Structure and Behavior of Active Sites in Fe-ZSM-5 DeNO$_x$ Catalysts: New Insight by Spectroscopic In situ-studies

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Introduction

In recent years, Fe-ZSM-5 zeolites have been recognized as highly efficient catalysts for a number of reactions, among them selective catalytic reduction (SCR) of NO_x by NH_3 [1] and hydrocarbons [2]. The outstanding catalytic activity of these materials has been related in most cases to isolated [2], dimer [3] and/or small cluster-like FeO_x species of only few Fe atoms, the formation of which is favored by the confinement of the ZSM-5 pore geometry. However, it has been shown that reliable identification of the structure and function of single Fe sites co-existing with FeO_x clusters is not straightforward even when using several spectroscopic techniques [2]. In this work, in situ-EPR and in situ-UV/VIS-DRS spectroscopy were used to monitor the behavior of Fe species during heating in air and reactant flow in differently prepared Fe/ZSM-5 catalysts used for SCR of NO by isobutane. Thus, changes of Fe^{3+} species in dependence on the preparation conditions were studied and active Fe sites being accessible by gas phase molecules could be identified.

Results and Discussion

Fe-ZSM-5 samples with 5.0 – 5.4 wt.-% Fe were prepared from the H-form of commercial Na-ZSM-5 by chemical vapor deposition (CVD) using $FeCl_3$ followed by washing with 1 l (W_1) or 10 l water per 5g catalyst (W_{10}) and calcination at 873 K with heating rates of 0.5 K/min ($C_{0.5}$) or 5 K/min (C_5). Preparation details as well as results of ex situ-characterization and catalysis are described in [2]. The following samples were studied: 1) W_1 (without calcination), 2) W_1C_5, 3) $W_1C_{0.5}$, 4) $W_1C_{0.5}U$ (after use in SCR), 4) $W_{10}C_{0.5}U$, 5) SSIE (prepared by solid state ion exchange using $FeCl_3$ without subsequent washing and calcination, Fe content 8.7 wt.-%). Spectroscopic in situ-studies up to 773 K were performed using a home-made flow reactor for EPR [4] and a commercial diffuse reflectance accessory (Harrick) for UV/VIS-DRS measurements.

EPR spectra of all samples show signals of isolated Fe^{3+} ions in strong rhombically ($g' \approx 4.3$) and axially distorted environment ($g' \approx 6.0$) as well as a broad line at $g' \approx 2$ arising from oxidic clusters. UV/VIS-DRS spectra are characterized by $Fe^{3+} \leftarrow O$ charge-transfer (CT) bands below 250 nm (isolated tetrahedral Fe^{3+}), at 300 – 450 nm (oligomeric Fe^{3+}) and above 450 nm (larger clusters with octahedral Fe^{3+}) [5]. Depending on the preparation conditions, the relative intensity of the EPR signals and UV/VIS bands differs markedly.

Effect of calcination: During calcination the amount of isolated Fe^{3+} sites in fresh samples W_1 and SSIE decreases markedly in favor of Fe_xO_y clusters. Comparison of

samples $W_1C_{0.5}$ and W_1C_5 suggests that this effect is slightly more pronounced at higher calcination rates.

Effect of washing: In comparison to sample $W_1C_{0.5}U$, EPR and UV/VIS spectra of sample $W_{10}C_{0.5}U$ indicate a higher relative percentage of isolated Fe^{3+} species and the temperature dependence of the g´≈ 2 EPR signal points to a decrease of the Fe_xO_y cluster size in sample $W_{10}C_{0.5}U$.

Interaction with gas phase molecules: By evacuating sample SSIE at 293 K (Fig. 1) or heating to 773 K, the EPR signal at g´≈ 6 disappears and the one at g´≈ 4.3 increases suggesting that octahedral Fe sites (g´≈ 6) might release adsorbed water ligands and become tetrahedral (g´≈ 4.3). This process is reversible in ambient atmosphere at 293 K. In contrast, the g´≈ 2 signal remains unchanged suggesting that larger Fe_xO_y clusters are less sensitive to the interaction with gas phase molecules and, therefore, may play a minor role in the SCR reaction as concluded in [2].

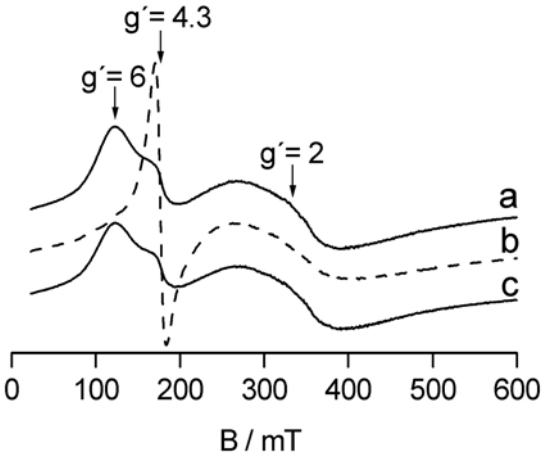

Fig. 1. EPR spectra of sample SSIE at 293 K: a) in air, b) in vacuum, c) re-exposed to air

Effect of catalytic reaction: Both EPR and UV/VIS spectra of samples $W_1C_{0.5}$ and $W_1C_{0.5}U$ reveal that Fe_xO_y clusters form during SCR of NO_x at the expense of isolated Fe^{3+} sites, in particular, of those giving rise to the g´≈ 6 EPR signal. In situ-experiments with reactant molecules such as NO and isobutane being under way are expected to shed more light on the role of the different isolated Fe^{3+} species under reaction conditions.

In summary, the experiments have shown that in situ-EPR and -UV/VIS spectroscopy are powerful tools to distinguish different co-existing Fe^{3+} species in ZSM-5 matrices and to follow their structural changes in dependence on temperature and gas atmosphere.

References

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