

**Experiment title:**

Investigation of the vanadium surrounding in VAION catalysts by XANES and EXAFS

Experiment number:

26-01-703

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Shifts:**Local contact(s):**

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*Received at ESRF:***Names and affiliations of applicants (* indicates experimentalists):****H.Poelman^a, S. Delsarte^{b*}, M. Florea^b, R. De Gryse^a**^a Department Solid State Sciences, Ghent University, Krijgslaan 281 S1, B-9000 Gent, Belgium.^b Unité de catalyse et chimie des matériaux divisés, Université catholique de Louvain-la-Neuve, Place Croix du Sud 2/17, B-1348 Louvain-la-Neuve.**Report:****Introduction**

Vanadium-aluminium-oxy-nitrides, VAION, systems are active catalysts in the ammoxidation of propane for the production of acrylonitrile (ACN). The VAION catalysts are made in two steps. First a vanadium-aluminium-oxide precursor, VAIO is prepared via the co-precipitation of NH_4VO_3 and $\text{Al}(\text{NO}_3)_3$. After drying in air, this oxide precursor is nitrated with NH_3 at 500°C , to form the VAION. The following parameters have an influence on the ACN selectivity: 1) The V/Al ratio in the co-precipitation solution, 2) The drying temperature of the oxide precursor, 3) The nitridation procedure. The nitridation can be performed as a pre-treatment before introduction in a catalytic reactor (“ex-situ samples”); or can be performed during reaction (“in-situ samples”); the VAIO is then introduced in the catalytic reactor and becomes a VAION during reaction, which takes place under a mixture of ammonia, propane and oxygen.

The catalyst with the highest selectivity is obtained with a V/Al ratio of 0.25, dried at 60°C and nitrated during reaction.

These differences in catalytic properties might be related to the V-structure in the powder catalyst. The goal of this experiment was therefore to determine the local structure around the V-atoms in the VAIO and VAION. Samples are noted as VAIO(0.XX) and VAION(0.XX), with 0.XX being the V/Al ratio.

Experimental

V K-edge spectra were recorded in transmission mode at the XAS station of the DUBBLE beamline (BM26A). Ex-situ samples were recorded at room temperature in air. A chemical cell, constructed at the Department Solid State Sciences of the Ghent University (Belgium), was used for the in-situ nitridation at 500°C in 5% NH_3/He and for the in-situ calcination study of VAIO(0.25) and VAION(0.9).

Results*The VAIO precursor*

The XANES spectra for VAIO(0.25) and VAIO(0.9) are given in Figure 1. The vanadium in the oxide precursors is in the V^{5+} oxidation state and is tetrahedrally co-ordinated with oxygen. The XANES spectra for the oxide precursors resemble the one for NH_4VO_3 very well. This reference compound has a tetrahedral “ VO_4 ” co-ordination with two vanadyl bonds ($\text{V}=\text{O}$) and two single V-O bonds. This structure is chosen as initial

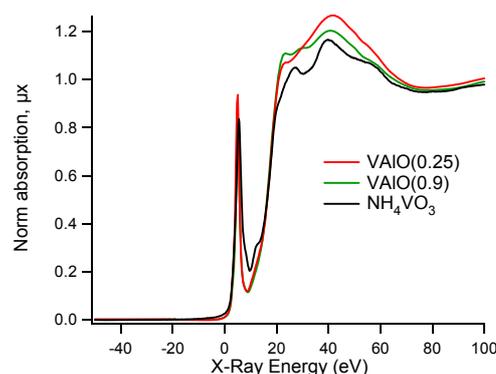


Figure 1: XANES spectra for the VAIO precursors with V/Al ratio 0.25 and 0.9.

guess in the EXAFS fits. The k^1 -weighted Fourier Transform (FT) spectra for experiment and fit and the resulting structural model is proposed in Figure 2. The two oxide precursors have the same tetrahedral coordination. For the VAIO(0.9) a V-V contribution at 3.2 Å is present.

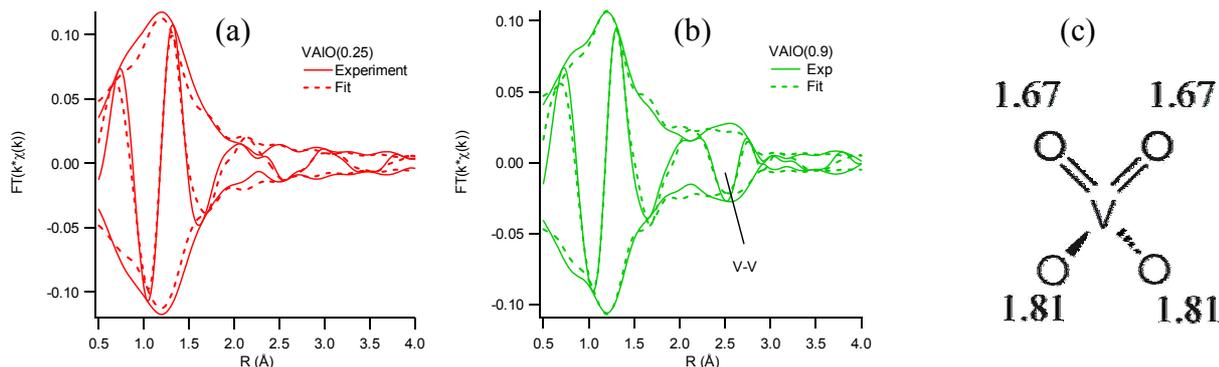


Figure 2: Experimental and fit FT($k \cdot \chi(k)$) for (a) VAIO(0.25) and (b) VAIO(0.9), (c) the corresponding tetrahedral “VO₄” model

In-situ nitridation

The nitridation of a VAIO(0.25) and a VAIO(0.9) was followed with *in-situ* XAS. The oxide precursor is first heated from room temperature to 500°C in 5%NH₃/He and kept at this temperature for up to 10 hours. XAS spectra were taken during heating and at 500°C after different nitridation times. The XANES spectra showed that the pre-edge peak intensity diminishes strongly during nitridation. This means that we pass from a tetrahedral co-ordination to an octahedral one. The structural changes already started during heating and are almost completed at 500°C. A fit of the EXAFS spectra after full nitridation was possible. The resulting FT structural model is presented in Figure 3. The ligands of the octahedron are O or N. As the two atoms are neighbouring elements in the Periodic Table they have similar scattering properties for EXAFS, which makes it difficult to differentiate between N and O with this technique.

The VAIO(N) system

The drying temperature of the oxide precursor before nitridation has an influence on the ACN selectivity. In Figure 4 the EXAFS spectra for three VAION(0.25) samples with drying temperatures of 60, 120 and 500°C are compared with the oxide precursor and the fully nitrided oxy-nitride. The VAION were obtained after nitridation during reaction in NH₃/O₂/C₃H₆. The EXAFS spectra can be seen as a linear combination of the spectra for the oxide precursor and the fully nitrided sample. The structure of the VAION(0.25) is a mixture of the oxide precursor tetrahedrae and the oxy-nitride octahedrae. The corresponding percentages octahedrae are indicated on Fig. 4. So it seems that during reaction a mixture of the oxide precursor tetrahedrae and oxy-nitride octahedrae is present. The ratio tetrahedrae/octahedrae may explain the chemical selectivity.

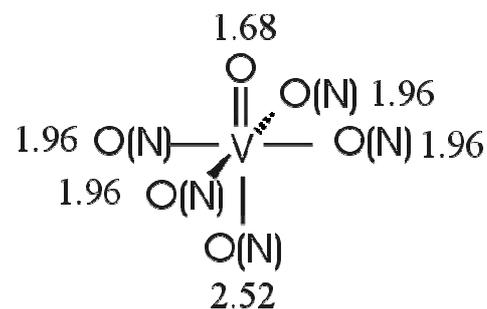


Figure 3: Structural model for the fully nitrided VAION(0.25)

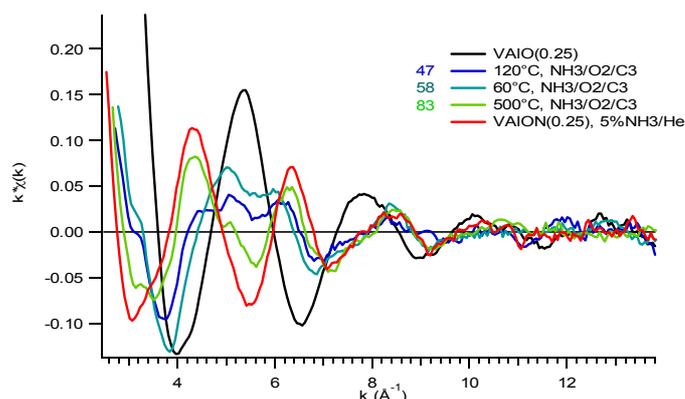


Figure 4: EXAFS spectra for VAION(0.25) catalysts with different drying temperatures, compared with the VAIO(0.25) oxide precursor and the fully nitrided VAION(0.25).

Publication/Presentation

The first results of this study were already presented on a Belgian national symposium on the use of synchrotron radiation. After finalisation of the treatments of all spectra a publication will follow.