The dynamic changes of Mn species in MnSiBEA catalyst for NH_3-SCR under realistic conditions monitored by high resolution XAS spectroscopy

Stanislaw Dzwigaj[a,*], **Rafal Baran**[b,*]

[a]*Sorbonne Universités, UPMC Univ Paris 06, CNRS, UMR 7197, Laboratoire de Réactivité de Surface, F-75005, Paris, France*

[b]*ESRF – The European Synchrotron, 71 Avenue des Martyrs, Grenoble, France*

**Corresponding authors: stanislaw.dzwigaj@upmc.fr, rafal.baran@esrf.fr*

Abstract: To be able to properly investigate the mechanism of SCR of NO with NH_3 the possession of model catalyst with well-established active centers is required. To achieve this condition we applied two-step postsynthesis method to introduce Mn ions into zeolite framework and obtain MnSiBEA material with isolated, mononuclear Mn species. We used this zeolite catalyst in the in-situ/operando X-ray absorption spectroscopy involving high resolution XANES and EXAFS experiments at synchrotron radiation facilities. The results revealed reason of manganese species reactivity and their behaviors under model conditions.

Keywords: zeolite, SCR, XAS, operando

1. Introduction

The emission of nitrogen oxides (NO, NO_2 and N_2O) to the atmosphere has severe impact on the environment that can be mitigated by catalytic reduction of NO_x ($DeNO_x$). Despite numerous studies fundamental questions concerning the catalytic mechanism, intermediate complexes and site products formation remain unanswered [1–2]. Moreover, currently proposed solutions for industrial application are not sufficiently good to fulfil all environmental requirements, thus improvements should be implemented.

Unrevealing a mechanism for $deNO_x$ reaction requires study under realistic conditions with catalyst containing well defined active centers and powerful spectroscopic techniques. Thus, we decided to study the chemical state and coordination of Mn species in zeolite MnSiBEA, obtained by two-step postsynthesis method [3,4], with high resolution XANES and EXAFS under operando conditions.

2. Experimental

The MnSiBEA catalyst was obtained by two-step postsynthesis method proposed by Dzwigaj et al. A detail description of the preparation method is reported elsewhere [3]. The XAS measurements were carried out at ID26 beamline of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France equipped with an emission spectrometer with five Ge(333) crystal analyzers in Roland circle geometry. High-Energy Resolution Fluorescence Detected X-ray Absorption Spectra (HERFD-XAS) were recorded by scanning the incident energy and detecting the fluorescence at the maximum of $K\alpha_1$ emission line. The Maxthal® in situ cell integrated in a devoted gas-flow setup was used as a reactor in operando experiments. The desired concentrations of O_2 (12 vol. %), NO (1000 ppm) and NH_3 (1000 ppm) were obtained by mixing pure gases with He as inert carrier. The gas flow was kept at 35 cm^3 min^{-1}. The gas evolutions were monitored by μGC analyzer equipped with MS5A (10 m) and PPU (8 m) columns and TCD detector.

3. Results and discussion

The two-step postsynthesis procedure of zeolite BEA modification allowed introducing Mn into framework positions as isolated mononuclear species. The successful incorporation of Mn ions in the framework of BEA zeolite has been confirmed by XRD, FTIR, UV-Vis and EPR as we reported in previous work [5]. We extensively investigated zeolite samples by various ex-situ spectroscopic techniques to gain information on the electronic structure and environment of Mn in the framework of Mn-containing SiBEA zeolites. However, to establish changes in the oxidation state and coordination of Mn over $deNO_x$ reaction it is necessary to use element-specific spectroscopic technique under realistic conditions. It has been demonstrated [6] that the synchrotron-based techniques (XAS and XES) combined with catalytic set-up are powerful tools to study mechanism of various catalytic reactions. The HERFD-XANES spectra (shown on Figure 1A) 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 (O_2) 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 NH_3. This may indicate 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. The analysis of the pre-edge features in the XANES spectrum after subtraction from white line (inset of Fig 1A) brings additional confirmation of Mn species transition during modulation of experiment conditions. For example, the pre-edges obtained under O_2 consists of a pronounced feature at 6540 eV and another peak at 6541.8 eV typical for Mn(III) while spectrum recorded under NH_3 exhibits one pronounced peak at 6439.7 eV characteristic for Mn(II) [7]. Moreover, the results of EXAFS analysis (Fig. 1B) clearly show that modification of reaction conditions influences the Mn–O bonds distances in first coordination shell as well as coordination number.

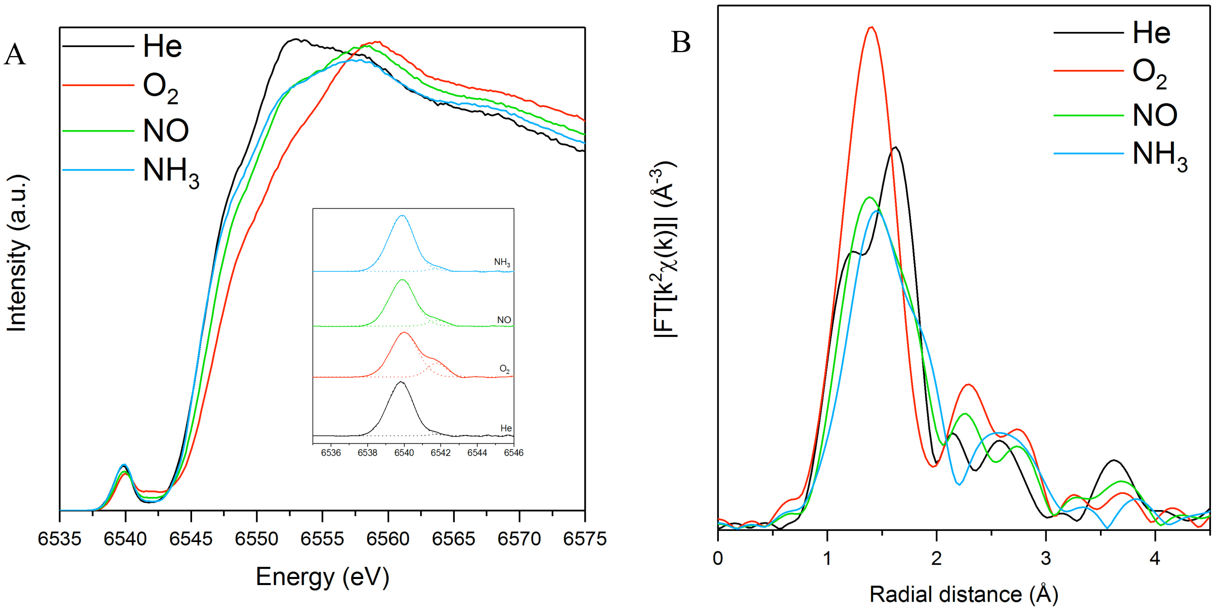

Figure 1. Kα$_1$-detected high resolution XANES spectra of MnSiBEA zeolite recorded under model SCR conditions. The inset shows the pre-edge features after main absorption line subtraction (A); Magnitude of the phase-uncorrected FT EXAFS spectra obtained by transformation the k^2-weighted $\chi(k)$ curves in the 2 – 11 $Å^{-1}$ range (B).

4. Conclusions

The two-step postsynthesis method of zeolite BEA modification allows introduction of Mn into zeolite framework in form of isolated Mn species. The analysis of the high resolution XANES and EXAFS spectra demonstrates a strong impact of the reaction conditions on structure and coordination of Mn centers and indicate that high redox dynamics of Mn(II)/Mn(III) is responsible of catalyst remarkable activity in NH_3-SCR.

References

1. R. Baran, F. Averseng, D. Wierzbicki, K. Chalupka, J.M. Krafft, T. Grzybek, S. Dzwigaj, Appl. Catal. A Gen. 523 (2016) 332.
2. L. Castoldi, R. Bonzi, L. Lietti, P. Forzatti, S. Morandi, G. Ghiotti, S. Dzwigaj, J. Catal. 282 (2011) 128.
3. S. Dzwigaj, M.J. Peltre, P. Massiani, A. Davidson, M. Che, T. Sen, S. Sivasanker, Chem. Commun. (1998) 87.
4. S. Dzwigaj, P. Massiani, A. Davidson, M. Che, J. Mol. Catal. A Chem. 155 (2000) 169.
5. R. Baran, L. Valentin, S. Dzwigaj, Phys. Chem. Chem. Phys. 18 (2016) 12050.
6. A. Boubnov, H.W.P. Carvalho, D.E. Doronkin, T. Gu, E. Gallo, A.J. Atkins, C.R. Jacob, J. Grunwaldt, J. Am. Chem. Soc. 136 (2014) 13006.
7. R. Baran, L. Valentin, J.-M. Krafft, T. Grzybek, P. Glatzel, S. Dzwigaj, Phys. Chem. Chem. Phys. 19 (2017) 13553.