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Local environment of vanadium in V/Al/O-mixed oxide catalyst for propane ammoxidation: Characterization by *in situ* valence-to-core X-ray emission spectroscopy and X-ray absorption spectroscopy

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ABSTRACT

The local environment of vanadium in V/Al/O amorphous oxide catalyst has been studied under propane ammoxidation reaction conditions. *In situ* valence-to-core X-ray emission spectroscopy (XES) and X-ray absorption spectroscopy (XAS) at the V K-edge showed that acrylonitrile production starts when vanadium in the bulk structure of the oxide material changes its formal oxidation state from +4.8 to +3.8 ± 0.1. Exposure of the catalyst to pure NH_3 at 500 °C leads to further reduction of vanadium. Valence-to-core XES has also proved that the level of bulk nitridation of vanadium in the active catalyst was rather small. XPS analysis performed *ex situ* after the catalytic tests confirmed the presence of significant amounts of N^{3-}, NH_x, and –NN– species on the catalyst surface. It can be concluded that activation of V/Al/O catalyst on-stream is mainly associated with reduction of vanadium in the bulk structure of the material and nitridation of vanadium atoms on the surface.

1. Introduction

The substitution of alkenes by alkanes as a feedstock is a challenging task for industries producing chemicals, plastics, and synthetic fibers. It is also important for lowering the prices and risks of chemical storage, which become crucial due to the continuous increase of the worldwide demand for chemicals and the reinforcement of the legislation rules on their manipulation.

The challenge lies mainly in the difficulty of breaking the first C–H bond in alkane and the lack of stability of the products formed. The process of acrylonitrile (ACN) production from propane is one of the closest to be industrialized. In general nitriles are much more stable than the corresponding aldehydes or acids, which can also be produced from alkanes. Furthermore, the yield of nitriles can be high enough to sustain an industrial application. The known catalysts for propane ammoxidation into ACN are mainly based on either rutile-type metal antimonates (V/Sb/O, V/Al/Sb/O) [1–5] or mixed molybdates (Mo/V/Te(Sb)/Nb/O) [6–9]. Attempts to optimize these materials by tuning their composition were successful but not good enough for industrialization [10–12]. Recently discovered V/Al/O-mixed amorphous oxides catalysts have shown to be very promising for propane ammoxidation [13–18]. Moreover, it was demonstrated that catalytic performance of these oxides could be improved after their exposure on-stream under catalytic conditions or after preliminary annealing in NH_3 at high temperatures. These phenomena were explained by partial substitution of nitrogen for oxygen in the mixed oxide structure of the catalyst. Maximal concentration of nitrogen observed in this kind of material was 3–5 wt% [17]. The activity of V/Al/O catalysts was explained by a Mars–van Krevelen-type mechanism related to the lattice oxygen and nitrogen mobility as well as the redox activity of vanadium [17,18]. It was also demonstrated that catalytic performance of these materials strongly depends on various parameters such as: (i) the V/Al ratio, (ii) the pH during synthesis, (iii) the vanadium concentration in solution, and (iv) the nitridation protocol (temperature, nitridation mixture, and time) [16].

The V/Al/O catalytic system seems to be rather simple and has potential to be further improved. However, these materials have amorphous structure, which makes rather difficult understanding of relationships between their structure, composition, and catalytic properties. Recently, *in situ* XAS studies have shown that under reaction conditions of ACN production, vanadium in the bulk oxide structure changes its local coordination from tetrahedral (similar

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to NH_4VO_3) to octahedral and a small decrease in vanadium degree of oxidation occurs [18]. However, using EXAFS it was difficult to prove the presence of V–N bonds in the bulk catalyst structure, because using this technique it was impossible to distinguish N and O ligands in the first coordination shell of vanadium. The only direct technique, which was used by now to identify the presence of V–N bonds in the catalyst, was X-ray photo-electron spectroscopy (XPS). XPS can be used for the analysis of surface species; however, it requires high vacuum conditions, which makes extremely difficult to apply it to *in situ* studies. In the present work we tried to get more information about the reactivity of lattice nitrogen in this catalyst and local environment of vanadium using *in situ* valence-to-core XES at V Kβ fluorescence line. A catalyst with V/Al ratio of 0.25, which was shown in the previous studies to be the most active, was prepared following the synthesis protocol mentioned in the literature [14] with the same reaction conditions (500 °C, O_2:C_3H_8:NH_3 = 3:1.25:1). *In situ* XAS at V K-edge vanadium also measured in the same experiment provided us complimentary information on the local structure and the oxidation state of vanadium in the catalyst. The data obtained by valence-to-core XES and XAS should correspond to the average material composition from 3 to 5 μm layer, which we considered as the bulk structure. The *ex situ* XPS analysis was performed after the catalytic tests in order to confirm the presence and the nature of surface species.

2. Experimental

A V/Al/O catalyst with V/Al molar ratio of 0.25 was prepared according to a published protocol [14]. The catalyst was produced by co-precipitation of solutions containing 0.01 M ammonium metavanadate and 0.01 M aluminum nitrate at 60 °C. Ammonium metavanadate was dissolved in hot water (60 °C) under stirring and then nitric acid (50 wt%) was added until the pH reached 3.0. When the solution of aluminum nitrate was added to the mixture, the latter became red-orange with pH of 2.5. Then the pH was increased up to 5.5 by adding ammonium hydroxide solution (25 wt%) and the mixture was maintained in these conditions for 1 h. The yellow precipitate was washed with ethanol and dried in vacuum at 120 °C.

Valence-to-core XES experiments at V Kβ line were performed at ID26 (X-ray absorption and emission spectroscopy beamline) at ESRF (Grenoble, France). The electron energy of the storage ring was 6.0 GeV; the ring current varied between 150 and 200 mA. The incident energy (5500 eV), which was 35 eV above the V K-edge, was selected by means of a pair of Si(2 2 0) single crystals. Higher harmonics were suppressed by two Si mirrors at 3.0 mrad. The beam size on the sample was 0.3 mm horizontal and 1 mm vertical with a total flux of about 10^{13} photons/s. We used an analyzer that employs the (3 3 3) Bragg plane of one spherically bent (*R* = 850 mm) Ge wafer, 89 mm in diameter. The energy bandwidth in the X-ray emission detection was 0.6 eV. An avalanche photodiode (APD) was used as the detector. The counting time per XES spectrum was 5 min. The XES spectra were recorded continuously during the whole period of catalytic test. The Kβ main and Kβ satellite lines were measured from 5390 to 5442 eV with 0.5 eV step and normalized by the integral spectral intensity. To perform quantitative analysis of the valence-to-core XES data we fitted the $K\beta_{1,3}$ main line contribution using pseudo-Voigt functions and subtracted it as a background. After each XES spectrum one V K-edge XAS spectrum of the catalyst was measured in a quick scan mode from 5442 to 5742 eV with 0.1 eV step (2 min scan per scan) using Si diode detector, which recorded the total fluorescence yield. The XAS spectra were normalized to the edge jump equal to 1. Analysis of the pre-edge region was conducted after subtracting the edge step contribution. The "pre-edge intensity" was defined to be the maximum intensity in this net pre-edge multiplet. The "pre-edge peak centroid" was defined to be the center of mass of this multiplet. For better understanding the effect of li-

Table 2
List of the consequent treatments of V/Al/O catalyst.

Treatment	Gas atmosphere	Temperature (°C)	Time of exposure (h:min)
A – initial state[a]	Air	25	–
B	O_2:C_3H_8:NH_3 = 3:1.25:1	280	During 5 °C/min ramp
C	O_2:C_3H_8:NH_3 = 3:1.25:1	500	2:00
D	O_2:C_3H_8:NH_3 = 3:1.25:1	500	3:00
E	O_2:C_3H_8:NH_3 = 3:1.25:1	500	3:25
F	O_2:C_3H_8:NH_3 = 3:1.25:1	500	4:22
G	O_2:C_3H_8:NH_3 = 3:1.25:1	500	5:35
H	O_2:C_3H_8:NH_3 = 3:1.25:1	500	9:20
I	O_2:C_3H_8:NH_3 = 3:1.25:1.25	500	1:25
J	NH_3	500	4:50
K	He	50	–

[a] Initial state corresponds to the state after drying at 120 °C.

Table 1
List of reference compounds with corresponding vanadium environment.

Compounds	Formal valence	Bond type	Number of bonds	Symmetry[a]	Bond distance (Å)	Reference
VB	0	V–B	7		2.26 × 4, 2.29 × 2, 2.40	[28]
		V–V	4		2.74 × 4	
VC	4	V–C	6	O_h	2.09	[29]
VN	3	V–N	6	O_h	2.07	[30]
V_2O_3	3	V–O	6	O_h	1.96, 2.06	[31]
V-bearing magnetite	3	V–O	6	O_h	2.0	[32]
Goldmanite $V_{1.2}Al_{0.47}Ca_{2.9}Fe_{0.33}Mg_{0.08}Mn_{0.02}Si_3O_{12}$	3	V–O	6	O_h	1.99	[33]
V_2O_4	4	V–O	6	O_h	1.76, 1.86, 1.87, 2.01, 2.03, 2.05	[34]
Cavansite $Ca(VO)(Si_4O_{10})\cdot 4H_2O$	4	V–O	5	P_y	1.60, 1.98 × 4	[35]
V_2O_5	5	V–O	5	P_y	1.58, 1.78, 1.89 × 2, 2.02	[36]
Vanadinite $Pb_5(VO_4)_3Cl$	5	V–O	4	T_d	1.70	[37]
Palenzonaite $As_{0.24}Ca_{2.3}Mn_2Na_{0.7}O_{12}Si_{0.3}V_{2.46}$	5	V–O	4	T_d	1.72	[38]
VF_4	4	V–F	6	O_h	1.70 × 2, 1.92 × 4	[39]

[a] O_h, octahedral; T_d, tetrahedral; and P_y, pyramidal.