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Kinetic study on propane ammoxidation to acrylonitrile over V–Sb–O/TiO_2(B)

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Abstract

Kinetic study on propane ammoxidation to acrylonitrile over V–Sb–O/TiO_2(B) was undertaken by a strict mathematical analysis of experimental rate dependencies on reactant pressure in order to obtain expression describing completely the data.

Keywords: V–Sb–O; TiO_2(B); Acrylonitrile

1. Introduction

There are two main technological options for the conversion of propane to acrylonitrile, a two-stage process based on a first dehydrogenation step of propane to propene integrated to a second conventional unit for propene to acrylonitrile, or a direct conversion to acrylonitrile [1,2]. The first option is already commercially available, but the relative high cost of the dehydrogenation unit for propane and even the cost of propene feedstock (about 5–6 times more than the cost of propane) limits the interest in this solution; the one-stage propane conversion to acrylonitrile appears more attractive [3]. Catalytic systems based on V-antimonate with a rutile structure [2–6] and systems based on a Bi–Mo–V scheelite structure [7,8] was investigated. Based on the patented results, V-antimonate system appears to be more active and selective in acrylonitrile formation. In addition to this metal oxide catalysts the activities of V-, Mo-, Bi–Mo-supported mixed oxides modified with various additives [9], and alumina-supported V-antimonate systems have also been reported [10]. Among the mechanistic investigation of the propane ammoxidation to acrylonitrile, various primary intermediates were suggested by different authors. The kinetic investigation over V–Sb–Al-oxides [10] and V–Sb–O [11] has been concluded that acrylonitrile forms mainly from propene intermediate. In contrast to this hypothesis, considering data from a vacuum transient technique in temporal analysis of products, published by Buchholz and Zanthoff [12] and the IR spectroscopy results [13] using V–Sb-oxides indicate that acrolein might be an intermediate in acrylonitrile formation from the ammoxidation of propane.

Against this background, kinetic study on propane ammoxidation to acrylonitrile over V–Sb–O/TiO_2(B) was undertaken. For this purpose, a strict

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mathematical analysis of experimental rate dependencies on reactant pressure was performed, in order to obtain expression describing the data completely. The corresponding mechanism was then derived, concerning the formation of acrylonitrile and CO_x.

2. Experimental

The support precursor preparation [14] and the active phase impregnation [15] were achieved as described in the literature.

X-ray diffraction of the catalyst was carried out on a Philips XRD instrument PW1840 and Cu K_α radiation; surface area was detected with a Carlo Erba Instrument Sorpty 1750, using adsorption of nitrogen at liquid nitrogen temperature. The Sb/V ratio was controlled with atomic absorption (Perkin Elmer 2380 spectrophotometer).

X-ray diffraction analysis showed that the precursor was pure TiO_2(B). The catalyst was prepared with an amount of active phase of 10% and a ratio Sb/V of 5.0: the surface area is 16 m^2/g.

The catalytic performance was studied in the ammoxidation of propane to acrylonitrile. An isothermal plug-flow reactor was used in the experiments; the products and unreacted propane were analyzed with a GC system (FID). The methanation system was used for the detection of carbon dioxides.

3. Kinetic and rate equation

Figs. 1 and 2 (respectively rate formation of acrylonitrile and CO_x) show the kinetic behavior of the V–Sb–O/TiO_2(B) in the ammoxidation of propane at 370°C, 400°C, and 430°C in differential condition; the trend of the rate formation of propylene is similar to acrylonitrile one. Linearization method and in some case nonlinear regression with the method of flash position was used to determine the rate constant (Tables 1–3) of the rate equation Eqs. (1)–(3):

$$r_{\mathrm{ACN}} = k_1\left(\frac{a_1P_{\mathrm{A}} + P_{\mathrm{A}}^2}{1 + a_2P_{\mathrm{A}} + a_3P_{\mathrm{A}}^2}\right)\left(\frac{a_4P_{\mathrm{O}} + P_{\mathrm{O}}^2}{1 + a_5P_{\mathrm{O}} + a_6P_{\mathrm{O}}^2}\right) \times \left(\frac{P_{\mathrm{P}}}{1 + a_7P_{\mathrm{P}}}\right), \tag{1}$$

Table 1
Kinetic constant of the rate equation for acrylonitrile formation at 370°C, 400°C and 430°C

Acrylonitrile	370°C	400°C	430°C
k_1 (mol/m^2 min kPa^5)	3.37E−05	4.21E−05	3.35E−05
a_1 (kPa)	1.94E+01	1.07E+01	1.60E+00
a_2 (kPa^{-1})	2.23E−04	5.58E−04	1.35E+00
a_3 (kPa^{-2})	1.62E−02	3.73E−02	4.13E−02
a_4 (kPa)	1.25E+01	1.77E+01	1.50E+02
a_5 (kPa^{-1})	1.44E−02	6.09E−02	6.27E−02
a_6 (kPa^{-2})	1.09E−01	3.16E−02	9.97E−03
a_7 (kPa^{-1})	1.77E−01	8.26E−02	1.12E−01

Table 2
Kinetic constant of the rate equation for propylene formation at 370°C, 400°C and 430°C

Propylene	370°C	400°C	430°C
k_3 (mol/m^2 min kPa^5)	2.93E−06	2.34E−05	1.37E−05
b_1 (kPa)	3.00E+02	5.00E+01	1.20E+01
b_2 (kPa^{-1})	2.03E−02	4.07E−03	8.59E−04
b_3 (kPa^{-2})	2.56E−03	5.96E−03	1.50E−02
b_4 (kPa)	6.00E+00	7.00E+00	4.00E+01
b_5 (kPa^{-1})	8.13E−04	4.30E−02	7.93E+02
b_6 (kPa^{-2})	1.23E−01	1.14E−01	2.57E−02
b_7 (kPa^{-1})	3.02E−02	4.21E−02	1.25E−01

Table 3
Kinetic constant of the rate equation for carbon oxides formation at 370°C, 400°C and 430°C

Carbon oxides	370°C	400°C	430°C
k_3 (mol/m^2 min kPa^3)	8.91E−01	1.02E−02	1.82E−04
c_1 (kPa)	2.04E+00	9.21E+00	2.26E+02
c_2 (kPa^{-1})	2.00E+01	4.70E−01	5.00E−02
c_3 (kPa^{-1})	5.41E−01	6.16E−02	7.55E−03
c_4 (kPa^{-1})	2.08E−01	1.14E−01	3.94E−02

$$r_{\mathrm{C_3H_6}} = k_2\left(\frac{b_1P_{\mathrm{A}} + P_{\mathrm{A}}^2}{1 + b_2P_{\mathrm{A}} + b_3P_{\mathrm{A}}^2}\right)\left(\frac{b_4P_{\mathrm{O}} + P_{\mathrm{O}}^2}{1 + b_5P_{\mathrm{O}} + b_6P_{\mathrm{O}}^2}\right) \times \left(\frac{P_{\mathrm{P}}}{1 + b_7P_{\mathrm{P}}}\right), \tag{2}$$

$$r_{\mathrm{CO}_X} = k_3\left(\frac{c_1 + P_{\mathrm{A}}}{1 + c_2P_{\mathrm{A}}}\right)\left(\frac{P_{\mathrm{O}}}{1 + c_3P_{\mathrm{O}}}\right)\left(\frac{P_{\mathrm{P}}}{1 + c_4P_{\mathrm{P}}}\right). \tag{3}$$

In order to gain more information on the reaction mechanism in acrylonitrile synthesis from propane, a

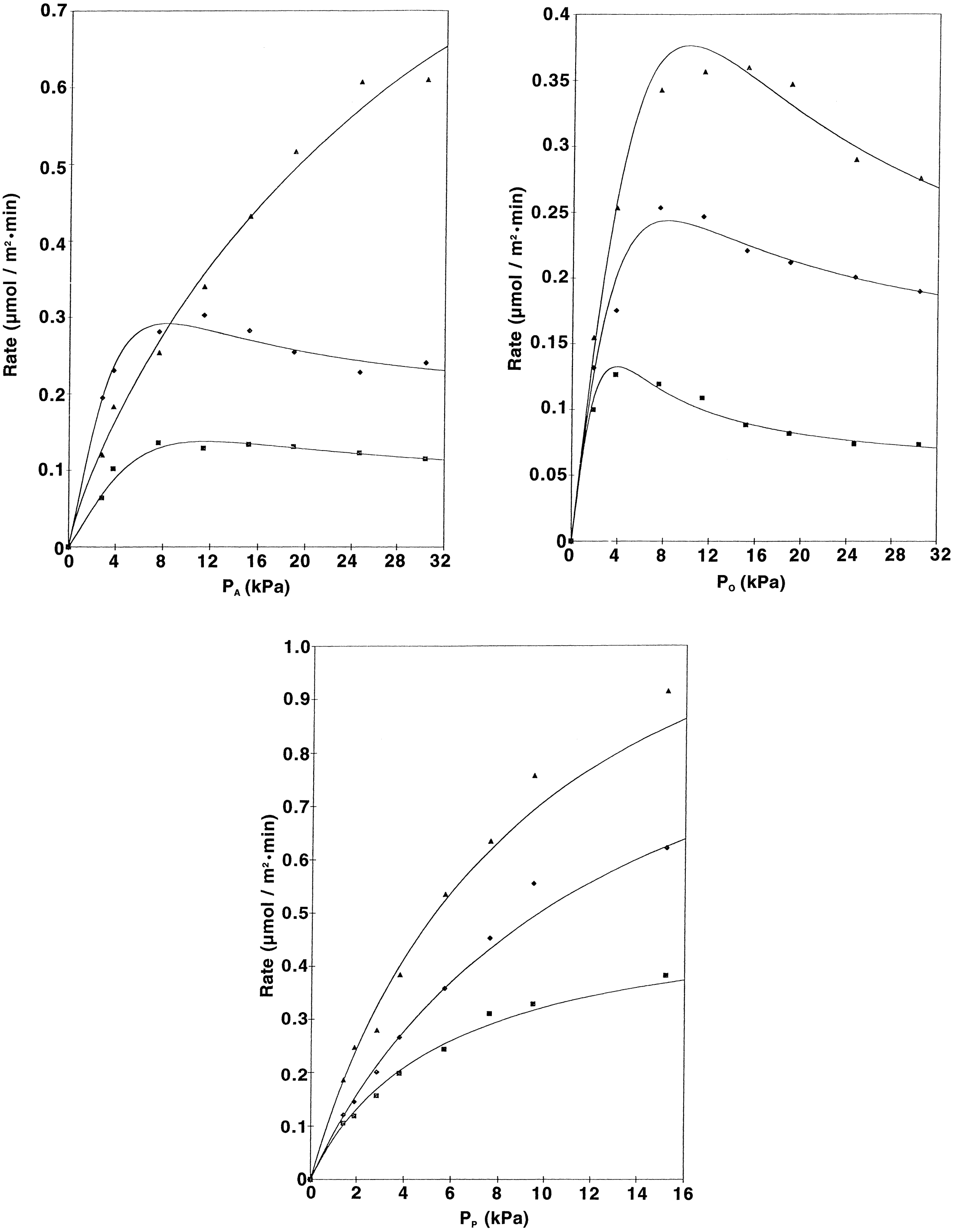

Fig. 1. (a) Rate of acrylonitrile formation as a function of ammonia partial pressures for the reaction temperature of 370°C (*n*), 400°C (*u*) and 430°C (*s*). P_O=15.2 kPa and P_P=3.8 kPa. (b) Rate of acrylonitrile formation as a function of oxygen partial pressures for the reaction temperature of 370°C (*n*), 400°C (*u*) and 430°C (*s*). P_A=15.2 kPa and P_P=3.8 kPa. (c) Rate of acrylonitrile formation as a function of propane partial pressures for the reaction temperature of 370°C (*n*), 400°C (*u*) and 430°C (*s*). P_A=15.2 kPa and P_O=15.2 kPa.

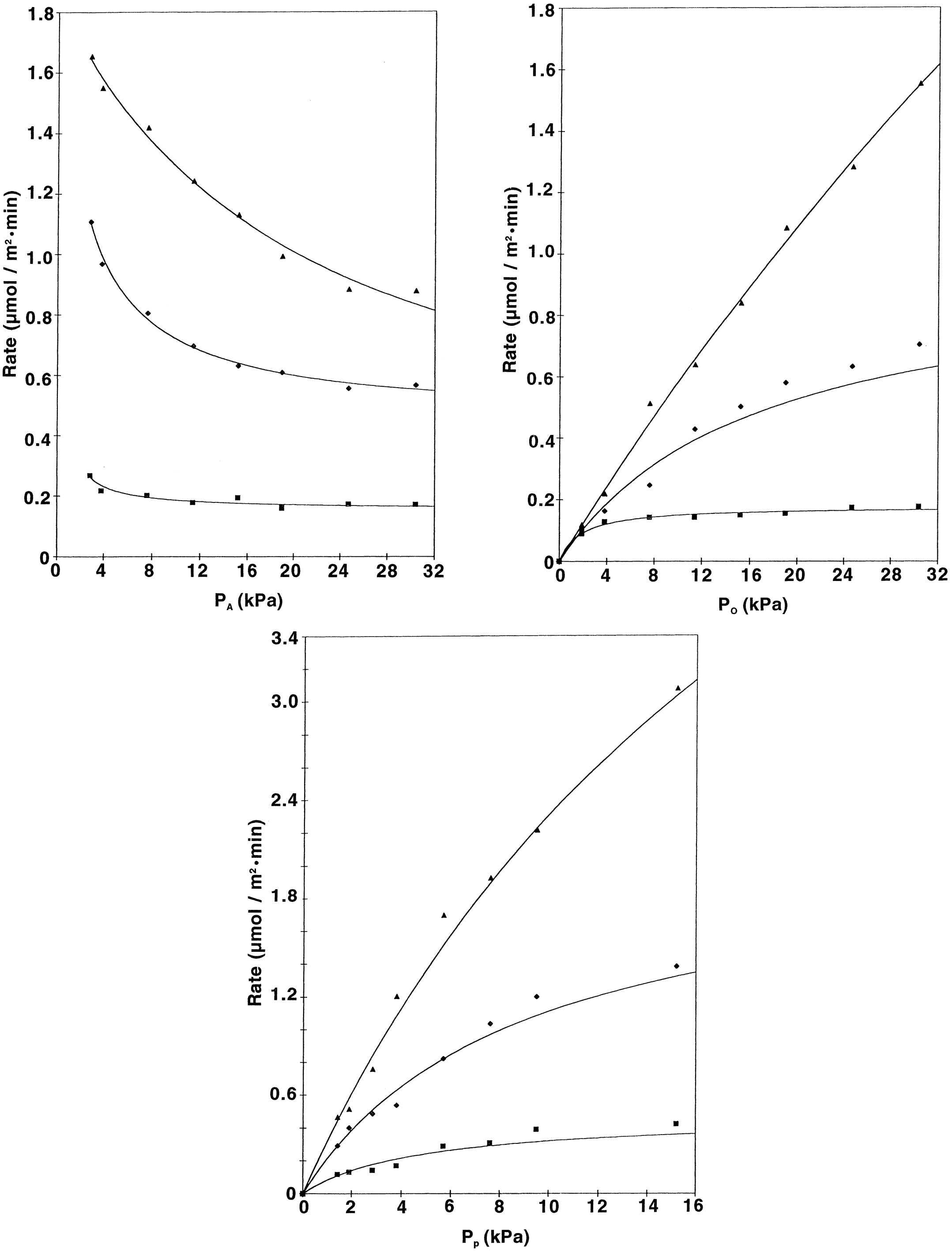

Fig. 2. (a) Rate of carbon oxides formation as a function of ammonia partial pressures for the reaction temperature of 370°C (*n*), 400°C (*u*) and 430°C (*s*). P_O=15.2 kPa and P_P=3.8 kPa. (b) Rate of carbon oxides formation as a function of oxygen partial pressures for the reaction temperature of 370°C (*n*), 400°C (*u*) and 430°C (*s*). P_A=15.2 kPa and P_P=3.8 kPa. (c) Rate of carbon oxides formation as a function of propane partial pressures for the reaction temperature of 370°C (*n*), 400°C (*u*) and 430°C (*s*). P_A=15.2 kPa and P_O=15.2 kPa.

kinetic study was performed on the V–Sb–O/TiO_2(B) catalyst. Fig. 1 reports the variation of the rate for formation of the acrylonitrile with the partial pressures of ammonia (Fig. 1(a)), propane (Fig. 1(b)), and oxygen (Fig. 1(c)) at three reaction temperatures measured in a differential type flow reactor. The rates of acrylonitrile (Fig. 1) and propylene formation vs. the partial pressures of ammonia and oxygen have a similar dependence on the reagent concentration. As ammonia and oxygen pressures increase, the rates for the formation of acrylonitrile and propylene pass through maxima. This behavior can be due to competitive adsorption between reactants [14]. Analysis of these rate dependencies by plotting the functions $P_A/r=f(P_A)$ and $P_O/r=f(P_O)$ (where r is related to acrylonitrile or propylene) and its corresponding linearized form showed the following rate expressions:

$$r=\left(\frac{a_1P_A+P_A^2}{1+a_2P_A+a_3P_A^2}\right), \tag{4}$$

$$r=\left(\frac{a_4P_O+P_O^2}{1+a_5P_O+a_6P_O^2}\right). \tag{5}$$

However in all cases a Langmuir–Hinshelwood dependence on the partial pressure of propane was observed. It was found that the dependence of the rate for formation of acrylonitrile and propylene on the partial pressure of propane could be linearized by using the function $1/r=f(1/P_P)$. Analysis of slope and intercept showed the following rate expression:

$$r=\left(\frac{P_P}{1+a_7P_P}\right). \tag{6}$$

The dependencies expressed by expressions (4) and (5) have to be combined with those of (6): in such a way that the final rate expressions obtained are mechanistically significant. Hence, the dependencies for the formation of acrylonitrile and propylene are similar and the rate expressions for the formation of these products that fit the experimental data (i.e. shown in Fig. 1) are the rate Eqs. (1) and (2). Reported in Tables 1 and 2 are the kinetic parameter of these two rate equations, calculated at three temperatures.

The denominator of the final rate expression (1) contains sites with the partial pressure of ammonia and oxygen or a combination of both, which is in agreement with the reaction network [10] for the side reaction of ammonia oxidation to nitrogen and with the assumption that a large fraction of ammonia is not utilized for the selective insertion in acrylonitrile molecules. Fig. 3 proposes a reaction scheme that obeys the general features of the mechanisms as concluded from consideration of the final rate expression for the formation of acrylonitrile. The description is of course rather general, since no structural information about reaction intermediate can be obtained from a rate expression; the proposed mechanism intermediate is chosen considering information available in literature. The active site is considered to be an ensemble of vanadyl species with antimony site [Sb–O–Sb], the latter was postulated to be active for the transformation into acrylonitrile [16], while the oxygen bonded vanadia participates in the dehydrogenation step. The scheme in Fig. 3 shows that acrylonitrile can be formed from two routes. One route (Fig. 3(a)) involves reaction with the acrolein intermediate where one ammonia molecule has been adsorbed. This route is predominant at low partial pressures of ammonia. The acrolein intermediate further transforms to an acrylate species. At high partial pressures of ammonia, another route (Fig. 3(b)) comprising reaction of acrylate species with two adsorbed ammonia species becomes important, the preadsorbed ammonia desorbs from the catalyst in a later step. In both routes, some type of surface reaction constitutes a slow and rate-determining step, which is followed by desorption of acrylonitrile and formation of a reduced surface site. The reoxidation step comprises a fast adsorption of molecular oxygen followed by a slow dissociation, which probably is not rate-limiting under the conditions used in the present work, i.e. low conversion and an excess of oxygen. The adsorption of ammonia is in the both routes a fast step. The assumption of acrolein being an intermediate in acrylonitrile formation is supported by pulse experiment investigations of ammoxidation of propane on a V–Sb–O catalysts by Buchholz and Zanthoff [12]. If propene and ammonia were pulsed simultaneously, the desorbed products at the reactor outlet were in the sequence acrolein, then acrylonitrile and finally carbon oxides: from this it is possible to conclude a sequential formation of acrylonitrile from acrolein. In the same experiment it was observed that, with a decreasing of NH_x species on the surface, the yield of acrolein at the reactor outlet was increased and the formed acrylonitrile was decreased. Centi and

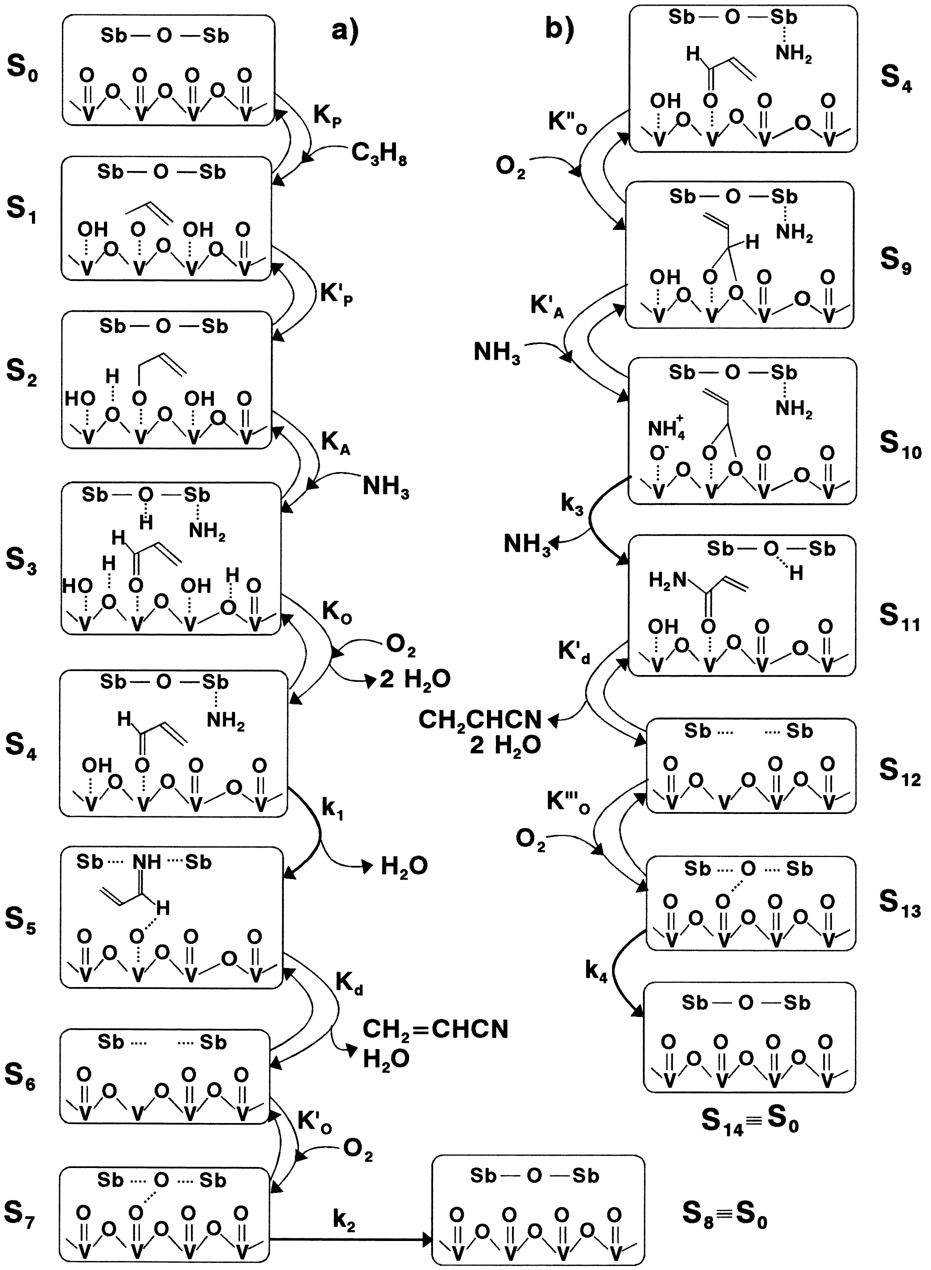

Fig. 3. Proposed mechanism about propane ammoxidation to acrylonitrile.

Marchi [13] observed acrylate and acrolein structure in IR spectroscopic investigation during ammoxidation of propane on V–Sb oxides. From these results they also concluded acrolein to being the intermediate for acrylonitrile formation. The consecutive transformation of acrolein to acrylonitrile over a $SbVO_4$ with excess α-Sb_2O_4 has been reported for ammoxidation of propene [17]: the interpretation was that the excess crystals of α-Sb_2O_4 form sites which are active for allylic oxidation. The mechanistic view, supported by the present results, agrees with that proposed by Centi and Marchi [13] on propane ammoxidation.

The variation of the rate for CO_x formation with the partial pressures of ammonia, oxygen and propane is given in Fig. 2. Fig. 2(a) shows that the rate for the CO_x formation decreases, increasing ammonia pressure. The observed decrease in rate for combustion with increasing the partial pressure of ammonia was explained as being due to competitive adsorption between ammonia and oxygen resulting in a decrease of both the rate of reoxidation and the concentration of electrophilic oxygen species that are active for degradation [18]. A similar behavior has also been observed in the ammoxidation of toluene over V_2O_5/TiO_2 catalysts [19,20]. The decrease in rate was claimed to be due to the fact that ammonia stabilizes the initial intermediate of toluene activation and, thus, prevents it from being burnt off. From analysis of experimental data by plotting inverse rate vs. P_A, and the corresponding linearized form, it can be concluded that the dependencies are as the following equation:

$$r = \left(\frac{c_1 + P_A}{1 + c_2 P_A}\right). \tag{7}$$

The dependencies for CO_x formation vs. oxygen and propane (Fig. 2(b) and (c)) are of the Langmuir–Hinshelwood type; see the following equations:

$$r = \left(\frac{P_O}{1 + c_3 P_O}\right), \tag{8}$$

$$r = \left(\frac{P_P}{1 + c_4 P_P}\right). \tag{9}$$

The final rate expression that fits to all the data was obtained by combining Eqs. (7)–(9). This gives Eq. (3).

Unfortunately, there is not much information on the nature of the intermediates available on the combustion routes for the ammoxidation reaction. In the kinetic investigation for the ammoxidation of propane on V–Sb–O catalysts obtained by Trifirò et al. [3–6,19,20], a combustion routes, on the basis of a dynamic approach to selectivity have been proposed. The first is that for the formation of nitrile and CO_x, the existence of a common adsorbed precursor or intermediate has been concluded in the kinetic study. According to this approach, parallel reaction of CO_x from propylene, direct oxidation of propane to CO_x and consecutive transformation of acrylonitrile to CO_x were concluded.

The numerator of the final rate expression of the CO_x (3) consists of terms with a combination of the partial pressures of the reactants, ammonia, oxygen and propane on the basis of the participation of propane, oxygen and ammonia in the rate-limiting step.

However, although the reported rate equation for the formation of CO_x probably indicates the existence of a parallel pathway via the formation of an intermediate and the consecutive oxidation to carbon oxides, it is not possible to deny completely the direct oxidation of propane to CO_x.

References

[1] J.F. Brazdil, D.D. Suresh, D.A. Omdoff, R.K. Grasselli, US Patent 4 788 173 (1988).

[2] A.T. Gutman, R.K. Grasselli, J.F. Brazdil, US Patent 4 746 641, 4 788 173 and 4 837 233 (1988).

[3] G. Centi, R.K. Grasselli, F. Trifirò, Catal. Today 13 (1992) 661.

[4] G. Centi, R.K. Grasselli, E. Patane, F. Trifirò, in: F.G. Centi, F. Trifirò (Eds.), New Developments in Selective Oxidation, Elsevier, Amsterdam, 1990; Stud. Surf. Sci. Catal. 55 (1990) 515.

[5] G. Centi, F. Trifirò, R.K. Grasselli, La Chimica and L'Industria (Milan) 72 (1990) 617.

[6] R. Catani, G. Centi, F. Trifirò, R.K. Grasselli, Ind. Eng. Chem. Res. 31 (1992) 107.

[7] D.D. Sureh, D.A. Ornoff, J.F. Brazdil, L.C. Glaeser, M.S. Friedrich, US Patent 4 760 159 (1988).

[8] L.C. Glaeser, J.F. Brazdil, M.A. Toft, US Patent 4 843 655, 4 835 125 and 4 837 191 (1988).

[9] G. Minow, K.H. Schnable, G. Ohlmann, Z. Phys. Chemie (Lipzig) 65 (1984) 145.

[10] A. Andersson, S.L.T. Andersson, G. Centi, R.K. Grasselli, M. Sanati, F. Trifirò, Proceedings of the 10th International Congress on Catalysis, Akademiai Kiado, Budapest, 1993, p. 691.

[11] V.D. Sokolovskii, A.A. Davydov, O.Y. Ovsitser, Catal. Rev.-Sci. Eng. 37 (1995) 425.

[12] S.A. Buchholz, H.W. Zanthoff, Heterogeneous hydrocarbon oxidation, Am. Chem. Soc. 41 (1996) 210.

[13] G. Centi, F. Marchi, in: J.W. Hightower, W.N. Delgass, E. Iglesia, A.T. Bell (Eds.), Proceedings of the 11th International Congress on Catalysis, 40th Anniversary, Studies in Surface Science Catalalysis, vol. 101, Elsevier, Amsterdam, 1996, p. 277.

[14] M. Sanati, A. Andersson, Ind. Eng. Chem. Res. 30 (1991) 312.

[15] R. Nilsson, T. Lindblad, A. Andersson, J. Catal. 148 (1994) 501.

[16] R. Nilsson, T. Lindblad, A. Andersson, C. Song, S. Hansen in: V. Cortes Corberan, S. Vic Bellon (Eds.), New Developments in Selective Oxidation II, vol. 82, Elsevier, Amsterdam, 1994, p. 293.

[17] R. Nilsson, T. Lindblad, A. Andersson, Catal. Lett. 29 (1994) 409.

[18] A. Andersson, S. Hansen, M. Sanati in: R.K. Grasselli, W. Sleight (Eds.), Structure – Activity and Selectivity Relationships in Heterogeneous Catalysis, Elsevier, Amsterdam, 1994; Stud. Surf. Sci. Catal. 67 (1991) 43.

[19] P. Cavalli, F. Cavani, I. Manenti, F. Trifirò, Catal. Lett. 1 (1987) 245.

[20] P. Cavalli, F. Cavani, I. Manenti, F. Trifirò, M. El-Sawi, Ind. Eng. Chem. Res. 26 (1987) 804.