Catalysis Today 142 (2009) 152–157

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Role of V in supported V–Sb–O catalysts for the ammoxidation of propane to acrylonitrile: Multilayered $VO_x/SbO_x/Al_2O_3$ catalysts

M. Olga Guerrero-Pérez *, Miguel A. Bañares

Catalytic Spectroscpy Laboratory, Instituto de Catálisis y Petroleoquímica, CSIC, Marie Curie 2, E-28049 Madrid, Spain

A R T I C L E I N F O

Article history:
Available online 13 December 2008

Keywords:
V–Sb–Al
V–Sb–O
Oxidation
Ammoxidation
Propane
Acrylonitrile
Structure-activity relationship
In situ Raman
XRD

A B S T R A C T

A synthesis method for multilayered V–Sb–O catalysts on Al_2O_3 is described and compared to coimpregnated series; these catalysts are tested for propane ammoxidation. With this preparation method, vanadium and antimony are added sequentially. First, alumina support is impregnated with a loading corresponding to a monolayer of antimony dispersed, it is dried and calcined; then; this solid is impregnated with a vanadium oxide precursor solution. The data obtained are compared with previous papers with catalysts prepared adding both antimony and vanadium at the same time. The new method facilitates the reaction between vanadium and antimony to form the rutile $VSbO_4$ active phase. The presence of dispersed vanadium oxide species along with the rutile $VSbO_4$ phase improves propane conversion.

1. Introduction

Acrylonitrile is widely used as intermediate for the preparation of synthetic rubbers, synthetic resins and fibbers. It is industrially produced nowadays by ammoxidation of propylene on fluid bed reactors with catalysts made of promoted Fe–Bi–Mo–O (BP America) or promoted Fe–Sb–O (Nitto) [1]. Thus, direct conversion of propane into acrylonitrile by ammoxidation of propane is an alternative route to the conventional propylene ammoxidation since propane is substantially cheaper than propylene. More recently, ammoxidation of renewables would be a new route to acrylonitrile formation [2].

There is an important body of research on propane ammoxidation, and the major part of the reported work concentrates on two types of catalysts: the antimonates with rutile structure [3–7] and the molybdates [8–12], both systems usually incorporate vanadium as the key element. Mo–V catalysts modified with niobium and tellurim may afford near 50% yield to acrylonitrile [12] while it reaches 40% on the antimonate system [7,13–14]. Sb–V–O catalysts with an excess of V are highly active and selective for propane oxidative dehydrogenation (ODH) while an excess of Sb affords Sb–V–O catalysts more efficient for propane ammoxidation [15].

Several synthesis methods have been studied for the Sb–V–O based catalysts and it is reported that the synthesis method affects dramatically the activity behavior of catalysts [16]. The most usually studied correspond to patents deposited on 1988 by Standard Oil Co [5–7] and consist on keep a reflux during some hours an aqueous dispersion of NH_4VO_3 or V_2O_5 and Sb_2O_3. Others studies try to keep vanadium as V^{4+} on oxalic acid and then add antimonic acid to this solution [17] or prepare catalysts with a dissolution of VCl_3 and $SbCl_5$ on HCl [18], and Brazdil et al. have developed a sol-gel method synthesis for this kind of catalysts [19].

A previous work studied a new synthesis route with Sb–V catalysts supported on alumina [20,21]. With this new method, antimony is added as a soluble tartrate complex. Thus, antimony remains dispersed on the alumina support surface as a monolayer. This work evaluates the relevance on structure, activity and selectivity of sequential vs. simultaneous addition of vanadium and antimony on alumina substrate.

2. Experimental and methods

2.1. Preparation of samples

Alumina-supported V–Sb–O catalysts were prepared using two procedures. A *two-step process*, where alumina is doped with

---

* Corresponding author at: Departamento de Ingeniería Química, Universidad de Málaga. Campus de Teatinos, E-29071 Málaga, Spain.
E-mail address: oguerrero@uma.es (M. Olga Guerrero-Pérez).

0920-5861/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2008.10.040

antimony, and vanadia is added to SbO_x/Al_2O_3, and a *single-step process* in which vanadium and antimony are coimpregnated. The alumina impregnated with antimony (SbTAl) was prepared dissolving the necessary quantity of antimony acetate (Aldrich) on tartaric acid (Sigma) 0.3 M. This solution was stirred until all antimony dissolves; then, γ-Al_2O_3 (Versal) was added to the solution. The resulting dissolution was dried in a rotatory evaporator at 80 °C. The resulting solid was dried at 115 °C for 24 h and then calcined at 400 °C for 4 h. SbTAl was prepared so that a total coverage of antimony would correspond to 8 atoms per nm^2 of alumina support (this loading would be close to monolayer coverage). Next, the SbTAl modified support was added to an aqueous solution of NH_4VO_3 (Sigma) to prepare the vanadium catalysts. The resulting solution was dried in a rotatory evaporator at 80 °C and the resulting solid was dried at 115 °C for 24 h and, finally, calcined at 400 °C for 4 h. This synthesis method is denominated as "*two steps*". This catalyst was prepared so that a total coverage of vanadium would correspond to 25%, 50%, 100% and twice their dispersion limit on the support. This dispersion limit loading, understood as the maximum surface loading of VO_x units that remain dispersed, with no crystalline V_2O_5, was determined by Raman spectroscopy to be near 9 VO_x units per nm^2 of alumina support, in accordance to previous reports on other supports [22,23]. For the sake of simplicity, these supported catalysts are labeled as "*xV/SbTAl*" where x represent the nominal fraction of dispersion limit ("monolayer" coverage) of V atoms on the support.

For comparative purposes, another series of catalysts is prepared, in which both vanadium and antimony are coimpregnated on alumina support. Alumina is added to a solution containing antimony acetate (Aldrich) dissolved in tartaric acid (Sigma) 0.3 M and NH_4VO_3 (Sigma) solutions; this synthesis method is denominated as "*one step*". In a similar fashion to the two-steps series, 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 a total coverage of V + Sb would correspond to the dispersion limit on the alumina support. Three samples were prepared with Sb/V molar ratios of 1, 2 and 4. These supported catalysts are labeled as "1SbyV/Al" where y represents the Sb/V molar ratio.

2.2. Characterization

Nitrogen adsorption isotherms (−196 °C) were recorded on an automatic Micromeritics ASAP-2000 apparatus. Prior to the adsorption experiments, samples were outgassed at 413 K for 2 h. BET areas were computed from the adsorption isotherms ($0.05 < P/P_o < 0.27$), taking a value of 0.164 nm^2 for the cross-section of the adsorbed N_2 molecule at −196 °C. X-ray diffraction patterns were recorded on a Siemens Krystalloflex D-500 diffractometer using Cu Kα radiation ($\alpha = 0.15418$ nm) and a graphite monochromator. Working conditions were 40 kV, 30 mA, and scanning rate of 2°/min for Bragg's angles (2θ) from 5° to 70°. In some cases, the peaks of Al from the sample holder are present.

Raman spectra were run with a single monochromator Renishaw System 1000 equipped with a cooled CCD detector (−73 °C) and holographic super-Notch filter. The holographic Notch filter removes the elastic scattering while the Raman signal remains very high. The samples were excited with the 514 nm Ar line; spectral resolution was ca. 3 cm^{-1} and spectrum acquisition consisted of 20 accumulations of 30 seconds. The spectra were obtained under dehydrated conditions (ca. 120 °C) in a hot stage (Linkam TS-1500). Hydrated samples were obtained at room temperature after and under exposure to a stream of humid synthetic air.

2.3. Activity measurements

Activity measurements were performed using a conventional quartz microreactor fitted to an on-line gas chromatograph, equipped with a flame ionization and thermal conductivity detector. The correctness 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 (±10%). 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. The axial temperature profile was monitored by a thermocouple sliding inside a tube inserted into the catalytic bed. Tests were made using the following feedstock: 25% O_2, 9.8% propane, 8.6% ammonia in helium. The total flow rate was 20 ml/min corresponding to a gas-space velocity (GHSV) of about 3000 h^{-1}. Yields and selectivities in products were determined on the basis of the moles of propane feed and products, considering the number of carbon atoms in each molecule.

3. Results

The BET surface areas of the catalyst are listed in the Table 1. The BET area values decrease with surface coverage on Al_2O_3 from ca. 265 to 44 m^2/g for the two-step catalyst series. The BET area decrease is less marked for the one-step catalyst series—from 265 to 111 m^2/g. For a given vanadium oxide loading, BET area values are higher for the one-step catalyst series.

The XRD patterns of fresh and used catalysts are shown in Fig. 1. Reference samples Sb_2O_3, α-Sb_2O_4, VSbO4 and V_2O_5, were characterized in a previous work [14]. The XRD pattern of the alumina-supported antimony oxide (sample SbTAl) and that of the samples with lower vanadium coverages prepared with the *two-steps* synthesis method (0.25V/SbTAl and 0.5V/SbTAl) exhibit no diffraction pattern, the diffraction pattern of $VSbO_4$ phase (JCPDS file 16-0600) becomes increasingly apparent for 1V/SbTAl and 2V/SbTAl (Fig. 1A) and it grows more intense upon aging in reaction. At the highest vanadium loading, V_2O_5 diffraction pattern (JCPDS file 41-1426) is observed for fresh 2V/SbTAl. All aged samples exhibit an increase in the diffraction pattern of $VSbO_4$ phase. The interaction between antimony and vanadium appears promoted during reaction; 0.5V/SbTAl exhibits the features of $VSbO_4$ phase. For 2V/SbTAl, the diffraction pattern of V_2O_5 is lost and that of $VSbO_4$ grows stronger. This trend of vanadium to react with antimony during reaction has been described previously [24].

Fig. 1B shows the XRD patterns of the *one-step* series. There are significant differences with the two-step series. The fresh samples generate no diffraction pattern; however, aged 1Sb1V/Al and 1Sb2V/Al exhibit the $VSbO_4$ diffraction pattern. Which is consistent with the trend described above.

Table 1
Composition and BET area of alumina-supported Sb–V–O catalysts.

Catalyst	Synth. Meth.	Sb/V	%Sb	%V	BET area (m^2/g)
Al_2O_3	–	–	–	–	265
SbTAl	–	–	29.1	–	178
0.25V/SbTAl	Two steps	4	27.3	2.3	117
0.5V/SbTAl	Two steps	2	25.5	5.2	97
1V/SbTAl	Two steps	1	22.4	11.3	66
2V/SbTAl	Two steps	0.5	18.1	18.0	44
1Sb4V/Al	One step	4	13.23	1.38	114
1Sb2V/Al	One step	2	11.49	2.39	111
1Sb1V/Al	One step	1	9.38	3.77	139