On the reaction mechanism of ammoxidation of propane over vanadium containing oxide catalysts

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Vacuum transient pulse and continuous flow investigations on the ammoxidation of propane over VSb_xO_y ($x = 1$, 2 and 5) and $(VO)_2P_2O_7$ catalysts reveal that propene and acrolein are reaction intermediates over both types of oxides. However, the N-insertion step and the formation of total oxidation products proceed significantly different. Short-lived NH_3 or NH_4^+ species are involved in the N-insertion step over V–Sb–O, whereas strongly bound, long-lived NH_x species are participating in the reaction on V–P–O. Only lattice oxygen is involved in the hydrocarbon reaction pathway over V–Sb–O, whereas additionally adsorbed oxygen species lead to total oxidation over V–P–O.

Keywords: ammoxidation of propane, reaction mechanism, vacuum transient technique, V–Sb oxides, V–P oxides, catalytically active sites

1. Introduction

The formation of acrylonitrile by direct ammoxidation of propane is an economically promising alternative route to the conventional propene-based SOHIO/BP process which is presently applied for more than 90% of acrylonitrile production capacity worldwide [1]. Different kinds of catalysts have been developed for this reaction and especially solids containing vanadium, e.g., $(VO)_2P_2O_7$ [2], modified V–Sb oxides [3], and Mo–V–Te–Nb oxides [4], were shown to be highly active and/or selective towards acrylonitrile. Although the fundamental work performed up to now on physico-chemical properties and their relation to catalytic performance of model catalysts, i.e. mainly VSb_xO_y and $(VO)_2P_2O_7$, show that vanadium is the key element in these types of catalysts, the nature of the active sites and the detailed reaction scheme for the different catalysts is still a matter of discussion. The acrylonitrile formation on V–Sb–O catalysts is suggested to occur sequentially via the intermediates

$$C_3H_8 \rightarrow C_3H_6 \rightarrow CH_2{=}CH-CHO \rightarrow CH_2{=}CH-CN$$

based on vacuum transient investigations by Zanthoff and Buchholz [5] and atmospheric kinetic investigations of Andersson et al. [6] and Albonetti et al. [7]. In contrast, Centi et al. [8] proposed in a recent FTIR spectroscopic study that different pathways to ACN exist on V–Sb–O catalysts. The main one being via intermediate formation of propene, allyl alcoholate and acrylimine. For the $(VO)_2P_2O_7$ catalyst Centi and Perathoner [9] proposed the formation of propylamine or acrylate species as intermediates in ACN formation. $NH_{3,ads}$ or NH_4^+ have been suggested by Zanthoff et al. [10] as the N-species to be inserted, whereas amido or imido like species were proposed by Centi and Perathoner [9].

It is the intention of the present work to compare the two catalysts $(VO)_2P_2O_7$ and VSb_xO_y with respect to elementary reaction steps in the partial oxidation and ammoxidation of propane in order to gain further insight into the nature of the catalytically active sites. The results presented focus on the role of ammonia and oxygen in the selective and non-selective reaction pathways. A vacuum transient technique, the temporal-analysis-of-products reactor (TAP), was used to minimise the influence of homogeneous gas phase reactions which are well known to influence the reaction pathways [1]. Labelled oxygen ($^{18}O_2$) was used to distinguish between adsorbed and lattice oxygen. The catalysts were characterised by surface area measurement (BET), XRD, IR and TEM/EDX.

2. Experimental

2.1. Catalysts

The VSb_xO_y catalysts were prepared by a redox reaction of NH_4VO_3 and Sb_2O_3 in aqueous medium with subsequent calcination of the dried precursor in air up to 900 K. XRD and TEM/ EDX analyses revealed the presence of α-Sb_2O_4, $\sim$$SbVO_4$ and small amounts of V_2O_5 (micro crystalline). The average vanadium oxidation state, determined by potentiometric titration, amounted to 4.3 (VSb_1O_x), 4.2 (VSb_2O_x) and 3.9 (VSb_5O_x). The BET surface area (1-point method) of the

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samples used amounted to 10 ± 1.5 m^2/g. The $(VO)_2P_2O_7$ catalyst was prepared by calcination of a $VOHPO_4 \cdot 0.5H_2O$ precursor obtained by evaporation of a solution of V_2O_5 and oxalic acid in diluted H_3PO_4 in N_2 at 753 K. The resulting solid was activated in a flow of a 1.5% butane-in-air mixture. Only reflexes of crystalline $(VO)_2P_2O_7$ were detected by XRD. The average vanadium oxidation state was 4.0. The BET surface area (1-point method) amounted to 5.8±0.4 m^2/g. Additionally, an α-$(NH_4)_2[(VO)_3(P_2O_7)_2]$ single-phase catalyst was prepared by heating of a mixture of V_2O_5 and $(NH_4)_2HPO_4$ and a small amount of inoculating crystals [5]. This catalyst is isostructural to α-$K_2[(VO)_3(P_2O_7)_2]$ [11] exhibiting a tunnel structure containing the ammonium cations [12].

2.2. Methods

A detailed description of the principles of the temporal-analysis-of-products reactor (TAP) applied is given elsewhere [13,14]. The operating conditions in the present work are as follows: the amount of catalyst, usually about 200 mg ($d_P = 250$–355 μm), is placed in the isothermal zone of a stainless-steel micro catalytic fixed-bed reactor between two layers of quartz. Gas pulses (10^{15}–10^{17} molecules/pulse) enter the reactor containing the catalyst sample and are analysed at the reactor outlet using a quadrupole mass spectrometer. Gas transport in the reactor exclusively occurs by diffusion processes under these conditions. Additionally, continuous flows of gas mixtures were passed through the reactor and mass spectra (amu = 1–60) were taken subsequently to follow the changes in gas composition with time. The average gas flow amounted to ~0.4 ml/min (STP). The pressure in the reactor was calculated to < 1 kPa under these conditions (no direct measurement possible). No gas phase reactions occurred in the absence of a catalyst. Quantification of the data for calculation of conversions, yields and selectivities was possible using Ne as internal standard. Conversions were calculated from the product yields.

3. Results

Under the low-pressure conditions applied, propene, acrolein, acrylonitrile, CO, CO_2, N_2, NO and N_2O were observed as reaction products over all catalysts. No indication was observed for other products as propylamine, allylimine or others. Pulsing gas mixtures of $C_3H_8/O_2/NH_3/Ne$ over the $(VO)_2P_2O_7$ catalyst, the mean residence times of the products increase in the following order: non-converted $C_3H_8 \approx C_3H_6$ < acrolein < acrylonitrile < CO_2. A similar sequence has been observed for V–Sb–O catalysts [5]. In the following, results are reported concerning the differences in the role of oxygen and ammonia in the ammoxidation of propane.

3.1. Role of ammonia in the N-insertion step

3.1.1. V–Sb–O catalysts

Sequential pulse experiments were performed pulsing first NH_3 followed by a pulse of propene after a time interval Δt to study the interaction of the gaseous hydrocarbon with preadsorbed ammonia. The dependence of the yield of the selective products acrolein and acrylonitrile on the delay time Δt for a VSb_5O_x catalyst at $T_B = 697$ K is shown in figure 1. The yield of acrylonitrile decreases from 6.5 to 1.6% with Δt increasing from 0.1 to 1.4 s, while the respective yield to acrolein increases from 6.5 to 16.5%.

3.1.2. V–P–O catalysts

The results of the sequential pulse experiments, where NH_3 is pulsed first, followed by a pulse of propene over the $(VO)_2P_2O_7$ catalyst look similar to those of the V–Sb–O catalysts. The yield to acrylonitrile decreases with increasing delay time Δt, whereas that of acrolein increases (cf. figure 2). However, the decrease in the acrylonitrile formation is much lower over the V–P–O catalyst. Even for a delay time of 90 s the yield to acrylonitrile amounted to about 1/2 compared to a delay time of 0.1 s. The respective increase in acrolein, however, is lower compared to the decrease in acrylonitrile. In an additional pulse experiment a propene/Ne mixture was pulsed over the α-$(NH_4)_2[(VO)_3(P_2O_7)_2]$ phase, which contains NH_4^+ ions in the lattice. Acrylonitrile is formed over this catalyst in addition to acrolein and CO_x. The response signals at the reactor outlet for acrolein and acrylonitrile are shown in figure 3.

3.2. Role of oxygen in the reaction pathways

3.2.1. V–Sb–O catalysts

In a transient pulse experiment a $C_3H_8/NH_3/Ne$ mix-

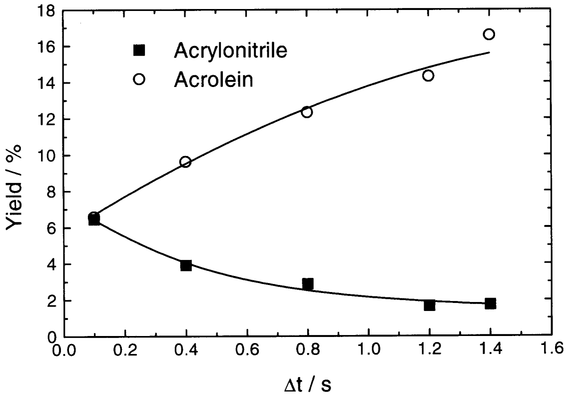

Figure 1. Dependence of the yields to acrolein and acrylonitrile on the time difference Δt when sequentially pulsing (1) NH_3 and (2) C_3H_6 over a VSb_5O_x catalyst ($m_{cat} = 0.15$ g, $T_B = 697$ K).

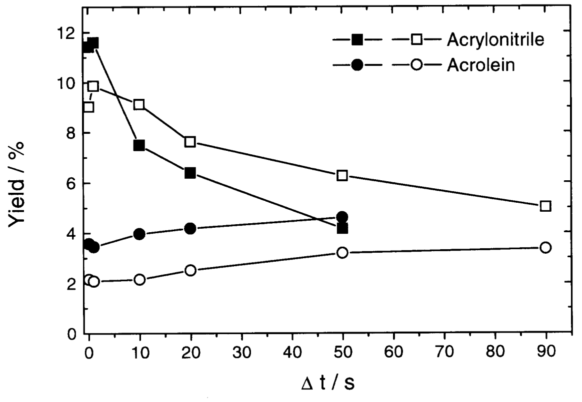

Figure 2. Dependence of the yields to acrolein and acrylonitrile on the time difference Δt when sequentially pulsing (1) NH_3 and (2) C_3H_6 over a $(VO)_2P_2O_7$ catalyst ($m_{cat} = 0.24$ g, $T_B = 738$ K, solid symbols: fresh catalyst; open symbols: catalyst reduced by propene).

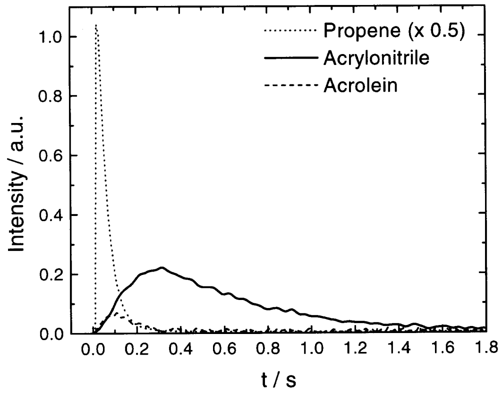

Figure 3. Formation of acrylonitrile during pulsing of C_3H_6/Ne = 1 : 3 over α-$(NH_4)_2[(VO)_3(P_2O_7)_2]$ in the absence of NH_3 ($T_B = 653$ K, $m_{cat} = 0.20$ g).

ture with and without oxygen ($C_3H_8 : NH_3 : O_2 :$ Ne = 1 : 2.5 : 2.5 : 4 or 1 : 2.5 : – : 6.5) was pulsed over the V–Sb oxides in vacuum at $T_B = 791$ K. The presence or absence of oxygen in the feed gas did not significantly affect the reaction to the hydrocarbon products (the total amount of gas pulsed did not significantly change the surface oxidation state). For the VSb_2O_x catalyst (cf. table 1) a propane conversion of $44.3 \pm 0.1\%$ was observed for the fresh sample. The fresh VSb_2O_x catalyst is quite unselective. The yields to the major products CO_x amounted to 43.9%, whereas the yields to the selective products acrolein and acrylonitrile only attained 0.2 and 0.07%. On the fresh catalyst no significant amount of propene was detected. After a pretreatment in a continuous flow of $C_3H_8/O_2 = 1 : 2.5$ propane conversion decreased to $13.5 \pm 0.3\%$. Simultaneously, the yields to the total oxidation products decreased ($Y_{CO_x} = 10.2\%$), but those of the selective products propene, acrolein and acylonitrile increased to 2.3, 0.84 and 0.36%, respectively.

The role of gas phase oxygen in the conversion of C_3H_8 over V–Sb oxides was further investigated using isotopic-labelled oxygen in the feed gas mixture. A continuous flow of $C_3H_8/^{18}O_2$/Ne was fed to the $VSb_2{}^{16}O_x$ catalyst and the isotopic distribution in the products was followed with time-on-stream. Both propane and oxygen react on the catalyst under these conditions, and acrolein, CO and CO_2 were observed as products. In the initial stages of the reaction only ^{16}O containing products were observed at the reactor outlet. The formation of ^{18}O labelled products, however, increased with time-on-stream. Figure 4 shows the dependence of the isotopic oxygen distribution on the reaction time and consequently on the amount of $^{18}O_2$ reacted from the gas stream for CO. At $t = 0$ min only $C^{16}O$ is observed, whereas the ^{18}O portion increased with time-on-stream, amounting to 82% after 165 min. This corresponds to a conversion of 1.3×10^{20} molecules of $^{18}O_2$. A similar behaviour was observed for the other V–Sb oxide catalysts.

3.2.2. $(VO)_2P_2O_7$ catalyst

In a transient pulse experiment a mixture of propane, ammonia and neon with and without oxygen ($C_3H_8 : NH_3 : O_2 :$ Ne = 1 : 2.5 : 2.5 : 4 or 1 : 2.5 : – : 6.5) was pulsed over the $(VO)_2P_2O_7$ catalyst in the vacuum at $T_B = 778$ K. Under these conditions the sample used was less active compared to the VSb_2O_x catalyst. Only a conversion of $X_{C_3H_8} = 5.5\%$ was calculated in the absence of gas phase oxygen. In the presence of oxygen the conversion was slightly higher amounting to $X_{C_3H_8} = 6.4\%$. Also differences in the product yields were detected (cf. table 2). The CO_2 yield increased in the

Table 1
Yields and conversions during pulse experiments over VSb_2O_x. A: fresh catalyst; B: after pretreatment with C_3H_8/O_2 for 60 min ($m_{cat} = 0.200$ g; $T_B = 791$ K; pulse size: 8.1×10^{16} molecules/pulse)

	Feed composition				X (%)	Y (%)				
	C_3H_8	NH_3	O_2	Ne		C_3H_6	ACHO	ACN	CO_x	$N_2 + NO_x$
A	10	25	–	65	44.2	–	0.20	0.07	43.92	76.3
A	10	25	25	40	44.4	–	0.20	0.06	44.18	62.1
B	10	25	–	65	13.6	2.2	0.84	0.37	10.12	86.5
B	10	25	25	40	13.8	2.4	0.84	0.35	10.23	90.3

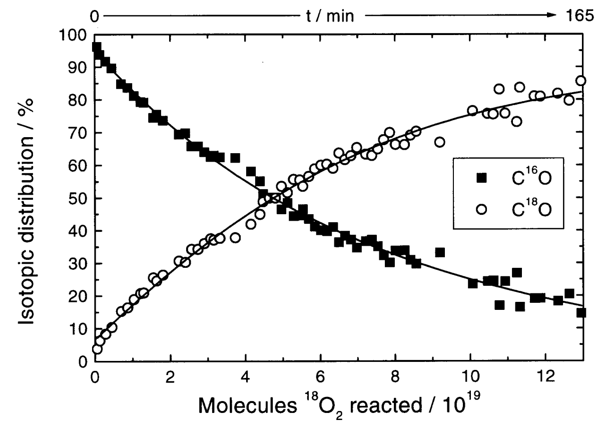

Figure 4. Distribution of oxygen isotopes in CO during continuous flow of $C_3H_8/^{18}O_2$/He over VSb_2O_x ($m_{cat} = 0.20$ g; $T_B = 920$ K).

presence of O_2 from 2.2 to 3.0% whereas the yield to acrylonitrile decreased from 0.80 to 0.76%. The yield to propene increased from 2.49 to 2.54%, respectively. After treating with a $C_3H_8/O_2/Ne$ mixture (1 : 2.5 : 6.5), the activity of the sample remained quite the same amounting to $X_{C_3H_8} = 6.9\%$ in the absence and $X_{C_3H_8} = 7.8\%$ in the presence of oxygen. The yields to the selective products were found to be increased by a factor of two ($Y_{ACHO} = 0.13\%$ and $Y_{ACN} = 1.56\%$) whereas the total oxidation yields increased to 2.60% only. Again, in the presence of oxygen in the feed gas higher yields to propene ($Y_{C_3H_6} = 2.78\%$) and CO_x ($Y_{CO_x} = 3.49\%$) were obtained.

Continuous flow experiments using isotopic-labelled oxygen were performed similar to those described for the V–Sb oxide catalyst. Acrolein, CO and CO_2 were observed as reaction products, too. However, even in the initial stage of the reaction ^{18}O-labelled products were observed, increasing in number with progressive reaction time. The dependence of reaction time (equal to the converted amount of $^{18}O_2$) on isotopic distribution in the product CO is shown in figure 5. At $t = 0$ min the ^{18}O content in CO amounted to about 15%, reaching a portion of 80% after 63 min (7.5×10^{20} molecules $^{18}O_2$ reacted).

4. Discussion and conclusions

The observed product sequence as well as the opposite trend of acrolein and acrylonitrile formation in the NH_3/propene sequential pulse experiments shows that the hydrocarbon reaction intermediates over $(VO)_2P_2O_7$ are similar to those over VSb_xO_y, i.e. propene and acrolein. This result is in accordance with the ammoxidation of toluene to benzonitrile over $(VO)_2P_2O_7$ via intermediate formation of the aldehyde [11]. The acrolein might form acrylate species on the surface as was proposed by Centi and Perathoner [9]. This is supported by the rapid oxygen exchange of the oxygen in the aldehyde group of acrolein on V–Sb oxides observed in vacuum pulse experiments using ^{16}O-acrolein pulses over an ^{18}O-exchanged V–Sb–O catalyst.

4.1. Role of ammonia in the N-insertion step

The present results reveal that the N-insertion steps differ significantly on V–Sb and V–P oxides. The decrease in ACN formation during sequential NH_3/propane pulses with increasing delay time Δt observed for both catalysts indicates that short-lived NH_x species, most probably NH_3 or NH_4^+ [5,8], are involved in this reaction step. The calculated half-life times amounted from $t_{1/2} = 0.5$ s for the VSb_5O_x up to $t_{1/2} = 5$ s for an alumina-modified VSb_5O_x/Al_2O_3 catalyst. The disappearance of the N-species can be explained by the fact that these species are also intermediates in the undesired N_2 formation from ammonia [10] over these catalysts (cf. tables 1 and 2). For $(VO)_2P_2O_7$ the calculated half-life time is larger than 90 s, indicating that either the oxidation rate of the ammonia to N_2 is lower compared to the V–Sb oxides or that additionally long-lived NH_x species are involved in the insertion mechanism. The pulse experiments using the α-$(NH_4)_2[(VO)_3(P_2O_7)_2]$ phase show that even lattice ammonium ions can participate in ACN formation over V–P–O catalysts. Therefore, it is assumed that at least part of the adsorbed NH_3 is converted to more stable surface NH_x species exhibiting a longer lifetime under the conditions applied. These species might be NH_4^+ or more probably NH_2^- because the

Table 2
Yields and conversions during pulse experiments over $(VO)_2P_2O_7$. A: fresh catalyst; B: after pretreatment with C_3H_8/O_2 for 60 min ($m_{cat} = 0.200$ g; $T_B = 778$ K; pulse size: 8.1×10^{16} molecules/pulse) [a]

	Feed composition				X (%)	Y (%)				
	C_3H_8	NH_3	O_2	Ne		C_3H_6	ACHO	ACN	CO_x	$N_2 + NO_x$
A	10	25	–	65	5.5	2.49	0.06	0.80	2.19	49.2
A	10	25	25	40	6.4	2.54	0.06	0.76	3.04	43.3
B	10	25	–	65	6.9	2.63	0.13	1.56	2.60	70.2
B	10	25	25	40	7.8	2.78	0.12	1.37	3.49	59.4

[a] Unknown product with fragment at amu = 29 could not be identified.

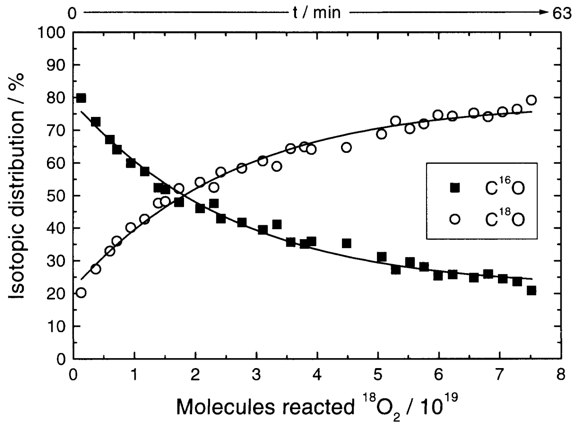

Figure 5. Distribution of oxygen isotopes in CO during continuous flow of C_3H_8/$^{18}O_2$/He over $(VO)_2P_2O_7$ (m_{cat} = 0.20 g; T_B = 920 K).

NH_2^- species were detected using FTIR spectroscopy on $(VO)_2P_2O_7$ during ammonia adsorption [9,15] but not on VSb_xO_y [16]. The higher stability of the NH_x species on $(VO)_2P_2O_7$, in consequence, leads to higher yields of ACN over this catalyst under the vacuum conditions applied. However, the intermediate acrolein, which should be observed on the V–Sb oxides instead, is partly oxidised to CO_x and cannot be detected in large amounts due to its lower thermal and oxidative stability compared to ACN [17]. Therefore, the selectivity of ACN + acrolein over VSb_2O_y only amounted to about 9% (cf. table 1B) compared to 32% reported under atmospheric conditions, i.e. in the presence of high partial pressures of ammonia [18].

4.2. Role of oxygen in the reaction pathways

Transient pulse as well as continuous flow experiments showed no direct effect of gas phase oxygen on the ammoxidation reaction over V–Sb-oxide catalysts. Therefore, it can be concluded that exclusively lattice oxygen is involved in the selective and total oxidation steps over this catalyst. However, for the $(VO)_2P_2O_7$ catalyst the larger conversion and yield of CO_x in the transient pulse experiments and the immediate presence of ^{18}O-containing products in the isotopic-labeling experiments reveal that short-lived oxygen species are participating in the activation of propane and the formation of total oxidation products over this type of catalyst. The participation of adsorbed oxygen in the reaction was also observed in vacuum transient studies on *n*-butane oxidation over the same $(VO)_2P_2O_7$ catalyst [19]. However, the participation in the selective pathway as was concluded by Centi et al. [20] could not be confirmed. Under the vacuum conditions applied in the present work the influence of the loosely bound oxygen species is low due to the low oxygen surface coverages resulting in a better catalytic performance of V–P–O compared to V–Sb–O. At atmospheric pressure, however, these species totally oxidise propane and decrease the yields of ACN. A higher catalytic performance towards acrylonitrile on V–P–O compared to that obtainable at propane/oxygen cofeed conditions might therefore be achieved in the absence of gas phase oxygen, i.e. using advanced reactor setups working with the riser/regenerator principle keeping the catalyst in its active state by reoxidation in a separate reaction vessel.

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