

Raman spectroscopy during catalytic operations with on-line activity measurement (*operando* spectroscopy): a method for understanding the active centres of cations supported on porous materials†

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Raman spectroscopy with on-line activity measurement (*operando* Raman spectroscopy) is used to reach a molecular understanding of the structure–activity relationship of supported vanadium oxide catalysts during alkane selective oxidation and ammoxidation reactions. The advantage of the *operando* methodology is that the molecular structures are recorded during true catalytic operation, thus affording information about the structures relevant to the catalytic performance. It is shown that efficient propane ammoxidation requires both surface mono-oxo vanadium oxide species and SbVO₄ phases.

Introduction

Despite the large reserves of alkanes, except for the conversion of butane to maleic anhydride on VPO catalysts,¹ no industrial process appears to be operative for the conversion of lighter alkanes. More abundant and economic than olefins, paraffins are very attractive as raw materials. Propane oxidative dehydrogenation (ODH) to propylene^{2–5} and the ammoxidation of propane to acrylonitrile (AN)^{6–9} are attractive valorisation routes for propane.

It is difficult to assess the exact nature of the surface-active phase in bulk mixed-metal oxides, since *in situ* molecular spectroscopies are usually dominated by the *bulk structure*. The use of model-supported systems may facilitate the determination of the structure–activity relationship, since it is possible to grow microcrystalline phases with a high surface-to-volume ratio.¹⁰ Knowledge of the molecular structures existing during true catalytic operation will lead to a deeper understanding of the molecular structure–activity/selectivity relationship.

Supported metal oxide catalysts consist of two-dimensional surface metal oxide overlayers on an oxide support (e.g. alumina, titania, zirconia, silica, etc.). The supported oxide cation (M) binds to the support cation (S) *via* bridging M–O–S bonds, which are formed in part by reaction with surface hydroxyl groups.^{11,12} The molecular structure of dehydrated supported vanadium oxide consists of one terminal V=O bond and three oxygens bridging to the support.¹³ Since the range of these surface structures is below one nanometer, the local environment is not affected by the porosity of the support.

Vanadium oxide is present in most of the catalysts used for selective oxidation of alkanes. Additives may tune vanadia performance for catalytic reactions. Alkaline additives (e.g. Ca, Na, K, ...) tend to coordinate to acidic surface vanadia sites, altering the M–O bonds^{14–17} and decreasing the redox and acidic properties. Sb reacts with V leading to the formation of Sb–V–O phases,^{10,18} increasing the redox properties of vanadia. The formation of Sb–V–O phases requires that the total surface coverage of Sb + V is at least one monolayer, as

has been observed for zirconia¹⁸ and alumina-supported¹⁰ Sb + V oxide systems.

While important details of the reaction mechanism for propane ODH^{19,20} and propane ammoxidation are known,^{21–25} the structure and nature of surface species during the catalytic operations are not fully understood. The molecular understanding of the catalyst requires detailed information on the nature of the active sites and their role in the catalytic cycle. Alumina-supported vanadium oxide catalysts afford their best performance for propane ODH at half-monolayer coverage.⁵ Propane ammoxidation requires the formation of Sb–V–O mixed oxide aggregates to be efficient and Sb–V–O phases form if Sb + V surface loading is at least one monolayer.¹⁰ Several studies about the nature of the active phase in Sb–V–Al mixed-metal oxide catalysts^{26,27} proposed a mixed Sb–V oxide phase, such as SbVO₄, in the presence of Sb₂O₄ as the active phase. However, details of the surface species and the changes that they undergo during propane ammoxidation are currently not fully understood. Scanning electron microscopy has revealed that SbVO₄ microcrystals appear to grow on top of Sb₂O₄ after a catalytic operation, and the combination of both phases together is more selective than either pure phase.^{28,29}

This work presents a study of model alumina-supported V–K–O and Sb–V–O catalysts for propane ODH and propane ammoxidation, respectively, with Raman and on-line GC measurements, so that both the structure and activity/selectivity information are simultaneously obtained. For the sake of simplicity, methodology which involves the simultaneous use of an *in situ* spectroscopy during catalytic operation and on-line activity measurement has recently been called *operando* spectroscopy.^{30–33} The combination of model catalysts and *operando* spectroscopy is used to provide information about the structure–activity/selectivity relationship in vanadium antimonate catalysts for propane ammoxidation and alkali-doped alumina-supported vanadia for propane ODH.

Experimental

The V–K–O/Al₂O₃ catalyst was prepared by impregnation of a commercial γ -Al₂O₃ support (Girdler Südchemie, 160 m² g⁻¹) with an aqueous solution of ammonium metavanadate. Due to the modest solubility of the vanadium salt, the solution was

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heated to 60 °C. The content of vanadium in the catalysts corresponds to half-monolayer coverage of VO_x, *i.e.* near 4 V atoms nm⁻² (7.9 wt.% V). The K-doped catalysts were prepared from aqueous solutions of potassium hydroxide by sequential impregnation with the vanadium oxide precursor on K-doped alumina. The concentration of potassium was 0.7 wt.%, which corresponds to a K/V atomic ratio of 0.1. After drying at 120 °C for 2 h, the samples were calcined at 450 °C for 4 h. This catalyst is denoted 4V/1KAl. The Sb–V–O/Al₂O₃ catalyst was prepared by the slurry method: Sb₂O₃ (Aldrich) was added to an aqueous solution of NH₄VO₃ (Sigma). This solution was stirred at 80 °C for 50 min and then γ-Al₂O₃ powder was added. The resulting solution was dried in a rotary evaporator at 80 °C. The resulting solid was dried at 115 °C for 24 h and then calcined at 400 °C for 4 h. The catalysts were prepared so that the total coverage of V + Sb was two monolayers on alumina and the Sb/V atomic ratio was 5 (named 2Sb₅V/Al). As a reference, this catalyst is compared with another that possesses a total coverage of V + Sb of one monolayer and Sb/V atomic ratio of 1 (named 1Sb₁V/Al).

The chemical analyses of the catalysts were carried out by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Perkin-Elmer Optima 3300 DV spectrometer. The BET areas of the catalysts were measured with a Micromeritics ASAP-2000 apparatus from N₂ adsorption isotherms. XRD spectra were recorded on a Siemens Krystalloflex D-500 diffractometer, using Cu-Kα radiation ($\lambda = 0.15418$ nm) and a graphite monochromator. The working conditions were 40 kV, 30 mA (1200 W); scan rate of 2° min⁻¹ for Bragg's angles (2 θ) from 5 to 70°. The X-ray photoelectron spectra (XPS) were recorded using a VG Escalab 200R apparatus equipped with a hemispherical electron analyzer and an Mg or Al X-ray source operating at 12 kV and 10 mA. Residual pressure in the analysis chamber was less than 5 × 10⁻⁹ mbar.

Raman spectra were run with a Renishaw Micro-Raman System 1000 equipped with a cooled CCD detector and a holographic super-Notch filter to remove the elastic scattering. The samples were excited with the 514 nm Ar line. *Operando* Raman-GC spectra were run with a home-made reaction cell that consists of a fixed-bed quartz microreactor contained by quartz wool plugs at both ends, the catalyst (*ca.* 150 mg) was in powder form. The reaction feed is controlled by mass flow controllers and the reactor outlet is connected on-line to a gas-chromatograph. The micro-reactor walls are of optical quality and no appreciable differences were observed between the activity data afforded by the Raman reaction cell and conventional fixed-bed reactors. Several Raman spectra were acquired at each reaction temperature, representative examples of which are presented. The laser power on the sample was kept below 9 mW to prevent local heating.

The above-mentioned reaction Raman cell was used to run propane ODH and propane ammoxidation experiments with on-line gas chromatographic analyses. For the ODH reaction, the catalysts (150 mg) were tested between 300–500 °C. The reactant gas mixture for propane ODH was C₃H₈–O₂–He (1:6:4), with a total flow rate of 67 cm³ min⁻¹. Analysis of products and unreacted propane was performed by on-line CG (HP-5890 Series II) connected at the exhaust of the Raman

reaction cell. Propene, carbon monoxide, and carbon dioxide were found to be the main reaction products. Propane ammoxidation activity measurements were analysed at the exhaust of the Raman reaction cell with an on-line gas chromatograph (Varian) using flame ionization and equipped with thermal conductivity detectors. The accuracy of the analytical determinations was checked for each test by verification that the carbon balance (based on the propane converted) was within the cumulative mean error of the determinations ($\pm 10\%$). In both reactions, to prevent participation of homogeneous reactivity, the reactor was designed to minimize gas-phase activation of propane. Tests were made using 0.2 g of sample with particle dimensions in the 0.25–0.125 mm range and employing the following feed: 25% O₂, 9.8% propane, and 8.6% ammonia in helium. These proportions were selected in order to obtain an O₂/He ratio similar to the O₂/N₂ ratio in air. The total flow rate was 20 ml min⁻¹, corresponding to a gas-space velocity (GHSV) of about 3000 h⁻¹. Yields and selectivities of the products were determined on the basis of the numbers of moles of propane feed and products, considering the number of carbon atoms in each molecule.

Results

Table 1 illustrates a variety of characterization data. All the catalysts were prepared on the same alumina support. However, 2Sb₅V/Al and 1Sb₁V/Al exhibit lower BET area values than 4V/1KAl. It should be underlined that alumina coverage on the latter is below monolayer coverage, which results in a moderate effect on the BET area. When Sb and V are supported at a total coverage above one monolayer, the system exhibits a moderate decrease in the BET area values. This trend has been observed on alumina¹⁰ and on zirconia.¹⁸ All the catalysts exhibit the diffraction pattern of alumina. In addition, fresh 2Sb₅V/Al exhibits a weak pattern due to Sb₂O₃ (JCPDS file 11-689), which is absent after its use in propane ammoxidation. Thus, if these samples possess crystalline structures, they must be smaller than 4 nm.

A 0.08 V/Al ratio is observed by XPS at a monolayer coverage of pure vanadium oxide on pure alumina.³⁴ However, the porosity of alumina support, which may reduce the XPS signal of some supported vanadium sites, and the presence of a second component, antimony or potassium, makes the evaluation of the V/Al atomic ratio by XPS difficult. The K/V atomic ratio in 4V/1KAl is significantly lower than its bulk K/V ratio (0.042 *vs.* 0.12) by XPS. This is due to the method of preparation of this sample, where vanadium species deposit on the K-doped alumina support.³⁵ The Sb/V atomic ratios from XPS in the fresh Sb–V–O/Al₂O₃ catalysts are much lower than the bulk ratio. However, after propane ammoxidation, these catalysts show increased exposure of vanadium oxide species on the surface that approaches the bulk Sb/V atomic ratio. Therefore, propane ammoxidation induces an extensive rearrangement of the supported vanadium and antimony oxides. It is interesting to note that the V/Al atomic ratio by XPS is essentially constant during this structural transformation. It may be indicative of the fact that redistribution is mainly due to a change in the nature of the antimony species. Therefore, it would be expected

Table 1 Characterization data for the catalysts

Catalyst	BET/m ² g ⁻¹	Metal content/wt.%			Surface density/atoms nm ⁻²			Status	XRD	XPS atomic ratio		
		V	Sb	K	V	Sb	K			V/Al	Sb/V	K/V
2Sb ₅ V/Al	78	2.4	26.8	—	2.6	13.4	—	Fresh	Al ₂ O ₃ trace Sb ₂ O ₃	0.06	13.7	—
										0.07	5.7	—
1Sb ₁ V/Al	91	7.0	16.7	—	4.0	4.0	—	Fresh	Al ₂ O ₃	0.06	5.2	—
										0.06	1.7	—
4V/1KAl	135	7.9	—	0.7	4.5	—	0.4	Fresh	Al ₂ O ₃	0.02	—	0.04

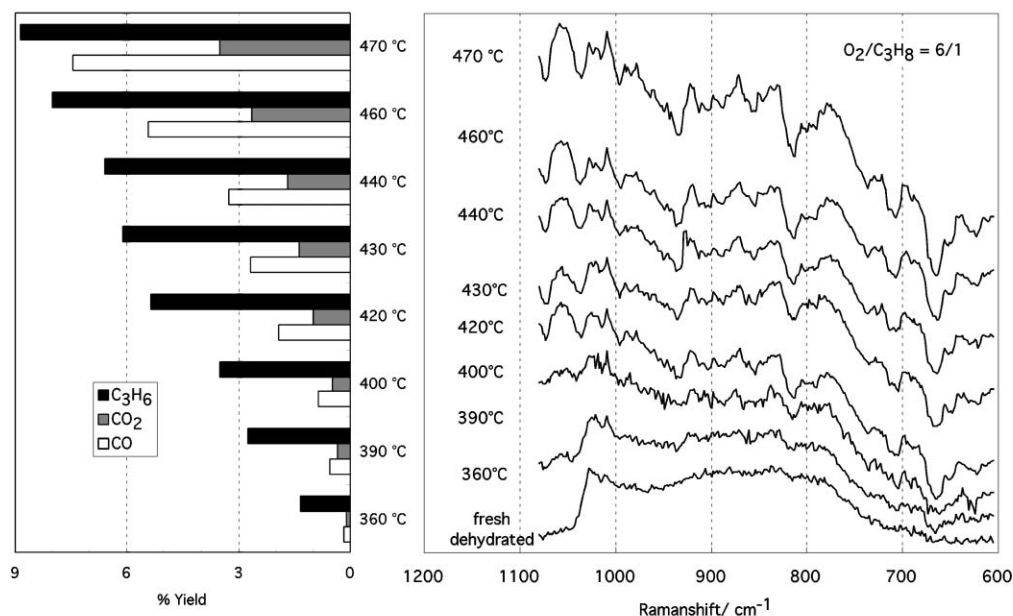


Fig. 1 (Right) *Operando* Raman spectra obtained during propane ODH on 4V/1KAl catalyst. (Left) Yields of the different products during Raman acquisition.

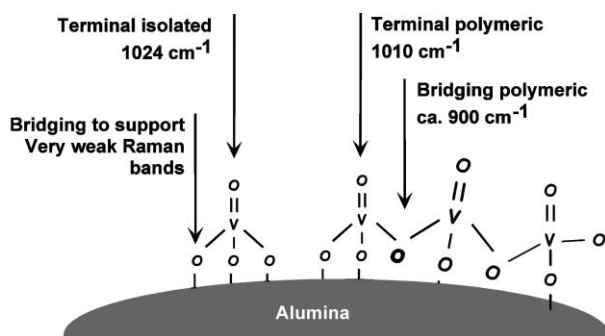
that vanadium exposure on V–Sb–O/Al₂O₃ catalysts is not significantly affected by the structural transformations occurring during catalytic operation.

Raman spectra obtained during catalytic operation are shown in the right panel of Fig. 1. The alumina support shows no Raman bands during blank catalytic operation runs for propane ODH reactions. The catalyst exhibits two Raman bands around 1024 and 1010 cm⁻¹ under dehydrated conditions (200 °C under synthetic air). These two Raman bands are not a doublet,^{31,36,37} but evidence vanadium sites in two different environments: surface isolated vanadium oxide species exhibit one terminal V=O bond near 1024 cm⁻¹, while the V=O mode in surface polymeric vanadium oxide species gives rise to a Raman band near 1010 cm⁻¹^{31,36,37} (Scheme 1). The broad Raman band around 900–800 cm⁻¹ corresponds to the bridging V–O–V mode of surface polymeric vanadium oxide species. Simultaneous activity data related to the corresponding Raman spectra during propane ODH are presented in Fig. 1. The conversion of propane increases with the reaction temperature. The main oxidation product is propylene, the yields of which approach 9% at 470 °C. The catalyst exhibits several weak Raman bands near 987, 923, 873, 836, 782, and 730 cm⁻¹ that may correspond to the incipient formation of potassium vanadate by reaction of surface vanadium oxide species with K, most likely KV₃O₈.³⁸ The Raman bands assigned to alkaline vanadate become more evident with propane conversion, most likely due to a moderate reduction in surface polymeric vanadium oxide species. The Raman spectra show a background

during propane ODH. This must be due to moderate fluorescence generated during reaction. In addition, two Raman bands at ca. 1059 and 690 cm⁻¹ become increasingly evident as the reaction temperature increases. These Raman bands correspond to the V–OC and VO–C modes of surface alkoxy species chemisorbed on surface vanadium oxide sites.³⁹ The alkoxy species disappear as soon as the propane feed is shut down. During these spectra, the catalyst reaches 20% propane conversion at 470 °C. Previous *in situ* Raman studies suggest that surface polymeric vanadia species are more reducible than surface isolated ones.^{31,32,36,37} *Operando* Raman studies during propane ODH on K-free alumina-supported vanadium oxide catalyst show preferential removal of surface polymeric vanadium oxide species as compared with the surface isolated ones.³² However, the presence of surface alkoxy species could not be recorded,³² as in another K-free V₂O₅/Al₂O₃ catalyst;³⁹ this has been attributed to a support-induced effect upon the electronic structure of the surface V–OR species that reduces the Raman scattering cross-section.³¹ The presence of K on the surface of the alumina support blocks this support effect and surface V–OR species give rise to appreciable Raman bands.

Surface vanadium sites during catalytic operation may exhibit a moderate degree of reduction, which has been quantified by *in situ* UV-Vis-NIR diffuse reflectance during ethane and propane ODH.^{40,41} The extent of reduction under alkane ODH conditions show a significant dependence on surface vanadia coverage and underlines the fact that surface polymeric vanadium oxide species are more reducible than surface isolated vanadium oxide species. Raman spectra during catalytic operation with simultaneous activity measurement show that surface polymeric species are indeed more reducible than surface isolated ones, but this has no appreciable effect on the activity.³²

Since it is difficult to assess the state of surface polymeric species from their weak Raman band around 900–800 cm⁻¹, characteristic of the V–O–V stretching mode, it is best to compare the relative Raman intensities of the V=O modes of surface isolated (1024 cm⁻¹) and surface polymeric (1010 cm⁻¹) vanadium oxide species (Fig. 2). Propane conversion increases with reaction temperature, and the polymeric-to-isolated surface vanadia species ratio (Raman intensity ratio 1010/1024) decreases by 1/3 as conversion increases from ca.



Scheme 1 Molecular structures of alumina-supported surface vanadium oxide species.

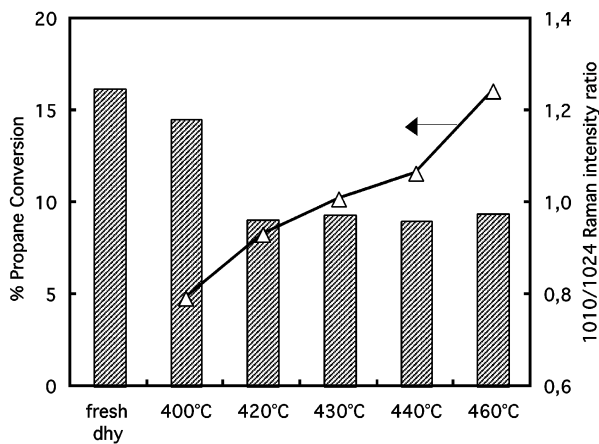


Fig. 2 Propane conversion and 1010/1024 Raman band intensity ratio during propane ODH *operando* Raman spectra of catalyst 4V/1KAl.

5% to ca. 9%. Due to the low signal-to-noise ratio in these spectra, it is not possible to obtain more quantitative statements. However, the additional increase in propane conversion does not result in extensive reduction of surface vanadium sites. Therefore, surface vanadium oxide species undergo some structural changes due to their coordination with propane molecules, which is reflected in a partial loss of surface polymeric vanadium oxide species. However, it is not possible to establish a direct correlation between the decrease of the surface polymeric-to-isolated vanadia species ratio and the extent of propane conversion. The average oxidation state during catalytic operation depends on the relative rates of propane conversion per V site and that of the reoxidation of V sites by molecular oxygen. On average, the system is essentially oxidized, in line with the UV-Vis-NIR diffuse reflectance studies.^{40,41}

Propane ammoxidation on alumina-supported Sb-V-O catalysts affords mainly acrylonitrile, CO₂, propylene, CO, and acetonitrile. However, these catalysts exhibit a transient activity period where propane conversion and acrylonitrile selectivity increase. During this transient activity period, the yields of acrylonitrile and propylene increase at the expense of CO.¹⁰ The results presented in Table 1 demonstrate that important

rearrangements occur on Sb-V-O/Al₂O₃ catalysts during propane ammoxidation. The Raman spectra in Fig. 3 were acquired during propane ammoxidation on a catalyst with 2 monolayers of Sb + V on alumina and an Sb/V atomic ratio of 5. The alumina support shows no Raman bands during blank catalytic operation runs for propane ammoxidation. The fresh 2Sb₅V/Al catalyst, under dehydrated conditions, exhibits Raman bands at 716, 451, 372, 255, and 190 cm⁻¹, characteristic of Sb₂O₃, and a broad band around 800 cm⁻¹ (deconvolution shows that it is constituted of two bands at 835 and 795 cm⁻¹). This broad Raman band is characteristic of the SbVO₄ phases.¹⁰ The 2Sb₅V/Al exhibits different Raman bands when it is under catalytic operation at 480 °C (60% propane conversion) (Fig. 3). The Raman bands of Sb₂O₃ are replaced by bands at 459, 399, 261, and 190 cm⁻¹, characteristic of α-Sb₂O₄, and the broad Raman band near 800 cm⁻¹ becomes more intense. Fresh dehydrated 1Sb₁V/Al exhibits Raman bands at 1024 and 900 cm⁻¹, characteristic of surface polymeric mono-oxo vanadium oxide species. Antimony oxide must be highly dispersed in this sample, since surface dispersed antimony oxide species do not show any appreciable Raman band.¹⁰ The Raman spectrum of 1Sb₁V/Al significantly changes during catalytic operation and exhibits new Raman bands characteristic of surface alkoxy (V-O-R) species, near 1060 and 670 cm⁻¹.^{31,33} Both catalysts are efficient for propane ammoxidation, but 2Sb₅V/Al exhibits no surface vanadium oxide species while 1Sb₁V/Al possess surface vanadium oxide species (Raman band at 1024 cm⁻¹). The absence of surface vanadium accounts for the lack of surface alkoxy V-O-R species on 2Sb₅V/Al. It is interesting that surface exposure of vanadium is similar on both catalysts (see Table 1); however, surface exposure of Sb on used catalysts is higher for 2Sb₅V/Al than for 1Sb₁V/Al (5.7 vs. 1.7, Table 1). The excess surface antimony species must combine with surface vanadium oxide species in 2Sb₅V/Al. Therefore, exposed vanadium sites are different to those in 1Sb₁V/Al, where dispersed surface mono-oxo vanadium oxide species are present (Raman band near 1024 cm⁻¹). Surface vanadium oxide species must be important sites for the catalytic performance of Sb-V-O alumina-supported catalysts for propane ammoxidation, since their presence in the catalyst results in higher conversion, yield, and selectivity towards acrylonitrile.

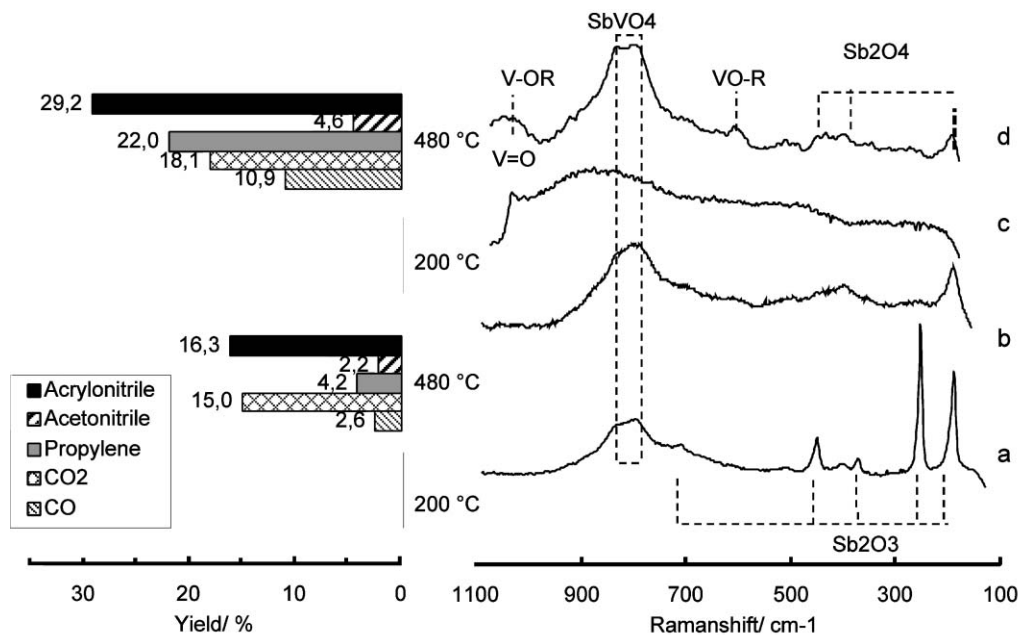


Fig. 3 (Right) *Operando* Raman spectra obtained during propane ammoxidation on 2Sb₅V/Al and 1Sb₁V/Al catalysts. (Left) Yields of the different products during Raman acquisition: (a) fresh dehydrated 2Sb₅V/Al; (b) 2Sb₅V/Al during propane ammoxidation at 480 °C; (c) fresh dehydrated 1Sb₁V/Al; (d) 1Sb₁V/Al during propane ammoxidation at 480 °C.

Discussion

Surface vanadium oxide species interact directly with propane molecules during both the propane ODH and propane ammoxidation reactions, as evidenced by the formation of surface alkoxy species. The interaction between propane and surface vanadium oxide species leads to a moderate reduction of surface vanadium oxide species, and surface polymeric species reduce more easily (Fig. 2). The extent of reduction is moderate, since the number of surface vanadium oxide species on 4V/1KAl does not appear to decrease significantly and the surface structures are not significantly affected during propane ODH on K-doped alumina-supported vanadium oxide catalyst.

The chemistry of mixed Sb–V oxides is different to that of mixed K–V–O oxides. K reduces the redox properties of surface vanadium oxide species,³⁵ whereas Sb significantly increases the redox properties of vanadium oxide species.⁴² The presence of an Sb–V–O phase is essential for the ammoxidation of propane to acrylonitrile on alumina-supported Sb–V oxide catalysts. Surface vanadium oxide species and antimony oxide species tend to combine into Sb–V–O phases during catalytic operation, as is reflected in the Raman spectra obtained during catalytic operation.

It has been reported that the Sb/V atomic ratio determines the performance of alumina-supported Sb–V–O catalysts.¹⁰ At very high Sb/V atomic ratios, the exposure of surface vanadium oxide species is low due to the excess Sb, as shown by the absence of surface vanadia and surface alkoxy species. The results presented above emphasize that surface vanadium sites must directly be involved in the active site for propane ammoxidation. This is in line with a recent study which suggests that surface vanadia species on SbVO₄ and Sb₂O₄ may be important in the redox cycle of V in SbVO₄ for propane ammoxidation reaction.³³

It is interesting to note that the formation of SbVO₄ and Sb₂O₄ becomes more evident after catalytic operation than after calcination of the starting catalyst precursor. This could indicate that the formation of SbVO₄ may require an environment that is not net oxidizing. The ammoxidation reaction feed composition has a moderately reducing character that may account for the more extensive formation of SbVO₄. This is consistent with the oxidation states in SbVO₄, where Sb(v) and V(III) have been identified by Mössbauer and EPR spectroscopy, respectively.^{43,44} Thus, the formation of SbVO₄ from surface vanadia and antimony oxide species requires a moderately reducing environment and its formation is partially reversed under more oxidizing conditions.³³ Therefore, V sites in SbVO₄ may undergo a redox cycle involving surface vanadium oxide species and Sb₂O₄. This cycle may be important for the propane ammoxidation reaction. The spectra in Fig. 3 demonstrate the interaction between surface vanadium oxide species and propane molecules, which may be critical for an efficient ammoxidation reaction. Therefore, an SbVO₄ phase is critical for propane ammoxidation, and the presence of surface vanadium oxide species on SbVO₄ makes the system more active and selective towards acrylonitrile.

Conclusions

The combination of Raman spectroscopy during catalytic operation with simultaneous on-line activity measurements (*operando* methodology) affords molecular understanding of the structure of cations dispersed on porous oxide supports. The results presented above show that the molecular structures of surface vanadium oxide species during catalytic operation are determined by the specific reaction and additional hetero-cations present on the system. Thus, K-doped alumina-supported vanadium oxide catalysts possess a stable surface structure where surface mono-oxo polymeric vanadium oxide species reduce to a moderate extent during propane ODH. On

the other hand, alumina-supported Sb and V oxides undergo significant structural transformations induced by the reaction environment. These structural transformations lead to a change in the dispersion of Sb oxide species into α -Sb₂O₄ and SbVO₄ phases. These phases may originate from highly dispersed Sb oxide or from crystallites of Sb₂O₃. The presence of SbVO₄ phases is critical for propane ammoxidation. If the Sb/V atomic ratio is low, surface mono-oxo vanadium oxide species decorate the surface of SbVO₄ phases. When surface mono-oxo vanadium oxide species are present in addition to SbVO₄ phases and α -Sb₂O₄, the system is significantly more active and selective. Thus, efficient propane ammoxidation requires both surface mono-oxo vanadium oxide species and SbVO₄ phases.

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