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In Situ ESR Monitoring of CuH–ZSM-5 up to 500°C in Flowing Dry Mixtures of NO (NO_2), C_3H_6 (C_2H_5OH), and Excess O_2

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A flow cell was used for ESR monitoring of the state of copper ions in Cu–ZSM-5 *in situ* at 20–500°C in a He stream containing C_3H_6 (or C_2H_5OH), NO, and O_2. The gas mixtures approximate those in the selective catalytic reduction of NO_x, save for the absence of steam. At room temperature, in propene flow, the formation of an oligomeric, carbonaceous material is accompanied by the reduction of a significant part of the Cu^{2+} cations. Heating of the sample at 200–300°C leads to quantitative reduction of the cupric ions. Ethanol is a less active reductant, and its sorption at 20–100°C results only in a coordination change of the Cu^{2+} by octahedral complex formation. The onset of the reduction of the Cu^{2+} ions in the [C_2H_5OH + He] flow is at ~200°C. The equilibrium oxidation state of the copper in CuH–ZSM-5 depends on both the temperature and the composition of the gas mixture. At 500°C in the presence of propene or ethanol and in an excess of oxidant, the condition prevailing during SCR, virtually all the copper remains in the Cu^{2+} state. At lower temperatures, in the 200–350°C range, in the same gas mixtures, a partial reduction of the Cu^{2+} ions takes place. High-temperature oxidation of the propene is accompanied by coke deposition on the outer surface of the zeolitic crystals.

INTRODUCTION

Cu–ZSM-5 has become the model catalyst in the study of the low-temperature decomposition of NO to elements and in the selective catalytic reduction (SCR) of NO_x in excess oxygen by organic compounds (1–3). In the past few years Cu–ZSM-5 samples have been examined by FTIR (4), XPS (5), MAS NMR (6), XANES (7), TPD (8), etc. The examined specimens varied widely in Cu loading, the SiO_2/Al_2O_3 ratio, and preparation procedures. Surface characterization methods yield contradictory results about the changes in the coordinative and valence states of the copper after treatment of the samples with different gas mixtures. A facile thermal transition from Cu^{2+} to Cu^{1+} was assumed or noted in several instances in an inert gas or in an oxidizing atmosphere (7, 9, 10). Correspondingly, several investigators considered the cuprous to be the active site for the decomposition of NO (9, 10) and in SCR (11, 12).

Previously, we have 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 nonpolar molecules (13–15). 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 (16–17). The next logical step is to apply the previously developed high-temperature *in situ* method (13) to the monitoring of the state of the copper at 300–500°C in a flow of complex mixtures, containing different reductants.

ESR spectroscopy is a very sensitive method for obtaining information on both the oxidation and the coordination states of copper ions, especially for such dilute systems as isolated Cu^{2+} cations in CuH–ZSM-5 (18–20). Spectra taken at high temperatures afford very specific, but not necessarily complete, information about the course of the catalytic reaction taking place in the flowing gas. The interaction of the copper ions with C_3H_6, C_2H_5OH, NO, O_2, and their mixtures, as registered by the changes in the ESR spectra, is presented in this paper.

EXPERIMENTAL

The ESR spectra were taken in the X band on a Bruker ESP300 spectrometer, equipped with a high-temperature ER4111 HT-VT cavity. The ESR signal from the Mn^{2+} ions in a diluted MnO/Al_2O_3 solid solution was used as an internal standard to ensure stable operation of the spectrometer (13). 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 normalization of the magnification by comparison of the narrow

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Mn^{2+} lines (fifth and sixth components) afforded an accuracy of intensity comparison, for different Cu^{2+} ESR spectra, of ±5%.

The ESR signals were registered in the field range of 2300–3800 G (two scans with a sweep time of 168 s). Resonances for various levels of microwave power were recorded to verify the lack of sample saturation.

A ion-exchanged sample of CuH–ZSM-5 (1.27 wt% Cu, or 67% of the protons exchanged *nominally* for Cu^{2+} into a zeolite with $SiO_2/Al_2O_3 = 50$) was used. For details of the sample preparation see Ref. (13). A coaxial quartz ampoule was designed for *in situ* treatment of the sample in the gas flow (13, 14). The gas flow was regulated by a four-channel readout mass flow controller (Model 247C, MKS Instruments). This system permitted one to change the composition of the gas by regulating the flow through any of the channels from 1.5 to 18 cc/min.

Pure He (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. The mixture [1.7 vol% C_2H_5OH + He] was obtained by bubbling the flow of pure He through absolute ethanol cooled to 0°C.

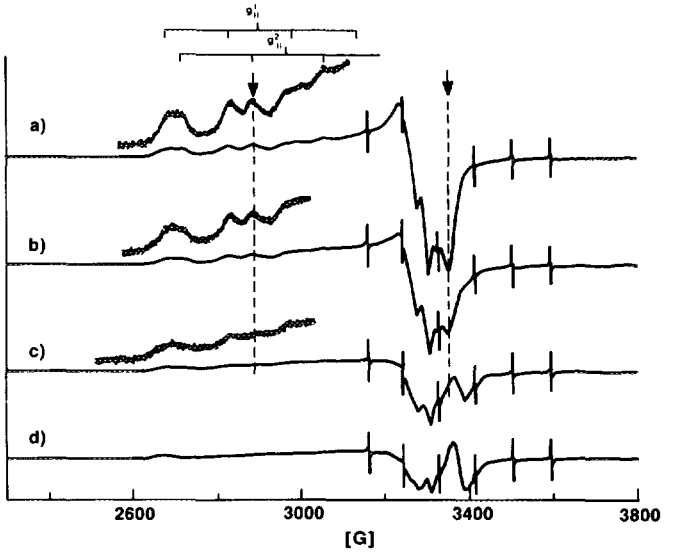

FIG. 1. ESR spectra, at 20°C, of CuH–ZSM-5 precalcined at 500°C in a [O_2 + He] flow: (a) purged by an He flow at 20°C; (b) after 25 min in a [C_3H_6 + He] stream (5 cc/min); (c) after 50 min; (d) after 85 min. The six narrow lines are Mn^{2+} ESR peaks from the internal standard; the line with $g = 2.004$ and $\Delta H \sim 22$ G is the ESR signal from oligomeric cation radicals.

RESULTS AND DISCUSSION

1. *Ambient Temperature Exposure of CuH–ZSM-5 to Flows Containing Hydrocarbons*

Treatment with C_3H_6 at 20°C. Figure 1 shows the gradual change, at 20°C, of the ESR signal of CuH–ZSM-5 (precalcined *in situ* at 500°C in a [O_2 + He] flow for 1 h and cooled to 20°C) in a 5 cc/min flow of [0.39% C_3H_6 + He]. The initial spectrum (Fig. 1a) is rather well resolved and represents the superposition of two main signals from isolated Cu^{2+} ions in two differing coordinations: square pyramidal, with $g_\parallel = 2.32$, $A_\parallel = 154$ G, and square planar, with $g_\parallel = 2.27$, $A_\parallel = 175$ G (13–15). These parameters were first assigned to Cu^{2+} ions in ZSM-5 in previous work (18). Treatment of the sample with a [0.39% C_3H_6 + He] flow is accompanied by the gradual irreversible change in the ESR spectrum shown in Fig. 1. The normalized integral intensity (DI/N) of the cupric ion signal decreases by a factor of 3 after 85 min on stream. Simultaneously, the process is accompanied by the appearance and growth of a new, narrow line, with traces of hyperfine splitting (hfs) ($g = 2.004$, $\Delta H \sim 22$ G; Fig. 1). There is no broadening of the Cu^{2+} ESR signal, formed after 1.5 h in a [C_3H_6 + He] flow, upon the introduction of oxygen into the gas flow. The temporal change of the intensity decrease of the Cu^{2+} ESR signal in the [C_3H_6 + He] stream is shown in Fig. 2 (curve 1).

As shown earlier (21, 22), fast oligomerization of alkenes takes place upon their sorption onto the H form of ZSM-5 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 presence of Cu^{2+} cations in the ZSM-5 channels does not stop this process, but the hfs of the ESR signal is less resolved (23). The appearance of the line at $g \sim 2.004$ (Fig. 1) indicates the formation of carbonaceous oligomers on the CuH–ZSM-5. The lack of influence of O_2 on the Cu^{2+}

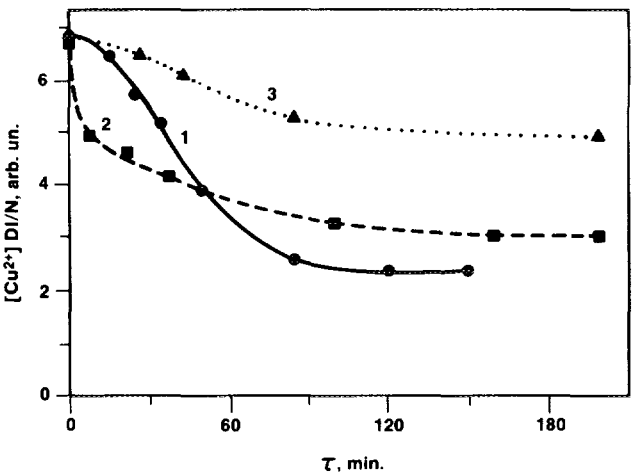

FIG. 2. Decrease in the intensity of the Cu^{2+} ESR signal (DI/N, normalized double integral) after treatment of CuH–ZSM-5, at 20°C, by propene-containing gas mixtures: (1) [0.39% C_3H_6 + He], 5 cc/min; (2) [0.04% C_3H_6 + 0.37% NO + He], 15 cc/min; (3) gas mixture (1) after NO_2 pretreatment.

ESR signal (Fig. 1d) in propene-free flows at ambient conditions (14) confirms once more the shielding of the residual cupric cations inside the zeolitic channels by the carbonaceous material.

There remains a question: is the 2/3 loss of the ESR signal upon sorption of the propene at 20°C (Fig. 2, curve 1) due to a redox process or is it caused by formation of a complex with Cu^{2+}? The spin cannot be lost by formation of a complex between the non-paramagnetic propene (or some secondary alkene formed upon oligomerization) and the Cu^{2+} ion. In the case of complex formation with charge transfer, subsequent heating of the sample in He flow should lead to the restoration of the original ESR signal shown in Fig. 1a, as a result of propene desorption. The heating of the sample in He flow at 100–200°C is accompanied by a further drop of the signal intensity down to a trace. Hence, the loss of the cupric ions due to the interaction between CuH–ZSM-5 and propene is irreversible. The reduction of the cupric cations by a reactive alkene is a facile process. The quantitative reduction of Cu^{2+} by the formed carbonaceous material takes place at 200°C even in a stream of [20.2% O_2 + He]. It is plausible that the reactive deposit blocks the access of the oxygen to the pores and the reduction of the residual cupric ions is faster than pore deblocking.

Referring back to the two main coordination sites of Cu^{2+} in CuH–ZSM-5 which differ in their reactivity, the present results confirm this representation: the interaction with propene at 20°C leads to a total loss of more reactive square-planar Cu^{2+} cations. This is shown in Fig. 1 by the more rapid disappearance of the signal associated with the square-planar configuration of Cu^{2+}, the resolved $g_{\|}$ and $g_{\perp}$ components of which are marked with arrows.

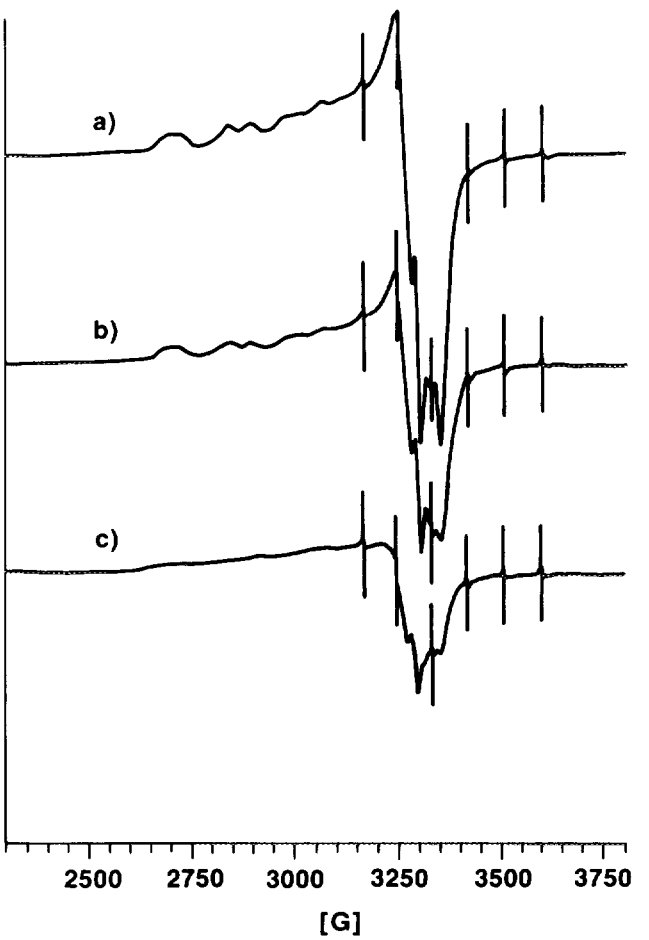

FIG. 3. ESR spectra of CuH–ZSM-5 precalcined at 500°C in a [O_2 + He] flow: (a) purged by He; (b) after 23 min in [0.04% C_3H_6 + 0.37% NO + He]; (c) after 100 min.

Treatment by [C_3H_6 + *NO*]. Treatment of CuH–ZSM-5, at 20°C, by the gas mixture [0.04% C_3H_6 + 0.37% NO + He] results in the gradual irreversible change in the Cu^{2+} ESR spectrum, as shown in Fig. 3. Two differences from the case mentioned above must be noted: (i) the narrow line at $g \sim 2.004$ does not appear upon the interaction of CuH–ZSM-5 with C_3H_6 in the presence of NO; and (ii) the intensity drop of the Cu^{2+} ESR signal occurs much *faster* (Fig. 2, curve 2) despite the much lower alkene concentration in the flow. The absence of the carbonaceous radicals may indicate the absence of the oligomers which may be due to the low concentration of propene or to the inhibition of the formation of the deposits by NO. Conversely the deposits may still be present, but the signal may be quenched by the pairing of spins between the NO and carbonaceous radicals. A similar behavior persists at 500°C (*vide infra*). Indeed, the presence of NO does not prevent the reduction of Cu^{2+} ions because some accumulation of reactive alkenic species inside the zeolite does take place during the treatment, and subsequent heating of the sample at 200°C, followed by a stoppage of the flow, results in a complete reduction of the cupric ions.

Interaction of C_3H_6 with CuH–ZSM-5 pretreated by [*NO* + O_2]. As shown previously (14), the treatment of CuH–ZSM-5, at 20°C, with [NO + O_2] results in the formation of a strong adsorption complex with NO_2 molecules. It is of interest to establish whether these strong ligands influence the subsequent interaction between the Cu^{2+} sites and propene molecules. Figure 4 shows the change in the Cu^{2+} ESR signal upon the interaction, at 20°C, between propene and CuH–ZSM-5 pretreated with [NO + O_2] flow. The loss of the integral intensity of the signal is shown in Fig. 2, curve 3. Figure 4 also demonstrates that the sorption of propene results in a noticeable change in the coordination of the cupric ion. At the same time, there is no drastic drop in the signal intensity (Fig. 2, curve 3), as distinct from the two cases discussed

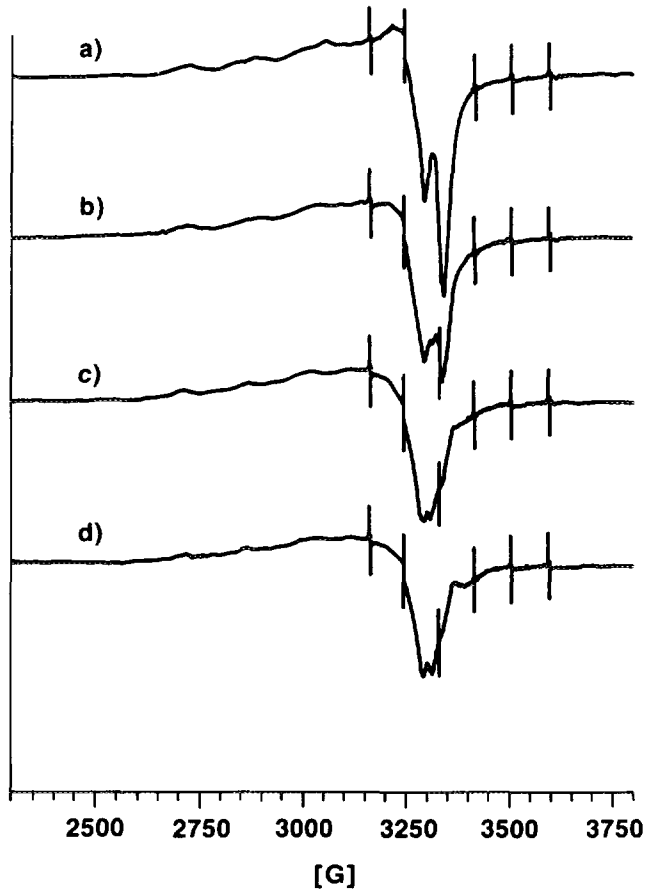

FIG. 4. ESR spectra, at 20°C, of CuH–ZSM-5: (a) after the saturation of the sample with NO_2 from a [NO + O_2] flow; (b) after 25 min in a [0.39% C_3H_6 + He] flow (5 cc/min); (c) after 43 min; (d) after 85 min.

above. Hence, the preadsorption of NO_2, which changes the coordination of the cupric ion (14), also inhibits the interaction with propene at ambient temperature. There have been suggestions (24) that in the selective catalytic reduction one of the effects of oxygen is to maintain the copper ions in the cupric state. As our data show, this is indeed the case at low temperatures.

Interaction of C_2H_5OH with Cu–ZSM-5 at 20–200°C. The sorption of ethanol onto CuH–ZSM-5 at 200°C is accompanied by a sharp change in the shape of the Cu^{2+} ESR signal without a decrease in the integral intensity. The new signal (Fig. 5a), with $g_{\|} = 2.38$ and $A_{\|} = 125$ G, is typical of octahedral complexes of Cu^{2+} which form, as a rule, with polar molecules. Spin-echo measurements from Sass and Kevan (19, 20) have shown that small alcohols link to Cu^{2+} cations inside H–ZSM-5 through the oxygen atom of the OH moiety. It was posited that the bonding with three or four alcohol molecules is accompanied by the displacement of cupric ions to the intersection of the channels, with the formation of the most symmetrical octahedral environment. Our results (Fig. 5a) agree very well with this representation. Both square-planar and pyramidal cupric cations participate in this complex formation. The comparison of the DI/N values for the original ESR signal and the spectrum obtained after the sorption of C_2H_5OH (Fig. 5a) shows that there is no change in the oxidation state of Cu^{2+} upon C_2H_5OH sorption at 20°C.

The spectrum shown in Fig. 5a is not altered by heating the sample at 100°C for 1 h and cooling in a C_2H_5OH stream. The most exact comparison by subtraction demonstrates the complete coincidence of the two spectra. A more severe treatment of the sample at 200°C for 1 h in a flow of [C_2H_5OH + He] does change the Cu^{2+} ESR signal (Fig. 5b). The signal retains only ~25% of its original intensity. The difference between the two spectra (Fig. 5c) is due to reduction by the ethanol at 200°C. Not surprisingly, ethanol is less active in the reduction of the cupric ions than propene.

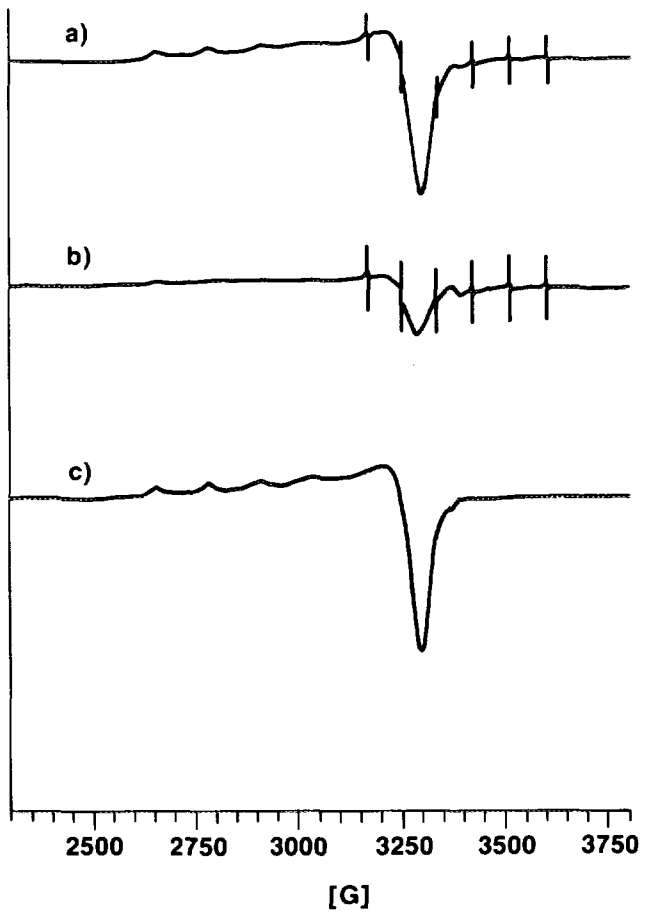

FIG. 5. ESR spectra of CuH–ZSM-5 treated with a [1.7% C_2H_5OH + He] flow: (a) saturated with C_2H_5OH at 20°C; (b) after heating at 200°C in the flow; (c) (a) − (b) (magnified ×3).

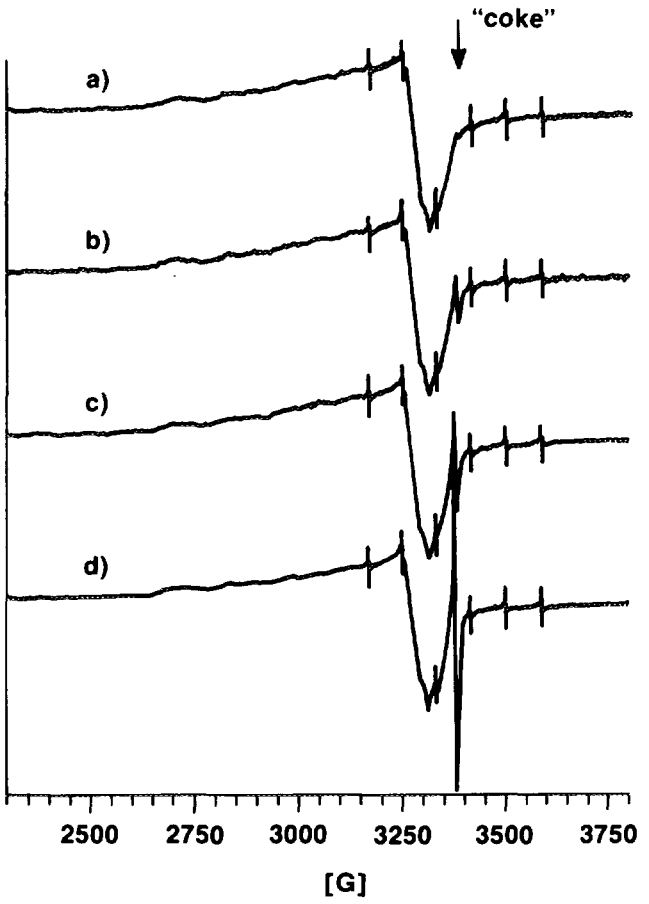

FIG. 6. Change in the Cu^{2+} ESR signal, at 500°C, after contact of CuH–ZSM-5 with [C_3H_6 + O_2] (15 cc/min): (a) in [2.7% O_2 + He] flow; (b) 20 min in [0.21% C_3H_6 + 2.7% O_2]; (c) 20 min in [0.26% C_3H_6 + 2.7% O_2] stream; (d) 15 min in [0.355% C_3H_6 + 1.84% O_2].

2. *High-Temperature Interaction of CuH–ZSM-5 with [Hydrocarbon + Oxidant] Gas Mixtures*

The dynamic state of CuH–ZSM-5 during the SCR catalytic process at 300–500°C in gas mixtures with changing ratios of components is of the most direct relevance to the understanding of the behavior of a catalytic site. To this end we followed the oxidation of propene and ethanol by O_2 and NO at 500 and 300°C.

Virtually all the cupric ions in our sample contribute to the ESR signal (15). When the gas flow is switched from the [O_2 + He] to the complex mixture containing both the oxidant and the reductant the drop in the DI/N reflects quantitatively the extent of Cu^{2+} reduction. The dynamic steady state is established rapidly at 300–500°C.

Oxidation of C_3H_6 by O_2 on Cu–ZSM-5 at 500°C. Figure 6a presents the spectrum of CuH–ZSM-5 taken at 500°C in a flow of [2.7% O_2 + He]. A switch of the gas flow to a strongly oxidizing propene-containing mixture [2.7% O_2 + 0.21% C_3H_6] results in a minor change of the spectral shape (Fig. 6b) during the first few minutes on stream. No further change of this signal occurs upon treatment of the sample for 20 min. Comparison of the double integrals of the spectra in Fig. 6, taken subsequently under identical conditions, shows, with an accuracy of ±5%, that no measurable reduction of CuH–ZSM-5 takes places at 500°C as a result of the switch from [2.7% O_2 + He] to the strongly oxidizing, propene-containing gas. Shifting the gas composition nearer to stoichiometry, as in a mixture of [1.84% O_2 + C_3H_6], where the O_2/C_3H_6 mole ratio is 5.3, compared to the stoichiometric ratio of 4.5, leads to a noticeable decrease in the signal intensity (Fig. 6d; ~84% of the initial value). Thus, the reduction of the cupric ions becomes measurable only when the excess of the oxygen becomes small. Under SCR conditions the excess is, as a rule, large. A further decrease in the oxygen/reductant mole ratio below 4.5 induces a sharp change in the catalyst state: a complete reduction of the copper occurs very quickly at 500°C, and the restoration of the parent state of the catalyst, with isolated Cu^{2+} cations, takes 1–2 h when treating the sample with a flow of [20% O_2 + He].

Figure 6 also shows that the catalytic oxidation of propene in excess oxygen, at 500°C, is accompanied by the appearance and gradual rise of a narrow ESR singlet ($\Delta H \sim 8$ 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 (21). Graphitized "coke" particles are too large for accommodation in the pores and can be located only on the outer surface of the zeolite crystals.

Interaction of CuH–ZSM-5 with [C_3H_6 + O_2] at 300°C. ESR spectra were also taken during the treatment of CuH–ZSM-5 with [C_3H_6 + O_2] at 300°C (Fig. 7). Distinct from the process at 500°C, the addition of 0.26% C_3H_6 to a stream of [2.7% O_2 + He] stream causes a measurable decrease in the Cu^{2+} in the sample: a 15% loss of the signal intensity after 70 min on stream. The reduction of the cupric ions is much faster when the concentration of propene in the flowing gas is adjusted to a oxygen/propene ratio of 5.3. The more reactive square-planar cupric ions are reduced first. Here, again, the appearance of the sharp signal due to coke formation is observed after only 5 min on stream.

Interaction of CuH–ZSM-5 with [C_3H_6 + O_2] at 500°C. At a NO/propene ratio of ~16 [0.024% C_3H_6 + 0.38% NO], 80% excess oxidant over stoichiometry, the Cu^{2+} signal does not change at 500°C after 1 h of treatment, within the ±5% accuracy of the measurement (Fig. 8). Increasing the propene concentration to 0.0365%, which corresponds to only 15% excess oxidant, induces a gradual reduction of the cupric ions. The switch to a flow of 0.38% NO in He does not quickly restore the signal.

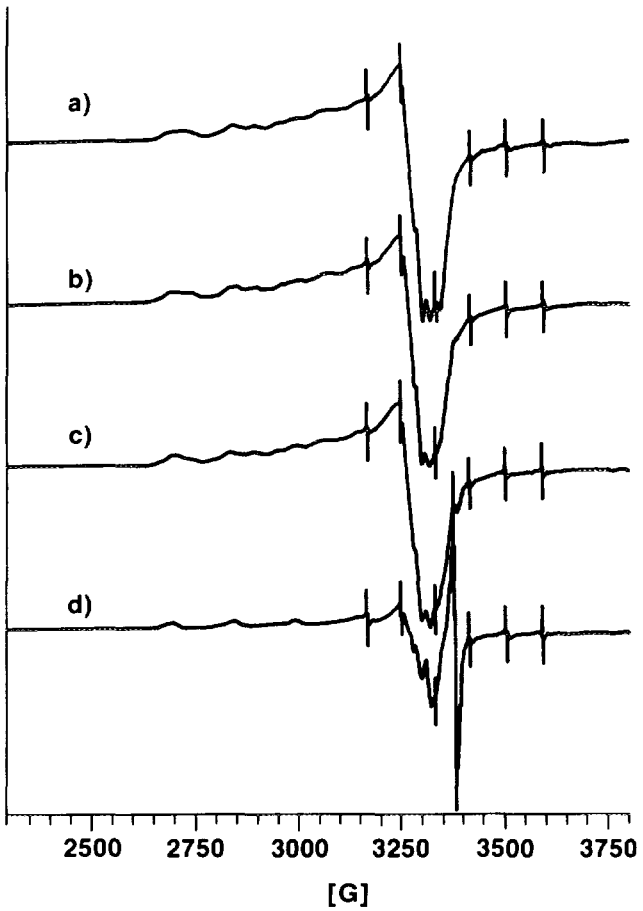

FIG. 7. Change in the Cu^{2+} ESR signal after contact of CuH–ZSM-5 with [$C_{36}6$ + O_2 + He] mixtures at 300°C: (a) in [2.7% O_2 + He] flow; (b) 22 min in [0.26% C_3H_5 + 2.7% O_2 + He]; (c) 70 min in the same flow; (d) 5 min in [0.355% C_3H_6 + 1.84% O_2 + He].

As could be expected, oxygen is more active than NO at reoxidizing the reduced copper ions.

As was noted at room temperature, at 500°C the presence of NO in the gas *strongly inhibits* the narrow ESR line associated with the carbonaceous deposits. Thus, the two spectra taken under close to stoichiometric conditions, one in the presence of O_2 (Fig. 6d) and the other in the presence of NO (Fig. 8d), differ greatly in the $g \sim 2.004$ signal. It is very prominent in the former and almost absent in the latter. Two explanations are possible: (a) very little carbonaceous deposit is formed in the presence of NO at relatively low propene concentrations or (b) the unpaired electron in the NO couples with the carbonaceous radicals, quenching the signal of the latter. There is indirect evidence that the bonding of NO to the carbonaceous deposits does take place on zeolitic catalysts (25), but more work is needed for confirmation.

Effect of the ternary gas mixture [C_3H_6 + O_2 + NO] at 500°C. Addition of 0.05 to 0.14% NO to the strongly oxidizing gas [2.7% C_3H_6 + 0.21% O_2] does not affect the equilibrium oxidation state of the copper in CuH–ZSM-5 at 500°C. No changes are discernible in the ESR spectra when using the most exact subtraction method.

Figure 9 summarizes the relations between the concentrations of the Cu^{2+} ions and the oxidant/propene ratio for all studied cases.

Oxidation of ethanol on CuH–ZSM-5 at 500°C. The contacting of Cu–ZSM-5, at 500°C, with flows of [20.2% O_2 + 1.7% C_2H_5OH] (a fourfold excess of oxidant) and [10.1% O_2 + 1.7% C_2H_5OH] (a twofold excess) does not change the ESR signal shape or decrease its intensity. The oxidation of ethanol engenders only a trace of the sharp line characteristic of carbonaceous residues. This agrees well with previous observation that the formation of coke is negligible during the oxidation of less reactive hydrocarbons.

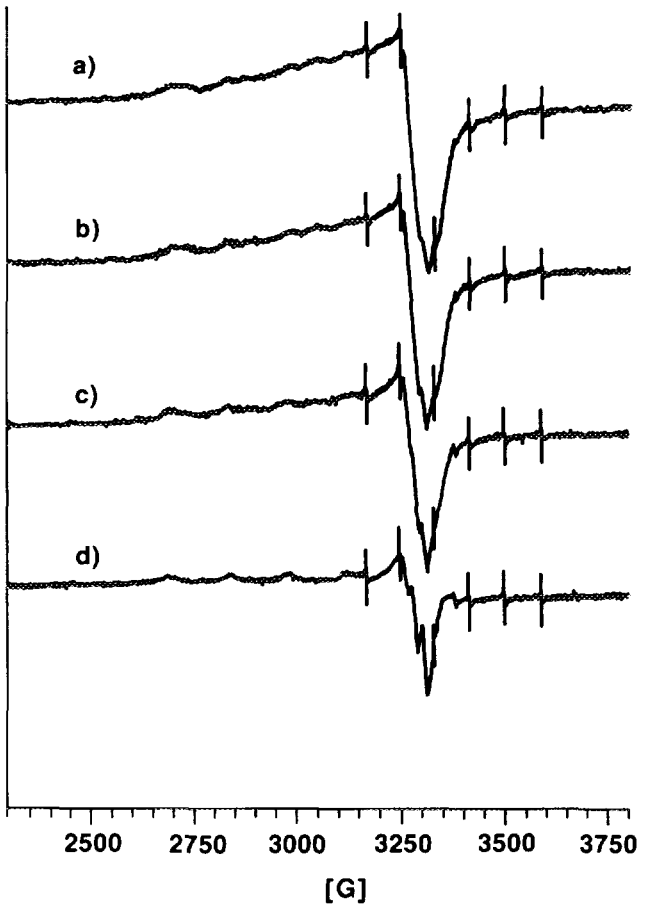

FIG. 8. Change in the Cu^{2+} ESR signal, at 500°C, after contact of CuH–ZSM-5 with [C_3H_6 + NO] (15 cc/min): (a) in [0.41% NO + He]; (b) 30 min in [0.024% C_3H_6 + 0.38% NO]; (c) 8 min in [0.0365% C_3H_6 + 0.38% NO] stream; (d) 35 min in [0.0365% C_3H_6 + 0.38% NO].

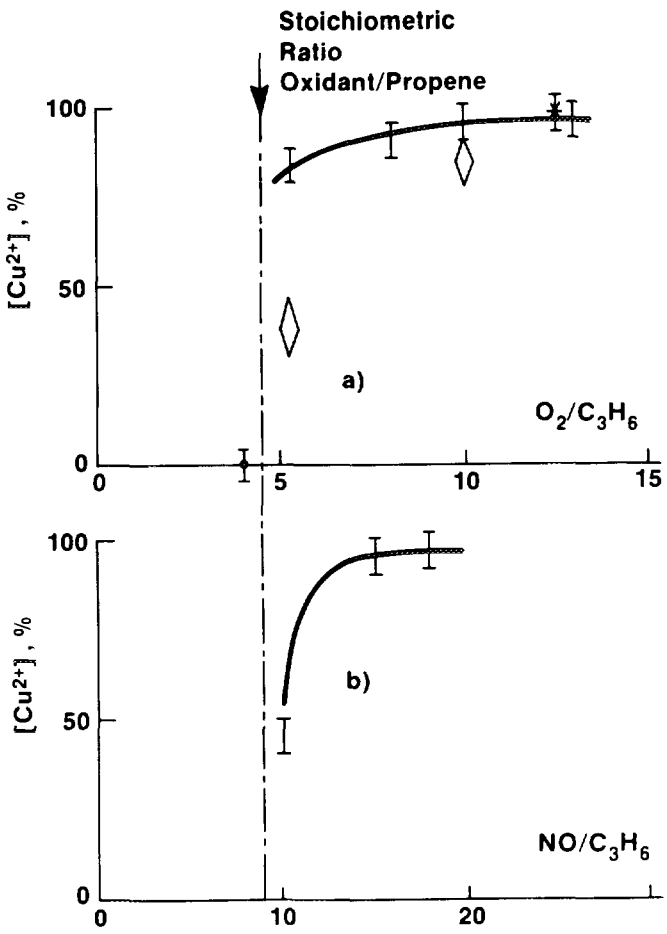

FIG. 9. Concentration of Cu^{2+} ions in CuH–ZSM-5 vs the ratio of oxidant/propene in the gas at 500°C: (a) [C_3H_6 + O_2]; (b) [C_3H_6 + NO]; (*) [C_3H_6 + $O2$ + NO]; (◇) 300°C.

CONCLUDING REMARKS

This work demonstrates unambiguously that at steady state, under typical conditions of selective catalytic reduction with a large excess of oxygen, virtually all of the copper is present in the Cu^{2+} state. The dynamic equilibrium $Cu^{2+} \leftrightarrow Cu^{+}$ is shifted completely to the left. The reoxidation of any reduced sites by O_2, or even more so by NO_2, is very fast. Only at lower temperatures and/or close to stoichiometry does this equilibrium begin to shift to the right.

The earlier results, that the square-planar isolated cupric ions are the most reactive, were confirmed. It is plausible that the same sites are also most susceptible to deactivation.

Exposure of CuH–ZSM-5 to a high-temperature reducing environment, i.e., oxygen-deficient gas mixtures, causes fast reduction of the copper, possibly with the formation of Cu^0 crystallites leading to deactivation. Subsequent reactivation in an oxidizing environment is sluggish. In this context, in practical automotive implementation one needs to avoid copious adsorption of hydrocarbons at cold start which may subsequently reduce the copper in the warm-up time period.

The results indicate the possibility of an interaction between NO and the carbonaceous deposits which entails spin-coupling between the radicals in both reactants. This must be confirmed further.

The present findings pertain strictly to CuH–ZSM-5 where the cupric ions are *isolated* and all are sensed by ESR (13, 14). The sample was deliberately chosen so as to avoid the ambiguities associated with "overexchange," extra-framework copper, etc.

REFERENCES

1. Ansell, G. P., Diwell, A. F., Golunski, S. E., Hayes, J. W., Rajaram, R. R., Truex, T. J., and Walker, A. P., *Appl. Catal. B* **2,** 81 (1993).
2. Valyon, J., and Hall, W. K., *J. Phys. Chem.* **97,** 1204 (1993).
3. Kharas, K. C. C., *Appl. Catal. B* **2,** 207 (1993).
4. Giamello, E., Murphy, D., Magnacca, G., Morterra, C., Shioya, Y., Nomura, T., and Anpo, M., *J. Catal.* **136,** 510 (1992).
5. Shpiro, E. S., Grunert, W., Joyner, R. W., and Baeva, G. N., *Catal. Lett.* **24,** 159 (1994).
6. Grinsted, R. A., Jen, H.-W., Montreuil, C. N., Rokosz, M. J., and Shelef, M., *Zeolites* **13,** 602 (1993).
7. Liu, D.-J., and Robota, H. J., *Catal. Lett.* **21,** 291 (1993).
8. Li, Y., and Armor, J. N., *Appl. Catal.* **76,** L1 (1991).
9. Iwamoto, M., and Hamada, H., *Catal. Today* **10,** 57 (1991).
10. Hall, W. K., and Valyon, J., *Catal. Lett.* **15,** 311 (1992).
11. Sepulveda-Escrivano, A., Marquez-Alvarez, C., Rodriguez-Ramos, I., Guerrero-Ruiz, A., and Fierro, J. L. G., *Catal. Today* **17,** 167 (1993).
12. Burch, R., and Millington, P. J., *Appl. Catal. B* **2,** 101 (1993).
13. Kucherov, A. V., Gerlock, J. L., Jen, H.-W., and Shelef, M., *J. Phys. Chem.* **98,** 4892 (1994).
14. Kucherov, A. V., Gerlock, J. L., Jen, H.-J., and Shelef, M., *Zeolites*, in press.
15. Kucherov, A. V., Gerlock, J. L., Jen, H.-J., and Shelef, M., *Zeolites*, in press.
16. Kucherov, A. V., Slinkin, A. A., Goryashenko, S. S., and Slovetskaya, K. I., *J. Catal.* **118,** 459 (1989).
17. Kucherov, A. V., Kucherova, T. N., and Slinkin, A. A., *Catal. Lett.* **10,** 289 (1991).
18. Kucherov, A. V., Slinkin, A. A., Kondrat'ev, D. A., Bondarenko, T. N., Rubinshtein, A. M., and Minachev, Kh. M., *Zeolites* **5,** 320 (1985).
19. Sass, C. E., and Kevan, L., *J. Phys. Chem.* **93,** 7856 (1989).
20. Sass, C. E., and Kevan, L., *J. Phys. Chem.* **92,** 5192 (1988).
21. Kucherov, A. V., Slinkin, A. A., Kondrat'ev, D. A., Bondarenko, T. N., Rubinshtein, A. M., and Minachev, Kh. M., *J. Mol. Catal.* **35,** 97 (1986).
22. Slinkin, A. A., Kucherov, A. V., Kharson, M. S., Bondarenko, T. N., and Minachev, Kh. M., *J. Mol. Catal.* **53,** 293 (1989).
23. Slinkin, A. A., Kucherov, A. V., Chuvylkin, N. D., Korsunov, B. A., Kliachko, A. L., and Nikishenko, S. B., *J. Chem. Soc. Faraday Trans. 1* **85,** 3233 (1989).
24. Petunchi, J. O., Sill, G. A., and Hall, W. K., *Appl. Catal. B* **2,** 303 (1993).
25. Yogo, K., Ogura, M., Ono, T., and Kikuchi, E., *Prepr. Div. Petr. Chem. Am. Chem. Soc.*, 159 (1994).