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**HERFD-XANES and valence-to-core XES studies of grafted V-W-TiO<sub>2</sub> catalysts for NO<sub>x</sub> removal by selective catalytic reduction by NH<sub>3</sub> and oxidation of organic model compounds**

**Experiment number:**  
CH-4751

<b>Beamline:</b> ID26	<b>Date of experiment:</b> from: 30 Mar 2016 to: 03 Apr 2016	<b>Date of report:</b>
<b>Shifts:</b> 14	<b>Local contact(s):</b> Pieter Glatzel Rafal Baran	<i>Received at ESRF:</i>

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## Report:

### Introduction

V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>-TiO<sub>2</sub> catalysts are extensively used for Selective Catalytic Reduction (SCR) of NO<sub>x</sub> with NH<sub>3</sub> and oxidation of hydrocarbons in the exhaust streams of heavy-duty diesel engines, marine engines and power plants. In addition, the vanadium containing catalysts could also be feasible oxidation catalysts for the less restrictive particulate matter emission standards in emerging countries, acting as a 2-way SCR/DPF system. This class of catalysts is relatively well described in literature, however, the corresponding reaction mechanism is still debated. While DRIFTS studies [1] claim adsorption of NO<sub>x</sub> and NH<sub>3</sub> on the catalyst, no proof for identification of the exact adsorption sites is provided which results in contradiction with the later kinetic [2] and DFT [3] studies. Previously, by combining *operando* High-Energy-Resolution Fluorescence Detected X-ray Absorption Near Edge Structure (HERFD-XANES) and valence-to-core X-ray Emission Spectroscopy (vtc-XES) we evidenced dynamics of oxidation state as well as structures of adsorption complexes on Fe and Cu sites in working Fe-/Cu-zeolite catalysts during SCR of NO<sub>x</sub> [4, 5]. In a next step we investigated a conventionally-prepared V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>-TiO<sub>2</sub> catalyst and the redox dynamics of V active sites were uncovered [6]. However, neither the coordination of NH<sub>3</sub> nor of NO at V could be observed. This basically rules out the direct adsorption of NH<sub>3</sub> [6], which is in contradiction to the SCR mechanism path claimed in [1] but supported by [3]. In the present study we used the advanced catalyst synthesis technique of grafting [7] to prepare a series of highly active model SCR catalysts containing predominantly V<sub>2</sub>O<sub>5</sub> monolayers with very high dispersion. This allowed us to examine once again the formation of direct V-N coordination which was previously not observed for the conventional V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>-TiO<sub>2</sub> catalyst [6].

### Experimental Section

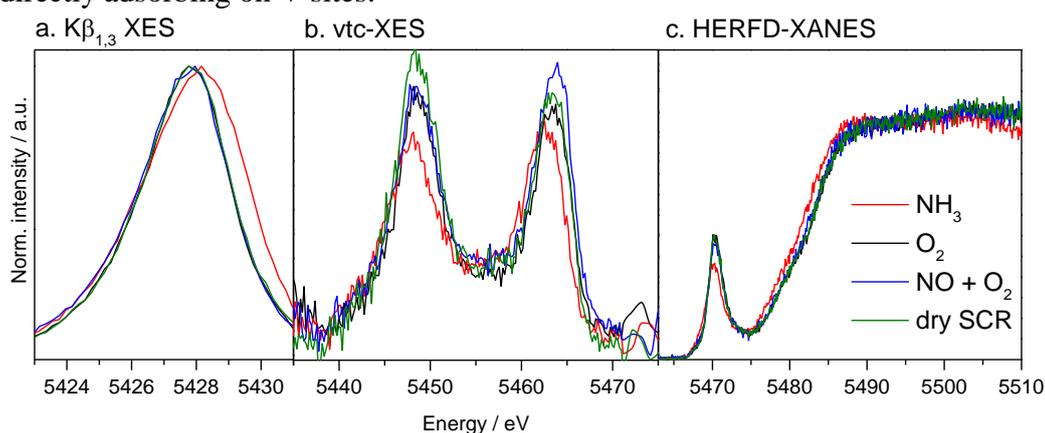
The grafted samples were synthesized according to Baiker et al. [7]. TiO<sub>2</sub> (anatase, Alfa Aesar or anatase+rutile, Degussa P25) was pre-conditioned at 10<sup>-4</sup> bar and 423 K for 3 h in a quartz-glass flask. Tungsten (when used) was loaded via the addition of tungsten(V) ethoxide (Alfa Aesar) in water-free hexane under stirring. The solution was stirred for 12 h at 323 K. Afterwards the solution was filtered and the

remaining powder was washed five times with water-free hexane. Next, V was added in form of vanadyl trisisopropoxide (Alfa Aesar) in water-free hexane. Again, the solution was stirred for 12 h at 323 K, filtered and the remaining powder five times washed with water-free hexane. The obtained powder was first calcined at 823 K (673 K for the sample without tungsten) for 4 h in N<sub>2</sub>. In a last step, the obtained powder was calcined at 823 K (673 K for the sample without tungsten) for 2 h in air.

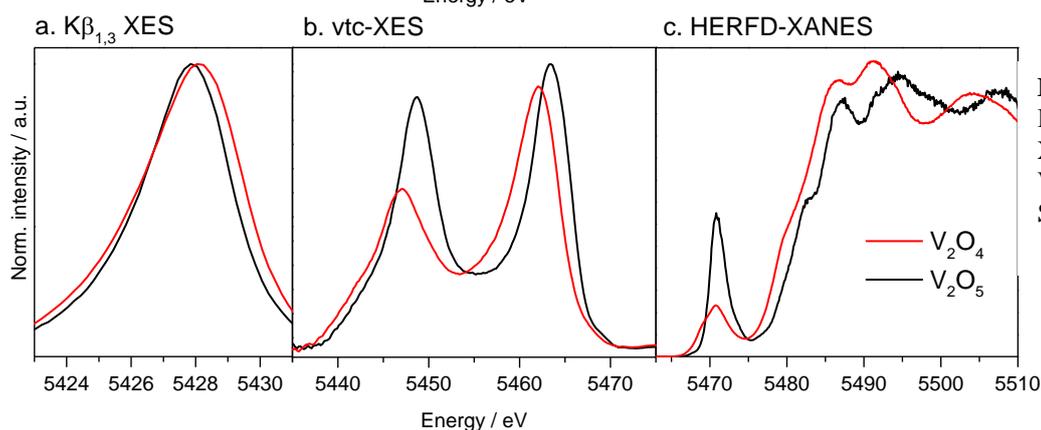
*Operando* XAS / XES measurements were performed at the ID26 beamline (ESRF, Grenoble, France). X-rays were generated by three mechanically independent undulators and monochromatized by a cryogenically cooled Si (111) double-crystal monochromator. The emission spectrometer was equipped with four spherically bent ( $r = 1$  m) Ge (422) analyser crystals installed in a Rowland geometry and an avalanche photodiode detector. Pressed and sieved catalysts (100-200  $\mu\text{m}$ ) were loaded in quartz capillary microreactors (plug flow geometry, diameter 1 mm, wall thickness 0.01 mm) heated by a hot air blower. Pure gases and gas mixtures were dosed to obtain the desired volume concentrations: 1000 ppm NO and/or 1000 ppm NH<sub>3</sub>, 5% O<sub>2</sub> and pure He as balance. The gas flow was 50 mL/min which results in a GHSV of 200 000 h<sup>-1</sup>. Gas analysis was performed using an FTIR gas analyzer (MultiGas™ 2030, MKS Instruments). Vtc-XES spectra were modeled using multiple scattering FEFF 9.6.4. *ab initio* code using a DFT-optimized model V site from [8].

## Results and Discussion

The previous *operando* HERFD-XANES and V2C XES study of a conventionally impregnated V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>-TiO<sub>2</sub> catalyst [6] has shown only a partial oxidation and reduction of V between V<sup>4+</sup> and V<sup>5+</sup> states under different SCR-related gas feeds. Furthermore, the changes in the XANES pre-edge region and in the vtc-XES were minimal indicating minor (if any) changes in the V site geometry, i.e. almost no adsorption-desorption of reactive species on the V sites. To confirm these results we measured HERFD-XANES and vtc-XES spectra for a series of model grafted V<sub>2</sub>O<sub>5</sub>-(WO<sub>3</sub>-)TiO<sub>2</sub> catalysts under the conditions which previously resulted in the most different spectra, i.e. NH<sub>3</sub>/He (reducing feed with a source of NH<sub>x</sub> ligand), O<sub>2</sub>/He and NO+O<sub>2</sub>/He (oxidizing feeds, the latter with a source of NO<sub>x</sub> ligand), and the SCR gas feed at 400 °C [4-6]. A typical example of the obtained spectra is shown in Fig. 1 and a set of reference spectra depicting V in different oxidation states but with the same type of nearest neighbor atoms (O) is reported in Fig. 2. Obviously, V sites exhibit reduction-oxidation (redox) dynamics during the SCR of NO<sub>x</sub>, which confirms the possible role of V as an electron acceptor/donor. On the other hand, as discovered earlier [6], XANES pre-edge and vtc-XES spectra change only slightly, which once again does not support the idea of NH<sub>x</sub> and NO<sub>x</sub> directly adsorbing on V sites.

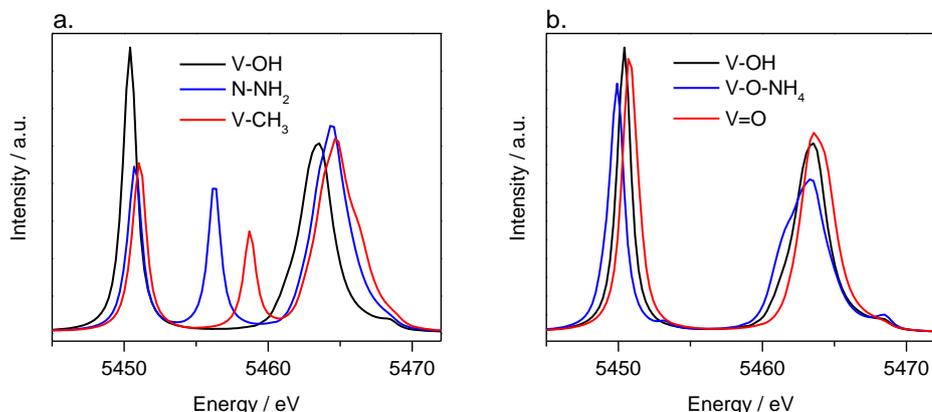


**Figure 1.** (a)  $K\beta_{1,3}$  and (b)  $K\beta''$ ,  $K\beta_{2,5}$  (vtc) XES and (c) HERFD-XANES spectra of grafted 4% V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>-TiO<sub>2</sub> under model SCR-related conditions.



**Figure 2.** (a)  $K\beta_{1,3}$  and (b)  $K\beta''$ ,  $K\beta_{2,5}$  (vtc) XES and (c) HERFD-XANES spectra of grafted 4% V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>-TiO<sub>2</sub> under model SCR-related conditions.

To further prove that the observed changes in the vtc-XES spectra are not caused by the changed the nature of nearest neighbor atoms (e.g. direct V-N bond formation instead of V-O) we calculated vtc-XES spectra of a model V/TiO<sub>2</sub> site directly coordinated with O, N, and C atoms (Fig. 3a). Considering the pronounced differences, the calculations clearly support the observation that only O neighbors and no V-N bond formation is observed in the experimental spectra (Fig. 1b). Nevertheless, a shift of Kβ'' and Kβ<sub>2,5</sub> emission lines to lower energies under reducing NH<sub>3</sub> feed (Fig. 1b) may indicate both a mere reduction of a V<sup>5+</sup> site to V<sup>4+</sup> (as seen in the reference spectra in Fig. 2b) or adsorption of ammonia via O atom similar to that seen in the case of Zeolites [4].



**Figure 3.** Calculated vtc-XES spectra for a model V site[8] (a) with different nearest neighbor atoms (V-X models) and (b) different polarization of an O atom (adsorption via O as V-O-X).

## Conclusions

A combination of *operando* HERFD-XANES and vtc-XES complemented by modeling allowed us to identify the role of V sites in the SCR of NO<sub>x</sub> with NH<sub>3</sub> over V<sub>2</sub>O<sub>5</sub>-(WO<sub>3</sub>-)TiO<sub>2</sub>. Kβ<sub>1,3</sub> XES and HERFD-XANES proved redox (electron accepting/donating) functionality of V sites, whereas their function as direct adsorption sites for NO<sub>x</sub> and NH<sub>3</sub> was not confirmed (contrary to earlier studies [1] but in line with recent DFT calculations [3]). Still, NH<sub>x</sub> may be adsorbed indirectly via the adjacent O atom (Fig. 3b) or at the interface with a neighboring Ti site from the titania support [3]. The obtained information [9] supports mechanisms derived from kinetic [2] and DFT [3] studies and allows better prediction of V-based catalyst behaviour.

## Acknowledgements

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