ESRF	**Valence-to-core XES studies of Cu-SSZ-13 for selective catalytic reduction of NOx with NH_3**	**Experiment number**: CH-4586
Beamline: ID26	**Date of experiment**: from: 18 Nov 2015 to: 23 Nov 2015	**Date of report**:
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Report:

Introduction

Selective catalytic reduction of NO_x by NH_3 (NOx-SCR) is the most widely used technique for the removal of nitrogen oxides from the exhaust of diesel vehicules and power plants. Zeolites with Chabazite structure ion-exchanged with Cu such as Cu-SSZ-13 and Cu-SAPO-34 are becoming the most widely used catalysts of NOx-SCR due to their high activity and high thermal stability. Efficient use of SCR catalysts requires deep understanding of mechanisms of catalytic reaction which in turn allows modelling and optimization of various process parameters. Modelling becomes even more important for automotive catalysts where process parameters such as flows, concentrations of gas species and temperature vary within a broad range. This leads to the necessity of studying a mechanism of NOx-SCR over Cu-SSZ-13 and the nature of active Cu species.

In a pioneering study of a NOx-SCR mechanism over CuSSZ-13 by *operando* HERFD-XANES and valence-to-core (V2C) XES we successfully exploited both techniques to obtain information about oxidation state, coordination environment and the nature of ligands at Cu sites for NOx-SCR carried out at one “low” temperature (200 °C) [1]. Cu-chabazites, however, exhibit a peculiar “dual-maxima” (also called a “seagull”) profile of NOx conversion with decreased NOx conversion at approx. 300-350 °C (Fig. 1) meaning that the low temperature mechanism may be not valid in the whole activity window. This justifies a current study which is an extension of the previous project CH-4184 [1] to high temperatures. The aim of the current study is to identify the reasons leading to the “dual-maxima” of the SCR activity of Cu-SSZ-13 which can be due to different active sites or different ligands at the active site at different temperatures and thus to extend the mechanism reported in [1] to higher working temperatures.

Experimental Section

1.2 wt.% Cu-SSZ-13 was obtained by ion-exchange with copper acetate of hydrothermally synthesized SSZ-13 zeolite (Si/Al = 16, Cu/Al = 0.2) [1]. *Operando* XAS / XES measurements were performed at ID26 beamline (ESRF, Grenoble, France). X-ray beam generated by 3 mechanically independent undulators was monochromatized using Si (111) double crystal monochromator. A secondary emission spectrometer (Rowland geometry) using a Ge (800) reflection of a spherically bent (1m) analyzer crystal and an APD detector was used to record HERFD-XANES and XES at Cu *K* absorption (scanning incident energy with the emission spectrometer set to the maximum of the Cu $K_{\beta 1,3}$ emission line) and Cu $K_{\beta 2,5}$ emission lines (keeping incident energy above Cu *K* absorption edge at 9100 eV and scanning the energy of the emitted X-rays). Pressed and sieved catalyst (100-200 µm, 6.4 mg, 6 mm bed length) was placed in a 1 mm quartz capillary (20 µm walls) which served as a plug-flow reactor [2] heated by a hot gas blower (FMB Oxford GSB-1300). Beam size was 0.2x0.5 mm (the probed sample position for XES was at 0.5 mm from the inlet of the catalyst bed, 5 points along the catalyst bed for XANES), energy resolution was below 1.5 eV. The catalyst response was followed at different temperatures between 150 and 500 °C in gas feeds containing one or several of the following components: 500 ppm NO, 500 ppm NO_2, 500 ppm NH_3, 10% O_2, 1.5% H_2O, and He balance. Total gas flow rate was 45 ml/min and GHSV amounted to 270 000 h^{-1}. Before each new experiment, the sample was treated 15 min at 500 °C in 10%O_2 / He to remove possible adsorbed species. HERFD-XANES and XES spectra were recorded after changing the gas atmosphere and/or temperature. Concentrations of NO, N_2O, NO_2, H_2O and NH_3 were monitored online using an MKS 2030 FTIR gas analyzer. XES modelling was performed using ORCA code.

Results and Discussion

Figure 1 reports NOx and NH_3 conversion profiles obtained over the studied catalyst during the spectral measurements. The shape of the NOx-SCR profile corresponds well to the previously observed results [1] and exhibits a distinctive drop of conversion at intermediate temperatures (approx. 350 °C). To study the origins of this activity drop we recorded HERFD-XANES and V2C XES spectra at the temperatures of 275, 350 and 425 °C. A decrease in activity at higher temperatures is explained by unselective NH_3 oxidation by O_2.

Several changes were identifed in the *operando* HERFD-XANES and XES spectra of Cu-SSZ-13 measured at temperatures around the activity drop. First, the study of ammonia adsorption and oxidation showed that NH_3 directly coordinated via Cu-N bond at low temperatures (T < 300 °C, also found in the previous studies of Cu-SSZ-13 by XES [1,3]) was displaced with O-containing ligands when heating up. Low amount of NH_3 could still be identified as adsorbed via O as Cu-OH-NH_2 (analogous to the Fe-zeolite case [4]) up to 425 °C but completely desorbed at higher temperatures. HERFD-XANES detected reduction of Cu^{2+} to Cu^+ at all studied temperatures.

Second, changes in interaction of NOx (mainly NO) with Cu sites were found depending on the temperature. Dosing NO and O_2 in He (without water) at low temperatures (T < 300 °C) resulted in XANES and XES spectra different from the reference spectra measured in the presence of O_2 in He. XES modelling suggests formation of Cu nitrosyl or isonitrosyl group as the explanation for the observed spectral change. However, this interaction disappeared in the presence of 1.5% H_2O which is always found in the real gas flow, the same behavior was observed by us in [1]. Contrary to this, at higher temperature interaction of Cu sites with NO and O_2 in the presence of water changes the spectral shape and intensity (XES spectra are normalized by the intensity of $K_{\beta 1,3}$ line) in both XES and XANES spectra (Fig. 2). The changes are mostly due to the temperature since similar changes were seen in the reference spectra measured in the atmosphere of O_2 and H_2O, however addition of NO causes significantly stronger changes, i.e. there is a certain interaction of NO with Cu sites at high temperatures in the realistic gas feed. The changes in this case might be due to desorption of water from the ligand shell of Cu mediated by NOx.

Third, changes in the branching ratio of the two main lines constituting $K_{\beta 2,5}$ emission line were observed with increasing temperature. Higher temperature leads to decrease of a peak at 8973 eV and increase of the peak at 8978 eV. According to the XANES modelling, an increase in intensity at lower energies is due to reduced Cu (Cu^+) and / or lower number of ligands in the coordination shell of Cu. According to the temperature behavior, intensity of the peak at 8973 eV reflects the number of ligands (it decreases in all cases during temperature increase) and intensity of the peak at 8978 eV reflects oxidation state of Cu (higher for Cu^{2+} and lower for Cu^+).

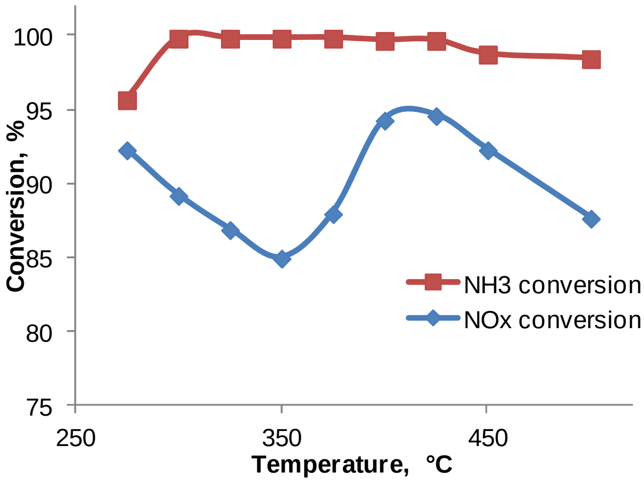

Figure 1. NOx and NH_3 conversion profiles measured during using the microreactor cell during the beamtime. Conditions: 500 ppm NO, 500 ppm NH_3, 10% O_2, 1.5% H_2O in He, GHSV = 270 000 h^{-1}.

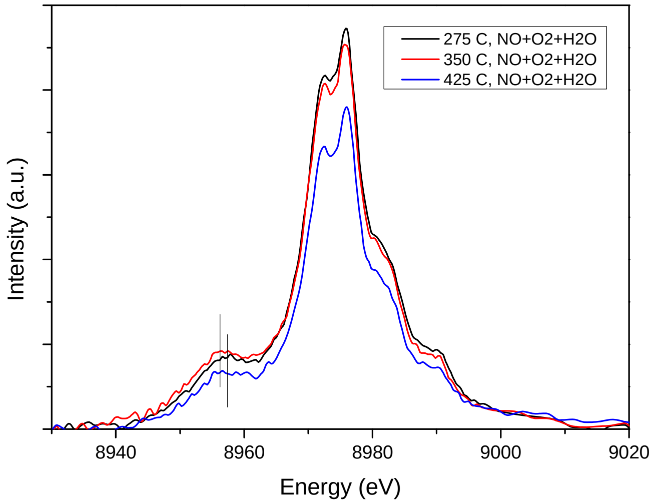

Figure 2. V2C XES of Cu-SSZ-13 measured at temperatures along the "seagull" NOx conversion profile. Conditions: 500 ppm NO, 10%O_2 in He, GHSV = 270 000 h^{-1}.

Conclusions

A combination of *operando* HERFD-XANES and V2C XES complemented by modeling allowed identifying several changes in the nature of Cu sites in Cu-SSZ-13 catalyst during NOx-SCR and related model reactions: a) adsorption, rearrangement and desorption of ammonia from Cu sites; b) competitive adsorption of NOx and water on the Cu sites; and c) dynamic changes in the oxidation state and coordination number of Cu sites. DFT modelling is currently underway to assemble a mechanism of NOx-SCR over Cu-SSZ-13 valid for both low- and high-temperature regimes.

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