction with the catalyst at 523 K. It was carried out as follows: after a pretreatment followed by the interaction with N<sub>2</sub>O to form (O)<sub>ad</sub>, the reactor was purged by He for 15 min and the mixture of 3 vol% CO in He (20 ml (STP)/min) was introduced for 6 min.

TPD measurements were performed in He (20 ml (STP)/min) after N<sub>2</sub>O interaction or after CO interaction with adsorbed oxygen. The gaseous composition was monitored in the range of 523–1250 K at a heating rate 30 K/min.

## 3. Results

### 3.1. Method of quantitative determination of active sites based on the transient response

The transient response method is widely used in catalytic research. In the present study the gas phase was monitored

in the reactor outlet after a step change of gas composition in the reactor inlet. The gas composition at the outlet as a function of time after a step change in the reactor inlet from He to a mixture of 2 vol%  $N_2O$ , 2 vol% Ar, and 96 vol% He for the HZSM-5<sub>1000Fe</sub> sample is presented in Fig. 1. The nonideal reactor behavior, as compared to the plug flow, is represented by the concentration–time profile of an inert tracer (Ar). In order to control if internal diffusion affects the responses, the blank experiment was carried out using quartz beads instead of the zeolite in the catalytic bed. The Ar responses were similar (Fig. 2), indicating that diffusion limitations do not play an important role.

It is seen from Fig. 1 that besides  $N_2O$  and Ar, also  $N_2$  appears, indicating the stoichiometric reaction (1) with concomitant formation of  $(O)_{ad}$ .  $N_2$  appears simultaneously

with Ar. A certain delay (about 35 s) is observed for  $N_2O$ . It can be concluded that when all active sites are blocked, the reaction stops. No molecular oxygen was detected at the outlet. The concentration of sites ( $C_{ad}$ ) is estimated from the amount of  $N_2$  released assuming that a single oxygen atom is chemisorbed on each active site and after the standard pretreatment the concentration found was  $C_{ad} = 4.9 \times 10^{17}$  sites/g.

In order to control if the formation of  $(O)_{ad}$  is reversible after interaction with  $N_2O$ , the reactor was purged by He and the transient response experiment with the  $N_2O$  mixture was repeated (Fig. 1). No evolution of  $N_2$  was detected, indicating that the formation of adsorbed oxygen was irreversible. At the same time, a delay in the  $N_2O$  response was again observed showing that  $N_2O$  is reversibly adsorbed. In-

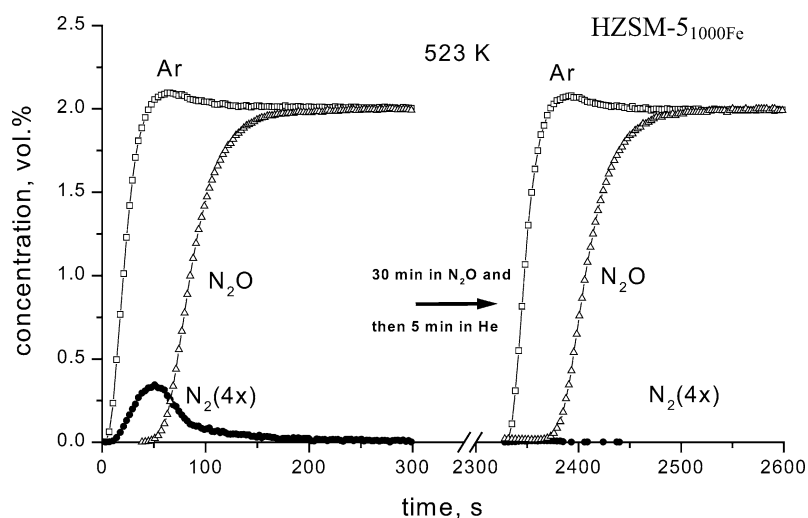


Fig. 1. Transient response curves obtained after introduction of the 2 vol%  $N_2O$ , 2 vol% Ar mixture in He on the HZSM-5<sub>1000Fe</sub> catalyst at 523 K after pretreatment in He at 823 K for 1 h.

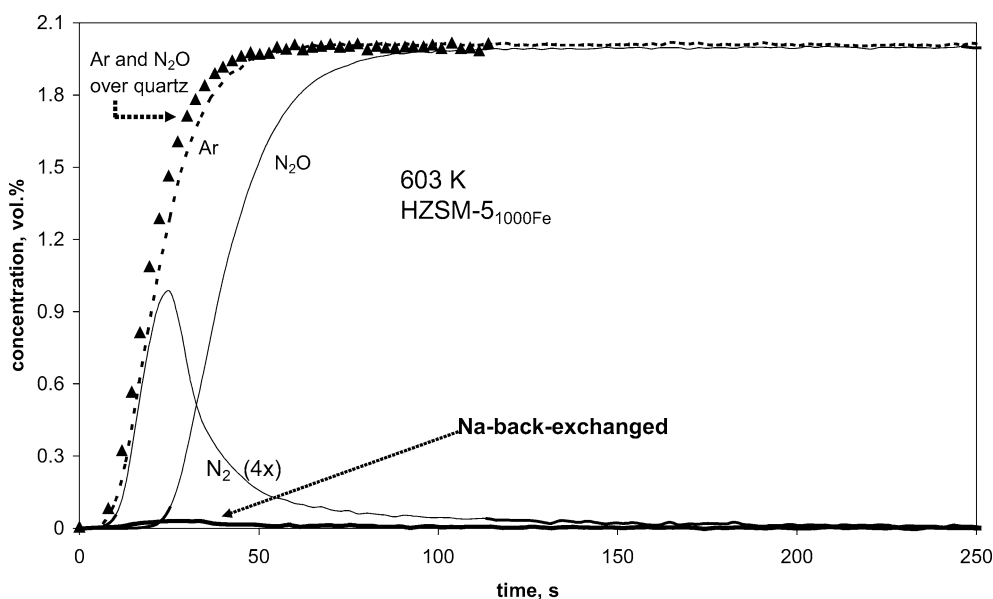


Fig. 2. Transient response curves obtained after introduction of the 2 vol.%  $N_2O$ , 2 vol% Ar mixture in He on quartz beads (triangles), HZSM-5<sub>1000Fe</sub>, and on the same sample after “non-aqueous back Na exchange” (only  $N_2$  response is shown) at 603 K after pretreatment in He at 823 K for 1 h.

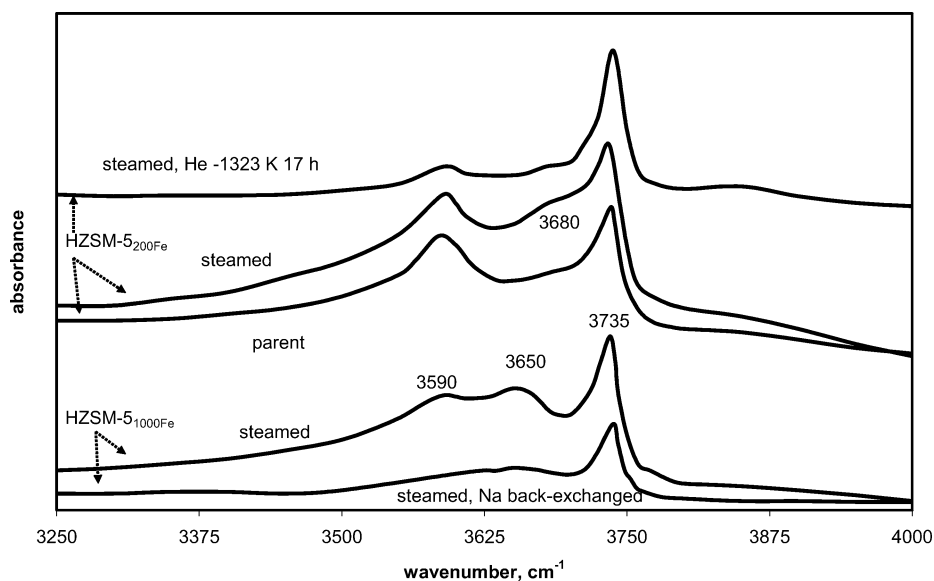


Fig. 3. DRIFT spectra of different HZSM-5<sub>200Fe</sub> and HZSM-5<sub>1000Fe</sub> catalysts taken with respect to KBr at 823 K after pretreatment in Ar in the in situ DRIFTS cell for 1 h at the same temperature.

tegration of the area between two responses (Ar and N<sub>2</sub>O) allows estimation of the amount of C<sub>N<sub>2</sub>O</sub>. It is worth noting that the amount of reversibly adsorbed N<sub>2</sub>O is more than one order of magnitude higher (C<sub>N<sub>2</sub>O</sub> = 12.0 × 10<sup>18</sup> sites/g) compared to the C<sub>ad</sub>. So, the C<sub>ad</sub> concentration was always determined from the N<sub>2</sub> released, but not from the amount of N<sub>2</sub>O consumed. This is in variance with the static method of Panov [3], which reported the equality of these amounts and used both of these values for the determination of the α-site concentration (corresponding in the present study to C<sub>ad</sub>). This variance is attributed to the higher partial pressure of N<sub>2</sub>O used in the present work (15 Torr instead of 0.2–0.4 Torr).

In order to verify the influence of the temperature on the concentration of active sites obtained (C<sub>ad</sub>), the transient response experiment was carried out at 603 K for the same catalyst (HZSM-5<sub>1000Fe</sub>) after the standard pretreatment (see Experimental). The results are presented in Fig. 2. The N<sub>2</sub> evolution is steeper, but the total amount of sites determined by the N<sub>2</sub>-peak integration remains almost the same: C<sub>ad</sub> = 5.7 × 10<sup>17</sup> sites/g. At the same time, the amount of reversibly adsorbed N<sub>2</sub>O diminished about 4 times: C<sub>N<sub>2</sub>O</sub> = 3.0 × 10<sup>18</sup> molecule/g, indicating a temperature dependence of the adsorption equilibrium constant.

### 3.2. DRIFT spectra of the samples after different treatments

Fig. 3 reports the spectra of the HZSM-5<sub>200Fe</sub> and HZSM-5<sub>1000Fe</sub> catalysts taken at 823 K after different treatments. The spectra consist of three main regions 3735, 3650–3680, and 3590 corresponding to terminal Si–OH, OH groups attached to extraframework cations, and bridged Si(OH)Al hydroxyls, respectively. It is seen from the spectra that zeolite steaming increases the OH groups on the extraframework cations (3680 cm<sup>-1</sup>) of the HZSM-5<sub>200Fe</sub> sample. Addi-

tional calcination of this catalyst at 1323 K in He results in a considerable decrease of OH groups, but they are still observed in the spectra.

### 3.3. Na-exchanged zeolites

The main difficulty in zeolite characterization used in this study is due to the low content of iron, hindering quantitative determination of their physico-chemical parameters. Therefore, the activated zeolites underwent a chemical treatment. It is known from the literature that sodium exchange of dealuminated ZSM-5 is not an easy process [12] since the exchange selectivity of HZSM-5 for various cations follows inversely their ionic radii. This favors the H<sub>3</sub>O<sup>+</sup> with an ionic radius of 1.5 Å versus sodium with an ionic radius of 0.95 Å. Even in the presence of large sodium excess under reflux and repeated operation, a complete exchange could not be observed. In order to prevent the active sites formed during catalyst activation (steaming and calcination) against the effect of water leading to the formation of H<sub>3</sub>O<sup>+</sup>, the Na exchange was performed from a nonaqueous solution of sodium methanolate in dried tetrahydrofuran (THF) called from now on “nonaqueous back Na exchange.” Under these “dry” conditions the ion exchange of H<sup>+</sup> (an ionic radius of 0.35 Å) will be favored toward Na<sup>+</sup> (an ionic radius of 0.95 Å) and should proceed to a much higher extent, if compared to the “aqueous conditions.”

The AAS analysis showed that iron was not removed after nonaqueous back Na exchange and its content remained 1000 ppm for the sample HZSM5<sub>1000Fe</sub>. The amount of Na introduced in this sample corresponded to 7650 ppm. In order to characterize Brønsted acidity, the DRIFT spectra were taken for the Na exchanged and H form of the ZSM-5<sub>1000Fe</sub> after standard pretreatment. The spectra are presented on the Fig. 3. It is seen that the amount of OH groups diminished,

especially in the region of more acidic hydroxyl groups ( $3650$  and  $3590\text{ cm}^{-1}$ ), which correspond to OH groups attached to extraframework cations and bridged Si(OH)Al hydroxyls.

At the same time the nonaqueous back Na exchange leads to a complete loss of the HZSM-5<sub>1000Fe</sub> activity in the benzene to phenol transformation [21]. Thus, at 623 K the benzene conversion over HZSM-5<sub>1000Fe</sub> (standard activation) was 25% with a phenol selectivity of 98%, but no conversion was observed over the same sample after nonaqueous back Na exchange. These results are at variance with the results reported by Sobolev et al. [22] who did not observe any change of activity after Na back exchange. We attribute this difference to the conditions of Na exchange, which was performed in a 1 M NaCl aqueous solution. Probably, under these conditions the protons in the active sites were not exchanged.

The transient response of N<sub>2</sub> over the HZSM-5<sub>1000Fe</sub> sample after nonaqueous back Na exchange is presented on Fig. 2. As it is seen, only small N<sub>2</sub> evolution was observed, indicating that almost no oxygen was deposited from N<sub>2</sub>O during its contact with the Na exchanged zeolite. So, the presence of Brønsted acidity in the zeolite seems to be important not only for the benzene reacting to form phenol by activation of the benzene molecule, but for the (O)<sub>ad</sub> formation as well. These results are in agreement with the observations by Notte [12], who reported a decrease of  $\alpha$ -site concentrations simultaneously with a decrease of Brønsted acid sites.

### 3.4. Relationship between (O)<sub>ad</sub> concentration and Fe content

Transient response experiments were carried out for the home-made catalysts after standard pretreatment and the N<sub>2</sub>

responses are shown in Fig. 4. The amount of (O)<sub>ad</sub> formed after N<sub>2</sub>O contact with zeolites is proportional to the total amount of iron (see inset in Fig. 4) and is independent on the Si/Al ratio. This is in agreement with similar observations for HZSM-5 zeolites with low Fe content reported [4,12].

### 3.5. Effect of calcination condition on the formation of active sites

The catalytic activity of Fe-containing HZSM-5 in N<sub>2</sub>O decomposition [16,18], genesis of  $\alpha$ -oxygen [3], and benzene hydroxylation by N<sub>2</sub>O [14] have been reported to be strongly dependent on the pretreatment conditions (catalyst activation), like temperature, time, and the gas atmosphere used. The activity in benzene oxidation to phenol and the concentration of (O)<sub>ad</sub> may vary by an order of magnitude [3], depending on the activation conditions, especially for the catalysts prepared from the isomorphously substituted HZSM-5 zeolites with a low Fe content. The necessity of mild steaming for these zeolites is well understood, but the conditions needed for the calcination step are not. To clear the latter points, after “standard steaming” (see Experimental), the calcination in He flow was performed for 1 h at different temperatures. After cooling the samples to 523 K, the active site concentration was measured by N<sub>2</sub>O decomposition under transient conditions. The results for HZSM-5<sub>200Fe</sub> are presented in Fig. 5 showing C<sub>ad</sub> as a function of the pretreatment temperature. Apparently, the calcination temperature strongly affects the C<sub>ad</sub> value. The temperature increase from 823 to 1023 K does not change the amount of active sites, heating further to 1173 K doubled their amount, and the calcination at 1323 K results in a drastic concentration change of more than one order of magnitude (from  $1.1 \times 10^{17}$  to  $1.2 \times 10^{18}$  sites/g). This agrees with the observations by Panov and co-workers who reported

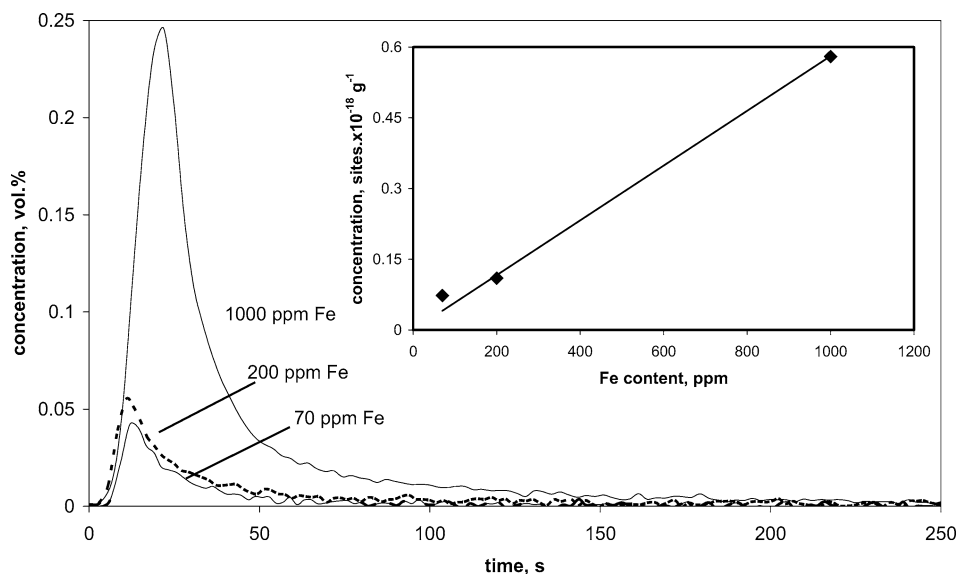


Fig. 4. N<sub>2</sub> response obtained after introduction of the 2 vol% N<sub>2</sub>O, 2 vol% Ar mixture in He on the HZSM-5<sub>1000Fe</sub>, HZSM-5<sub>200Fe</sub>, and HZSM-5<sub>70Fe</sub> catalysts at 603 K after pretreatment in He at 823 K for 1 h. Concentration of active sites as a function of the Fe content (inset).

a sixfold increase in  $\alpha$ -site concentrations after calcination in air at 1173 K [3]. If the calcination at 1323 K was performed for 8 h, the  $C_{ad}$  increased to  $2.1 \pm 0.1 \times 10^{18}$  sites/g and reached the stoichiometric maximum in the case of the sample HZSM-5<sub>200Fe</sub> with the total amount of Fe atoms of  $2.14 \times 10^{18}$  atoms/g. The response of N<sub>2</sub> at 523 K is shown for the catalyst pretreated in He at 1323 K in Fig. 6. No molecular oxygen was formed during this run; however, if the temperature was raised to 653 K, N<sub>2</sub>O decomposed stoichiometrically forming N<sub>2</sub> and O<sub>2</sub> with 100% conversion (see responses of O<sub>2</sub> and N<sub>2</sub> in Fig. 6).

According to Panov's work,  $\alpha$ -sites are the Fe(II)-containing sites, which cannot be oxidized by molecular oxygen at 823 K. In order to verify if the oxygen treatment can influence the  $C_{ad}$  value, the transient response was performed after pretreatment in He at 1323 K followed by an oxy-

gen calcination (10 vol% O<sub>2</sub> in He) at 823 K for 1 h. The results are shown on Fig. 7, indicating that the (O)<sub>ad</sub> concentration decreased about 20% from  $2.1 \pm 0.1 \times 10^{18}$  to  $1.75 \times 10^{18}$  atoms/g in a reproducible way. If the calcination in He flow at 1323 K was repeated, all active sites were regenerated. The effect of oxygen on the total amount of (O)<sub>ad</sub> was also checked with HZSM-5<sub>1000Fe</sub> calcined in He for 17 h. Similar to the HZSM-5<sub>200Fe</sub> catalyst, oxygen pretreatment at 823 K led to a small decrease ( $\sim 25\%$ ) of the total amount of active sites.

### 3.6. Effect of water on the formation of (O)<sub>ad</sub>

The presence of Brønsted acidity, as noted before, seems to be necessary for oxygen formation from N<sub>2</sub>O. From another view, a strong decrease of the zeolite activity in the

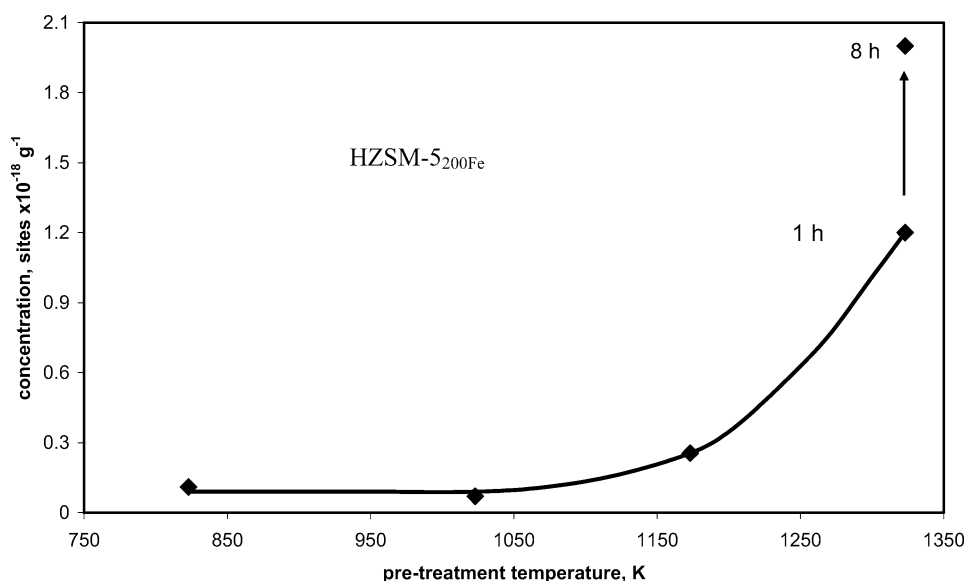


Fig. 5. Effect of the time and temperature pretreatment in He after steaming on the concentration of the active sites formed in the HZSM-5<sub>200Fe</sub> catalyst.

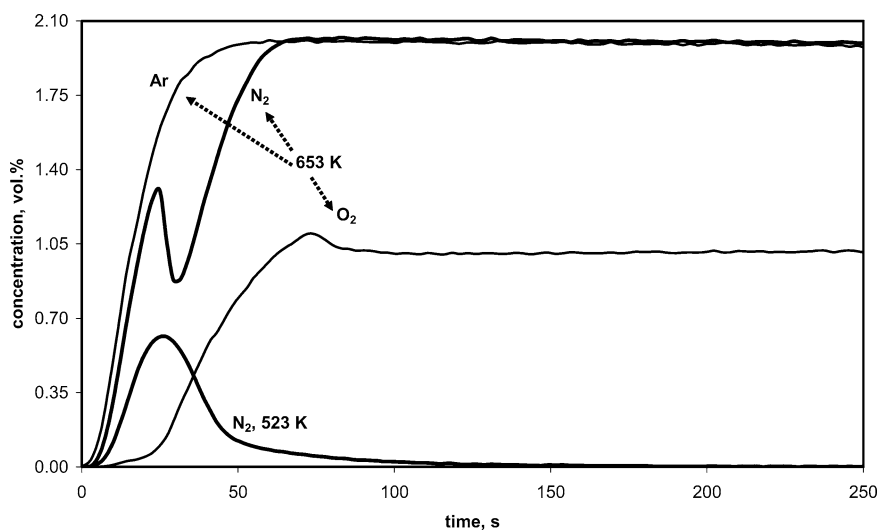


Fig. 6. Transient response curves obtained after introduction of the 2 vol% N<sub>2</sub>O, 2 vol% Ar mixture in He on HZSM-5<sub>200Fe</sub> at 523 K and at 653 K after pretreatment in He at 1323 K.

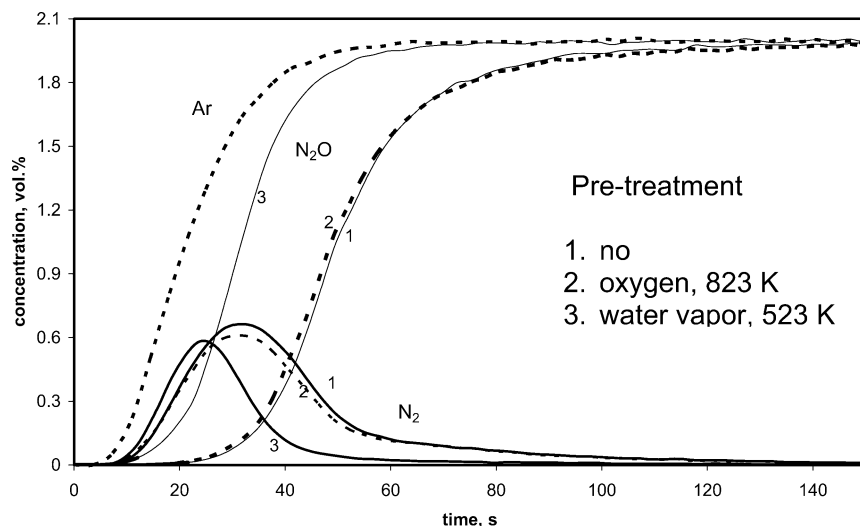


Fig. 7. Transient response curves obtained after introduction of the 2 vol%  $\text{N}_2\text{O}$ , 2 vol% Ar mixture in He on HZSM-5<sub>200Fe</sub> at 523 K after pretreatment in He at 1323 K (1) and after the same pretreatment followed by either oxygen (10 vol%  $\text{O}_2$  in He) calcination for 1 h at 823 K (2) or presaturation by water vapor at 523 K (3).

presence of water vapors has already been reported [17]. In order to understand this effect, we studied the influence of water on the  $(\text{O})_{\text{ad}}$  concentration. After the active site formation was completed, the sample HZSM-5<sub>200Fe</sub> was cooled to 523 K and water was introduced into the reactor by stepwise addition until saturation of the sites, which may adsorb water irreversibly. The transient response experiments are presented in Fig. 7. It is seen that the  $C_{\text{ad}}$  calculated from the  $\text{N}_2$  released decreases upon introduction of water. The  $(\text{O})_{\text{ad}}$  concentration of the sample saturated by water was  $C_{\text{ad}} = (1.0 \pm 0.1) \times 10^{18}$  sites/g, corresponding to about half of the active sites measured over dry zeolite. This result indicates that the chemisorption of oxygen atoms from  $\text{N}_2\text{O}$  is strongly affected by the presence of water.  $\text{H}_2\text{O}$  and  $\text{N}_2\text{O}$  molecules, both being highly polar, may compete for adsorption sites. It is interesting to note that only half of the sites are blocked by water and another half is still reactive toward  $\text{N}_2\text{O}$  decomposition.

To see the influence of the temperature on the blocking of the active sites by water,  $\text{N}_2\text{O}$  was reacted with zeolite at 473 K after  $\text{H}_2\text{O}$  was irreversibly adsorbed at the same temperature. The total amount of  $(\text{O})_{\text{ad}}$  almost did not change, as compared to 523 K, being equal to  $(0.9 \pm 0.1) \times 10^{18}$  sites/g.

In order to verify if this effect is valid for other catalysts, the  $(\text{O})_{\text{ad}}$  concentration was measured on the sample HZSM-5<sub>1000Fe</sub> before and after saturation by water as described above. The value  $C_{\text{ad}} = 0.53 \times 10^{18}$  sites/g was obtained on wet zeolite in comparison with  $C_{\text{ad}} = 1.01 \times 10^{18}$  sites/g measured on the dry sample pretreated in He at 1323 K for 1 h.

Fig. 7 shows a strong decrease in the amount of reversibly adsorbed  $\text{N}_2\text{O}$  after zeolite presaturation by  $\text{H}_2\text{O}$ , suggesting that the sites responsible for  $\text{N}_2\text{O}$  adsorption were also affected by  $\text{H}_2\text{O}$ .

### 3.7. Reactivity of $(\text{O})_{\text{ad}}$ in CO oxidation

The main particularity of the oxygen species formed by  $\text{N}_2\text{O}$  decomposition during its contact with (Fe)HZSM-5 is a high reactivity in oxidation reactions [4]. In the present study, the activity of  $(\text{O})_{\text{ad}}$  was characterized by the oxidation of CO. The  $\text{CO}_2$  responses during the CO interaction with the catalyst containing  $(\text{O})_{\text{ad}}$  deposited from  $\text{N}_2\text{O}$  are presented in Fig. 8. The responses differ depending if the sample was presaturated or not with water before oxygen deposition from  $\text{N}_2\text{O}$ . Thus, if  $(\text{O})_{\text{ad}}$  is formed on dry zeolite, a quick formation of  $\text{CO}_2$  was seen. The integration of the peak area gives the total amount of  $\text{CO}_2$  produced and characterizes the zeolite reactivity. For the dry zeolite the total amount of the  $(\text{O})_{\text{ad}}$  consumed (or  $\text{CO}_2$  formed) corresponds to about 65% of the total amount of  $(\text{O})_{\text{ad}}$  chemisorbed from  $\text{N}_2\text{O}$  ( $C_{\text{ad}}$ ). This means that the pool of deposited oxygen  $(\text{O})_{\text{ad}}$  consists of two different subpools: one with the oxygen capable of reacting with CO and the other subpool with the  $(\text{O})_{\text{ad}}$  being not active. The same result was reported by Sachtler and co-workers during the study of the isotopic exchange of oxygen on Fe/MFI [23]. The authors observed that the number of exchangeable oxygen atoms was smaller than the number of O atoms adsorbed from  $\text{N}_2\text{O}$ , and assigned this difference to the partial consumption of oxygen for the reoxidation of prerduced iron species. In the present study reductive pretreatment of zeolite in hydrogen was not carried out. But the calcination at high temperature in inert flow is also known to reduce strongly the Fe centers.

The oxidation of zeolite by molecular oxygen (10 vol% in He) at 823 K before interaction with  $\text{N}_2\text{O}$ , diminished the  $(\text{O})_{\text{ad}}$  concentration as noted above. Despite this pretreatment only  $\sim 70\%$  of deposited  $(\text{O})_{\text{ad}}$  is active in CO oxidation ( $C_{\text{ad}} = 1.75 \times 10^{18}$  sites/g,  $(\text{O})_{\text{ad}}$  active in CO oxidation is only  $1.27 \times 10^{18}$  sites/g) and this is an unexpected



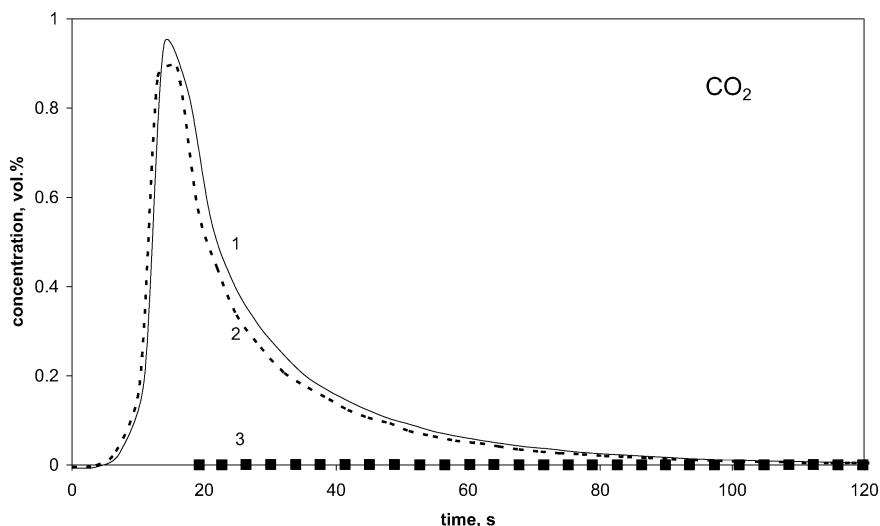


Fig. 8. CO<sub>2</sub> response curves obtained during interaction of CO (3 vol% CO in He, 523 K) with oxygen deposited from N<sub>2</sub>O on the HZSM-5<sub>200</sub>Fe catalyst at 523 K after pretreatment in He at 1323 K (1) and after the same pretreatment in He followed either by oxygen (10 vol% O<sub>2</sub> in He) calcination for 1 h, 823 K (2), or presaturation by water vapor ( $3.1 \times 10^{19}$  molecules/g) at 523 K (3).

Table 2

Concentration of oxygen (in O atoms  $\times 10^{-18}$ /g) after 5 min interaction with N<sub>2</sub>O at 523 K. The samples were activated in He at 1323 K for 8 h

Conditions of treatment (after He at 1323 K)	Deposited from N <sub>2</sub> O, 523 K	Reacted with CO at 523 K	Desorbed as O <sub>2</sub> in TPD up to 1323 K
–	1.9 ± 0.1	Not performed	1.2 ± 0.1 (sharp at 666 K)
–	2.0 ± 0.1	1.4 ± 0.1	0
10 vol% O <sub>2</sub> , 823 K, 1 h	1.8 ± 0.1	1.3 ± 0.1	0
10 vol% O <sub>2</sub> , 823 K, 1 h	1.8 ± 0.1	Not performed	1.2 ± 0.1 (sharp at 666 K)
Presaturation with water vapor at 523 K	1.0 ± 0.1	Not performed	0.8 ± 0.2 (broad at 940 K)
Presaturation with water vapor at 523 K	1.1 ± 0.1	0	0.7 ± 0.2 (broad at 940 K)

result. This indicates that molecular oxygen oxidized only a fraction of reduced iron sites and another fraction can be oxidized only by N<sub>2</sub>O. The high-temperature calcination in inert atmosphere (1323 K for 1 h) restored the initial value of  $C_{ad}$  and (O)<sub>ad</sub> concentration active in CO oxidation, showing that molecular oxygen was able to affect reversibly active sites.

Presaturation of zeolites with water drastically affects the surface reactivity. Not only the amount of O atoms chemisorbed from N<sub>2</sub>O becomes lower (see Fig. 7 and Table 2), but the oxygen species become inactive. Thus, after zeolite presaturation by water only half of (O)<sub>ad</sub> was formed ( $C_{ad} = 1.1 \times 10^{18}$  sites/g), if compared to the dry zeolite (Fig. 7). Even more important is that this oxygen species was not active for CO oxidation (Fig. 8, curve 3). A similar effect of water blocking the Fe sites for the isotopic exchange was reported by Sachtler and co-workers [23].

### 3.8. Temperature-programmed desorption of oxygen

TPD was applied to characterize the ability of (O)<sub>ad</sub> species to recombine forming O<sub>2</sub>. During CO oxidation

experiments two types of (O)<sub>ad</sub>, active and inactive, were detected upon pre-saturation by water with water, and therefore, the TPD measurements were performed over dry (Fig. 9a) and wet, or presaturated by water before interaction with N<sub>2</sub>O (Fig. 9b) of the HZSM-5<sub>200</sub>Fe sample. The evolution of O<sub>2</sub> from the dry sample appears as a sharp peak with a maximum at 666 K. Integration of the peak area gives the total amount of (O)<sub>ad</sub> recombined, which was found equal to the total amount of “active” (O)<sub>ad</sub> in CO oxidation. When TPD was performed from the catalyst reacted with CO, no O<sub>2</sub> evolution was observed (curve after CO, Fig. 9a). This indicates that (O)<sub>ad</sub>, which interacts with CO, corresponds to the oxygen desorbed at 666 K. This is characteristic of active (O)<sub>ad</sub> species.

The TPD profile of O<sub>2</sub> evolution from the sample pre-oxidized by molecular oxygen at 823 K is also presented in Fig. 9a. The form of the sharp peak at 666 K remains, but the total amount of the recombined oxygen did not change noticeably, being in quantitative agreement with the amount of (O)<sub>ad</sub> reacted with CO.

The TPD profile of O<sub>2</sub> evolution from the “water pre-saturated” sample (Fig. 9b) is completely different if com-

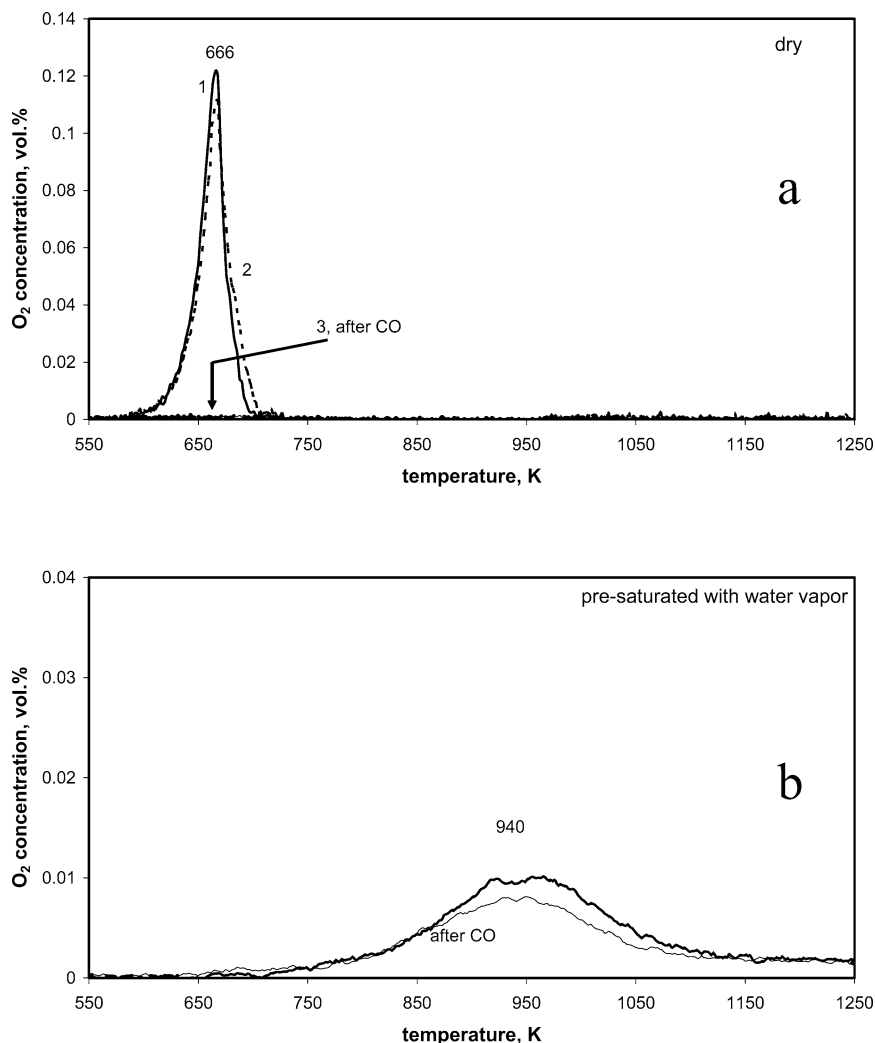


Fig. 9. TPD of oxygen after its deposition from  $N_2O$  (523 K) on the HZSM-5200Fe catalyst: (a) pretreated at 1323 K in He (curve 1) and after the same pretreatment followed either by oxygen (10 vol%  $O_2$  in He) calcination for 1 h at 823 K (curve 2) or after CO interaction at 523 K (curve 3); (b) after irreversible adsorption of water vapor at 523 K and after the same procedure followed by interaction with CO.

pared to the dry sample. Oxygen is desorbed showing a broad peak with a maximum at 940 K, indicating that another mechanism, like a surface spillover may be involved in  $(O)_{ad}$  recombination. If previous to the TPD experiment, CO was contacted with the pre-saturated by water catalyst, no  $CO_2$  was formed (Fig. 8). At the same time no significant change in the TPD profile was observed (response after CO, Fig. 9b). This confirms that  $(O)_{ad}$  formed on a wet surface is inactive. So, the TPD profile for the evolution of  $O_2$  can be considered as a characteristic (“fingerprint”) for active/inactive species.

It is worth noting that for the dry sample, the total amount of desorbed oxygen species ( $(1.2 \pm 0.1) \times 10^{18}$  atoms/g) is close to the amount removed during CO interaction ( $(1.3 \pm 0.1) \times 10^{18}$  atoms/g) and corresponds to about 65% of the  $(O)_{ad}$  chemisorbed from  $N_2O$  (concentration of active sites,  $C_{ad} = (2.0 \pm 0.1) \times 10^{18}$  atoms/g).

#### 4. Discussion

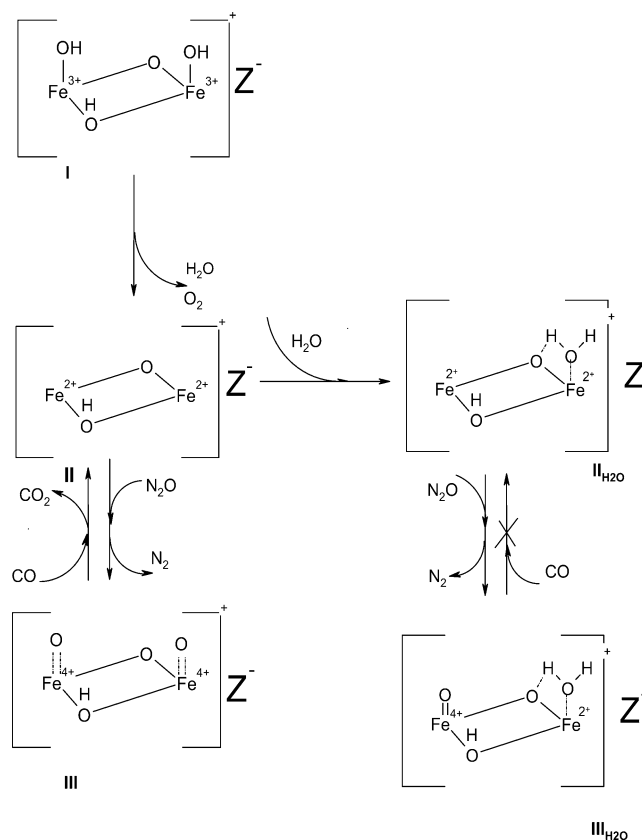
Based on the measurements of active site concentrations in HZSM-5 zeolites containing Fe in the range from 70 to 1000 ppm, it was found that the presence of Fe is essential for the formation of surface oxygen  $(O)_{ad}$  species from  $N_2O$ . Even Fe concentrations of 200–500 ppm, which are common in commercial or laboratory samples, make zeolite capable of  $(O)_{ad}$  chemisorptions from  $N_2O$  and zeolites become active in benzene to phenol oxidation by  $N_2O$ . This conclusion is in line with observations made by other groups [4,14].

It also follows from the present study that the presence of Fe in HZSM-5 is required, but not sufficient by itself to allow surface oxygen genesis and oxidative catalytic activity. The isomorphously substituted zeolites with Fe in the framework must be preactivated using mild steaming followed by high-temperature calcination in an inert atmosphere (see Fig. 5).

An important conclusion is that not all oxygen species formed on the surface from  $N_2O$  are chemically active for CO oxidation: the number of O atoms reacted with CO forming  $CO_2$  is not always identical to the number of  $(O)_{ad}$  deposited from  $N_2O$  after calcination in He at 1323 K. The maximum number of active  $(O)_{ad}$  species at temperature 523 K was  $\sim 65\%$  from the total amount of chemisorbed oxygen atoms. Moreover, the chemisorbed  $(O)_{ad}$  atoms formed on the zeolite presaturated by water were completely inactive in CO oxidation at 523 K. This unexpected result is at variance with the observations by Panov's group [24], who reported that all O atoms adsorbed (which they call  $\alpha$ -oxygen) and interacted with CO giving a stoichiometric amount of  $CO_2$ . The reason for this disagreement is not clear, but probably is related to the difference in the catalyst pretreatment. The oxidative treatment by molecular oxygen at 823 K was observed to decrease the total amount of  $(O)_{ad}$  with a concomitant decrease in the concentration of  $(O)_{ad}$  active in the CO oxidation. By the Panov group definition, the identity between the O species formed on the surface from  $N_2O$  ( $\alpha$ -sites) and the O species active in oxidative transformations is implicit. This assumption may be misleading when trying to explain the catalyst reactivity, since it may change drastically depending on the zeolite pretreatment.

In order to discuss the structure of iron-complex and active oxygen formation, based on the results of this study and taking into account the results reported on benzene to phenol transformations [3,12,15,21], some additional assumptions are necessary. The recent studies by the group of Sachtler on  $N_2O$  decomposition must be taken into consideration, despite the fact that the zeolites were prepared differently and contained a high amount of iron ( $Al/Fe = 1$ ,  $C_{Fe} = 4$  wt%) [17,23,25,26]. The active sites participating in the aforementioned processes seem to be identical, and seem to involve a binuclear Fe complex. Contrary to the present study, which deals mainly with the sample having a low content of iron, most of the studies were performed on zeolites with a high concentration of Fe. In these cases, besides an active binuclear Fe complex, other forms of iron may be present, as was confirmed experimentally. Combining these results with recent theoretical studies [27–29], a tentative structure for the active center and its formation can be proposed.

Water vapor was reported to accelerate the hydrolysis of Si–O–Fe bonds, leading to migration of Fe atoms from the crystalline lattice into the micropore space of the zeolite, thus facilitating Fe *ex*-framework formation. The *ex*-framework Fe center consists of a single metal oxo-cations ( $[FeO]^+$ , or  $[Fe(OH)_2]^+$ , as proposed by Bell and co-workers [30] and Sachtler and co-workers [17]. The steaming and calcination seem to induce surface migration forming a binuclear Fe center **I** (see Scheme 2). The presence of such binuclear Fe clusters in FeZSM-5 has been proven experimentally [19]. Although Prins and co-workers [19,31] considered two types of Fe clusters compensating one or



Scheme 2. Structure of  $[Fe_2O_2H]^+$  cluster formed during high-temperature calcinations of ZSM-5<sub>200</sub>Fe in inert flow and formation from  $N_2O$  of paired  $(O)_{ad}$  atoms active (**III**) in CO oxidation. Pathway of water interaction with  $[Fe_2O_2H]^+$  clusters and formation from  $N_2O$  a single  $(O)_{ad}$  inactive in CO oxidation.

two lattice charges, we include in our scheme only the first one. The cluster with structure **I** has only one Al atom in the vicinity for the charge compensation. This, in turn, increases the probability that such complexes exist, especially in the zeolites with high Si/Al ratios. Calcination at high temperature in inert atmosphere leads to dehydroxylation (as shown by DRIFTS experiments in this study) and concomitant autoreduction of binuclear center **I**, forming binuclear structure **II** according to the Scheme 2.

The existence of a reduced binuclear iron complex with bridging oxygen was previously postulated by Sachtler et al. [17,23], and Panov et al. [3,32,33] based on studies by IR, Mössbauer, ESR spectroscopies, and TPR. Literature results indicate that the Fe complexes should be located at the ion-exchange positions of the zeolite, having an overall monopositive charge. The structure of binuclear Fe complex **II** requires an Al-centered tetrahedral configuration in its vicinity for charge compensation. In Scheme 2 this is represented as  $Z^-$ , indicating that the zeolite framework itself  $\{(Si,Al)O_n\}^-$  acts as a crystalline acidic anion [34,35]. The presence of proton in the diamond core equilibrates the charge of the  $[Fe_2O_2]^{2+}$  complex. In this form it can act as extraframework monopositive  $[Fe_2O_2H]^+$  counterion.

The structure of active binuclear Fe center **II** is rather different from that proposed by Sachtler and co-workers [17]  $[\text{Fe}-\text{O}-\text{Fe}]^{2+}$ , which features both metal atoms bound at ion-exchange positions. The latter structure is also different compared to structure **B** proposed by Panov (see Scheme 1), which consists of a  $\mu$ -hydroxo group, but does not have the second oxygen atom bound to both Fe atoms. We propose the active Fe center in the form of  $[\text{Fe}_2\text{O}_2\text{H}]^+$  cluster featuring a “diamond core” structure similar to that of the monooxygenase enzyme [5,6,36,37]. From our point of view, structure **II** follows from the reductive dehydroxylation of complex **I**, the existence of which was confirmed by EXAFS experiments by Prins and co-workers [19]. No other structures of Fe-containing species are considered in this study due to the fact that for the sample HZSM-5<sub>200Fe</sub> all Fe atoms ( $2.1 \times 10^{18}$  atoms/g) were observed to be active toward  $(\text{O})_{\text{ad}}$  formation and water adsorption diminished this amount by one-half. For sample HZSM-5<sub>1000Fe</sub>, only part of Fe atoms was active, but after saturation by water a half also remained active toward  $(\text{O})_{\text{ad}}$  formation. We consider this result as an indirect sign of paired arrangement of Fe atoms in the active center.

When structure **II** reacts with  $\text{N}_2\text{O}$ , structure **III** is formed with two terminal ferryl groups  $[\text{Fe}=\text{O}]$ . This is in line with the prediction by DFT analysis for a terminal Fe–O group distance of 1.61 Å, indicating strong double-bond character [28]. We assume that CO interacts with the active terminal oxygen atoms forming  $\text{CO}_2$ .

The effect of zeolite presaturation by irreversibly adsorbed water is also shown in Scheme 2. The adsorption of one water molecule proceeds on two neighboring sites ( $\text{O}-\text{Fe}^{2+}$ ) forming structure **II**<sub>H<sub>2</sub>O</sub>, and the binuclear Fe center becomes a single Fe site. Therefore, the remaining part of the binuclear diamond core cannot accept a second  $\text{H}_2\text{O}$  molecule. But it is able to adsorb  $\text{N}_2\text{O}$  forming terminal oxygen in the structure **II**<sub>H<sub>2</sub>O</sub> and releasing  $\text{N}_2$ .

The assumption about  $\text{H}_2\text{O}$  blocking half of the Fe atoms may explain “a magic number” of  $0.5 \times C_{\text{ad}}$  obtained after saturation by water in two of the samples studied. The hydroxylated form of a binuclear Fe center acts as a single Fe site. This conclusion is in agreement with the results of DFT calculations [28], which showed that the hydroxylated form of a binuclear Fe center consists of one Fe ion completely saturated by water in the first coordination sphere. The result with  $\text{H}_2\text{O}$  blocking one-half of the Fe atoms also indirectly confirms the presence of proton in the binuclear diamond core, since otherwise two molecules of  $\text{H}_2\text{O}$  could be accommodated during adsorption on a  $[\text{Fe}_2\text{O}_2]^{2+}$  center.

It is important to note that the ability of zeolite to form active sites in the form of a binuclear Fe center depends on different factors like total Fe concentration, pretreatment conditions, and probably, Si/Al ratio. Thus, in the sample ZSM-5<sub>200Fe</sub> all the Fe atoms introduced in the zeolite were involved in the active sites forming  $(\text{O})_{\text{ad}}$ , contrary to the ZSM-5<sub>1000Fe</sub> sample, in which only a part of the Fe atoms was active. So, Fe atoms may be present in different forms

( $\text{Fe}_2\text{O}_3$  nanoparticles, single metal oxo-cations, framework ions, etc.), as observed by other groups for this type of zeolite, but these iron species were reported to be not catalytically active.

Temperature-programmed desorption results also support the structure stated above: coupling of neighboring  $(\text{O})_{\text{ad}}$  in structure **III** is more easy, if compared to the single  $(\text{O})_{\text{ad}}$  atoms recombination from the structure **III**<sub>H<sub>2</sub>O</sub>, which should involve surface diffusion. Therefore, the  $\text{O}_2$  evolution from complex **III** appears as a sharp peak at 666 K in the TPD profile, and from the complex **III**<sub>H<sub>2</sub>O</sub> as a broad feature between 600 and 1250 K with the maximum at 940 K.

The structure of the binuclear Fe center proposed explains the results obtained for the activity of  $(\text{O})_{\text{ad}}$  in CO oxidation. As shown the Scheme 2, structure **II** can accept two O atoms leading to the form **III**. We assume that CO interacts with active terminal oxygen atoms of structure **III** forming  $\text{CO}_2$ .

Only paired terminal O atoms adsorbed on the  $[\text{Fe}_2\text{O}_2\text{H}]^+$  sites of the binuclear center seem to be active in CO interaction, and the single  $\text{O}_{\text{ad}}$  atoms generated on an Fe site in the hydroxylated binuclear complex (**III**<sub>H<sub>2</sub>O</sub>) are inactive. This leads us to the conclusion about the importance in redox processes of the paired arrangement of active terminal oxygens bound to two Fe atoms in a diamond core geometry in analogy to the binuclear structure of active Fe sites in MMO. Another explanation of inactivity of single  $\text{O}_{\text{ad}}$ -atoms in the complex (**III**<sub>H<sub>2</sub>O</sub>) is based on its instability due to easy electron transfer from  $\text{Fe}^{2+}$  to  $\text{Fe}^{4+}$  resulting in the structure **I**. This activation becomes impossible in the complex saturated by water.

## 5. Conclusions

1. A method for quantitative determination of the active Fe-containing sites responsible for the formation of  $(\text{O})_{\text{ad}}$  species from  $\text{N}_2\text{O}$  is developed based on the transient response with a sensitivity level up to few dozen ppm of Fe.
2. The Fe presence in HZSM-5 is required, but not sufficient, for the surface-active site formation. The isomorphously substituted zeolites with a low content Fe in the framework must be preactivated using mild steaming followed by high-temperature calcinations in an inert atmosphere.
3. Based on the literature results and the findings of this study a tentative structure of an active binuclear Fe center featuring a diamond core geometry, similar to that of the monooxygenase enzyme, is suggested. It includes one  $\text{H}^+$  ion and has an overall monopositive charge  $[\text{Fe}_2\text{O}_2\text{H}]^+$ .
4. Only a part of  $(\text{O})_{\text{ad}}$  adsorbed from  $\text{N}_2\text{O}$  was active in CO oxidation at 523 K. This active oxygen quantitatively corresponded to the O atoms, which appeared in the TPD profile as a sharp peak at 666 K, indicating a desorption mechanism via direct recombination. These

active O atoms were assigned to the paired terminal oxygens each bound to one Fe site in the diferric  $[\text{Fe}_2\text{O}_2\text{H}]^+$  diamond core cluster.

5. Zeolite presaturated by water vapor, generates  $(\text{O})_{\text{ad}}$  species from  $\text{N}_2\text{O}$ , which appeared in a TPD profile as a broad peak with a maximum at 940 K, indicating a slow, probably diffusion-controlled recombination mechanism. The total amount of the adsorbed oxygen corresponded to half of the stoichiometric amount of Fe atoms in the sample. This suggests that water blocks one-half of the binuclear center, and the remaining part acts as a single Fe site. The  $(\text{O})_{\text{ad}}$  species adsorbed on single Fe sites were completely inactive in the CO oxidation.

## Acknowledgments

Authors highly appreciate the contributions of Dr. B. Louis, E. Casali, and A. Udriot to this work. Financial support from Swiss National Science Foundation is gratefully acknowledged.

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