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Rutile-type metal (Cr, V) niobates as catalysts for propane ammoxidation to nitriles: In situ characterization and operando reactivity

F. Cavani [a,*], N. Ballarini [a], M. Cimini [a], F. Trifirò [a],
M. Bañares [b], M.O. Guerrero-Pérez [b,c]

[a] Dip. Chimica Industriale e Materiali, V.le Risorgimento 4, 40136 Bologna, Italy
[b] Instituto de Catálisis y Petroleoquímica, CSIC, Marie Curie 2, E-28049 Madrid, Spain
[c] Departamento de Ingeniería Química, Facultad de Ciencias, Universidad de Málaga, E-29071 Málaga, Spain

Abstract

Rutile-type Cr/Nb and V/Nb mixed oxides were prepared by co-precipitation from ethanolic solutions, and calcination at 700 °C. The development of the rutile structure during the thermal treatment of the precursor was investigated by in situ TP–Raman spectroscopy. It was found that graphite-like carbon deposits build-up during calcinations in inert. Their decomposition provides the reducing agent that leads to the formation of rutile $VNbO_4$ at relatively mild conditions. Rutile Cr and V niobates were tested as catalysts for the ammoxidation of propane, under both hydrocarbon-rich and hydrocarbon-lean conditions. Catalysts were active but non-selective to acrylonitrile. The catalyst modifications occurring during reaction were followed by operando Raman–GC methodology. $VNbO_4$ transforms into a catalyst active and selective for acetonitrile under leaner hydrocarbon feed.

Keywords: Propane ammoxidation; Acrylonitrile; Acetonitrile; Rutile; Niobium oxide; Chromium niobate; Vanadium niobates; Operando Raman spectroscopy

1. Introduction

Acrylonitrile is conventionally prepared by the ammoxidation of propylene, but an interest exists for the development of a process that uses propane as the raw material, due to the lower cost of the paraffin as compared to the olefin [1–3]. BP, Mitsubishi Chemical and Asahi have announced the start-up of semi-commercial units or of pilot plants for the ammoxidation of propane [4,5]. The catalysts claimed are based either on rutile-type metal antimonates (V/Sb/O, V/Al/Sn/Sb/O, Fe/Sb/O) [6–10], or on mixed molybdates (Mo/V/Te(Sb)/Nb/O for the Mitsubishi and Asahi catalysts) [11–14]. These catalysts can be considered as multi-functional systems, in which the various components are aimed at different roles in the multi-electron, complex transformation of the alkane, including the propane activation and oxidehydrogenation, and the allylic ammoxidation of the unsaturated intermediate to acrylonitrile.

In multi-component systems for the oxidative transformation of hydrocarbons, Nb is claimed to play an important role [15–17]. This is particularly true in Mo/V/Te(Sb)/Nb/O catalysts for propane oxidation to acrylic acid, in which the addition of Nb leads to an increase of selectivity to the desired product [18–20]. Niobium affords specific crystalline structures and it may lead to new active sites, or tune existing active sites. Other authors claim a decrease of the catalyst acidity, which favours the desorption of acrylonitrile saving it from consecutive reactions [21]. The Mo/V/Nb/O system, originally disclosed by Union Carbide [22], and then studied by other authors [23,24], is very active and selective in the oxidation of ethane to ethylene or to acetic acid [25]; the role of Nb is to enhance the intrinsic activity of Mo/V/O, and to inhibit the combustion of ethane.

In the case of alkane ammoxidation, Nb is included in the formulation of Mitsubishi catalyst [11,13], but no specific role for this element in the reaction has been reported. The Nb/Sb/O

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* Corresponding author. Tel.: +39 051 2093680; fax: +39 051 2093680.
E-mail address: cavani@ms.fci.unibo.it (F. Cavani).

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system is claimed for the ammoxidation of ethane to acetonitrile [26], but their combination as $SbNbO_4$ renders the system inefficient for propane ammoxidation [27]. The combination of Bi/Mo/O and alumina-supported Nb_2O_5 gives good performance in the ammoxidation of isobutane to methacrylonitrile [28]. Nb is one component of the V/Nb/Sb/O catalyst for propane ammoxidation developed by Nitto Chem Ind [29]. In recent works, Bañares et al. found that when used as support for the V/Sb mixed oxide, Nb_2O_5 forms new phases during reaction conditions; these phases were responsible for an increased selectivity to acrylonitrile and are associated to mixed V/Nb oxides promoted by Sb [27,30].

Previously, we studied the reactivity of Cr/Sb and of Cr/V/Sb mixed oxides [31–34] for the ammoxidation of propane to acrylonitrile. It was found that rutile-like Cr antimonate is active but fairly selective for propane ammoxidation; the addition of V considerably improves the catalyst activity, while the effect on selectivity to acrylonitrile depends on the (Cr + V)/Sb ratio. In the present work, we report about the catalytic performance and the structural stability of $VNbO_4$ and $CrNbO_4$, rutile-type compounds, in order to check the feasibility of using Nb as one component in rutile-type catalysts for propane ammoxidation.

2. Experimental

The catalysts were prepared by the co-precipitation technique, developed for the preparation of rutile SnO_2-based systems claimed by Rhodia [7]. The preparation involves the dissolution of $Cr(NO_3)_3 \cdot 6H_2O$, $VO(acac)_2$ and $NbCl_5$ in absolute ethanol, followed by dropping the solution into a buffered aqueous solution maintained at pH 7. A precipitate is obtained, which is separated from the supernatant liquid by centrifugation and filtration. The solid is then dried at 120 °C, and calcined either in N_2 (V/Nb/O sample) or in air (Cr/Nb/O) at 700 °C for 6 h, with a heating rate of $1^\circ\ \mathrm{min}^{-1}$.

The XRD patterns of the catalysts were taken with Ni-filtered Cu Kα radiation (λ = 1.54178 Å) on a Philips X'Pert vertical diffractometer equipped with a pulse height analyser and a secondary curved graphite–crystal monochromator.

A 514 nm Ar line laser was used for all the Raman spectra. In situ Raman spectra of dehydrated catalysts and during temperature-programmed (TP) Raman were obtained under controlled atmosphere (dry air or nitrogen) using a Renishaw 1000 instrument fitted to a hot stage (Linkam, TS-1500). The operando Raman–GC reaction studies were carried out with a home-made operando Raman reaction cell [35,36]. These reaction tests were made using 0.2 g of sample, using the following feed: 9.8% propane, 8.6% ammonia, 25% oxygen, remainder He; GHSV was $3000\ \mathrm{h}^{-1}$. The activity data in the operando Raman cell show no appreciable differences with those observed in the conventional reactors [37].

Conventional catalytic tests under steady-state conditions were carried out in a laboratory stainless steel fixed-bed reactor operating at atmospheric pressure. About 1.8 g of catalyst was loaded, shaped in particles ranging in size from 0.42 to 0.55 mm. The following reaction conditions were used: feed composition 25 mol% propane, 10% ammonia, 20% oxygen, remainder helium; residence time 2.0 s. The reactor outlet was kept at 170 °C. On-line sampling of a volume of either the feedstock or effluents was obtained by means of three heated valves. Three different columns were used for product identifications. Two of these were an Hay-sep T column (TCD detector) for the separation of CO_2, NH_3, $C_3H_8 + C_3H_6$, H_2O, HCN, acrolein, acetonitrile and acrylonitrile, and a MS-5A column (TCD detector) for separation of O_2, N_2 and CO. Both columns were arranged in parallel. Hay-sep T was also used as a filter to avoid contamination of MS-5A by CO_2. The third column, a packed one filled with Poropak QS (FID detector), was used for the separation of propane from propylene.

3. Results and discussion

3.1. Genesis of the rutile structure

The synthesis of rutile-type $VNbO_4$ was carried out by thermal treatment in N_2 of precursors having a V/Nb atomic ratio equal to 1 [38], at 700 °C (surface area of calcined sample was $12\ \mathrm{m}^2/\mathrm{g}$). X-ray diffraction patterns exhibit the features of the rutile $VNbO_4$ phase and traces of Nb oxide. However, the patterns evidence $VNbO_5$ (JCPDF 46-0046), VNb_9O_{25} (18-1447) and V_2O_5 (41-1426) if the treatment is carried out in air (Fig. 1). Unlike rutile $VNbO_4$, $CrNbO_4$ (34-0366) could be synthesized by thermal treatment of the precursor in air (700 °C) [39]. Its surface area was $14\ \mathrm{m}^2/\mathrm{g}$. Therefore, the compound was stable under oxidizing conditions. The X-ray diffraction pattern (Fig. 1) evidence the presence of small amounts of Cr and Nb oxides. To our knowledge, $CrNbO_4$ has never been used for catalytic applications; recently, the reactivity of Cr/V/Nb mixed oxides in ethane oxidehydrogenation was reported, but in this case Nb was a component present in minor amount [40].

Due to the relevance of the environment for V/Nb/O phases, the evolution of the precursor in inert atmosphere (helium) has been followed by in situ TP–Raman spectroscopy from room temperature to 600 °C (Fig. 2). Fluorescence dominates the spectra at lower temperatures. Two bands at 1560 and $1370\ \mathrm{cm}^{-1}$ become increasingly evident in the 200–400 °C

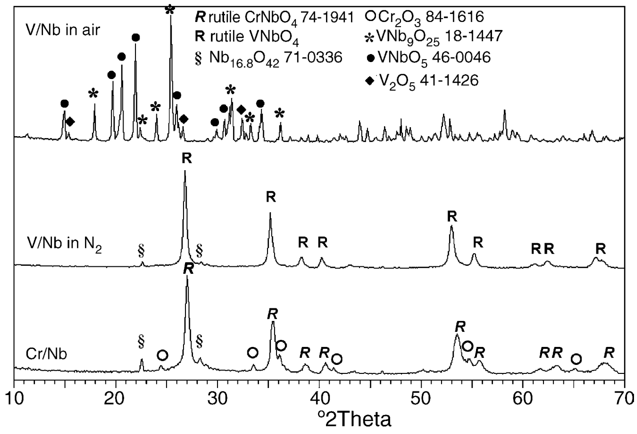

Fig. 1. X-ray diffraction patterns of V/Nb sample calcined in air and in N_2 at 700 °C, and of Cr/Nb sample calcined in air at 700 °C.

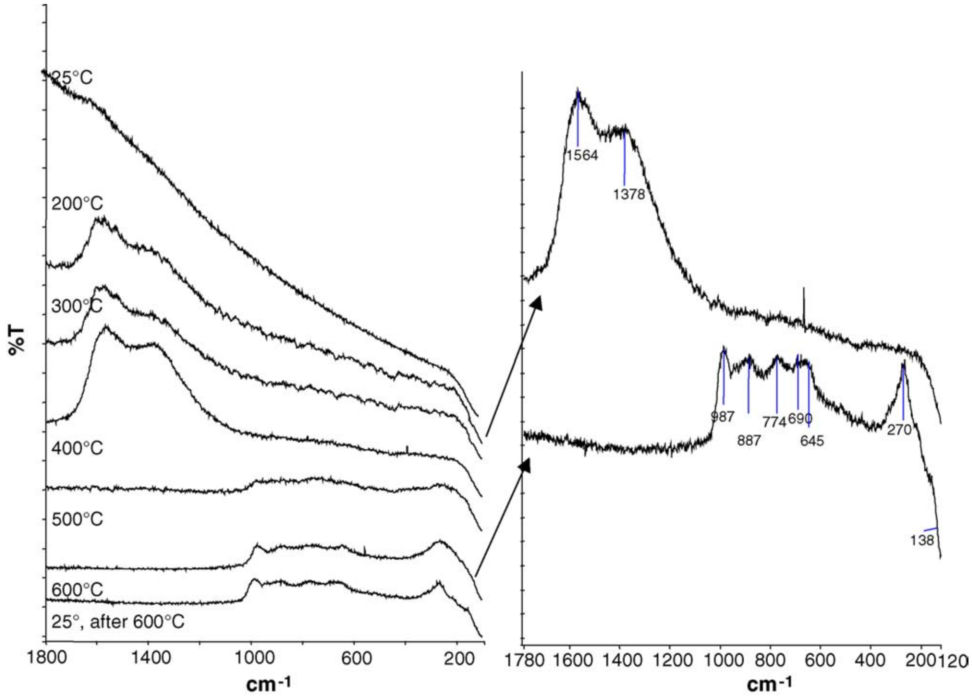

Fig. 2. In situ Raman spectra of V/Nb sample, treated in He at increasing temperature (left), and expanded spectra of samples after treatment at 200 and 600 °C.

(expanded spectrum in the right). These bands evidence the development of graphite-like carbon deposits [41,42]. The formation of carbon deposits was due to the residual organic compounds (ethanol, used for the preparation of the solution of metal salts) under non-oxidizing atmosphere. The Raman bands of carbon deposits are removed at 500 °C and above. This is associated to their oxidation at the expense of lattice oxygen since the new Raman bands (270, 690, 774, 887, 987 cm^{-1}) are characteristic of $VNbO_4$ [38]. Therefore, the reduction to V^{3+} by coke oxidation is necessary for the generation of rutile-type $VNbO_4$ since $VNbO_4$ has vanadium only as V^{3+} as demonstrated by XANES-measurements [43]. Further in situ Raman studies (not shown) demonstrated that no carbon deposits form if the precursors are treated in air; in this case the rutile-type compound did not form. These results are consistent with the XRD data. Regarding the formation of $VNbO_4$ at 500 °C, it is worth mentioning that the conventional synthesis of $VNbO_4$ occurs by solid-state reaction between NbO_2 and VO_2 at above 1000 °C in vacuum [44]. Our procedure (the co-precipitation of oxohydrates from an alcoholic solution) produces a precursor that, under thermal treatment in nitrogen, forms the rutile $VNbO_4$ phase at significantly lower temperature. The driving force for this decrease in the temperature must be found in the intimate contact between V and Nb afforded by the co-precipitation method, and in the reducing effect of coke.

3.2. Catalytic performance in propane ammoxidation of rutile-type metal niobates

The catalytic performance of $VNbO_4$ and $CrNbO_4$ is reported in Fig. 3, which plots the conversion of propane, and the selectivity to acrylonitrile and to nitrogen (the latter calculated as referred to ammonia converted) versus temperature. It also shows the selectivity to the various products at 460–470 °C. Catalysts were active, but quite unselective to acrylonitrile; major products were propylene and carbon oxides. Ammonia converted was almost exclusively transformed to N_2.

Due to the relevance of the environment, hydrocarbon-rich conditions were used in order to avoid the structural decomposition of $VNbO_4$. $VNbO_4$ decomposes under hydrocarbon leaner conditions. This was studied in detail versus reaction time by operando Raman–GC. Fig. 4 illustrates the Raman spectra and simultaneous yields to the products as functions of the reaction time under reaction conditions that are more oxidizing than those used for Fig. 3 (propane 9.8%, ammonia 8.6%, oxygen 25%, at 450 °C). The Raman bands corresponding to the rutile $VNbO_4$ (270, 650, 774, 887, 987 cm^{-1}) can be appreciated in the spectra recorded during the first 2 h on stream. In the last Raman spectrum, recorded at a reaction time of 334 min, incipient Raman bands at 143, 283, 405, 526, 698 and 994 cm^{-1}, indicate the formation of V_2O_5 oxide at the expense of the $VNbO_4$ rutile phase. Therefore, $VNbO_4$ is an unstable structure, and requires hydrocarbon-rich conditions in order to avoid the decomposition. This is consistent with previous observations that $VNbO_4$ is not stable in oxidizing environments, and transform into $VNbO_5$ or V_2O_5/Nb_2O_5 when treated in air at 400–450 °C, or when exposed to hydrocarbon-lean conditions during propane oxidehydrogenation [39]. In the operando study, such transformation is concomitant to a remarkable increase of the yield to acetonitrile. This can be attributed to the modification of catalyst features, and possibly to an increased acidity due to the in situ generation of segregated Nb oxide, or of Nb-rich V/Nb mixed oxides. The formation of

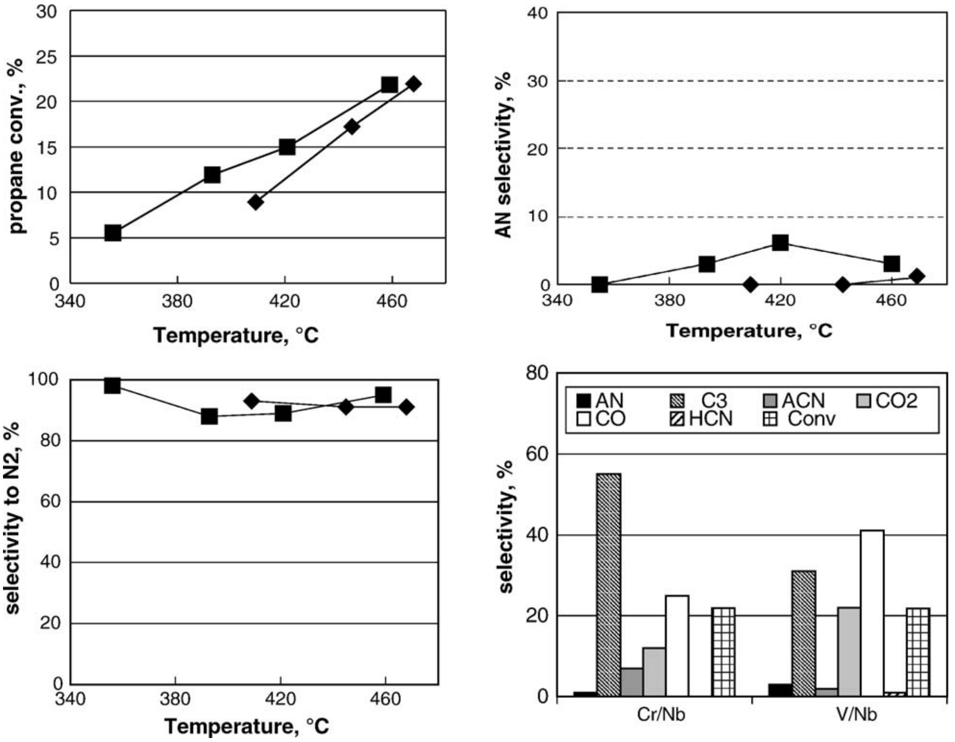

Fig. 3. Effect of temperature on propane conversion (top left), on selectivity to acrylonitrile (top right) and on selectivity to N_2 from ammonia combustion (bottom left). Distribution of products at ≈459–468 °C (bottom right). Catalysts Cr/Nb 1/1 (◆), V/Nb 1/1 (■). Reaction conditions: feed composition 25 mol% propane, 10% ammonia, 20% oxygen, remainder He; residence time 2.0 s. AN = acrylonitrile; C_3 = propylene; ACN = acetonitrile; CO_2 = carbon dioxide; CO = carbon monoxide; HCN = cyanhydric acid; Conv = propane conversion.

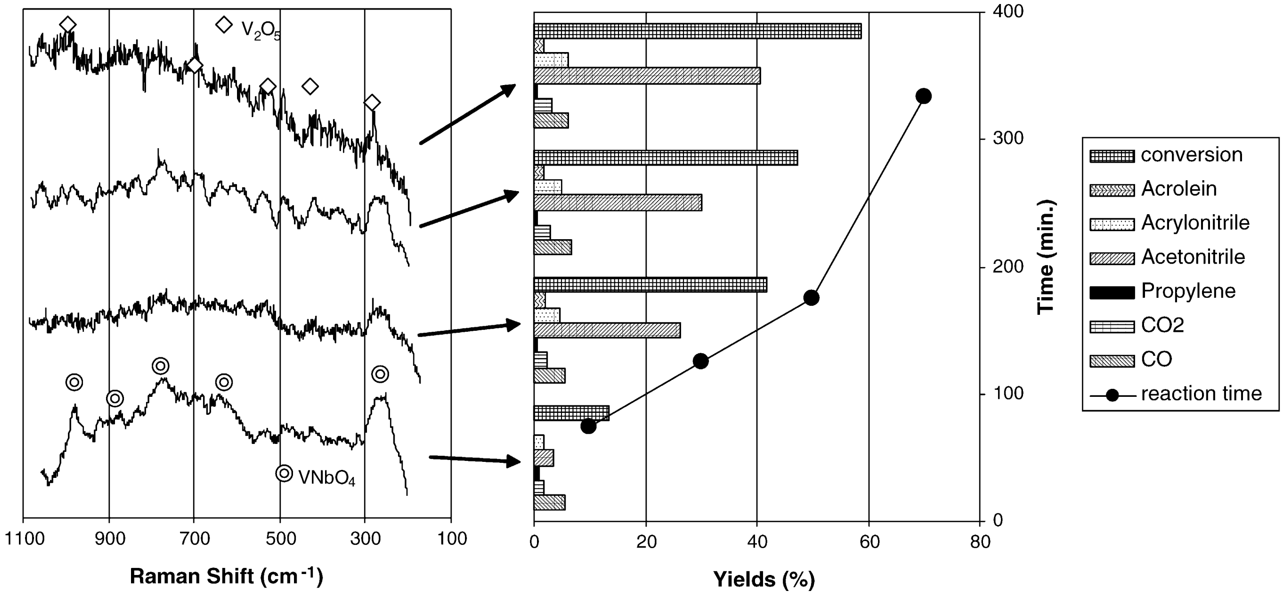

Fig. 4. Operando Raman–GC study during reaction at different reaction times (left) and the corresponding yields to products, measured in the operando Raman reactor. Reaction conditions: propane 9.8%, ammonia 8.6%, oxygen 25%, *T* 450 °C. Catalyst V/Nb 1/1 thermally treated in N_2.

$VNbO_4$ under mild calcination conditions (temperature as low as 500 °C) was thus facilitated by the development of intrinsically reducing conditions during the thermal treatment in N_2, due to the presence of residual organic compounds in catalyst precursor.

4. Conclusions

$CrNbO_4$ and $VNbO_4$ rutile phases require different conditions to be formed. Unlike $CrNbO_4$, the formation of $VNbO_4$ is strongly dependent on the conditions, being decomposed in oxidizing environment. The use of coprecipitation from an ethanolic solution method dramatically decreases the temperature for the formation of the rutile $VNbO_4$ phase.

In catalytic tests of propane ammoxidation, rutile $VNbO_4$ is sensitive to oxidizing conditions and is stable under hydrocarbon-rich reaction conditions, but decomposes into more oxidized, and probably, more acidic phases, during reaction under hydrocarbon-lean conditions. The new system is significantly more active, but essentially selective for acetonitrile formation.

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