Mechanism of ammoxidation of propane on a Sb/V/O system

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The mechanism of the direct ammoxidation of propane is investigated on a Sb/V mixed oxide catalyst (atomic ratio 5/1) in order to understand the sequence of the intermediates and the role of ammonia in the formation of acrylonitrile. The sample was characterized by different techniques (BET, FTIR, XRD and XPS) and tested in different conditions (oxidation and ammoxidation of propane and propene). It is proposed that propane is first converted to propene and hence to "oxidation products" (which could be acrolein or an intermediate absorbed on the catalyst surface, as allyl radical). In the absence of ammonia these "oxidation products" are converted to carbon oxide. But in its presence they are converted into acrylonitrile, which is appreciably more stable and undergoes minor degrees of oxidative degradation.

Keywords: mechanism, acrylonitrile, oxidation products, ammonia, oxygen

1. Introduction

Acrylonitrile (ACN) is produced nowadays by the ammoxidation of propene on catalysts made of promoted Fe–Bi–Mo–O (SOHIO process) or promoted Fe–Sb–O (Nitto process); nevertheless, in recent years some companies have decided to invest in the research of propane ammoxidation, and one of the more interesting catalytic systems for the direct ammoxidation of this paraffin is Sb/V/O [1–5].

The synthesis of these catalysts is usually made by solid-state reaction between V_2O_5 and Sb_2O_3 at a temperature of 700°C or by reaction between NH_4VO_3 and Sb_2O_3. Mössbauer analysis shows antimony to be mainly in its pentavalent state, indicating that a lot of vanadium is reduced, with the formation of $V^{III}Sb^{V}O_4$ and the possible presence of V^{IV} in substitutional or interstitial solid solution.

Centi et al. [3] and Nilsson et al. [4] have shown that an excess of antimony brings about an activity decrease, but also a large increase in the selectivities and in the yields in acrylonitrile and propene. The best catalyst for the synthesis of acrylonitrile from propane has a large excess of antimony ($Sb/V = 5.0$). This excess seems to facilitate the transformation of the intermediate propene to acrylonitrile; but an excess of vanadium, on the other hand, brings about an activity increase, but also a low selectivity in acrylonitrile due to the production of propene and carbon oxides.

In the past there have been many studies of the mechanism of propane or propene ammoxidation and the characterization of active sites. However, the catalyst structure and its mode of operation is far from completely understood. While propene is agreed to be the first intermediate formed, there is no agreement about the subsequent ones. From investigations over Sb–V–W–Al–O oxides Andersson et al. [2] and Catani et al. [6] proposed direct formation of acrylonitrile from propene on the catalyst, while acrolein is thought to form on the catalyst in a side reaction. Nilsson et al. [7] and Buchholz et al. [8], who performed a kinetic investigation on the pure Sb–V–O system, indicate that acrolein could be an intermediate in the formation of acrylonitrile.

Here, the mechanism of the direct ammoxidation of propane on the catalyst Sb–V–O is investigated. In particular we studied all the detectable species in order to understand the mechanism and especially the role of the ammonia. A sample with a relative molar ratio Sb/V of 5 was tested in the oxidation and ammoxidation of propane and propene, at different temperatures and contact times.

2. Experimental

2.1. Catalyst preparation

The sample was prepared with a coprecipitation technique chosen in order to achieve a homogeneous mixed oxide (a highly dispersed system), and to avoid a mixture of two single phases.

The coprecipitation of vanadium and antimony oxohydrates was achieved as follows: initially 100 ml of a solution of anhydrous $SnCl_4$ in an absolute ethyl alcohol was prepared; then vanadyl acetylacetonate ($VO(acac)_2$) was dissolved in the solution, in order to obtain the desired Sb/V ratio. The solution was added dropwise to 200 ml of an aqueous solution of CH_3COONH_4, having an initial pH of around 7.0

(about 2 M solution). During the precipitation of the oxohydrates the pH, which decreases due to the release of HCl, was kept constant by the addition of ammonia solution. The resulting precipitate was filtered, washed and dried overnight at 120°C; then it was calcined at 350°C for 1 h and at 700°C for 3 h.

2.2. Characterization

The catalyst was tested in a conventional apparatus with a tubular fixed-bed reactor working at atmospheric pressure. The analyses of propane, propene, acrylonitrile, acrolein, acetonitrile and uncondensable gases were made by gas-chromatographic techniques; ammonia and hydrogen cyanide were detected by absorption and titration. The feed composition and the contact time are described for each catalytic test, because they were changed in order to probe the reaction mechanism. The catalyst (2 ml) was loaded as grains (30–40 mesh). A thermocouple, placed in the middle of the catalyst bed, was used to verify that the axial temperature profile was within 3 K.

X-ray diffraction patterns (powder technique) were obtained using Ni-filtered Cu Kα radiation and a Philips computer-controlled instrument.

Surface area measurements were made using the BET method with nitrogen absorption at 77 K on a Carlo Erba Sorptomatic instrument.

Fourier transformed infrared (FT-IR) spectra were recorded using a Perkin-Elmer 7200 Fourier transform infrared spectrometer and the KBr disk technique.

XPS analyses were performed with a Perkin Elmer model Philips 5500.

3. Results and discussion

3.1. Characterization

The surface area of the catalyst is quite low (6 m^2/g).

The XRD pattern (figure 1) shows the presence of two different crystalline phases: the more intense reflections can be assigned to α-Sb_2O_4, the weaker ones to $SbVO_4$. The presence of the antimony oxide is due to the large excess of antimony ions with respect to vanadium; a sample, prepared with the same coprecipitation technique, but with an equimolar ratio of antimony and vanadium, gives only the $SbVO_4$ phase (figure 1).

The FT-IR spectra show the absorbance bands of α-Sb_2O_4 and a stretching absorbance of the V=O bond at around 988 cm^{-1} (different from the absorbance at 1022 cm^{-1} of the crystalline phase): the shift to lower frequencies of the stretching absorbance of the V=O double bond may be attributed to two effects: firstly to interactions between the vanadyl species and the rutile type $SbVO_4$ matrix and secondly to an electronic effect due to the presence of neighboring reduced vanadium sites. The rutile phase, shown in the diffractogram, is not revealed in the infrared spectra. The typical band of $SbVO_4$ at 550 cm^{-1} is absent.

The XPS characterization shows that the bulk composition is similar to that of the surface (Sb/V = 5.0 bulk vs. Sb/V = 5.1 surface). (A recent study on the

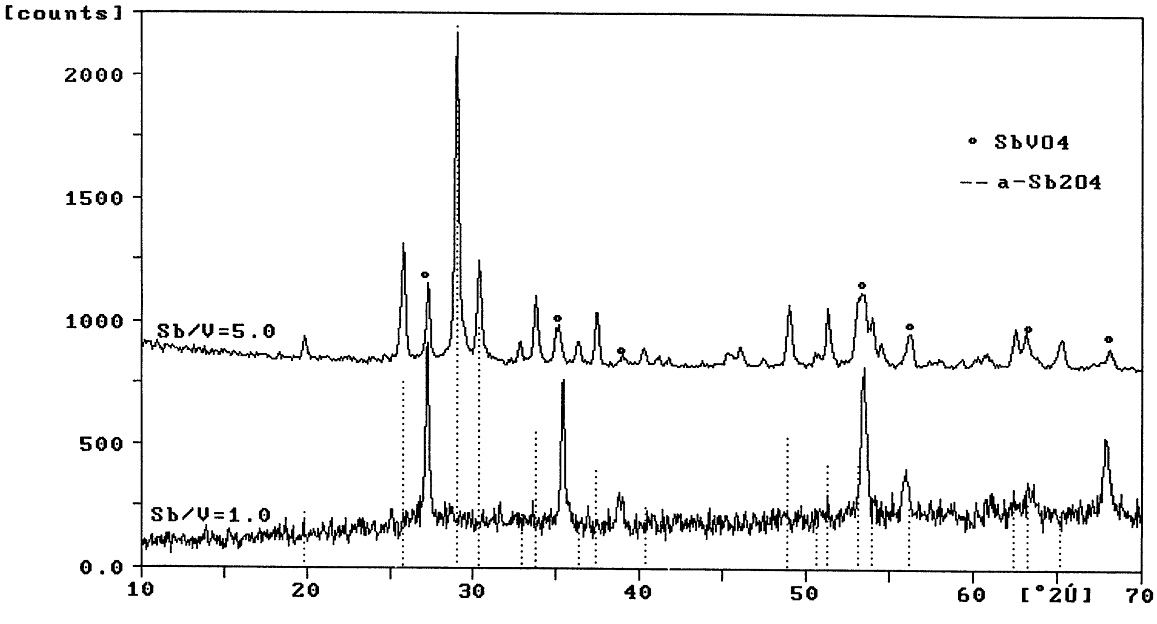

Figure 1. XRD spectra of the Sb/V sample, with two different atomic ratios: Sb/V = 1 : 0 and Sb/V = 5.0.

Sb/V system [7,9] revealed an antimony surface enrichment in samples with a molar ratio Sb/V > 5.)

3.2. *Catalytic tests*

3.2.1. *Ammoxidation of propane versus temperature*

The conversion of propane, oxygen and ammonia and the products yield as a function of the temperature for the Sb/V catalyst are respectively reported in figures 2 and 3; the feed is $C_3H_8 : O_2 : NH_3 : He = 25 : 20 : 10 : 45$ and the contact time is 2 s. At low temperature, propene is the main product and its yield remains similar at higher temperature. The acrylonitrile yield increases with increasing temperature up to 470°C, and then decreases due to the complete conversion of ammonia (figure 2). Owing to this minor amount of ammonia, the yield in propene and especially in carbon oxides increases; the olefin is converted in CO_x, not to acrylonitrile.

The olefin yield is quite high at all investigated temperatures, indicating that the catalyst is characterized by relative low activity in the transformation of propene to acrylonitrile.

In order to understand the mechanism of the propane ammoxidation and the role of propylene as possible intermediate, we have made some comparisons, under the same conditions, between oxidation and ammoxidation of propane and between ammoxidation of propane and propene.

3.2.2. *Oxidation and ammoxidation of propane versus feed oxygen concentration*

Figures 4 and 5 show respectively the conversion of propane and the products yield as a function of the oxygen concentration in the feed, with or without ammonia. In particular in figure 5 are reported the yield in propene and the sum of the yields in propene and carbon oxide for the oxidation; moreover, in the same figure are reported the yield in propene, the sum of the yields in propene and acrylonitrile and the sum of the yields of propene, acrylonitrile and carbon oxide for the ammoxidation. These tests were conducted at a temperature of

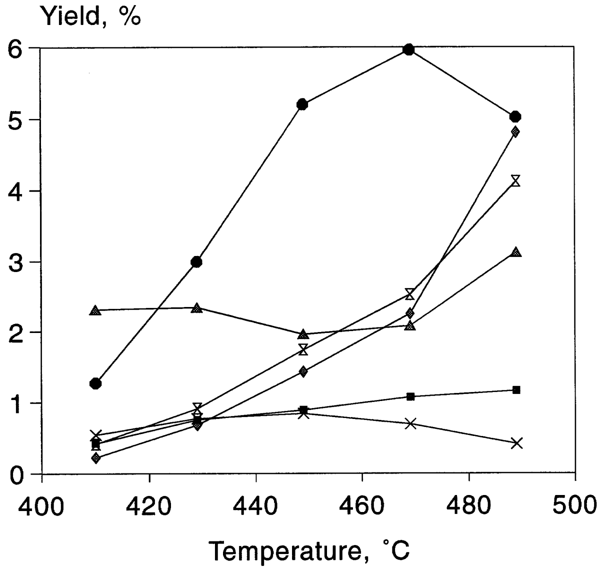

Figure 3. Products yield vs. temperature (ammoxidation of propane). Reaction conditions: $C_3H_8 : O_2 : NH_3 = 25 : 20 : 10$ and helium to 100; $\tau = 2.0$ s. (■) HCN, (×) CH_3CN, (●) ACN, (▲) C_3H_6, (⧗) CO, (◆) CO_2.

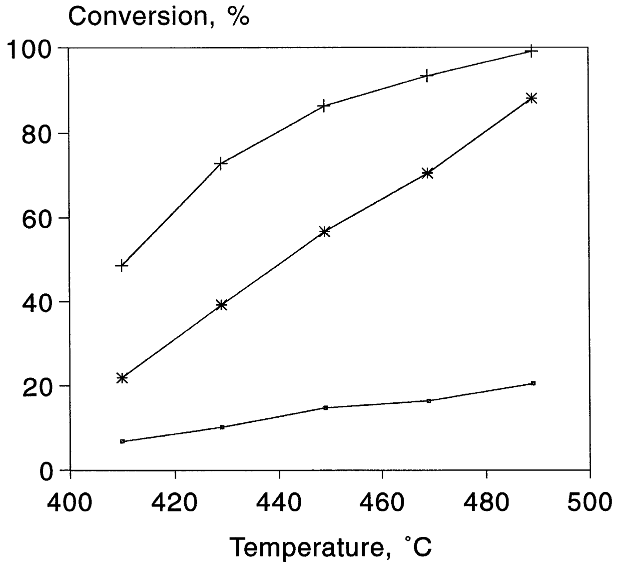

Figure 2. Conversion of propane (▪), ammonia (+) and oxygen (∗) vs. temperature (ammoxidation of propane). Reaction conditions: $C_3H_8 : O_2 : NH_3 = 25 : 20 : 10$ and helium to 100; $\tau = 2.0$ s.

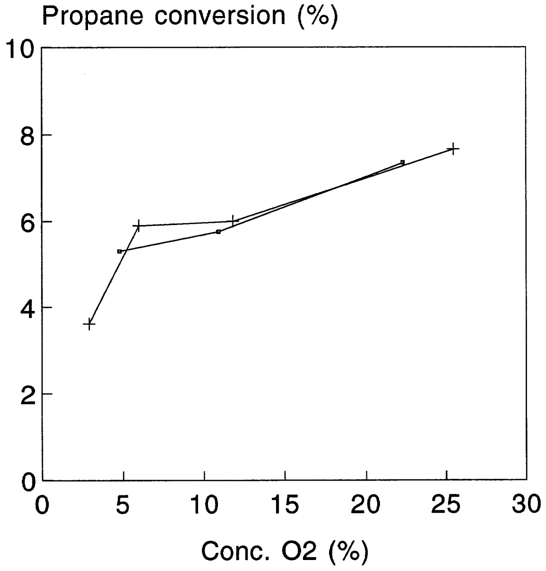

Figure 4. Conversion of propane vs. feed oxygen concentration, with (10%) and without ammonia (ammoxidation and oxidation of propane). Reaction conditions: $T = 430°C$ and $\tau = 2.0$ s; (▪) $C_3H_8 : O_2 : NH_3 = 25 : X : 10$ and (+) $C_3H_8 : O_2 = 25 : X$, the remainder to 100 is always helium.

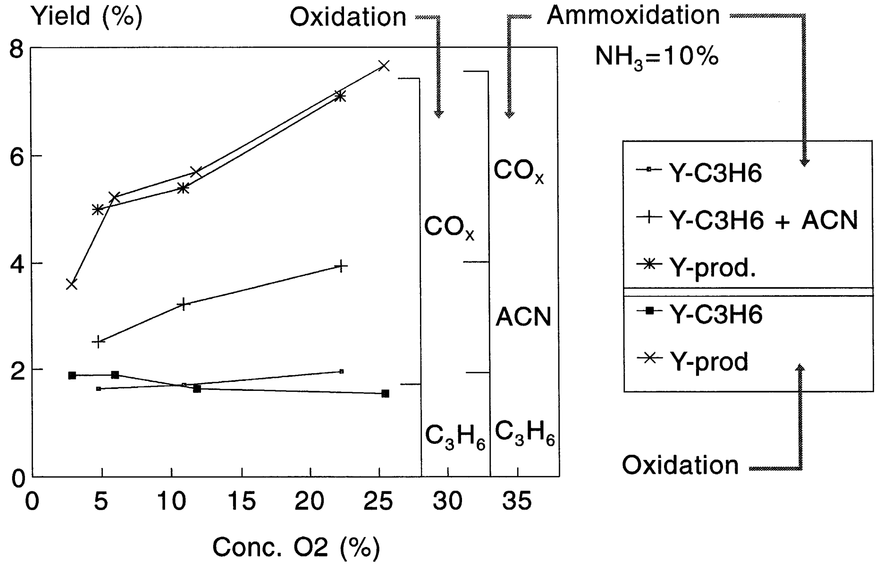

Figure 5. Products yield vs. feed oxygen concentration, with (10%) and without ammonia (ammoxidation and oxidation of propane). Reaction conditions: $T = 430°\mathrm{C}$, $\tau = 2.0$ s. Ammoxidation: $C_3H_8 : O_2 : NH_3 : He = 25 : X : 10 : 65 - X$; (▪) yield in propene, (+) sum of yield in propene and acrylonitrile, (∗) sum of yield in propene, acrylonitrile and CO_X. Oxidation: $C_3H_8 : O_2 : He = 25 : X : 75 - X$; (■) yield in propene; (×) sum of yield in propene and CO_x.

430°C, with a contact time of 2 s and with a feed of $C_3H_8 : O_2 : NH_3 = 25 : X : 10$ for ammoxidation and $C_3H_8 : O_2 = 25 : X$ for oxidation (X is the variable oxygen content and the remainder to 100 is helium). In this way it is easier to see the changes in the distribution of the products versus the feed oxygen concentration and to compare the behaviour of the catalyst under the oxidation and the ammoxidation conditions.

These figures show that the presence of ammonia influences neither the propene yield nor the propane conversion: hence the acrylonitrile is formed by interaction of ammonia with the intermediate of oxidation of propane and/or propene, which lead to carbon oxides. These intermediates might be acrolein or an other intermediate adsorbed on the catalyst surface as allyl radical. The production of acrylonitrile from these "oxidation products" is confirmed by the increase of the acrylonitrile yield with increase in the oxygen partial pressure of the feed.

This suggests the following considerations:

(1) the Sb/V system has quite a low catalytic activity for the ammoxidation of propene to acrylonitrile;

(2) ammonia influences neither propane conversion nor propene yield;

(3) the acrylonitrile is formed from "oxidation products" of propane and/or propene.

3.2.3. *Oxidation of propane versus contact time*

Some oxidation tests (without ammonia) were performed at different contact times in order to determine the oxidation intermediate of propane, which leads to carbon oxides or acrylonitrile. Figure 6 shows the selectivity in the products as a function of the contact time; the feed is $C_3H_8 : O_2 : He = 25 : 6 : 69$ and the temperature is 450°C. This figure shows that the yield in propene, and acrolein (slightly), increases with a decrease in contact time: this means that propene is the first intermediate. Moreover, extrapolating to zero contact time, the values of the selectivities to CO and CO_2 do not reach zero, but a value of around 18% for each. This means that propane also forms directly carbon oxides through a parallel reaction. Furthermore, at high contact time the selectivity in carbon oxides increases to the disadvan-

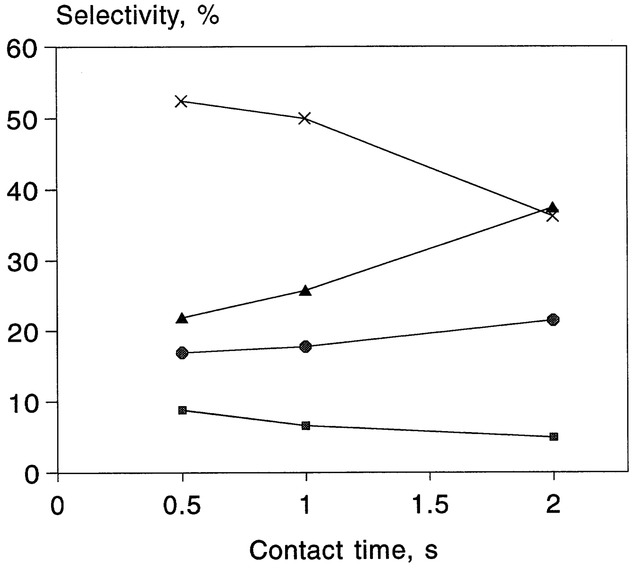

Figure 6. Products selectivity vs. contact time (oxidation of propane). Reaction conditions: $C_3H_8 : O_2 : He = 25 : 6 : 69$, $T = 450°\mathrm{C}$. (■) Acroleine, (×) C_3H_6, (●) CO, (▲) CO_2.

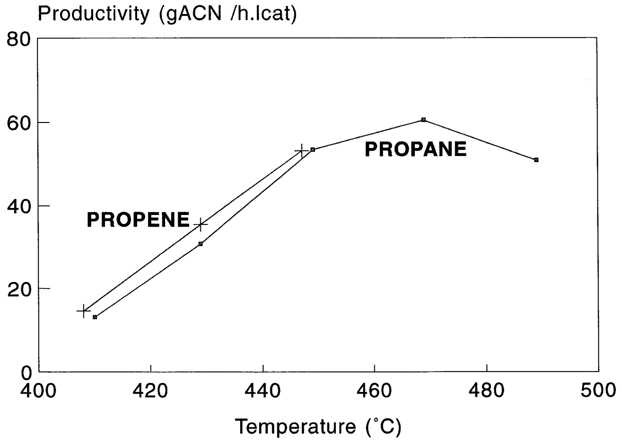

Figure 7. Productivity in acrylonitrile vs. temperature in the ammoxidation of propane (■) and propene (+).

tage of propene and acrolein: the total oxidation is consecutive to these intermediates.

These tests suggest the following considerations:

(1) the first intermediate is propene;

(2) the carbon oxides are formed from propane and from the intermediates propene and acrolein.

3.2.4. Ammoxidation of propane and propene

In order to ascertain if ammonia reacts with the "oxidation products" of propane or of propene, we have performed ammoxidation tests of the two hydrocarbons. The reaction conditions are the following: a contact time of 2 s, a feed of $C_3H_8 : O_2 : NH_3 : He = 25 : 20 : 10 : 45$ for the paraffin ammoxidation; in the case of olefin ammoxidation, keeping constant the ratio of ammonia and oxygen, the feed of propene is equal to the sum of propene and acrylonitrile produced from ammoxidation of propane at the same temperature (the remainder is always helium). The values of these catalytic tests are reported in figure 7 as the productivity of acrylonitrile (expressed as grams produced vs. hour of feed and litre of catalyst) as a function of the temperature.

This data shows that the quantity of acrylonitrile produced from the propane ammoxidation could be justified from the conversion of the "oxidation products" of propene (formed from propane): hence propene is the intermediate.

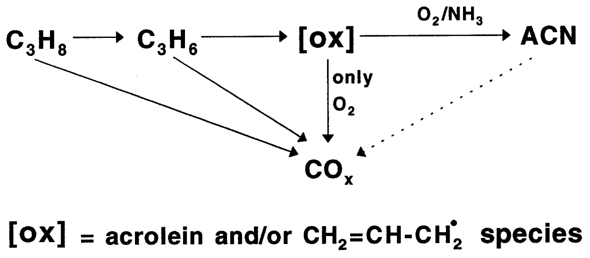

Figure 8. Mechanism of propane ammoxidation.

Therefore, even if the real identity of the "oxidation products" is not detected, it is possible to propose the mechanism given in figure 8 and to underline the role of the ammonia: it interacts with the "oxidation products", leading to acrylonitrile, a stable product.

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