Redox and photo-redox properties of isolated Mo^{5+} ions in MoH-ZSM-5 and MoH-beta zeolites: *in situ* ESR study

Alexei V. Kucherov * and Alexei A. Slinkin

Zelinsky Institute of Organic Chemistry, RAS, Leninsky Prosp. 47, Moscow 117913, Russia
E-mail: lab14@ioc.ac.ru

Received 20 June 1999; accepted 4 November 1999

Redox and photo-redox properties of isolated Mo^{5+} ions stabilized in H-ZSM-5 and H-beta zeolites are studied by *in situ* ESR in flowing O_2, NO, H_2, and C_3H_6. Upon oxidation of pre-reduced samples at 20 °C, NO demonstrates a higher oxidative ability, as compared with O_2. Interaction of Mo^{5+} ions with propene at 20 °C results in formation of a chemisorption complex with enhanced reactivity of Mo(V) toward NO. Illumination of the Mo^{5+}/HZSM-5 sample with UV-visible light causes measurable acceleration of Mo(V) oxidation by NO at 20 °C. Therefore, photochemical activation of the oxidation step could be realized, in principle, for Mo/zeolite catalysts. At 500 °C in the reaction mixture $NO + H_2$, the step of the catalytic site reduction is fast, and the dynamic equilibrium of the redox reaction Mo(VI) ↔ Mo(V) for MoH-ZSM-5 and MoH-beta seems to be strongly shifted to Mo^{5+}.

Keywords: Mo-ZSM-5, Mo-beta, redox and photo-redox properties, ESR

1. Introduction

It was shown earlier that a chemical transport reaction, with formation of reactive and mobile oxychloride fragments in the zeolitic bed, provides effective dissipation of the oxide phase and migration of active species into zeolitic channels at temperatures as low as 150–200 °C [1,2]. For example, thermal treatment of the mixture H-zeolite + MoO_3 with an air flow containing CCl_4 permits to prepare the samples MoH-ZSM-5 and MoH-beta with isolated cationic species stabilized in the zeolitic matrix [1,2]. Study of catalytic functions of isolated redox sites located in confined environments of zeolitic voids ("biomimetic" systems) is of great interest. Therefore, it seems to be important to use our disperse samples MoH-ZSM-5 and MoH-beta for more detail studying of redox properties of isolated Mo^{5+} sites, and Mo(V)-ESR spectroscopy can be used as a unique sensitive method for the study of these low-loaded samples.

Here we summarize the results of the *in situ* ESR study of the interaction of Mo^{5+} sites, in prereduced MoH-ZSM-5 and MoH-beta, with different individual compounds and gas mixtures (O_2, NO, propene, H_2) at 20–500 °C. An attempt to monitor the possible influence of UV-visible illumination on redox processes is also taken.

* Temporary address: Dr. A. Kucherov, Ford Motor Co, MD 3182, PO Box 2053-SRL, Dearborn, MI 48121-2053, USA. E-mail: akuchero@ford.com.

2. Experimental

2.1. Sample preparation

Molybdenum-containing samples, with ∼1.8 wt% of MoO_3, studied in previous work [1,2], were used in this investigation. Precalcined MoO_3 was mixed with H-forms of zeolites (ZSM-5, Si/Al = 25; beta, Si/Al = 5), pressed without binder and crushed into 5–10 mm pieces. Granulated samples were placed in a quartz reactor tube and calcined at 500 °C in an air flow for 2 h. After cooling the reactor to 20 °C the air flow was switched to the bubbler filled with CCl_4, the reactor temperature was raised during 1 h to a 200 °C, the sample was calcined in the stream of air saturated at 20 °C with CCl_4 vapor for 2 h, cooled to room temperature, and blown out with pure dry air for 2–3 h [1,2]. Before study the samples were reduced in 1% H_2 + He flow at 500–550 °C for 2 h. We suggest that our samples are cation-deficient because isolated complex cation species $(MoO_2)^+$, and not isolated Mo^{5+} ions, are coordinated in cation positions [1,3,4].

2.2. ESR measurements

The ESR spectra of paramagnetic species, at 20–280 °C and 500 °C, were taken in the X-band (9.6 GHz) on a Bruker ESP300 spectrometer, equipped with either a high-temperature cavity ER 4111 HT-VT or an optical cavity 4104 and a co-axial quartz gas flow cell [5]. Use of the cavity 4104 with optical slot permitted to combine *in situ* illumination of the sample by UV-visible light with sample heating up to 280 °C by flowing heated nitrogen. A mercury light source SP 200 (200 W) was used for sample

illumination. A cylindrical quartz filter filled with distilled water (6 cm length) was used to cut off the IR component of the spectrum and minimize the radiation sample heating. After absorption of the IR component the beam was focused inside the ESR cavity by a quartz lens (spot diameter $\sim 1/2$ inch).

The Bruker ESP300E software and the special Bruker program WIN-EPR (version 901201) were used for data treatment (baseline correction, double integration, and deconvolution). The ESR signals were registered, at modulation of 4 G and microwave power of 6.4 mW, in the field region of 2900–4100 G (2048 points). Two modes of resonance registration were used: (1) two scans with a sweep time of ∼21 s; and (2) ten scans with a sweep time of ∼42 s. The lack of sample saturation was verified for microwave power levels 0.64–12.2 mW.

The samples were crushed into 0.1–0.2 mm pieces, and 25–30 mg of a sample was placed in a co-axial quartz flow ampoule with an inner diameter of ∼4 mm for ESR measurements [5]. This cell was placed into the ESR cavity and connected, via long stainless-steel capillaries with Teflon ferrules, to a gas flow system. The setup permitted to calcine the cell in the outer high-temperature furnace (pre-reduction at 500–550 °C) and place it back into the 4104 cavity under the $H_2 + He$ gas flow. The gas flow, at a pressure of ∼1 atm, was regulated by a four-channel readout mass-flow controller (model 247C, MKS Instruments). This system permitted to change the composition of the gas mixture and to regulate the flow from 1.5 to 18 cm^3/min. Pure helium (99.999%) and the mixtures 10.1 vol% O_2+He, 0.41 vol% NO + He, 0.39 vol% C_3H_6 + He, and 1.0 vol% H_2 + He were used for *in situ* sample treatment.

3. Results and discussion

As shown earlier [1,2], thermal treatment of zeolites with an air + CCl_4 flow results in formation of defect sites capable of stabilization of O_2^- [6,7]. A rather weak ESR spectrum with $g_{xx} = 2.017$, $g_{yy} = 2.010$, and $g_{zz} = 2.004$, can be unambiguously assigned to the signal from O_2^- radical species [6–8]. However, the number of the defect sites formed (estimated by the intensity of this ESR signal) does not exceed 1% from the number of the lattice Al^{3+} ions in the sample [1]. Therefore, in our further discussion of the ESR data we neglect the appearance of a weak ESR triplet related with a minor dealumination of zeolites.

3.1. Interaction of isolated Mo^{5+} sites with O_2

Figure 1(a) presents the ESR spectrum from MoH-ZSM-5 pre-reduced in H_2 flow at 500 °C. In addition to the ESR signal typical of isolated Mo^{5+} ions ($g_0 = 1.945$; $I \approx 10^{19}$ spin/g), an additional weak triplet from O_2^- radical species is also seen. It seems that no essential interrelation between these defect sites mentioned above and Mo^{5+} stabilization exists.

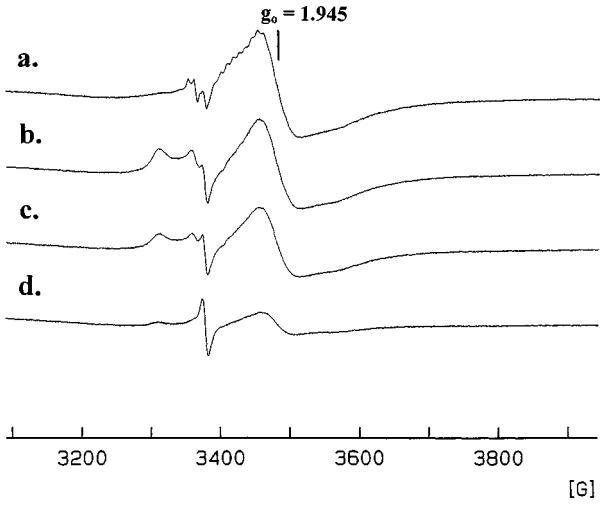

Figure 1. Transformation of the ESR spectra of MoH-ZSM-5 (pre-reduced by H_2 at 500 °C) upon interaction of the sample with NO at 20 °C: (a) pure He flow, (b) switch to 0.4% NO + He flow ∼3 min, (c) 6 min, and (d) 20 min.

The ESR line from isolated Mo^{5+} ions in reduced MoH-ZSM-5 demonstrates an informative peculiarity: an additional superhyperfine splitting (shfs), with $\Delta H = 7$–8 G, can be distinguished (figure 1(a)). The formation of the extra structure may be due only to a shf-interaction of the unpaired electron of Mo^{5+} with an outershell ^{27}Al nucleus. Earlier shfs of this type was detected for Cr^{5+} and V^{4+} species located in cationic positions of H-ZSM-5 [4,9,10].

The number of shf-components exceeds 6, so, formally, it can be explained either by interaction of the unpaired electron with 2 Al nuclei or by overlapping of $g_\parallel$ and $g_\perp$ components of the anisotropic spectrum from MoO_2^+ species interacting with one Al of the lattice ($I = 5/2$). Similarly, Cr(V)-ESR signals from CrH-ZSM-5 demonstrate the same overlapping of components, when taken in the X-band. However, the spectrum from Cr(V)-ZSM-5 becomes much better resolved in the Q-band, with sextets on $g_\parallel$ and $g_\perp$ confirming the interaction of the cationic species with one lattice Al^{3+} ion [4]. The same explanation seems to be also convenient for Mo(V) in high-silica ZSM-5, with large average distance between Al atoms in the framework.

Therefore, the shfs gives an evidence of the cationic location of the Mo^{5+} species, with the lattice Al^{3+} of the zeolite positioned in the second coordinative sphere [1].

In a recent study of Mo/ZSM-5 prepared from MoO_3 and H-ZSM-5 it was shown that MoO_x species migrate inside the zeolitic channels upon calcination, and each Mo atom replaces one H^+ during exchange [11]. Formation of $Mo_2O_5^{2+}$ species was supposed for the Mo(VI) valence state [11]. In our study of pre-reduced samples we suppose formation of MoO_2^+ species interacting with one exchange site. It is hard to suppose noticeable formation of Mo-species with lower oxidation states for the mild conditions of reduction used in our study.

It is known that high-temperature treatment of Mo/ZSM-5 samples with high Mo loading (>4–5 wt%) can

cause some dealumination of zeolite, with formation of unreducible and inactive $Al_2(MoO_4)_3$ domains [11]. This effect is negligible, however, for low-loaded samples [11]. So, we suppose that the majority of Mo in our reduced samples forms isolated MoO_2^+ species.

The Mo(V) oxidation state in pre-reduced MoH-ZSM-5 and MoH-beta is not resistant to oxidative calcination, and the sample treatment in 10% O_2 + He flow at 200 °C results in fast and quantitative disappearance of the Mo^{5+}-ESR signal pointing to a total oxidation of Mo(V). However, the Mo(V) state stabilized by the zeolites is quite stable at room temperature. Switch of the gas flow through the sample from pure He to 10% O_2 + He causes a noticeable broadening of the Mo^{5+}-ESR line due to dipole–dipole interaction of ions with paramagnetic O_2 molecules, but this broadening occurs without substantial loss in the integral intensity. Measurable decrease of the Mo^{5+}-ESR signal at 20 °C can be registered only after ∼30 min in O_2 + He flow. Oxidation of Mo^{5+} in pre-reduced MoH-beta by oxygen is also quite slow at room temperature. These results agree with earlier data demonstrating slow oxidation of Mo^{5+}H-ZSM-5 in air at 20 °C [1,3]. *In situ* illumination of the samples by UV-visible light does not cause measurable acceleration of Mo^{5+} oxidation by oxygen at 20 °C.

3.2. Interaction of isolated Mo^{5+} sites with NO

NO demonstrates higher oxidative ability, as compared with O_2, upon oxidation of pre-reduced Mo^{5+}/H-ZSM-5 and Mo^{5+}/H-beta samples at 20 °C. Changes in ESR signals caused by switch of the gas flow from He to 0.4% NO + He are shown in figures 1 and 2. A fast appearance of a new, quite intense ESR spectrum occurs first, reaching maximum in 2–4 min, and when a gradual decrease in intensities of both new-formed spectrum and Mo^{5+}-ESR signal takes place (figures 1 and 2). An attempt to separate the spectrum formed upon the first step of interaction between NO and MoH-beta is demonstrated in figure 2(c) as a result of subtraction ($[\Delta] = [a] - 0.8[b]$). The resulting spectrum, with $g^1 = 2.041$, $g^2 = 2.009$, and non-resolved g^3-component (figure 2, dotted line), resembles surprisingly well ESR signals from nitroxyl radicals (>NO•) with hindered rotation [12]. In spite of the unclear structure of the paramagnetic species formed, one can assume that a fast formation of the transient complex occurs upon NO chemisorption on the Mo^{5+} site, with a quite slow subsequent oxidation of Mo(V) to the Mo(VI) state. The process takes place much faster at 100 °C, and our method of measurement is too slow to monitor kinetics of either the complex formation or the Mo^{5+} oxidation.

Illumination of the Mo^{5+}/HZSM-5 sample with UV-visible light causes measurable acceleration of Mo(V) oxidation by NO at 20 °C. Kinetics of disappearance of the Mo^{5+}-ESR signal in dark and under illumination is compared in figure 3. Taking into account a quite low accuracy of quantitation of the ESR signal by double integration (deviation > ±10%), changes in the signal intensity were evaluated by subtraction (accuracy ±5%).

Contribution of the "nitroxyl" species was not included.

The position of the two kinetics lines differs markedly (figure 3), and the difference cannot be ascribed to some thermal heating of the sample by the beam. Use of the water filter permits to cut off the IR part of the light and minimize radiation heating. A thermocouple placed inside the illuminated ESR ampoule shows that the temperature rise caused by the beam does not exceed 1 °C. Therefore, the result obtained demonstrates, in our opinion, that photochemical activation of the oxidation step could be realized, in principle, for heterogeneous catalysts Mo^{5+}/zeolite. It was mentioned above that on the first step of interaction NO chemisorption results in fast formation of the transient complex without change of the Mo(V) valence state, with subsequent oxidation of Mo(V) to Mo(VI). In our opin-

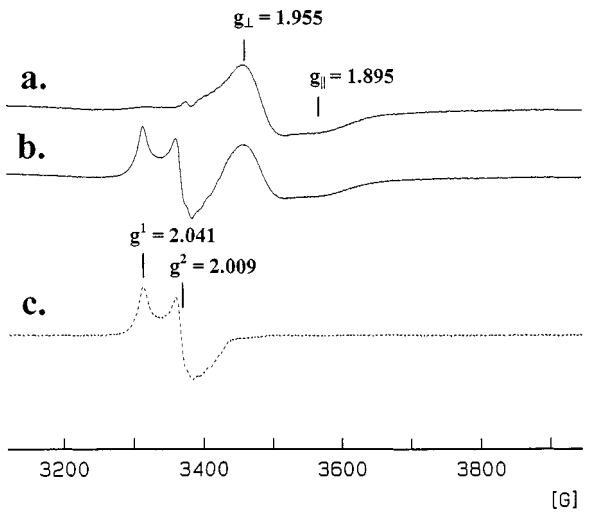

Figure 2. Transformation of the ESR spectra of MoH-beta (pre-reduced by H_2 at 500 °C) upon interaction of the sample with NO at 20 °C: (a) pure He flow, (b) switch to 0.4% NO + He flow ∼5 min, and (c) result of subtraction of the two spectra mentioned above, $[\Delta] = [b] - 0.8[a]$.

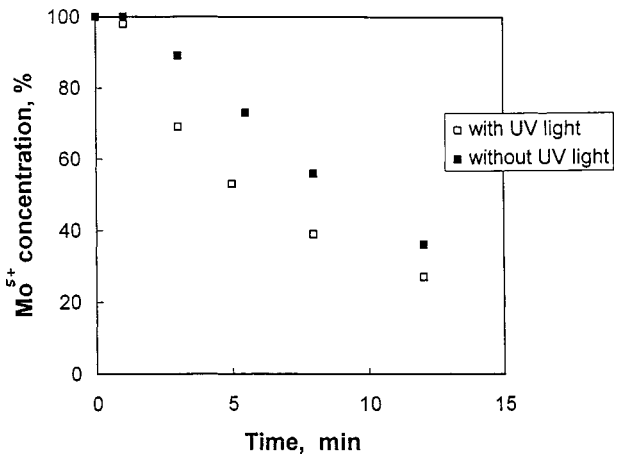

Figure 3. Kinetics of the Mo^{5+}-ESR signal disappearance upon interaction of pre-reduced MoH-ZSM-5 with 0.4% NO + He flow at 20 °C: (■) no illumination and (□) illumination with UV-visible light.

ion, illumination accelerates just the second slow step of transformation of the transient complex.

A broad UV-visible spectrum was used in our present preliminary study, so it is impossible to evaluate the minimum value of the energy quantum capable of photoinitiating oxidation. The data obtained (figure 3) are qualitative only: the cylindrical ampoule illuminated from one side does not provide a uniform photo-treatment of the catalyst charge. Use of a more powerful light source, with different filters, combined with a flat flow reactor could help to obtain further insight into the problem. However, even preliminary qualitative data are of principal interest, from our point of view.

Reduction, by H_2, of the samples oxidized by NO was studied *in situ* at 20–280 °C. No formation of Mo(V) was detected both in dark and upon illumination. Thermal reduction takes place with measurable rate at temperatures >400–450 °C, and our equipment does not allow to study photo-reactions at such a high temperature.

3.3. Propene chemisorption on Mo^{5+} sites and subsequent interaction of the complex with NO

Change in the ESR signal from MoH-ZSM-5 caused by propene sorption at 20 °C is shown in figure 4. Interaction with C_3H_6 results in a rather small transformation of the Mo^{5+}-ESR line (figure 4(b)) indicating that some change in the local crystal field occurs upon the site interaction with additional ligand. No measurable change in the integral intensity of the signal takes place, i.e., all the paramagnetic sites preserve the Mo(V) state. Subsequent purging of the sample with a flow of pure He (20 °C, 2 h) causes no back change of the ESR signal formed (figure 4(b)). Therefore, a relatively strong chemisorption complex is formed upon propene sorption on the Mo^{5+} site in H-ZSM-5. The same effect accompanies propene chemisorption on MoH-beta.

Interaction of samples containing pre-sorbed propene with NO at 20 °C causes a fast decrease in the Mo^{5+}-ESR signal intensity (figure 5 (■)). The rate of the Mo(V) loss in this case exceeds the rate of oxidation of the propene-free sample by a factor of ∼2 (see figures 3 and 5). Thus, formation of the chemisorption complex between Mo^{5+} site and C_3H_6 (or secondary oligomer) increases noticeably the reactivity of the Mo(V) toward oxidation by NO. Kinetics of disappearance of the Mo^{5+}-ESR signal in dark and on light is compared in figure 5. Some acceleration of the process by illumination can be noted for Mo^{5+}/C_3H_6 in H-ZSM-5 but the effect is less pronounced than that registered in the absence of propene (figure 3). Taken into account the accuracy of the method it is difficult to make the conclusion about efficient photooxidation in this case.

An oxidized by NO MoH-ZSM-5/propene sample was heated in pure He flow. After treatment at 200 °C for 30 min a relatively weak ESR signal from isolated Mo^{5+} ions reappears demonstrating reduction of some part of cations. No influence of illumination was detected in this case. Therefore, thermal reduction of Mo sites by organic species chemisorbed by zeolite is much more effective, as compared with reduction of oxidized MoH-ZSM-5 by H_2. This effect could point to different distribution of oxidized sites in the two cases: organic fragments tightly bonded inside zeolitic channels can prevent aggregation of Mo(VI) during oxidation. If so, no redispersion of aggregated species is required upon subsequent reductive treatment.

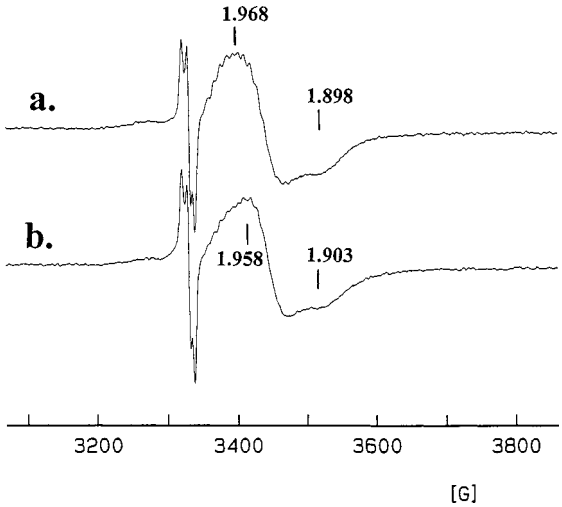

Figure 4. Transformation of the ESR spectra of MoH-ZSM-5 (pre-reduced by H_2 at 550 °C) upon interaction of the sample with C_3H_6 at 20 °C: (a) pure He flow and (b) 0.5% C_3H_6 + He flow ∼7 min + pure He flow ∼60 min.

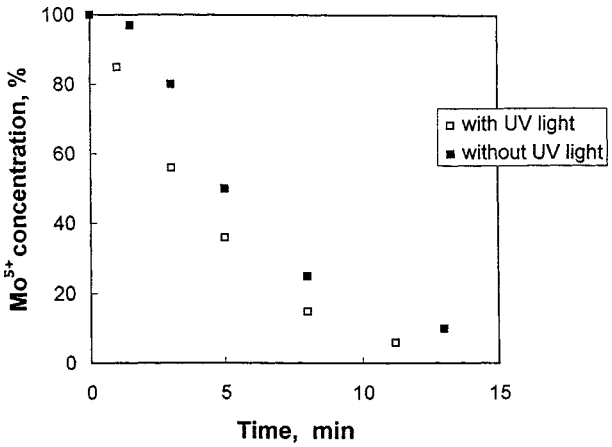

Figure 5. Kinetics of the Mo^{5+}-ESR signal disappearance upon interaction of MoH-ZSM-5, with propene pre-sorbed, with 0.4% NO + He flow at 20 °C: (■) no illumination and (□) illumination with UV-visible light.

3.4. In situ ESR monitoring of Mo^{5+}/H-ZSM-5 and Mo^{5+}/H-beta in flowing gas mixtures (H_2 + NO) at 500 °C

The Mo^{5+}-ESR signal from the reduced Mo^{5+}/H-ZSM-5 taken at 500 °C in He flow (figure 6(a)) is not altered noticeably by heating save for an intensity decrease due to the Curie–Weiss law. When treated with a flow of 1% H_2 + He the ESR signal associated with the isolated Mo^{5+} ions did

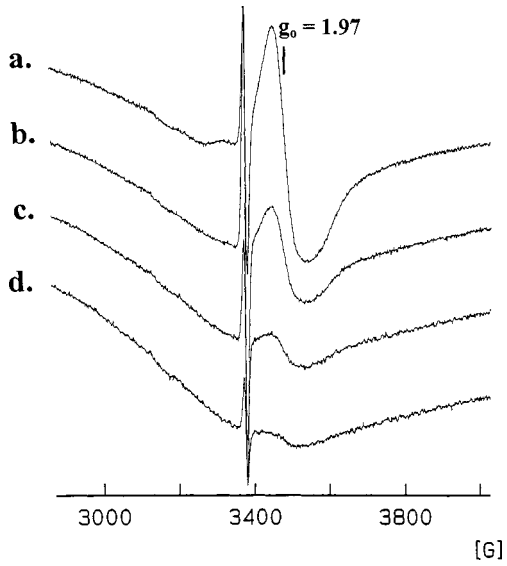

Figure 6. Transformation of the ESR spectra of pre-reduced MoH-beta upon treatment of the sample with He + NO + H_2 gas mixtures at 500 °C: (a) 1% H_2 + He flow and mixtures He + NO + H_2 with $X = H_2/NO$ = 5.8, 3.6, and 1.25; (b) $X = 0.8$, 5 min; (c) $X = 0.3$, 5 min; and (d) 0.4% NO + He flow, 5 min.

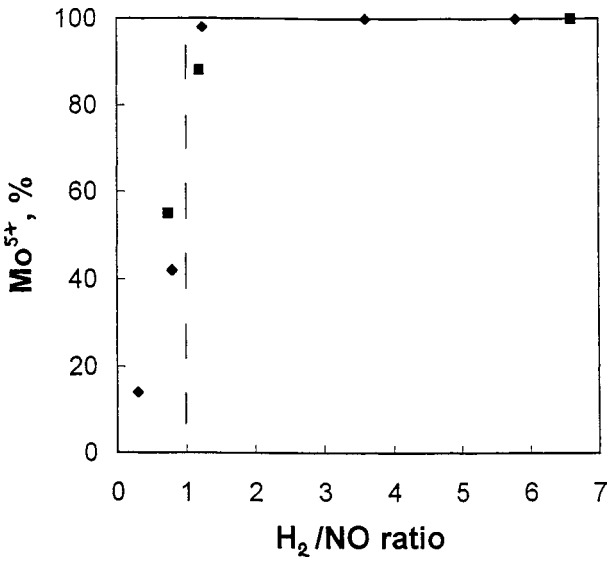

Figure 7. Relative concentration of Mo^{5+} ions in MoH-ZSM-5 (■) and MoH-beta (♦) vs. stoichiometric ratio, H_2/NO, in the gas mixture He + NO + H_2 at 500 °C.

not change the shape in the temperature range from 20 to 500 °C.

The ESR signal from Mo^{5+} ions, taken *in situ* at 500 °C in a flow cell [5], does not decrease in a flow of He + H_2 + NO at different stoichiometries, going from a molar ratio, H_2/NO, of ∼7 to 1.2 (figure 6(a)). Going to stronger oxidizing conditions results in a noticeable drop of this signal (figure 6 (b)–(d)) but the signal decrease is completely reversible upon back switch to the reducing gas mixture. Therefore, a short-term exposure of the catalysts to oxidizing conditions at the common temperature of the catalytic process does not cause irreversible formation of Mo(VI) agglomerates. Figure 7 shows the dependence of the relative concentration of Mo^{5+} vs. the stoichiometry of the gas mixture. One can conclude that at 500 °C in the reaction mixture of NO and H_2 the step of the catalytic site reduction is fast, and the dynamic equilibrium of the redox reaction $Mo^{5+} \leftrightarrow Mo^{6+}$ seems to be strongly shifted to the Mo^{5+} state.

4. Conclusions

NO demonstrates a noticeably higher reactivity than O_2 in oxidation of pre-reduced Mo^{5+}/H-ZSM-5 and Mo^{5+}/H-beta samples at 20 °C.

Illumination of the Mo^{5+}/HZSM-5 sample with UV-visible light causes a measurable acceleration of Mo(V) oxidation by NO at 20 °C. So, photochemical activation of the oxidation step could be realized, in principle, for Mo/zeolite catalysts.

Interaction of Mo^{5+} sites with propene at 20 °C results in the formation of a chemisorption complex with enhanced reactivity of Mo(V) toward NO.

At 500 °C in the NO+H_2 mixture the step of the Mo-site reduction is fast, and the dynamic equilibrium of the redox reaction Mo(VI) ↔ Mo(V) for MoH-ZSM-5 and MoH-beta is strongly shifted to Mo^{5+}. Catalysts are not vulnerable to a short-term exposure to oxidizing conditions.

Acknowledgement

This work was supported by Russian Foundation for Basic Researches (Grant 98-03-32010). AVK thanks Dr. John L. Gerlock (Ford Scientific Research Labs.) for the help with the ESR spectrometer.

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