

Dynamic changes of Mn species in MnSiBEA zeolite under NH₃-SCR realistic conditions monitored by XAS and XES spectroscopies

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The emission of nitrogen oxides to the atmosphere has severe impact on the environment that can be mitigated by catalytic reduction of NO_x. Despite numerous studies fundamental questions concerning the catalytic mechanism, intermediate complexes and site products formation remain unanswered. Unrevealing a mechanism for deNO_x reaction requires investigation under realistic conditions with catalyst containing well defined active centers and powerful spectroscopic techniques. In this work, we decided to put into action synchrotron based photon-in/photon-out techniques under operando conditions to study the chemical state and coordination of Mn species in zeolite MnSiBEA obtained by two-step postsynthesis method [1].

The two-step postsynthesis method proposed by Dzwigaj et al. [1] was applied to obtain single-site zeolite catalyst – MnSiBEA. The detail description of the preparation method is reported in previous work [2]. The high resolution XAFS measurements were carried out at ID26 beamline of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France equipped with an emission spectrometer. High-Energy Resolution Fluorescence Detected X-ray Absorption Spectra (HERFD-XAS) at the maximum of K α_1 emission line. The in-situ cell integrated in a devoted gas-flow setup was used as a reactor in operando experiments.

In our work, we applied the two-step postsynthesis method because this procedure allows introduction Mn into framework positions of BEA structure as isolated mononuclear species. It has been proved by complementary studies with XRD, FTIR and EPR as well as by calculation involving FDMNS code. The HERFD-XANES spectra recorded under various model conditions exhibit significant differences in spectral features and edge positions. The changes of the atmosphere from inert (He) to oxidant one (O₂) considerably impacted the state of the Mn centers. The shift of the edge position (determined as maximum of 1st derivative) toward higher energy by ~1 eV suggests increase in oxidation number. An inverse trend was observed when the oxidized sample was contacted with an atmosphere containing NH₃. This confirms that a large fraction of Mn(III) is reduced to Mn(II) due to adsorption of ammonia. When the catalyst was exposed to the NO/He gas mixture the absorption edge appeared between the two extremes indicating rather mild interaction between nitric oxide and Mn species. Furthermore, the pre-edge features subtracted from XANES spectrum show under O₂ a pronounced feature at 6540 eV and another peak at 6541.8 eV typical for Mn(III) while spectrum obtained under NH₃ exhibits one pronounced peak at 6439.7 eV characteristic for Mn(II). Moreover, the results of EXAFS analysis clearly show that modification of reaction conditions influences the Mn–O bonds distances in first coordination shell as well as the interactions of Mn with the zeolite framework (2 – 3 Å range of Mn–Si distance).

The analysis of the high resolution XANES and EXAFS spectra demonstrates a strong impact of the reaction conditions on electronic structure and coordination of Mn centers and indicate high redox dynamics of Mn(II)/Mn(III).

1. S. Dzwigaj, M.J. Peltre, P. Massiani, A. Davidson, M. Che, T. Sen, S. Sivasanker, Chem. Commun. (1998) 87.
2. S. Dzwigaj, P. Massiani, A. Davidson, M. Che, J. Mol. Catal. A Chem. 155 (2000) 169.