Catalysis Today 139 (2008) 202–208

Contents lists available at ScienceDirect

Catalysis Today

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

Sb–V–O-based catalysts for the ammoxidation of propane with a fluidized bed reactor

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ARTICLE INFO

Article history:
Available online 2 September 2008

Keywords:
V–Sb–Al
V–Sb–Si
V–Sb–Nb–Si
V–Sb–O
Fluid bed
Ammoxidation
Propane
Acrylonitrile
Structure–activity relationship

ABSTRACT

Propane ammoxidation is usually investigated with fixed-bed reactors at laboratory scale; however, this kind of reactions takes place over fluid-bed reactors in industry. The present paper investigates the catalytic ammoxidation of propane over supported Sb–V–O catalysts using a fluidized bed microreactor. The effect of support, Sb/V atomic ratio, Sb + V total coverage, synthesis procedures, as well as the effect of Nb as additive of the Sb–V–O system were evaluated. The activity results show that the selectivity trends are quite similar to those obtained with a fixed-bed reactor but a higher amount of active phase is necessary for the fluidized bed catalysts to obtain similar acrylonitrile yields.

1. Introduction

The majority of the industrial organic products are manufactured with oil and natural gas. Nearly 25% of these compounds are prepared via selective oxidation and ammoxidation reactions using heterogeneous catalysts; so, paraffin selective ammoxidation to nitriles is a very important process to obtain organic products traditionally generated from petroleum [1–3]. Propane ammoxidation is especially important since it would be an alternative to the actual propylene ammoxidation. Thus, in 1997 British petroleum (bp) started a demonstration plant to make acrylonitrile, using propane, and estimated to decrease production costs ca. 20% compared with conventional propylene-based technology [4].

There are several studies about catalysts used for propane ammoxidation, but the major part of the reported work is concentrated on two types of catalysts [1–3], the antimonates with rutile structure [5–11] and the molybdates [12–15], both systems usually incorporate vanadium as the key element. Alumina has been described as a good support of this system and there are several patents with synthesis procedures for the Al–Sb–V–O system [16], the selectivity to acrylonitrile and propylene was found to be higher on catalysts supported on alumina than on unsupported, especially for higher conversions [17]. Previous results with a micro-fixed-bed reactor, showed a good performance of supported Sb–V–O catalysts [18,19]; and it was found that the support determines both structure and catalytic behavior of catalysts [20].

The fixed-bed reactor is widely used due to the simple technology that it requires; under certain premises, fluidized bed reactors are necessary. Pressure built-up can be quite important for large reactor lengths and reactants fluxes. In practice, the pressure increase becomes the factor that determines the smallest particle diameter that can be used. Larger particles present internal diffusional resistance, so, they cannot be used [21]. Processes with a high rate of heat exchange, e.g. strongly exothermic reactions, pose serious limitation on the temperature control in a fixed-bed reactor, which can result in catalyst or reactor damage. Uncontrolled temperature increase may decrease selectivity values; which is the case for the oxidation and ammoxidation of propane. Industrially, propane ammoxidation would only take place in a fluid-bed reactor; yet only a few works report fluidized Sb–V–O catalysts [22,23].

Sb–V–O and Sb–V–Nb–O fluid-bed catalysts supported on Al_2O_3 and SiO_2 are studied in present paper. Catalysts were prepared

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doi:10.1016/j.cattod.2008.07.021

according to two different synthesis methods, the standard, in which antimony is added as a Sb_2O_3 suspension, and a new method in which antimony is added as soluble tartrate complex [24,25]. This paper evaluates the role of the support, the synthesis method and the role of Nb as an additive on supported Sb–V–O catalysts. The results are compared with those previously reported with a conventional fixed-bed reactor.

2. Experimental and methods

2.1. Preparation of samples

Two series of catalysts are prepared, the (Nb)–Sb–V/support-(Sb_2O_3) and the Nb–Sb–V/support-(SbT) series, which use Sb_2O_3 suspension (slurry) or a molecularly dissolved Sb precursor (tartrate). The (Nb)–Sb–V/support-(Sb_2O_3) catalyst series was prepared by a slurry method. Sb_2O_3 (Aldrich, p.a.) was added to an aqueous solution of NH_4VO_3 (Sigma, p.a.) and an ammonium niobium soluble complex (Niobium Products), heating and stirring at 80 °C for 50 min, then, γ-Al_2O_3 (Versal, 265 m^2/g) or SiO_2 (XPO 2407, Grace Division) was added. The resulting solution was dried in a rotavapor at 80 °C. The resulting solid was dried at 115 °C for 24 h and then was calcined in air at 400 °C for 4 h. The Nb–Sb–V/support-(SbT) catalysts were prepared dissolving the necessary quantity of antimony acetate (Aldrich) on tartaric acid (Sigma) 0.3 M [24,25]. This solution was kept under stirring until all antimony was dissolved. Then, NH_4VO_3 (Sigma), ammonium niobium soluble complex (Niobium Products) and γ-Al_2O_3 or SiO_2 were added. The resulting solution was dried in a rotavapor at 80 °C. The resulting solid was dried at 115 °C for 24 h and then was calcined in air at 400 °C for 4 h.

The catalysts were prepared so that a total coverage of V + Sb or V + Sb + Nb would correspond to the dispersion limit or four times this value on the corresponding support (i.e., total of 9 atoms/nm^2 of support on alumina or total of 1 atom/nm^2 of support on silica). The dispersion limit was determined by Raman spectroscopy in a VO_x/Al_2O_3 series, as the maximum surface loading of VO_x units that remain dispersed, with no crystalline V_2O_5 (at V/nm^2) [26]. The Sb/V and Sb/V atomic ratio changed in the one to three intervals for de Sb/V and was fixed to one for the Nb/Sb 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 ($0.05 < P/P_0 < 0.27$), 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 (α = 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.

The particle size distribution was determined with a Mastersizer apparatus (Malvern). It has been used laser light dispersion in small angle, commonly called laser diffraction. The sample is like a powder and is pushed with air with a pressure of 2 bar. The apparatus uses a laser of He–Ne.

Raman spectra were run with a single-monochromator Renishaw System 1000 equipped with a cooled CCD detector (200 K) and holographic Notch filters. The holographic Notch filters remove the elastic scattering. The samples were excited with the 514 nm Ar line; spectral resolution was ca. 3 cm^{-1} and spectrum acquisition consisted of 10 accumulations of 30 s. The spectra were obtained under dehydrated conditions (ca. 390 K) 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. Silica-supported catalysts could not be characterized by Raman spectroscopy due to an overwhelming fluorescence background.

2.3. Activity measurements

Activity measurements were performed using a microplant with feed lines for air, nitrogen and ammonia. The fluid-bed reactor is made of quartz, it has a porous plate in the base that distributes the flux and then it has two porous plates to achieve a good fluidization. It has an internal tube for the thermocouple. At the end of the reactor there is an expansion camera. A glass carcass protects the reactor. External resistances that heat the system surround it and permit to see the interior of the reactor during reaction. CO, CO_2, ethylene, oxygen, nitrogen, propylene and propane are analyzed on line with a 5890 Hewlett Packard gas chromatograph. The CG also has a FID detector for the analysis of acrylonitrile, acrolein and acetonitrile that are recovered in absorbed lunges with HCl; in this case, the sample is injected with an automatic injector. NH_3 and HCN were determined by titration methods. 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. 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%). Tests were made using the following feedstock: 9.8% propane, 8.6% ammonia and the rest air. The total flow rate was 20 N L h^{-1} and 40 g of catalysts were used. Such parameters were experimentally determined to reach a good fluidization regime [27]. Temperature reaction was 450 °C. To verify the reliability of our micro-fluid-bed reactor, a test of propylene ammoxidation with a commercial catalyst was made. 90% propylene conversion was obtained at 430 °C and selectivity to acrylonitrile was higher than 70%.

3. Results and discussion

3.1. Alumina-supported catalysts

Table 1 shows the BET surface areas, the composition obtained by ICP, the Sb/V molar ratios and the Sb + V total coverage values. The BET area values for the Sb–V catalysts decrease when the surface coverage increases. The atomic Sb/V ratios do not appear to have a clear effect on BET area values. Catalysts prepared with tartaric acid present higher BET area values. Fig. 1 shows the granulometric distributions for Sb–V–O/Al catalysts. The distribution shows a maximum near 100 μm and another small maximum

Table 1
Composition determined by ICP and BET area of alumina-supported Sb–V–O catalysts

Catalyst	Sb + V total coverage	Sb/V molar ratio	%Sb	%V	BET area (m^2/g)
1Sb1V/Al–(SbT)	1	1	5.2	12.4	177
1Sb3V/Al–(SbT)	1	3	2.4	17.0	130
4Sb1V/Al–(SbT)	4	1	9.1	21.8	71
4Sb3V/Al–(SbT)	4	3	3.9	28.2	58
1Sb1V/Al–(Sb_2O_3)	1	1	6.1	14.7	138
1Sb3V/Al–(Sb_2O_3)	1	3	3.0	21.6	125
4Sb1V/Al–(Sb_2O_3)	4	1	12.6	30.1	67
4Sb3V/Al–(Sb_2O_3)	4	3	6.1	43.5	36