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In situ ESR of CrH-ZSM-5 up to 500°C in flowing gas containing O_2, H_2O, CCl_4, NO, NO_2, and C_3H_6

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A flow cell was used for the in situ ESR monitoring of the state and reactivity of chromium ions in Cr-ZSM-5. Calcination of $Cr(NO_3)_3/NH_4$-ZSM-5 in air at 500°C is accompanied by migration of chromium ions inside the zeolitic channels and stabilization of *isolated* Cr^{5+} cations near lattice Al^{3+} ions. Calcination of Cr-ZSM-5 at 750°C leads to a gradual disappearance of the isolated Cr^{5+} cations and formation of α-Cr_2O_3 microcrystals. All the Cr^{5+} cations are accessible to gas-phase molecules: O_2 strongly broadens the dipole–dipole signal; H_2O sorption increases the local crystal field symmetry; admission of CCl_4 results in a small change of the Cr^{5+} local coordination; strongly stabilized complexes on Cr-ZSM-5 are observed upon sorption of either NO or NO_2. The sorption of C_3H_6 on Cr-ZSM-5 at 20°C is accompanied by a gradual reduction of the Cr^{5+} sites. At 500°C in [$C_3H_6 + O_2$ + He] flow, even at a large excess of oxidant, the reduction of a noticeable part of Cr^{5+} ions takes place. At 400°C, in the same gas mixtures, a deeper reduction of Cr^{5+} occurs. Closer to stoichiometric conditions, in a [C_3H_6 + NO + He] flow with 120% excess of oxidant the Cr^{5+} is completely reduced at 500°C. The oxidation of propene is accompanied by coke deposition on the surface of the catalyst. The implications of the results are discussed.

Keywords: in situ ESR; CrH-ZSM-5; flowing gas

1. Introduction

The ability of the ZSM-5 matrix to stabilize transition metal ions as isolated cationic species in unusually low-coordination environments (Cu^{2+}, Fe^{3+}, Mn^{2+}) and with rarely prevailing oxidation states (Cr^{5+}, V^{4+}) was shown in a series of publications [1–9] and summarized in a review [10]. Such materials are of interest as catalysts. Firstly, comparative catalytic studies may elucidate the influence of local crystal field symmetry on the intrinsic catalytic properties of isolated transition metal ions. Secondly, one can compare the intrinsic catalytic properties of different ions located in the same environment. CuH-ZSM-5 which was found to be active

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in the selective catalytic reduction (SCR) of NOx by hydrocarbons [11–16] was accorded most attention. Few data were obtained for CrH-ZSM-5 and the results were not quantitative [17–19].

Previously, we have shown that ESR spectroscopy may be effectively used for in situ monitoring of the state of the paramagnetic ions in Cu-ZSM-5. For ion-exchanged samples with low copper content (no over-exchange) the ESR signal is associated with the majority of Cu^{2+} introduced into zeolite [20,21]. It was shown that isolated cupric cations in a H-ZSM-5 matrix preserve their oxidation state up to 500°C in the absence of reactive hydrocarbons (or hydrogen) and in the presence of other polar and non-polar molecules [20–23]. Also, the catalytic activity of CuH-ZSM-5 in total oxidation reactions was correlated with the concentration of coordinatively unsaturated square-planar Cu^{2+} cations in CuH-ZSM-5 [23–25]. For CrH-ZSM-5 it was shown that these catalysts are stable and effective in total burn-up of hydrocarbon traces (300–500 ppm) in a very large excess of O_2 [17,18]. The intrinsic activity of CrH-ZSM-5, per chromium ion, exceeds the activity of supported Cr/SiO_2 or of Cr/SiO_2–Al_2O_3 by a factor of $\sim$30. At the same time, the increase of hydrocarbon concentration in the gas mixtures leads to an irreversible decrease in the intrinsic activity [26].

The aim of this work is to study the interaction of different molecules with CrH-ZSM-5 and to compare the results to those obtained, using the same experimental approach, with a CuH-ZSM-5 catalyst made from the same batch of ZSM-5 zeolite [20–23].

2. Experimental

The ESR spectra were taken at 20–500°C in the X-band (microwave frequency 9.485 GHz) on a Bruker ESP300 spectrometer, equipped with a high temperature cavity ER 4111 HT-VT. The Bruker ESP300E software and the special Bruker program WIN-EPR (version 901201) were used for the treatment (baseline correction, double integration, and subtraction) of the recorded spectra.

The ESR signals of Cr^{5+} were registered in the field region 3225–3625 G (resolution 2048 points; 10–25 scans with a sweep time of 42 s; modulation frequency 100 kHz; modulation amplitude 1.9 G). Resonances for microwave power 0.64–6.41 mW were recorded to verify the lack of sample saturation. A few spectra were taken also in the field region 50–4050 G to observe the possible appearance of a broad ESR line from the antiferromagnetic Cr_2O_3 phase.

The sample of CrH-ZSM-5 was prepared by impregnation of the NH_4-form of the zeolite having a SiO_2/Al_2O_3 ratio of 50 (Si/Al = 25) (PQ Chemicals) by a $Cr(NO_3)_3$ solution with subsequent drying and calcination at 500°C. While the intent was to prepare a 1 wt% Cr sample, the analysis by inductively coupled plasma atomic emission spectroscopy (ICP-AES) gave 0.87 wt% Cr. This analysis

also confirmed the atomic Si/Al ratio as 25.15. The Cr/Al atomic ratio of the sample was 0.36. Hence the sample contained isolated Cr ions.

The zeolite was pressed without binder and crushed into 0.1–0.2 mm pieces. Then it was placed in a quartz ampoule for ESR measurements and precalcined in dry air at 500–750°C. A co-axial quartz cell was used for in situ treatment of the sample in gas flow at 20–550°C [20]. The cell, containing the sample (15–25 mg), was placed in the ESR cavity and connected with stainless steel capillaries of the flow system by Teflon ferrules. The gas flow was regulated by a 4-channel readout mass flow controller (model 247C, MKS Instr.). This system permitted to change the composition of the gas mixture and to regulate the gas flow from 1.5 to 18 cm^3/min.

Pure helium (5.0 grade) and the mixtures [20.2 vol% O_2 + He], [0.41 vol% NO + He], and [0.39 vol% C_3H_6 + He] were used for in situ sample treatment. To study the interaction with H_2O or CCl_4 the sample was treated with a flow of pure He saturated by the vapors at 15°C.

3. Results and discussion

Chromium ions, in an aqueous solution, cannot be exchanged into NaZSM-5 or HZSM-5. Conversely, a high-temperature calcination of H- or NH_4-forms of ZSM-5 impregnated by $Cr(NO_3)_3$ or with addition of CrO_3 causes a solid-state migration of chromium species in the zeolitic channels and stabilizes isolated Cr^{5+} ions in cationic positions [2,7,8]. By the formal requirement of charge neutrality, the ion with no extra-lattice ligands must replace five singly charged cations. This is impossible even in the case of exchanged zeolites with lower SiO_2/Al_2O_3 ratios [27]. In high-Si zeolites with a large distance between lattice Al^{3+}-ions, only one positive charge of the Cr^{5+}-ion is satisfied by the negative charge associated with the tetrahedrally coordinated lattice Al^{3+}. Four other negative charges have to be extralattice oxygens or hydroxyl ions. As discussed in our previous publications and also by others [2,7,8,27], we assume the stabilization of the pentavalent chromium $(CrO_2)^+$ cationic species.

Because of the rarity of materials containing Cr^{5+} there is no easily available quantitative calibration standard for the ESR spectra. However, the calibration for CuH-ZSM-5 [21] showed that the ESR signal is associated with all the copper introduced into a sample containing 1.27% Cu in an identical matrix. Also, in the study of co-introduction of copper and chromium ions into H-ZSM-5 [28] it was demonstrated that the two ions are located at the same sites. The Cr^{5+}-ions in cationic positions of the H-ZSM-5 were exchanged for Cu^{2+}-ions during high temperature calcination of 1% CrH-ZSM-5 with CuO [28]. The aforesaid may serve as an indirect calibration indicating that the Cr^{5+}-ESR signal is also representative of all the Cr ions in our CrH-ZSM-5 sample as was the case in the similar CuH-ZSM-5 material [21].

3.1. ESR SPECTRA OF CrH-ZSM-5 IN O_2 AND He

3.1.1. CrH-ZSM-5 in O_2 and He flow at room temperature

Fig. 1a shows the ESR spectrum of CrH-ZSM-5 calcined in situ at 500°C in a [O_2 + He] flow for 1 h and cooled to 20°C. This broad spectrum is typical of calcined CrH-ZSM-5 in the presence of oxygen. To reveal the structure of the spectrum it is necessary to prevent the strong broadening of the Cr^{5+} ESR signal caused by the dipole–dipole interaction of the cations with the paramagnetic O_2 molecules [2,7]. Fig. 1b shows the signal obtained after treatment of the sample in He flow (10 cm^3/min) for 5 min at room temperature. A quasi-symmetrical spectrum ($g_0 = 1.975$; $\Delta H = 45$ G) with additional super-hyperfine (shf) splitting ($\sim$7.4 G) coincides very well with previously registered spectra [2,7,8], and shows that the sample contains isolated Cr^{5+} cations located near lattice Al^{3+} in a low symmetry crystal field.

The Bruker ESP300E software affords double integration of the ESR spectra with a rather high accuracy. The quantitative comparison of two spectra (fig. 1a and 1b) demonstrates that the signal broadening in presence of O_2 is accompanied by a pronounced decrease of the signal intensity. The change in both form and intensity is completely reversible when switching the gas flow. Oxygen removal by the flow of He leads to an increase of the integral intensity of the signal by a factor of $\sim$3. Such a large difference in the integral intensities of the signals (fig. 1a and 1b) is evidence of considerable electronic interaction between the Cr^{5+} ions and the oxygen in the zeolitic channels. We propose that the observed behavior is due to a weak physical adsorption of paramagnetic O_2 molecules, at room temperature, which decreases the density of unpaired electrons on the Cr^{5+} ions, reducing the ESR signal intensity. The quenching of the signal as a result of spin-coupling between the paramagnetic ion and a paramagnetic molecule located in its first coordinative sphere could take place without charge transfer. Although a decrease in

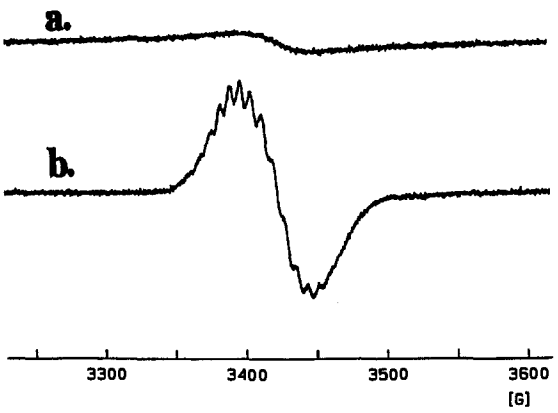

Fig. 1. ESR spectra, at 20°C, of CrH-ZSM-5 precalcined at 500°C in [O_2 + He] flow: (a) in [O_2 + He]; (b) purged by He flow.

the Cr^{5+} concentration due to formation of Cr^{6+} and surface O_2^- radical ions as a result of charge transfer could be also formally written, we reject this explanation because it is difficult to visualize such a redox process, with O_2^- radical formation, as a step in a weak and fully reversible physical adsorption.

3.1.2. CrH-ZSM-5 in O_2 and He flow at 500°C

Fig. 2a presents the ESR spectrum of CrH-ZSM-5 taken at 505°C in an [O_2 + He] flow. The switch of the flow to pure He (5 cm^3/min) results in an appearance of shf-splitting with a minor decrease of the spectrum width, from 50 to 45 G (fig. 2b), during the first few minutes on stream. No further change of this signal occurs upon heating of the sample in He flow for 30 min. The trace c of fig. 2 is the subtraction between the two spectra. Comparison of the normalized signal intensity (DI/N values) for these two spectra (fig. 2a and 2b), taken subsequently under identical conditions, shows the absence of spontaneous thermal reduction of the Cr^{5+} ion to within an accuracy of ±10%. This result is germane to the issue of spontaneous thermal reduction of transition metal ions exchanged into the ZSM-5 structure which was claimed for Cu^{2+} ions in CuH-ZSM-5. In our experience this does not take place if the exchanged ions are *isolated.* At 505°C the presence of paramagnetic O_2 molecules in the zeolite channels broadens the ESR peaks of the shf-structure (fig. 2a and 2b), but the interaction with O_2 molecules which broadens the entire signal, causing the sharp fall in intensity at 20°C, becomes negligible at 505°C.

The gradual decrease in the signal intensity with the temperature rise of the spectrum registration, from 20 to 505°C is in accordance with Curie's law, without noticeable change in the spectrum fine structure (compare figs. 1b and 2b). The good resolution of the spectrum shown in fig. 2b confirms that spin–lattice interaction between the Cr^{5+} cations and the zeolite framework does not increase with the rise of the temperature up to ~500°C.

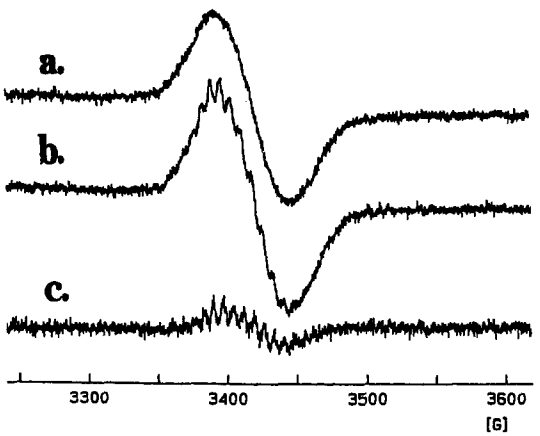

Fig. 2. ESR spectra, at 505°C, of CrH-ZSM-5: (a) in [O_2 + He] flow; (b) purged by He; (c) subtraction of (a) from (b).

Heating of the sample, whose ESR signal is shown in fig. 1b, at 750°C for 2 h leads to a noticeable decrease in the intensity. At the same time, a broad line ($\Delta H \approx 750$ G; $g = 1.98$) appears when registering the ESR signal at 20°C. The intensity of this broad line ($\Delta H \approx 600$ G; $g = 1.98$) increases when the spectrum is recorded at 100°C. This ESR line originating from Cr^{3+} ions in antiferromagnetic α-Cr_2O_3 crystals, is observable above the Néel temperature (51°C), confirming the formation of a Cr_2O_3-phase on the outer surface of zeolitic crystals [7].

3.2. INTERACTION OF CrH-ZSM-5 WITH H_2O

Fig. 3 shows changes in the ESR spectrum of CrH-ZSM-5 during gradual saturation of the sample with H_2O at 20°C. Shf-splitting disappears completely and the integral intensity decreases by a factor of ~ 10 as a result of filling of the channels by water molecules. Subsequent stepwise heating of the sample in He flow is accompanied by a gradual restoration of the parent signal, as shown in fig. 4. The removal of physically adsorbed H_2O molecules at 100–200°C does not increase the intensity markedly (fig. 4a, 4b). Even after the sample purging by He at 400°C the DI/N value reaches only 55% of the initial value (fig. 4d). A more thorough dehydration at 500°C fully restores the signal demonstrating that the process is reversible. Therefore, formation and destruction of strongly chemisorbed complexes are responsible for the observed behavior. This should not be mistaken for evidence of reduction–oxidation of Cr^{5+} cations, in CrH-ZSM-5, by H_2O. The argument in favor of our interpretation is that only the Cr^{5+} ions in a local crystal field of a rather low symmetry give the ESR signal at 20°C [29]. If bonding with strong ligands increases the symmetry of the local environment of the Cr^{5+} ions, the relaxation time sharply increases making these ions inaccessible to ESR at room

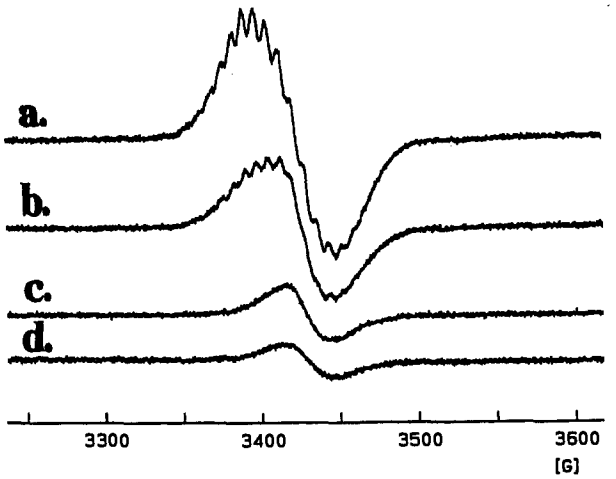

Fig. 3. ESR signal of CrH-ZSM-5 at 20°C: (a) in He ($DI/N = 100\%$); (b) ~ 14 min in [H_2O + He] flow ($DI/N = 53\%$); (c) 24 min ($DI/N = 14\%$), (d) 36 min ($DI/N = 7.5\%$).

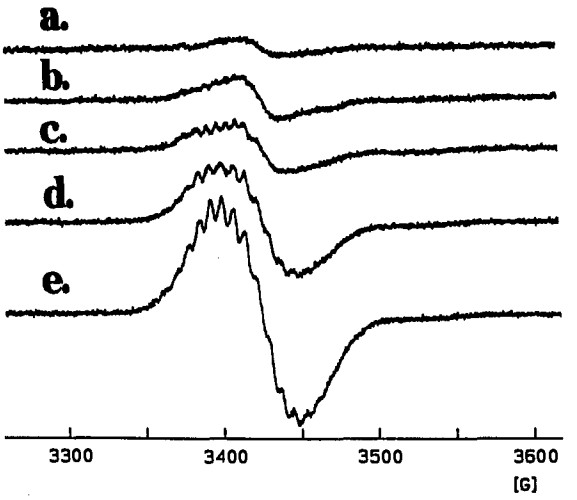

Fig. 4. ESR signal, taken at 20°C, during dehydration of CrH-ZSM-5 in He flow: (a) 100°C, 20 min ($DI/N = 5\%$); (b) 200°C, 30 min ($DI/N = 15\%$); (c) 300°C, 20 min ($DI/N = 25\%$); (d) 400°C, 20 min ($DI/N = 55\%$); (e) 500°C, 15 min ($DI/N = 100\%$).

temperature. The drastic change in the signal intensity can be explained without invoking a change in the oxidation state of the chromium ions upon interacting with strong ligands.

3.3. ADSORPTION OF CCl_4 ON CrH-ZSM-5 AT 20°C

In previous work it was observed that the ESR signal of CuH-ZSM-5 is sensitive to the presence in the zeolite channels of chemically "inert" molecules such as Xe, *n*-hexane and CCl_4 [30]. The weak sorption of these species affected the Cu^{2+} ions only in one of the two configurations of Cu^{2+} present in Cu-ZSM-5. We attempted here to ascertain whether a similar effect can also be observed in CrH-ZSM-5. Indeed, a small but measurable and completely reversible attenuation of the Cr^{5+} ESR signal intensity takes place when admitting CCl_4 into the zeolite at 20°C.

3.4. INTERACTION OF CrH-ZSM-5 WITH NO AND [NO + O_2]

Below 400°C reversible formation of NO_2 takes place in gas mixtures of [NO + O_2] with the equilibrium being shifted far towards NO_2 at 20°C. Fig. 5 shows that adsorption of NO_2 at 20°C induces a sharp change in the Cr^{5+} ESR signal. Treatment of the sample in a [0.33% NO + 4.0% O_2 + He] flow results in a fast and irreversible loss of the shf-structure and a drop in the signal intensity by a factor of ~ 10. This new state is quite thermally stable: treatment of the sample in an He stream at 300°C for 30 min does not change in the ESR signal (fig. 5d) noticeably. Even the heating of the sample in He flow at 400°C for 30 min does not

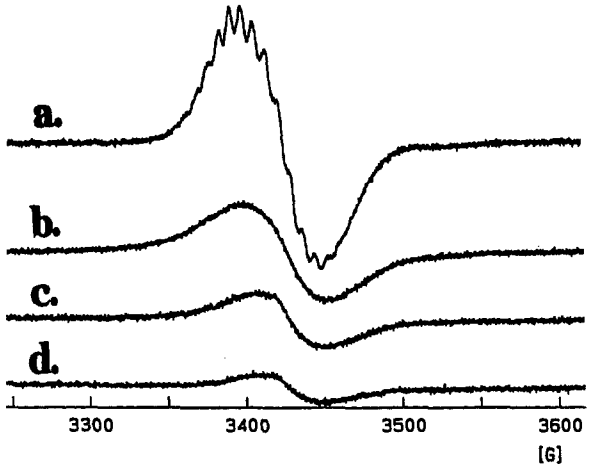

Fig. 5. ESR signal, at 20°C, after contact of CrH-ZSM-5 with: (a) in He flow; (b) ~3 min in [0.33% NO + 4.0% O_2 + He] flow (15 cm^3/min); (c) ~11 min; (d) 60 min.

eliminate all the ligands, and the DI/N value reaches only 50% of the original signal intensity. At 505°C the gas phase equilibrium is shifted far towards NO and there is no measurable influence of [NO + O_2] flow on the state of the Cr^{5+} cations. Similarly, a complete restoration of the initial spectrum (fig. 5a) occurs by heating the sample with adsorbed NO_2 at 500°C in a flow of pure He. The results indicate that NO_2 adsorbed at lower temperatures is bonding strongly to the Cr^{5+} cations in H-ZSM-5.

As could be expected from the above, at 505°C the passage of a [NO + O_2] flow over the CrH-ZSM-5 does not affect the ESR signal. At room temperature the change in the Cr^{5+} ESR spectrum upon NO sorption at 20°C resembles that observed in NO_2 sorption: a fast loss of shf-structure and the signal intensity diminishes by a factor of ~3 after 20 min in [NO + He] flow. The effect of NO sorption at 20°C is also irreversible. The treatment of the sample with a stream of pure He at different temperatures leads to a gradual restoration of the parent ESR signal. Purging by He at 200°C restores the DI/N value from 17 to 27% of the original value and at 400°C to 71%. To restore completely the parent spectrum it is necessary to treat the sample in the flow at 500°C.

The comparison of the NO and NO_2 adsorption on Cr^{5+} and Cu^{2+} in H-ZSM-5 points to a difference in the properties of the two ions. NO adsorption is weak even on the most reactive square-planar Cu^{2+} sites, and the nitrosyl complexes formed can be removed by He flow at ~150°C [21]. The interaction between NO_2 and the Cu^{2+} sites is much stronger, and the complex formed can be removed in He flow at only ~400°C. In the case of the Cr^{5+} sites the difference in the bonding strength for NO and NO_2 is much smaller, a very strong chemisorption of the two reagents takes place, causing a decrease in the ESR signal intensity. The formation of a strong complex as a result of interaction with such weak a ligand as NO can

be rationalized by the possibility of a reaction between NO and the $(CrO_2)^+$ species. The reaction of NO (or NO_2) with extralattice oxygens can lead to the formation of NO_2^- and NO_3^- ligands strongly bonded to chromium ion. The oxidation of Cr^{5+} to Cr^{6+} may also not be excluded in this case.

3.5. INTERACTION OF CrH-ZSM-5 WITH PROPENE

Fig. 6 shows the gradual change, at 20°C, of the ESR signal of CrH-ZSM-5, precalcined in situ at 500°C in a [O_2 + He] flow for 1 h and cooled to 20°C, in a 15 cm^3/min flow of [0.39% C_3H_6 + He]. There is observed a progressive, irreversible loss of the shf-structure and a decrease in the signal intensity. The DI/N value of the Cr^{5+} ion signal decreases by a factor of 3.3 after 90 min on stream (fig. 6a → 6d). There is no appearance of any new line. There are two possible reasons for the 2/3 loss of the ESR signal upon sorption of the propene at 20°C: (1) reduction of the Cr^{5+} ions by the olefin; (2) formation of a more symmetric complex of Cr^{5+} which is ESR-inactive at room temperature. Heating of the sample in He flow at 100°C for 15 min is accompanied by a further drop of the Cr^{5+} signal intensity down to a trace (fig. 6e). A slow ramping of the temperature up to 400°C during sample purging by He did not restore the Cr^{5+} ESR signal. Thus, the irreversible loss of the signal indicates a rather facile reduction of Cr^{5+} ions by the interaction of CrH-ZSM-5 with propene.

As shown in earlier work [32,33], fast oligomerization of alkenes takes place on their sorption on the H-form of high-silica zeolites at 20°C, and the oligomer formed can be identified by ESR. The typical signal parameters are: $g = 2.004$ and a splitting of ~7 G between components. The appearance of the trace line at

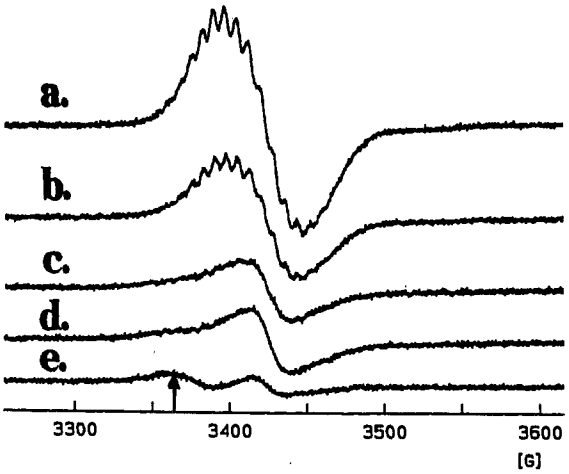

Fig. 6. ESR signal, at 20°C, after contact of CrH-ZSM-5 with: (a) in He flow (DI/N = 100%); (b) 10 min in [0.39% C_3H_6 + He] flow (DI/N = 60%); (c) 43 min (DI/N = 31%); (d) 90 min in flow (DI/N = 29%); (e) after heating at 100°C for 15 min in He flow (DI/N = 5%).

$g = 2.004$ (marked by the arrow on fig. 6e) indicates the formation of carbonaceous oligomers on the CrH-ZSM-5 at 100°C. Further heating of the sample is accompanied by transformation of this line into a more intense symmetric singlet with $g = 2.002$ and $\Delta H \approx 10$ G typical of carbonaceous deposits.

3.6. HIGH-TEMPERATURE INTERACTION OF CrH-ZSM-5 WITH [C_3H_6 + OXIDANT] GAS MIXTURES

The dynamics of the presumed active sites in the CrH-ZSM-5 during the redox catalytic process at $T \approx 500$°C in gas mixtures with varying ratios of components is of the most direct relevance. To this end we followed the oxidation of propene by O_2 and NO at 500 and 400°C. When the gas flow is switched from [O_2 + He] to the complex mixture containing both the oxidant and the reductant, the drop in the ESR signal intensity reflects quantitatively the extent of Cr^{5+} reduction. The dynamic steady-state is established rapidly at 400–500°C.

3.6.1. Oxidation of C_3H_6 by O_2 on Cr-ZSM-5 at 400 and 500° C

Fig. 7a shows the spectrum of CrH-ZSM-5 taken at 505°C in a flow of [10.1% O_2 + He]. A switch of the gas flow to a strongly oxidizing propene-containing mixture [10.1% O_2 + 0.2% C_3H_6] changes the shape of the signal (fig. 7b) during the first few minutes on stream. Longer treatment for 30 min causes only a minor additional change. Comparison of the double integrals of the spectra in fig. 7, taken subsequently under identical conditions, shows, with an accuracy of ±5%, that ~20% reduction of CrH-ZSM-5 takes place at 505°C when switching the flow from [O_2 + He] to the strongly oxidizing propene-containing gas. Shifting the gas composition nearer to stoichiometry leads to a further decrease in the signal intensity

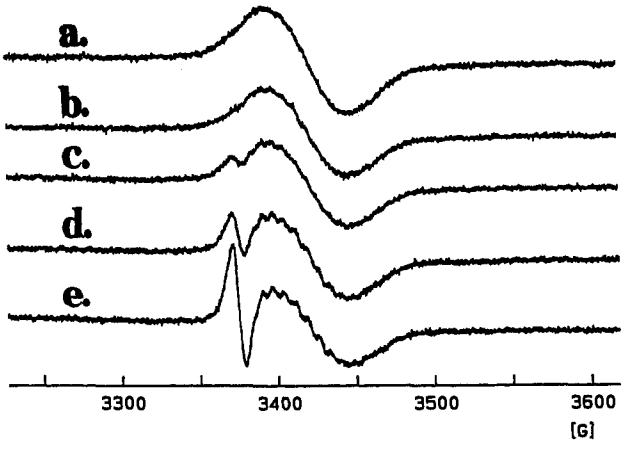

Fig. 7. ESR signal after contact of CrH-ZSM-5 with [$C_3H_6 + O_2$ + He] mixtures at 505°C: (a) in [O_2 + He] flow; (b) $O_2/C_3H_6 = 52$; (c) $O_2/C_3H_6 = 34.5$; (d) $O_2/C_3H_6 = 17.3$; (e) $O_2/C_3H_6 = 8$.

(fig. 7e, ~69% of the initial value). Thus, partial reduction of the Cr^{5+} ions takes place even when the excess of the oxygen is very large.

Fig. 7 also shows that the catalytic oxidation of propene in excess oxygen, at 505°C, is accompanied by the appearance and gradual growth of a narrow ESR singlet ($\Delta H \approx 8$ G; $g = 2.004$) typical of carbonaceous residue. The dependence of the intensity of this line on oxygen concentration, noted at 20°C, is evidence of graphitization [10]. Graphitized "coke" particles are too large to fit into the pores and can be located only on the outer surface of the zeolite crystals.

Backswitching the gas flow, at 505°C, from the reaction mixture to [O_2 + He] gradually restores the parent signal of Cr^{5+} (fig. 7e → 7a) and the narrow line due to coke deposit disappears. Both processes are rather slow: the full restoration of the signal fig. 7a takes place in ~20 min in a [20.2% O_2 + He] stream and the coke residue is completely removed after 100 min of oxidative treatment.

ESR spectra were also taken during the treatment of CrH-ZSM-5 with [C_3H_6 + O_2] at 400°C. The reduction of the Cr^{5+} ions is deeper at this lower temperature than under comparable conditions at 500°C: a ~40% loss of the signal intensity is noted in a mixture where $O_2/C_3H_6 = 48$. Here, again, the appearance of the sharp signal due to "coke" formation is observed after only 10 min on stream. Reoxidation at 400°C is very slow: switching of the flow back to [O_2 + He] causes only a minor rise in the Cr^{5+} ESR signal after 15 min on stream.

3.6.2. CrH-ZSM-5 in [C_3H_6 + NO] at 500°C

At an NO/C_3H_6 molar ratio of ~20, 120% excess oxidant over stoichiometry, the Cr^{5+} signal disappears completely at 505°C after 10 min of treatment. The switch to a flow of 0.38% NO in He does not affect the signal during 30 min. As could be expected, oxygen itself is much more active than NO in the reoxidation of the reduced Cr^{5+} ions. Neither does the addition of NO, in the concentration range of interest from 0.05 to 0.14%, to the strongly oxidizing gas [10.1% O_2 + He] alter the steady-state concentration of the Cr^{5+} in CrH-ZSM-5 operating at 505°C.

4. Concluding remarks

The object of this work was to use an exchangeable, transition metal ion in ZSM-5, different from Cu^{2+} but similarly amenable to ESR analysis (i.e. having an unpaired electron) to augment our understanding of the behavior of such ions in the zeolite structure. Cr^{5+} is such a species. In general terms the two ions behave similarly: (a) they exchange, in high Si/Al zeolites and at low loadings, as one ion per one Al^{3+}-site, regardless of the formal valency; (b) they do not reduce thermally in the absence of a reducing agent; (c) the adsorptive behavior of both ions towards most molecules is largely alike, with the exception of NO sorption.

But there are also important differences associated with the different thermodynamic stability of these ions. Under oxidizing conditions, in air, at high temperatures of >750°C the cupric ion changes coordination while still remaining as an

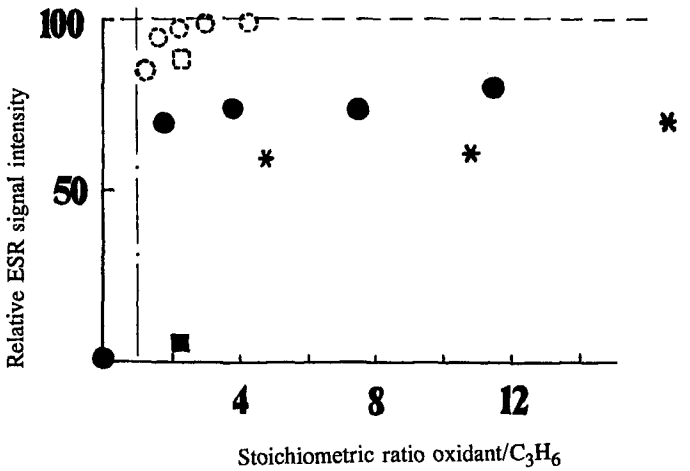

Fig. 8. Relative intensities of ESR signals of CrH-ZSM-5 vs. oxidant/C_3H_6 stoichiometric ratio in the gas mixture: (●) at 505°C in [$C_3H_6 + O_2$]; (■) at 500°C in [$C_3H_6 + NO$]; (*) at 400°C in [$C_3H_6 + O_2$]. For comparison, CuH-ZSM-5: (○) at 500°C in [$C_3H_6 + O_2$]; (□) at 500°C in [$C_3H_6 + NO$] [23].

isolated entity [31]. The pentavalent Cr-ions are oxidized to the hexavalent state and, even though present at a very low concentration, migrate out of the zeolite forming chromia particles.

The less stable Cr^{5+} is also more prone to reduction by olefins than Cu^{2+}. Fig. 8 summarizes the relationship between the concentration of Cr^{5+} ions and the oxidant/propene ratio for all cases studied. For comparison, the data for the catalyst with 1.27% CuH-ZSM-5 [23] are also plotted. The difference between the stability of the transition metal sites in CrH-ZSM-5 and CuH-ZSM-5, under identical conditions, is clearly apparent. In circumstances typical in SCR, even with a large excess of oxygen, the relative extent of reduction of the Cr^{5+} cations in CrH-ZSM-5 is much higher than that of Cu^{2+} cations in CuH-ZSM-5. Not much information is available on CrH-ZSM-5 as a catalyst for the selective reduction of NO_x by hydrocarbons but if an ion like Cr^{5+}, or a $(CrO_2)^+$ moiety, is required as the active site, the stability of such a catalyst will be very low. On the other hand the CrH-ZSM-5 zeolite is quite active and stable in the burn-up of *traces of alkane* in streams containing excess oxygen [17,18].

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References

[1] A.V. Kucherov and A.A. Slinkin, Zeolites 6 (1986) 175.

[2] A.V. Kucherov and A.A. Slinkin, Zeolites 7 (1987) 38.
[3] M.W. Anderson and L. Kevan, J. Phys. Chem. 91 (1987) 4174.
[4] A.V. Kucherov and A.A. Slinkin, Zeolites 7 (1987) 583.
[5] B. Wichterlova, S. Beran, K. Bednarova, L. Nedomova, L. Dudikova and P. Jiru, Stud. Surf. Sci. Catal. 37 (1988) 199.
[6] S. Beran, B. Wichterlova and H.G. Karge, J. Chem. Soc. Faraday Trans. I 86 (1990) 3033.
[7] A.A. Slinkin, A.V. Kucherov, S.S. Goriaschenko, E.G. Aleshin and K.I. Slovetskaya, Zeolites 10 (1990) 111.
[8] A.V. Kucherov, A.A. Slinkin, H.K. Beyer and G. Borbely, J. Chem. Soc. Faraday Trans. I 85 (1989) 2737.
[9] A.V. Kucherov and A.A. Slinkin, Zeolites 8 (1988) 110.
[10] A.V. Kucherov and A.A. Slinkin, J. Mol. Catal. 90 (1994) 323.
[11] G.P. Ansell, A.F. Diwell, S.E. Golunski, J.W. Hayes, R.R. Rajaram, T.J. Truex and A.P. Walker, Appl. Catal. B 2 (1993) 81.
[12] K.C.C. Kharas, Appl. Catal. B 2 (1993) 207.
[13] E. Giamello, D. Murphy, G. Magnacca, C. Morterra, Y. Shioya, T. Nomura and M. Anpo, J. Catal. 136 (1992) 510.
[14] M. Iwamoto and H. Hamada, Catal. Today 10 (1991) 57.
[15] A. Sepulveda-Escrivano, C. Marquez-Alvarez, I. Rodriguez-Ramos, A. Guerrero-Ruiz and J.L.G. Fierro, Catal. Today 17 (1993) 167.
[16] R. Burch and P.J. Millington, Appl. Catal. B 2 (1993) 101.
[17] A.A. Slinkin, A.V. Kucherov, S.S. Goriaschenko, E.G. Aleshin and K.I. Slovetskaya, *Proc. 8th Soviet–French Seminar Catal.*, Novosibirsk (1990) p. 153.
[18] A.A. Slinkin, A.V. Kucherov, S.S. Goriaschenko, E.G. Aleshin and K.I. Slovetskaya, *Proc. 9th Soviet–Japanese Seminar Catal.*, Novosibirsk (1990) p. 224.
[19] S. Sato, Y. Yu-u, H. Yahiro, N. Mizuno and M. Iwamoto, Appl. Catal. 70 (1991) L1.
[20] A.V. Kucherov, J.L. Gerlock, H.-W. Jen and M. Shelef, J. Phys. Chem. 98 (1994) 4892.
[21] A.V. Kucherov, J.L. Gerlock, H.-W. Jen and M. Shelef, Zeolites 15 (1995) 9.
[22] A.V. Kucherov, J.L. Gerlock, H.-W. Jen and M. Shelef, Zeolites 15 (1995) 15.
[23] A.V. Kucherov, J.L. Gerlock, H.-W. Jen and M. Shelef, J. Catal. 151 (1995), in press.
[24] A.V. Kucherov, A.A. Slinkin, S.S. Goryaschenko and K.I. Slovetskaya, J. Catal. 118 (1989) 459.
[25] A.V. Kucherov, T.N. Kucherova and A.A. Slinkin, Catal. Lett. 10 (1991) 289.
[26] T.N. Kucherova, unpublished.
[27] J.-F. Hemidy and D. Cornet, J. Chim. Phys. Phys.-Chim. Biol. 71 (1974) 739.
[28] A.V. Kucherov and A.A. Slinkin, Zeolites 7 (1987) 43.
[29] V.A. Shvets, Thesis, Inst. Org. Chem., Moscow, Russia (1982).
[30] A.V. Kucherov and A.A. Slinkin, J. Phys. Chem. 93 (1989) 864.
[31] A.V. Kucherov, C.P. Hubbard and M. Shelef, J. Catal., submitted.
[32] T. Ichikawa, M. Yamaguchi and H. Yoshida, J. Phys. Chem. 91 (1987) 6400.
[33] A.V. Kucherov, A.A. Slinkin, D.A. Kondrat'ev, T.N. Bondarenko, A.M. Rubinstein and Kh.M. Minachev, J. Mol. Catal. 35 (1986) 97.