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Operando Raman study of alumina-supported Sb–V–O catalyst during propane ammoxidation to acrylonitrile with on-line activity measurement

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***Operando* Raman spectra during propane ammoxidation show partially reversible structural transformations of the active phases as a function of reaction environment.**

The ammoxidation of propane to acrylonitrile (ACN) constitutes an alternative route to conventional propylene ammoxidation since propylene is more expensive than propane. Some of the best performances in the synthesis of acrylonitrile from propane are achieved with V–Sb–O,[1,2] Al–V–Sb–O[3,4] and Al–V–Sb–W–O[5,6] systems.

Several studies about the nature of the active phase on Sb–V–Al mixed metal oxide catalysts[7,8] proposed a mixed Sb–V oxide phase, such as $SbVO_4$, in the presence of Sb_2O_4 as the active phase. However, the details about the surface species and the changes that they undergo during propane ammoxidation are currently not fully understood. Scanning electron microscopy reveals that $SbVO_4$ microcrystals appear to grow on top of Sb_2O_4 after catalytic operation, and the combination of both phases together is more selective than either pure phase.[9,10] However, 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 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.[4] Evaluation of the structures before and after catalytic operation provides some relevant information, but knowledge of the exact molecular structures existing during catalytic operation will lead to a deeper understanding of the molecular structure–activity/selectivity relationship. This work investigates the structures of an alumina-supported Sb–V–O catalyst during propane ammoxidation with Raman and on-line GC measurements so that both the structure and activity/selectivity information are simultaneously obtained. The methodology that involves the use of *in situ* spectroscopy during catalytic operation with on-line activity measurement has recently been denoted *operando* spectroscopy.[11,12]

An alumina-supported Sb–V–O catalyst was prepared as described previously.[4] The catalyst loading was selected so that the total coverage of V + Sb would correspond monolayer surface coverage.[4] The Sb/V atomic ratio was fixed at 1. Raman spectra were obtained with a single monochromator Renishaw System 1000 described elsewhere.[4,12] The acquisition time was 200 s. The Raman–GC spectra were measured with a home-made reaction cell that consists of a fixed-bed quartz-microreactor contained by quartz wool plugs on both ends with the catalyst in powder form. No appreciable differences in conversion and selectivity can be observed between the Raman reaction-cell and a conventional fixed-bed microreactor. The laser power at the sample was kept below 9 mW to prevent local heating. The reaction feed was controlled by mass-flow controllers and the reactor outlet was connected on-line with a gas-chromatograph equipped with flame ionization and thermal conductivity detectors (Varian 3800). The reactor was designed to minimize gas-phase activation of propane. Tests were made using 0.2 g samples with particle size in the range 0.25–0.125 mm. The catalytic reaction employed the following feed composition: 25% O_2, 9.8% propane, 8.6% ammonia in helium. The total flow rate was 20 ml min^{-1} (GHSV = 3000 h^{-1}). Yields and selectivities of the various products were determined on the basis of the moles of propane in the feed and the products, taking into account the number of carbon atoms in each molecule.

The Raman spectra of the fresh catalyst prior to and during propane ammoxidation are shown in Fig. 1. The spectrum of the fresh dehydrated catalyst shows a Raman band near 1024 cm^{-1}, typical of the terminal V=O stretching vibration, and a broad Raman band centered at 900 cm^{-1}, typical of the stretching vibration of the bridging V–O–V bond of the surface vanadium oxide species. The fresh catalyst does not exhibit the Raman bands of any antimony oxide phases.[4] Surface dispersed antimony oxide species on alumina do not appear to exhibit any strong Raman bands, but the corresponding crystalline phases give rise to strong Raman bands.[4] The Sb and V oxides are highly dispersed on the surface of the alumina support for the fresh dehydrated catalyst. During catalytic operation, the intensity of the Raman band of the surface vanadium oxide species near 1024 cm^{-1} tends to disappear, and the shape of the broad Raman band centered at 900 cm^{-1} also changes. As the reaction temperature increases, propane ammoxidation becomes measurable and a broad Raman band becomes evident around 800 cm^{-1} (deconvolution shows that it is constituted by two Raman bands at 835 and 795 cm^{-1}). This broad Raman band is characteristic of the $SbVO_4$ (rutile) phase.[4] At 480 °C, the catalyst becomes more selective to ACN formation (Fig. 1(e)), and corresponds to a transformation of surface vanadia species into microcrystalline $SbVO_4$ and of Sb_2O_4. In contrast, CO_2 and propylene were the main products at lower reaction temperatures. This dramatic change in product distribution with reaction temperature is not observed for other alumina-supported Sb–V–O catalysts if the $SbVO_4$ phase does not form.[4] The broad Raman bands near 1060 and 620 cm^{-1} correspond to V–OC and VO–C vibrations, of adsorbed alkoxy species, respectively.[13] The concomitant loss of surface vanadium oxide species and decrease of CO_2 and propylene formation is indicative of a change in the nature of the active phase. The remarkable increase in the selectivity towards acrylonitrile corresponds to a structural change in the catalyst leading to $SbVO_4$ formation at the expense of surface vanadium and antimony oxide species. Surface antimony oxide species show no appreciable catalytic activity for alkane activation; however, alumina-supported vanadia species are active for propane ODH. The concomitant formation of $SbVO_4$ and Sb_2O_4 and a significant alteration in the product distribution towards acrylonitrile underlines the transformation of a surface efficient for propane ODH to an active phase efficient for propane ammoxidation.

It is interesting to note that the formation of $SbVO_4$ and Sb_2O_4 become more evident after catalytic operation than after calcination of the starting catalyst precursor. This may be indicative that the formation of $SbVO_4$ may require an environment that is not net oxidizing. A significant benefit of *operando* Raman spectroscopy is that it provides direct evidence on the relevance of the environment on the oxidation states of V and Sb oxide species in the Sb–V–O phases. The ammoxidation reaction feed composition has a moderate

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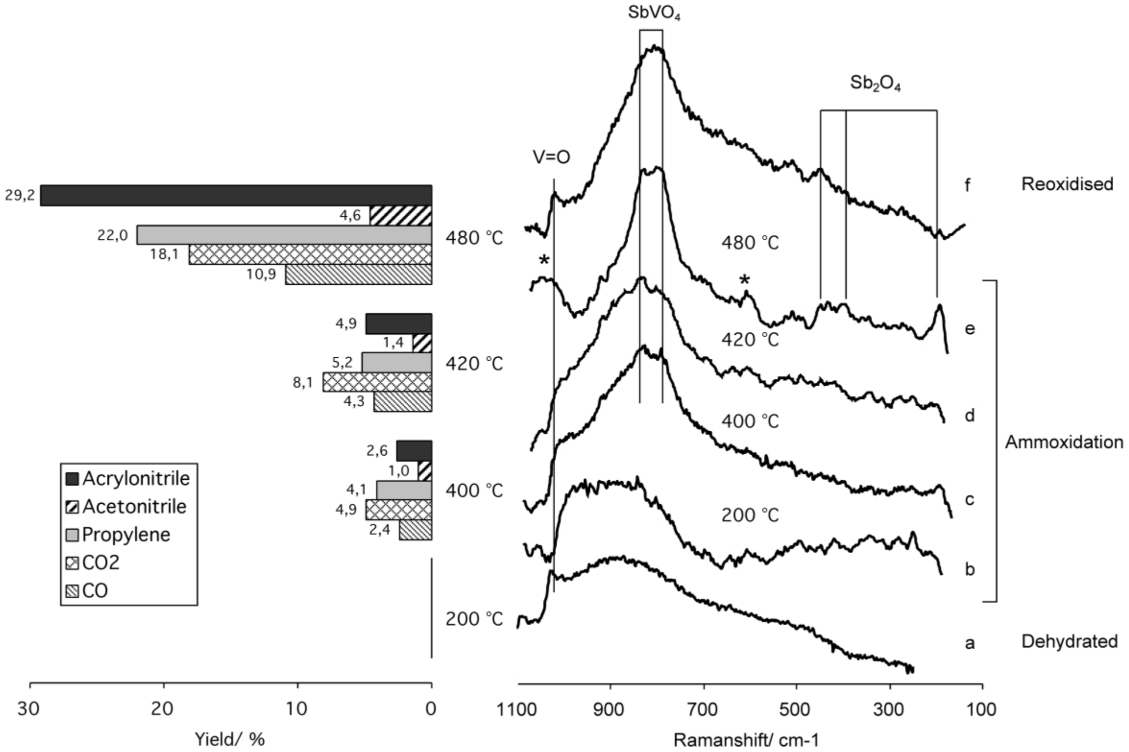

Fig. 1 Raman spectra of Sb–V–O/Al$_2$O$_3$ catalyst during propane ammoxidation reaction and other conditions: dehydration at 200 °C (a); ammoxidation at 200 °C (b), 400 °C (c), 420 °C (d) and 480 °C (e), reoxidation at 440 °C (f). The corresponding yield values are presented in the left panel. *Reaction conditions*: 200 mg of catalyst, total flow 20 ml min^{-1}; feed composition (% volume); C$_3$H$_8$–O$_2$–NH$_3$–H$_2$O–He (9.8 : 25 : 8.6 : 0 : 56.5).

reducing character that may account for the more extensive formation of SbVO$_4$. This is consistent with the oxidation states in SbVO$_4$, where Sb(V) and V(III) have been identified by Mössbauer and EPR spectroscopy, respectively.[14,15] Thus, this reaction environment leads to a more extensive formation of SbVO$_4$. Along this line, it is interesting to follow the transformation that may occur to the Sb–V–O/Al$_2$O$_3$ catalyst upon further exposure to an oxidizing environment at elevated temperatures. Thus, the reaction temperature was decreased to 200 °C and ammonia was removed from the reaction feed, under such ODH (propane, oxygen and helium) conditions the V sites in SbVO$_4$ exhibit a moderate reoxidation towards surface vanadium oxide species (Raman band at 1023 cm^{-1}). This trend becomes more evident as the reaction temperature is further increased to 400 °C. The removal of propane from the reaction feed at 400 °C leads to a more extensive reoxidation of the vanadium species. This reoxidation in O$_2$ + He feed becomes more evident as the temperature is increased from 400 to 520 °C (a representative Raman spectrum at 440 °C is shown in Fig. 1(f)). The conversion of surface V(V) oxide species into V(III) species in SbVO$_4$ during ammoxidation and the restoration of surface V(V) species after reoxidation is in agreement with the enhancement of the redox properties of vanadium oxide when combined with antimony oxide.[16] Thus, the formation of SbVO$_4$ from surface vanadia and antimony oxide species requires a moderate reducing environment and its formation is partially reversed under more oxidizing conditions. Therefore, V sites in SbVO$_4$ may undergo a redox cycle involving surface vanadium oxide species and Sb$_2$O$_4$. This cycle may be important for the propane ammoxidation reaction.

The novel *operando* methodology has shown that during propane ammoxidation the surface Sb and V oxides interact to form SbVO$_4$ as well as Sb$_2$O$_4$. SbVO$_4$ must be directly involved in the rate-determining step for acrylonitrile formation and surface vanadia species on alumina are not the active site for this reaction. The structural transformations are partially reversible since exposure to an oxidizing atmosphere restores surface vanadium oxide species and Sb$_2$O$_4$ disappears from the surface. Thus, the surface vanadia species on SbVO$_4$ and Sb$_2$O$_4$ may be important in the redox cycle of V in SbVO$_4$ for propane ammoxidation reaction.

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