

AMMOXAN

Novel ammoxidation catalysts with tailored anion structures based on transition metal nitrides and oxynitrides.

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J. Bilde¹, C. Janke², C. Lorentz¹, P. Delichere¹, S. Lorient¹, A. Brückner², J.M.M. Millet¹

¹ IRCELYON, UMR5256 CNRS-Université Claude Bernard Lyon 1, 2 av. A. Einstein 69626 Villeurbanne France.

² Leibniz-Institut für Katalyse e.V. an der Universität Rostock Warmemünde Seestrasse 15 18119 Rostock Germany.

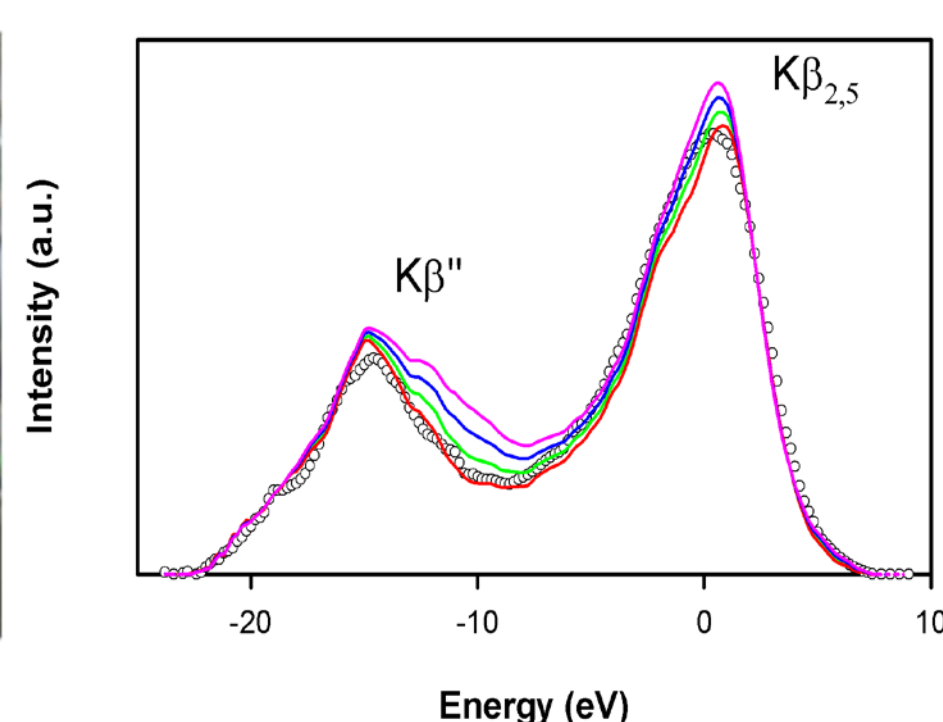
Introduction

Acrylonitrile is an important intermediate in chemical industry for the synthesis of various polymers and coatings. It is currently produced by ammoxidation of costly and increasingly scarce propylene.

This project aimed at developing novel catalysts allowing the **use of cheaper and abundant propane**, which is of industrial interest, economic potential and sustainability.

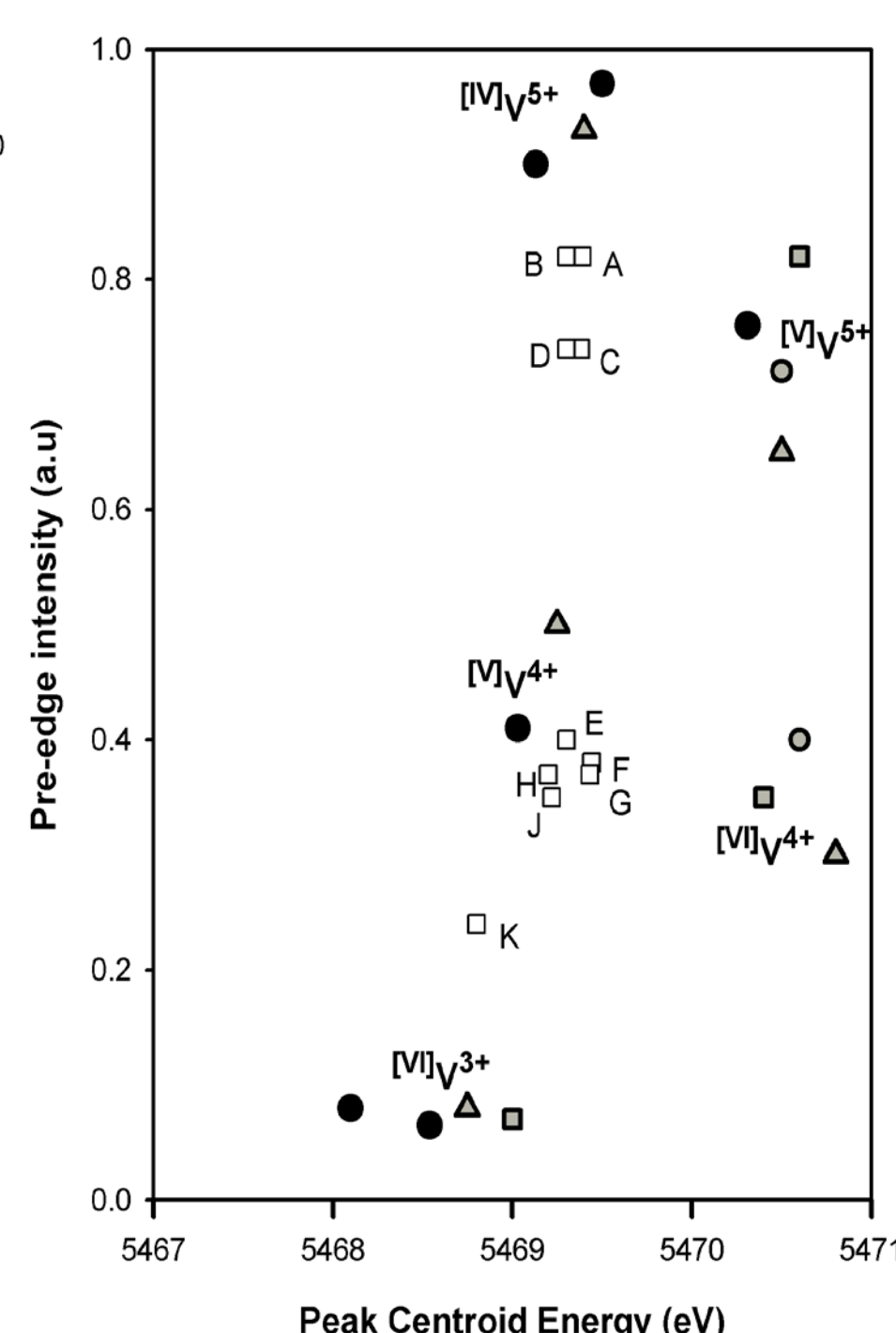
Totally novel routes to tailored catalysts have to be developed. For that we tried to exploit the unique properties of **nitrides and oxynitrides**.

Use of XES spectroscopy to characterize catalysts in operando conditions



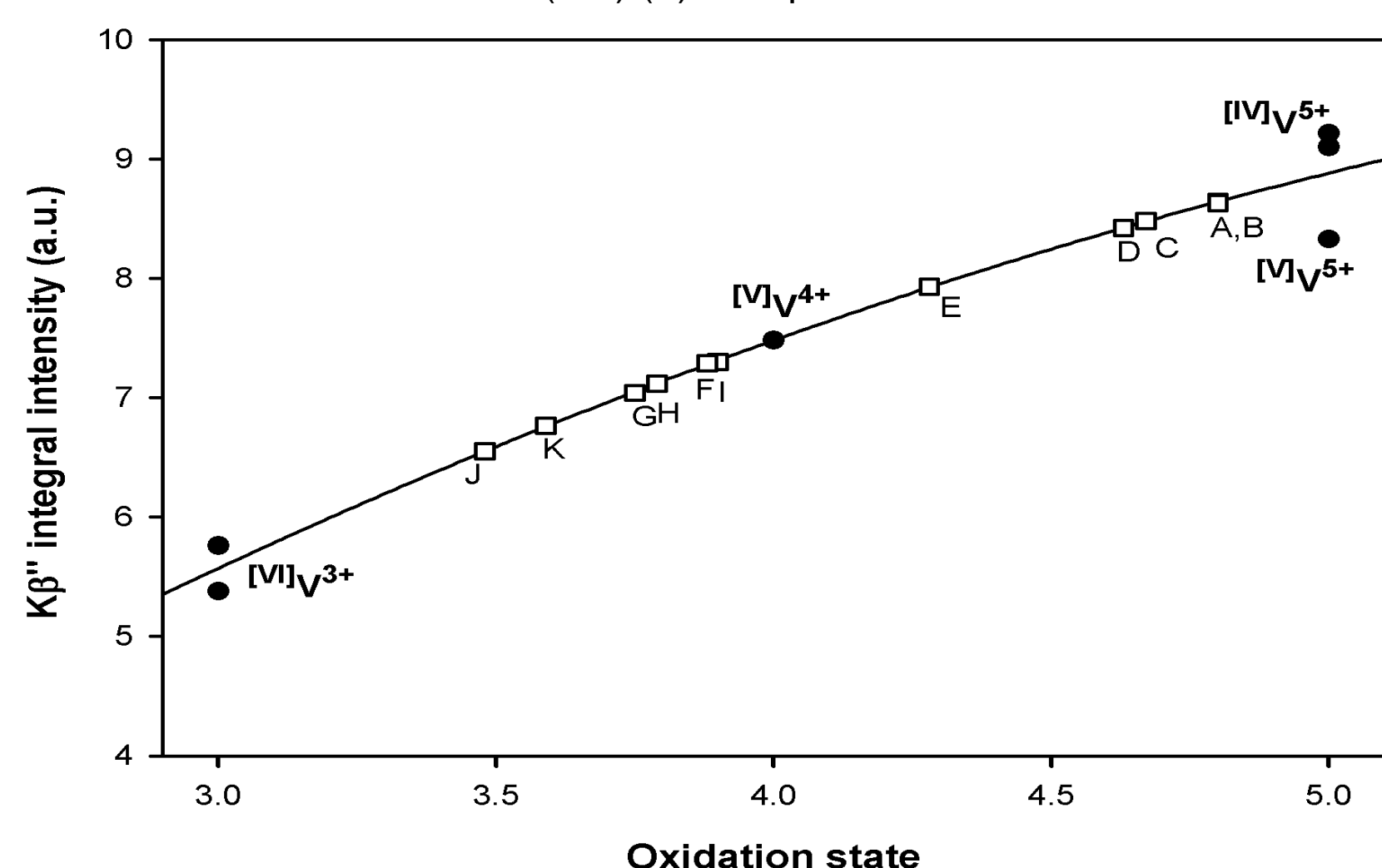
XES :

○ XES data at V K-edge and ●/○/□/△ correspond to linear combination of V-magnetite:cavancite:VN with ratios 6:4:0, 5:4:1, 4:4:2, 3:4:3, corresponding to N content of 0, 2, 4 and 6 w%.



XANES :

Pre-edge intensity vs. pre-peak centroid energy for V/Al/O catalyst under different reaction conditions (A-J) (□): comparison with data from references.

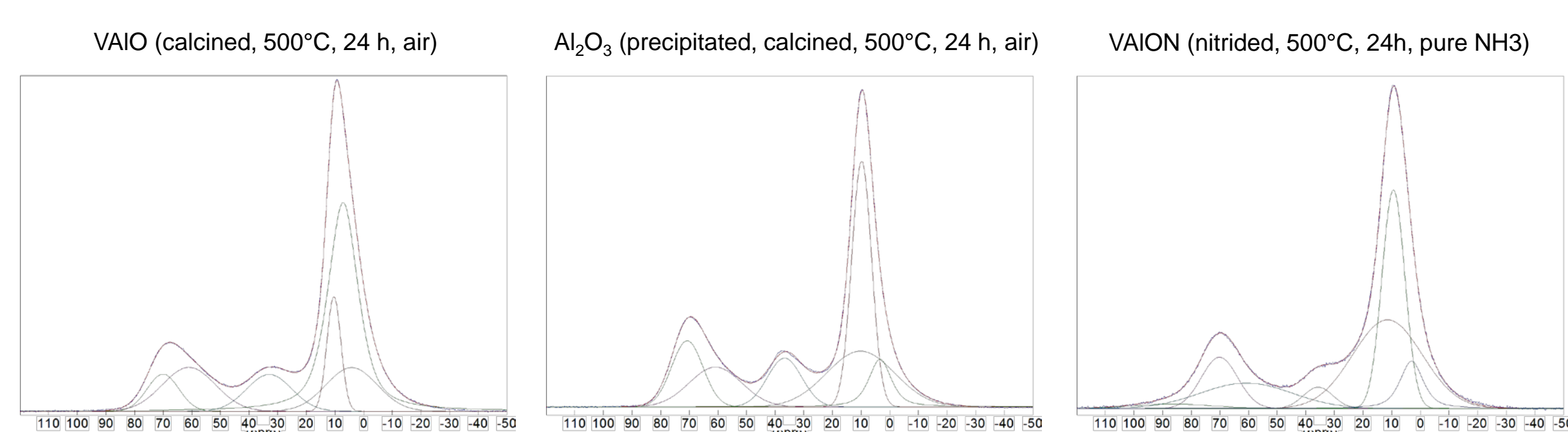


Correlation of Kβ'' intensity with oxidation state based on bond length.

Activation of VAIO catalyst on-stream is associated with reduction of V in the bulk (**mean oxidation state 3,8**) and nitridation of V atoms on the surface, with a **N bulk content of around 1w%**.

Multi-techniques approach of catalytic sites

²⁷Al high field solid NMR (800MHz, 30kHz MAS) :

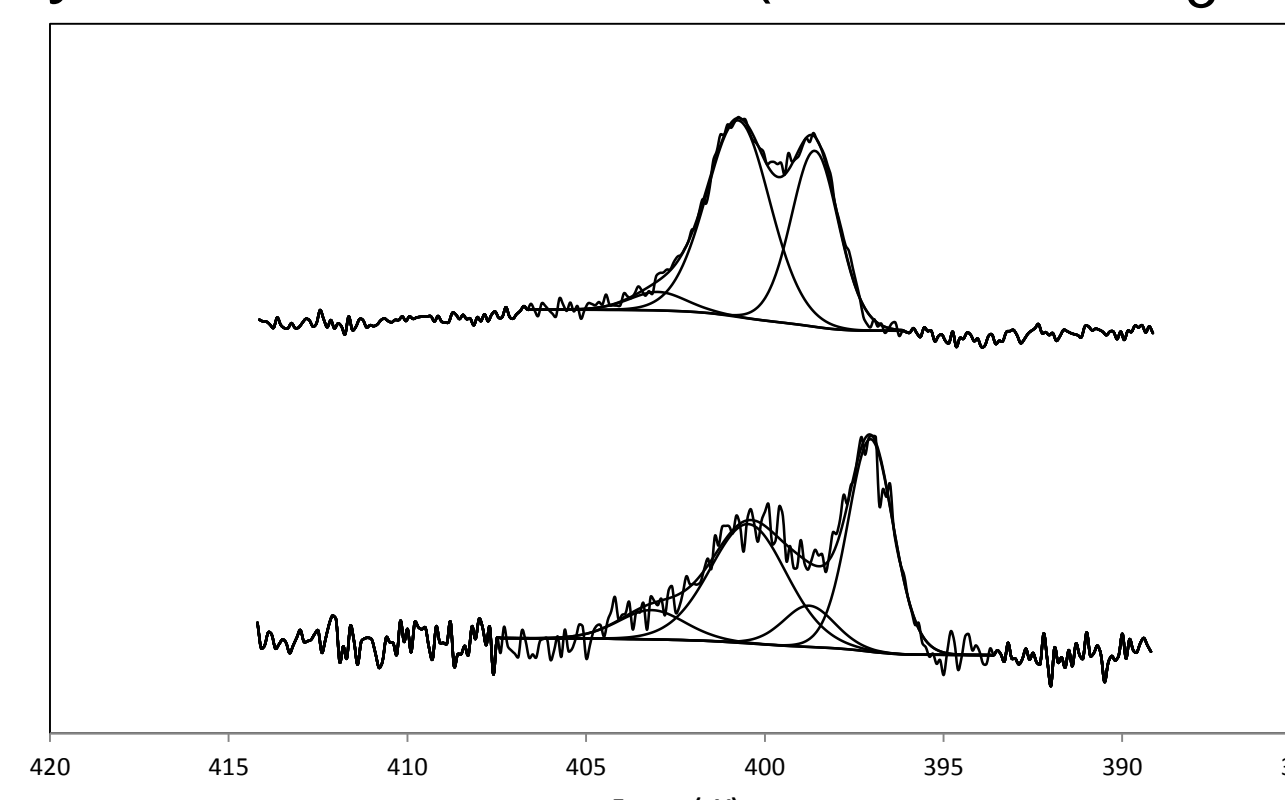


XRD :

VAION have the structure of **γ-alumina**, in agreement with NMR.

XPS analyses :

NH²⁻ and **N³⁻** species are formed during nitridation. In reaction conditions only **NH²⁻** are formed (shift of AlO₃N NMR signal from 86 to 83 ppm).

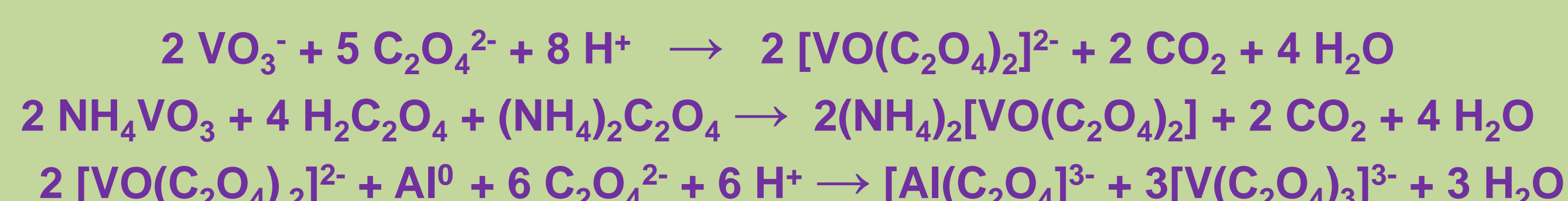


V is present as both **V³⁺**, **V⁴⁺** and **V⁵⁺** ($V^{3+}/V^{4+}/V^{5+}=7/20/73$). V/Al ratio is always slightly lower than that of the bulk and N/O has been determined (0,012).

The ammoxidation sites have been identified as **V-NH²⁻-AlO₃** sites. Alkane activation sites could correspond to **isolated VO₆** sites.

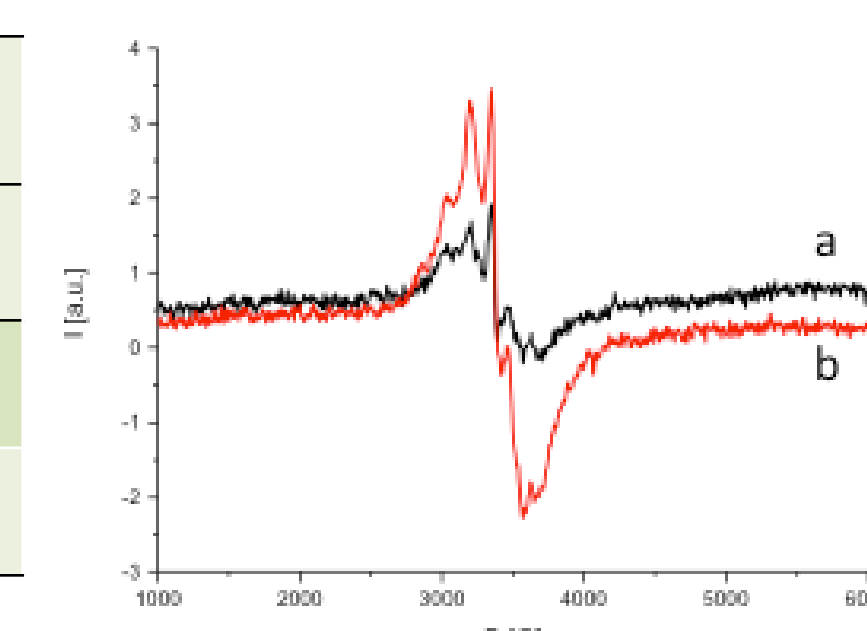
New original preparation method

A **mixed oxalate** (NH₄)₃[Al_xV_z(C₂O₄)₃] is prepared and transformed to oxide by **ozonation** in O₃/air (1.1 ppmv, 70mL.min⁻¹, 480h) at 180° C.



The oxalate contains V and Al mixed at atomic scale, V has a low oxidation state (V³⁺/V⁴⁺). Ozoned oxide is nitrided in reaction conditions at 500° C.

Catalyst	Mass (mg)	S _(BET) (m ² .g ⁻¹)	Conv (%)	Selectivity (%)			
				ACN	ACeN	C ₃ H ₆	CO _x
VAION-Ref	100	170	58	51	5	11	34
VAION-oz	28	40	49	55	5	12	30



The increased activity and selectivity to ACN is ascribed to a **better dispersion (isolation) of V species** in the bulk and at the surface.

Conclusions

- **XES in operando conditions** can be applied to characterize catalysts. For VAION, it allows determining V mean oxidation state and bulk N/O ratio.
- **A multi-techniques approach** of the characterization of the catalyst leads to propose sites for alkane activation and N insertion.
- **A new preparation method** of catalysts has been finalized. It can be applied to the syntheses of binary or ternary oxides and enable to increase the distribution of metallic elements in these oxides.

CONTACT :

Jean-Marc MILLET, Institut de Recherche sur la Catalyse et l'Environnement de Lyon, CNRS
jean-marc.millet@ircelyon.univ-lyon1.fr



Université Claude Bernard Lyon 1

