



Transient response method for characterization of active sites in HZSM-5 with low content of iron during N₂O decomposition

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Abstract

The surface active Fe-sites in HZSM-5 with low content of iron (<1000 ppm) activated by steaming and high temperature (up to 1323 K) calcination in inert lead to the formation of surface oxygen (O)_{ad} species from N₂O and were characterized quantitatively by transient response method. Only a part of (O)_{ad} deposited on zeolite by decomposing N₂O was active in CO oxidation at 523 K. A binuclear Fe-center is suggested as an active center, featuring a “diamond core” structure, similar to that of the monooxygenase enzyme. The active O-atoms were assigned to the paired terminal oxygen atoms each bound to one Fe-site in the binuclear [Fe₂O₂H]⁺-cluster.

Zeolite pre-saturated by water vapor at 473–523 K generates (O)_{ad} species from N₂O completely inactive in the CO oxidation. The total amount of the oxygen, (O)_{ad}, deposited on the pre-saturated by water zeolite corresponds to a half of stoichiometric amount of the surface Fe-atoms and suggests that water blocks a half of the binuclear [Fe₂O₂H]⁺-center, the remaining acting as a single Fe-site.

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1. Introduction

The nature of active sites in HZSM-5 zeolites with low content of Fe-ions (herein after H(Fe)ZSM-5) during benzene oxidation to phenol and direct N₂O decomposition is the focus of much interest. There is a wide consensus concerning the Fe-ions activity, but the specific nature of the active sites, especially the Fe nucleation, remains an open question. Activity was assigned by Panov and co-workers [1] to binuclear iron clusters in the zeolite extra-framework, where each Fe²⁺-site would be able to generate one active O-atom from N₂O, called α-oxygen. This α-oxygen was claimed to have high oxidative power converting CO to CO₂, or forming phenol from benzene at low temperatures [1,2]. But the experimental evidence for the stabilization of isolated iron cations after zeolite steaming has also to be taken into account [3,4]. Besides, the Fe²⁺-sites were studied experimentally [5], theoretically [6,7] and the DFT calculations of a benzene oxidation assuming mononuclear iron site have been recently published by Kachurovskaya et al. [8].

In spite of significant efforts, the characterization of active sites in H(Fe)ZSM-5 materials remains a challenge mainly due to low content of iron. Until now the concentration of active Fe-sites has been measured in a static vacuum set-up from the amount of the N₂ released or the N₂O consumed [1]. Another question: Is every oxygen atom deposited on the surface from N₂O able to participate in oxidative reactions? Only Panov's group has addressed this point.

We report herein the first application of a transient response method to determine quantitatively the iron active sites concentration starting from a few dozens of ppm. It is important to note that the measurements are carried out under normal pressure and at the reaction temperature. The number of active sites is defined as the number of N₂O molecules that can be decomposed on the zeolite



We concentrated on answering the two questions: (1) how the pre-treatment of the H(Fe)ZSM-5 influences the (O)_{ad} formation and its activity and (2) has every oxygen atom (O)_{ad} deposited on the surface from N₂O the same oxidative power? Activity of the deposited oxygen was characterized by its ability to oxidize CO.

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2. Experimental

The hydrothermal synthesis of $\text{HZSM-5}_{200\text{Fe}}$ has been described in details in our recent publication [9]. It is important to note that iron source was not added to the synthesis solution in order to obtain zeolite samples containing “natural”, impurity level of Fe. The deionized water was used in the preparation of $\text{HZSM-5}_{200\text{Fe}}$ with iron concentration of 200 ppm and $\text{Si/Al} = 42$ as measured by atomic absorption spectroscopy in a Shimadzu AA-6650 spectrometer. The $\text{HZSM-5}_{1000\text{Fe}}$ with Si/Al ratio = 25 was kindly provided by Uetikon SA (Switzerland).

For activation, the samples were pre-treated by steam (310 mbar) in nitrogen at 823 K for 3 h and calcined in flow of He for 1 h at 823 K.

The active sites concentration measurements, 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 gas phase. The catalysts (1.04–1.09 g) after pre-treatments were cooled down in He to the temperature of the transient response (523–653 K). The latter was performed by a quick switch of the He flow to the flow of gaseous mixture: 2 vol.% N_2O /2 vol.% Ar/96 vol.% He at a flow-rate 20 ml (STP)/min. N_2O reacts with the catalyst resulting in the formation of gaseous nitrogen and oxygen bound by the catalyst according to the reaction (1). The amount of active sites was calculated by integration of the nitrogen peak area. In the experiments with water, H_2O was pulsed to the reactor at 523 K using a 0.5 μl syringe via a special injector controlling the sample saturation by the mass-spectrometer.

Reactivity of adsorbed oxygen was characterized by CO oxidation to CO_2 by the catalyst containing $(\text{O})_{\text{ad}}$ deposited from N_2O at 523 K. The reactor was purged by He for 15 min after sample interaction with N_2O , temperature was set to 523 K and the mixture of 3 vol.% CO in He (20 ml (STP)/min) was introduced for 6 min.

3. Results and discussion

3.1. Quantitative determination of Fe-sites by the transient response method

The gas-phase composition was monitored in the reactor outlet after a step change of gas composition in the reactor inlet. The results for the $\text{HZSM-5}_{1000\text{Fe}}$ sample are shown in Fig. 1. The non-ideal reactor behavior, as compared to the plug-flow, is represented by the concentration-time profile of an inert tracer (Ar). 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 $(\text{O})_{\text{ad}}$. 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 covered by $(\text{O})_{\text{ad}}$, the reaction stops. No molecular oxygen was detected at the outlet since N_2O decomposition on N_2 and O_2 starts at higher temperatures (9). The concentration of active Fe-sites (C_{Fe}) is estimated from the amount of N_2 released and after the standard pre-treatment was $C_{\text{Fe}} = 5.8 \times 10^{17}$ molecules/g.

In order to control if the formation of $(\text{O})_{\text{ad}}$ is reversible, after interaction with N_2O the reactor was purged by He and the transient response experiment with the N_2O mixture was

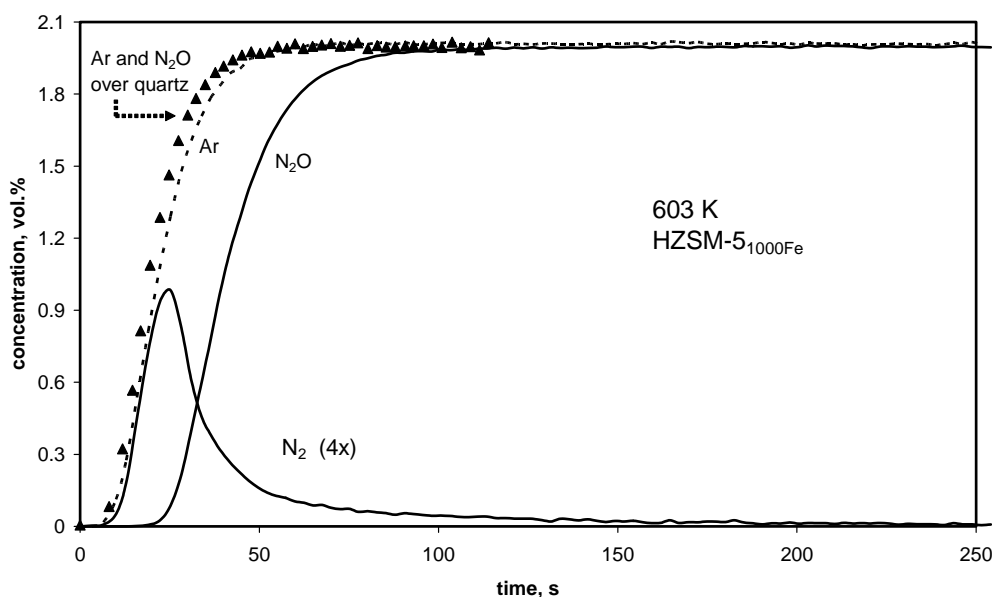


Fig. 1. Transient response curves obtained after introduction of the 2 vol.% N_2O , 2 vol.% Ar mixture in He on quartz beads (\blacktriangle), $\text{HZSM-5}_{1000\text{Fe}}$ at 603 K after standard activation and pre-treatment in He at 823 K for 1 h.

repeated. No evolution of N_2 was detected indicating that the formation of adsorbed oxygen was irreversible.

3.2. Effect of the catalyst pre-treatment on the formation of active Fe-sites

The catalytic activities of Fe-containing HZSM-5 have been reported to be strongly dependent on the pre-treatment conditions (catalyst activation), like temperature, time, and the gas atmosphere used. Therefore, after “standard pre-treatment” the calcination in He flow was performed during 1 h at different temperatures and the C_{Fe} concentration was measured by transient response method. The results for HZSM-5_{200Fe} are presented in Fig. 2 showing C_{Fe} as a function of the pre-treatment temperature and time. 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 1.1×10^{17} to 1.2×10^{18} sites/g). If the calcination at 1323 K was performed for 8 h, the C_{ad} increased up to $2.1 \pm 0.1 \times 10^{18}$ sites/g and reached the stoichiometric maximum for the sample HZSM-5_{200Fe} with the total amount of Fe-atoms of 2.14×10^{18} atoms/g. It is important to note that the active Fe-sites *once formed do not disappear* due to re-hydroxylation. The sample HZSM-5_{200Fe} after calcinations in He at 1323 K for 8 h was exposed for an ambient atmosphere, and even saturated by water vapors at 473 K, but after standard calcinations at 823 K for 1 h the same amount of $C_{Fe} = (2.0 \pm 0.1) \times 10^{18}$ sites/g was detected. So, the isomorphously substituted zeolites with Fe in the framework must be pre-activated by mild steaming followed by high temperature calcination in an inert (see Fig. 2). Water

vapor was reported to accelerate the hydrolysis of Si–O–Fe bonds, leading to Fe ex-framework formation as a single oxo-cations ($[FeO]^+$, or $[Fe(OH)_2]^+$ [10,11]. Surface migration of iron may lead to the binuclear Fe-center **I** (see Scheme 1), and its presence in FeZSM-5 has been proven experimentally [12]. Calcination in inert at high temperature leads to dehydroxylation and auto-reduction of binuclear center **I**, forming structure **II** according to the scheme.

The influence of water on the concentration of oxygen (O_{ad}) deposited from N_2O was studied. After the active Fe-sites formation was completed, the HZSM-5_{200Fe} was cooled down to 523 K and water was introduced into the reactor until saturation. The transient responses are presented in Fig. 3. It is seen that the (O_{ad}) concentration deposited on the sample saturated by water was much less as compared to the “dry” sample being $(1.0 \pm 0.05) \times 10^{18}$ atoms/g. This corresponds to about half of the active Fe-sites measured over “dry” HZSM-5_{200Fe}. It is interesting to note that only a half of sites are blocked by water and another half is still reactive towards N_2O decomposition. In order to verify if this effect is valid for other catalysts, the (O_{ad}) concentration was measured on the sample HZSM-5_{1000Fe} before and after saturation by water as described above. The value $C_{ad} = (0.5 \pm 0.05) \times 10^{18}$ sites/g was obtained on “wet” zeolite in comparison with $C_{ad} = (1.0 \pm 0.05) \times 10^{18}$ sites/g measured on the “dry” sample pre-treated in He at 1323 K for 17 h. We consider this result as indirect sign of paired arrangement of Fe-atoms in the active center. The structure of binuclear Fe-complex **II** requires an Al-centered tetrahedral configuration in its vicinity for charge compensation. In the scheme this is represented as Z^- indicating that the zeolite framework itself $[(Si, Al)O_n]^-$ acts as a crystalline acidic anion [13].

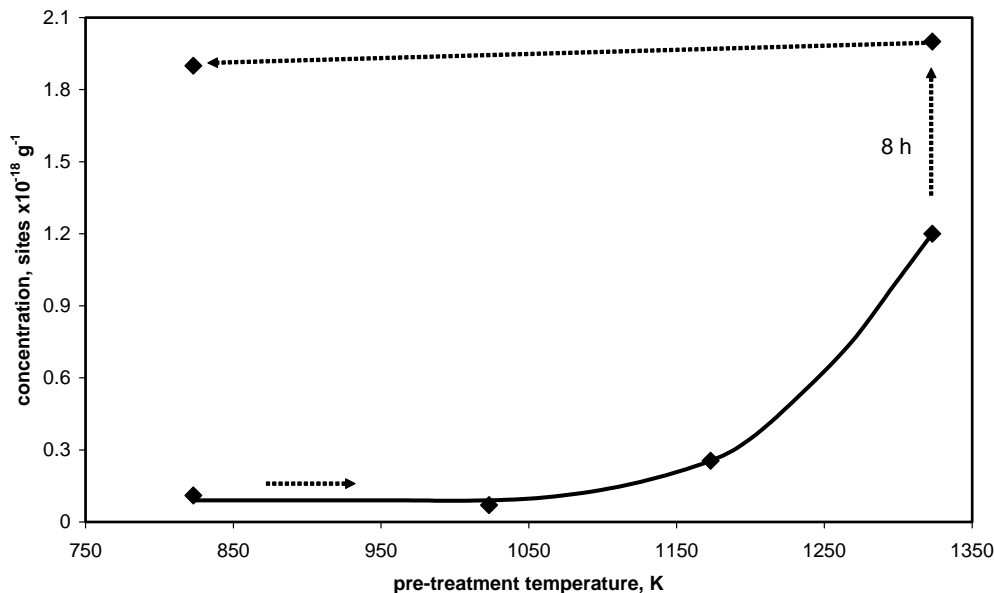
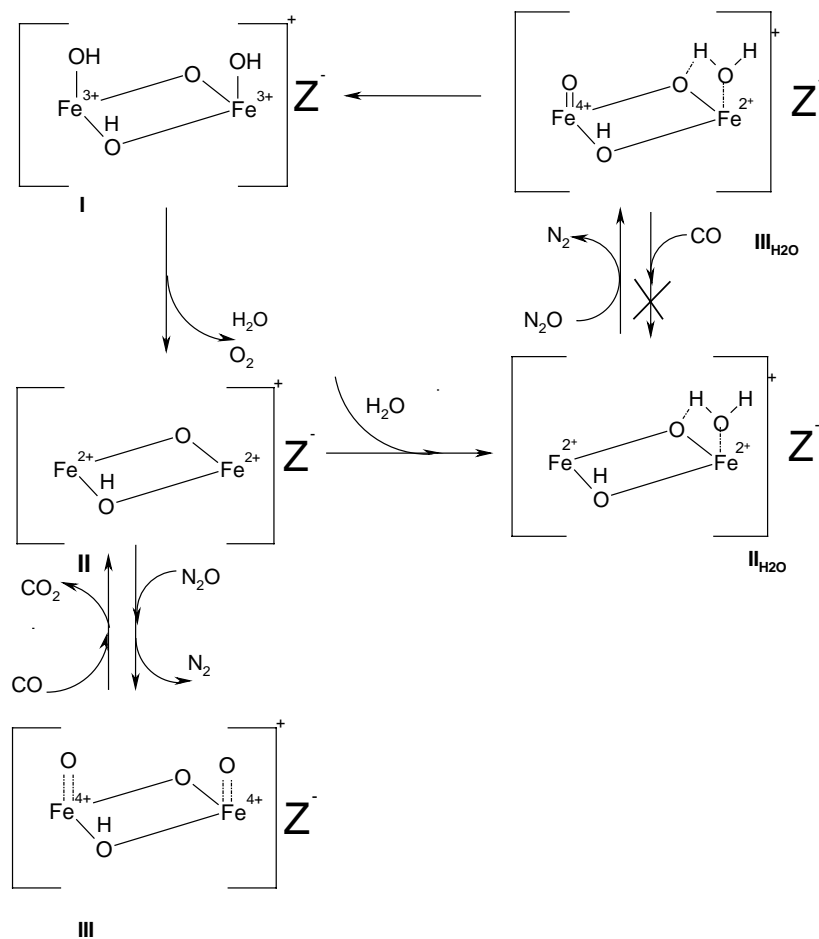


Fig. 2. Effect of the pre-treatment temperature (in He) and time on the concentration of active sites in the HZSM-5_{200Fe} catalyst.



Scheme 1. Structure of $[\text{Fe}_2\text{O}_2\text{H}^+]$ -cluster formed during high temperature calcinations of ZSM-5_{200Fe} in inert flow and formation from N_2O of paired $(\text{O})_{\text{ad}}^{\text{act}}$ species active in CO oxidation (III). Pathway of water interaction with $[\text{Fe}_2\text{O}_2\text{H}^+]$ -clusters leading to the zeolite inactive in CO oxidation.

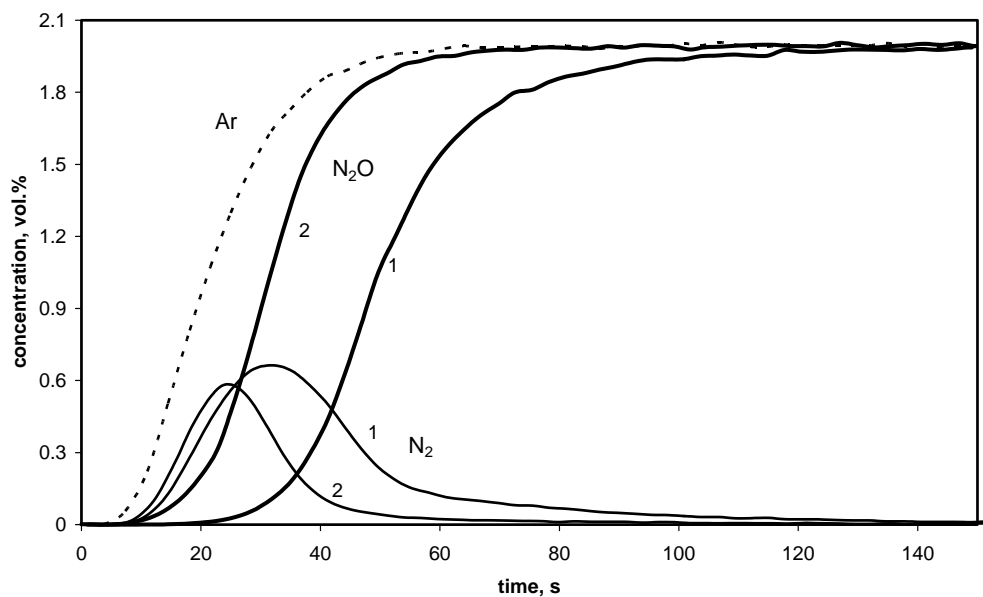


Fig. 3. Transient response curves obtained after introduction of the 2 vol.% N_2O , 2 vol.% Ar mixture in He on HZSM-5_{200Fe} at 523 K after the pre-treatment in He at 1323 K (1) and after the same pre-treatment followed by pre-saturation by water vapor at 523 K (2).

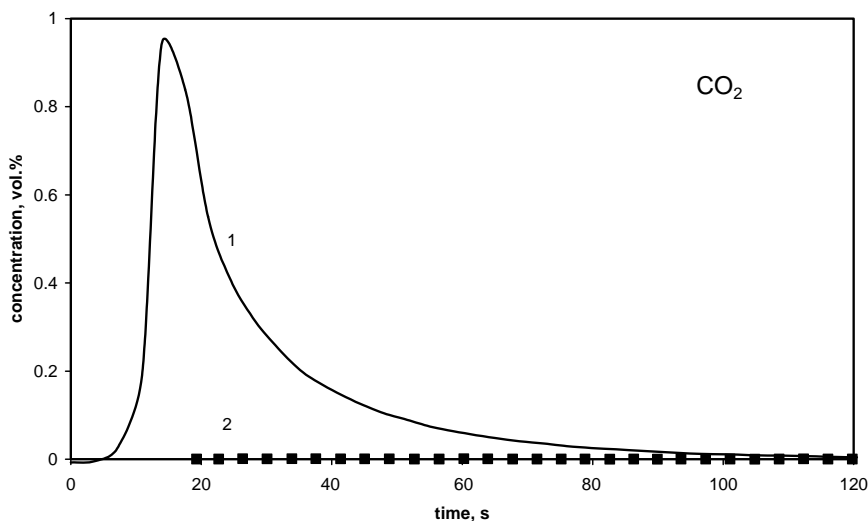


Fig. 4. CO₂ response curves obtained during interaction of CO (3 vol.% CO in He, 523 K) with oxygen deposited from N₂O on the HZSM-5_{200Fe} catalyst at 523 K after the pre-treatment in He at 1323 K (1) and after the same pre-treatment in He followed by pre-saturation with water vapor (3.1×10^{19} molecules/g) at 523 K (2).

3.3. Reactivity of (O)_{ad} in CO oxidation

The main particularity of the oxygen species formed by N₂O decomposition during its contact with H(Fe)ZSM-5, is a high reactivity in oxidation reactions [14]. In the present study, the activity of (O)_{ad} was characterized by its ability to oxidize CO. The CO₂ responses during the CO interaction with the catalyst containing (O)_{ad} deposited from N₂O are presented in Fig. 4 for the sample pre-saturated and not with water before oxygen deposition from N₂O. If (O)_{ad} is formed on “dry” zeolite, a quick formation of CO₂ was seen. The integration of the peak area gives the total amount of CO₂ produced and characterizes the zeolite reactivity. For the “dry” zeolite the total amount of the (O)_{ad}^{act} consumed (or CO₂ formed) corresponds to about 65% of the total amount of (O)_{ad} chemisorbed from N₂O (C_{Fe}). This means that the pool of deposited oxygen (O)_{ad} consists of two different sub-pools: one with the oxygen capable of reacting with CO ((O)_{ad}^{act}) and the other sub-pool with the inactive oxygen ((O)_{ad}^{inac}). Pre-saturation of zeolites with water drastically affects the surface reactivity: the oxygen species become inactive. Thus, after HZSM-5_{200Fe} pre-saturation by water only half of oxygen was deposited (C_{Fe} = 1.1×10^{18} sites/g), if compared to the “dry” zeolite and this oxygen species was not active for CO oxidation (Fig. 4, curve 2).

To explain the results obtain, we suggest the structure **III** formed with two terminal ferryl groups [Fe=O] when the structure **II** reacts with N₂O. 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 [15]. We assume that CO interacts with the active terminal oxygen atoms forming CO₂. The adsorption of one water molecule proceeds on two neighboring sites (O–Fe²⁺–) forming

structure **III**_{H₂O}, and the binuclear Fe-center becomes a single Fe-site. Therefore, the remaining part of the binuclear “diamond core” cannot accept a second H₂O molecule. But it is able to adsorb N₂O forming terminal oxygen in the structure **III**_{H₂O} and releasing N₂. The assumption about H₂O blocking half of Fe-atoms may explain “a magic number” of $0.5 \times C_{Fe}$ obtained after saturation by water. Hydroxylated form of binuclear Fe-center acts as a single Fe-site, in agreement with the results of DFT calculations [15], which showed that the hydroxylated form of binuclear Fe-center consists of one Fe-ion completely saturated by water in the first coordination sphere. The result with H₂O blocking one half of Fe-atoms also indirectly confirms the presence of proton in the binuclear “diamond core”, since otherwise two molecules of H₂O could be accommodated during adsorption on a [Fe₂O₂]²⁺-center.

The structure of the binuclear Fe-center proposed explains the results obtained for the activity of (O)_{ad} in CO oxidation. As shown in Scheme 1, structure **II** can accept two O-atoms leading to the form **III** with active terminal oxygen atoms able to form CO₂. Only paired terminal O-atoms adsorbed on the Fe-sites of the binuclear center [Fe₂O₂H]⁺ seem to be active in CO interaction, and the single O_{ad}-atoms generated on Fe-site in the hydroxylated binuclear complex (**III**_{H₂O}) are inactive. This result is in variance with the recently reported by Pérez-Ramírez et al. [16] high activity of isolated ex-framework iron sites in N₂O reduction by CO. This leads us to the conclusion that the inactivity of single O_{ad}-atoms in the complex (**III**_{H₂O}) may be due to (i) the necessity of CO activation via adsorption, which becomes impossible in the complex saturated by water, or (ii) the instability of the structure **III**_{H₂O} due to easy electron transfer from Fe²⁺ to Fe⁴⁺ resulting in the structure **I** consisting of two Fe³⁺.

4. Conclusions

1. A transient response method is shown to be suitable for quantitative determination of the active Fe-sites during catalytic N₂O decomposition with a sensitivity level up to few dozens ppm of Fe.
2. The surface active Fe-sites in isomorphously substituted H(Fe)ZSM-5 are formed by mild steaming followed by high temperature calcinations in inert atmosphere.
3. A tentative structure of active binuclear Fe-center is proposed featuring a “diamond core” geometry, similar to that of the monooxygenase enzyme, which includes one H⁺-ion and has an overall monopositive charge [Fe₂O₂H]⁺.
4. Not all of (O)_{ad}-atoms deposited from N₂O were active in CO oxidation at 523 K: only ~65% corresponded to (O)_{ad}^{act} and the rest were inactive.
5. H(Fe)ZSM-5 pre-saturated by water generates oxygen species inactive in CO oxidation, suggesting either the necessity of CO activation via adsorption, which becomes impossible in the complex saturated by water, or irreversible transformation of Fe²⁺ to Fe³⁺ due to oxidation by N₂O in the presence of water.

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