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Ammoxidation of propane to acrylonitrile on V-Sb-O catalysts. Role of ammonia in the reaction pathways

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Abstract

Transient experiments in the vacuum on the ammoxidation of propane over VSb_5O_x- and VSb_5O_x(30 wt%)/Al_2O_3 catalysts were performed. Additionally, the interaction of ammonia with the catalysts was investigated by means of TPD and DRIFT spectroscopic studies. The reported results reveal that short lived NH_x-species, most probably $NH_{3,ads}$ or NH_4^+, are active species in the formation of acrylonitrile from propane. These species are also involved in the formation of the non-selective side-product N_2, which is formed via the intermediates NO and N_2O.

Keywords: Ammoxidation of propane; Acrylonitrile; V-Sb-O catalysts; Ammonia

1. Introduction

Acrylonitrile (ACN) is currently technically produced by direct catalytic ammoxidation of propene. Maximum yields of about 80% can be achieved applying Bi-Mo or Fe-Sb based catalysts [1]. However, in recent years interest has increased in the development of alternative processes using propane as feed gas compound. Among the various catalysts developed for this reaction modified V-Sb oxides seem to be promising to make this process technically feasible [2]. ACN-yields of $Y_{max} = 39\%$ [2] were reported in the literature which is, however, much lower than can be obtained starting from propene. In order to develop catalysts exhibiting higher yields knowledge on the detailed reaction mechanism and the nature of the active sites is necessary. Although some scientific work dealt with these topics, e.g. [3–5], details of the reaction mechanism remained unclear. Especially the role of ammonia in the reaction pathways has to be elucidated.

Different N-species are discussed in the literature to be active in the ammoxidation reaction on different catalysts. For Fe-Sb oxides Sb-NH-Sb sites have been proposed for acrylonitrile formation from propene [6], which is generally agreed to be the primary intermediate in propane ammoxidation. In contrast to this hypothesis, NH_2^- groups are suggested to be active in the N insertion on Ga-Sb oxides [5]. NH_4^+, $NH_{3,ads}$, NH_2^- and imido groups (V = NH) are discussed for $(VO)_2P_2O_7$ [7]. The formation of N_2 which is the most undesired product of the reaction

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besides CO_2 on V-Sb-O catalysts is also unclear. Catani et al. [3] assumed a reaction pathway via nitrogen oxides which, however, could not be detected.

Against this background the presented work aimed at investigation of the role of ammonia in the reaction mechanism of the ammoxidation of propane on V-Sb- and V-Sb-Al-oxide catalysts. The interaction of (a) pure ammonia and (b) ammonia in the presence of propane and oxygen with the catalysts were studied in the vacuum applying transient and steady state experiments to identify intermediate reaction products and reaction pathways. NH_3-TPD and DRIFT experiments were used to obtain information on surface bonded N-species.

2. Experimental

2.1. Catalysts

VSb_5O_x- and VSb_5O_x(30 wt%)/Al_2O_3 catalysts were prepared by redox reaction in aqueous medium as described by Catani et al. [3]. The resulting catalyst was pelletized and granulated. Particles with a diameter of $d_p = 250–355$ μm were used in the experiments. The catalysts exhibited a BET-surface area of 3.6 and 110 m^2 g^{-1} for the VSb_5O_x- and VSb_5O_x(30 wt%)/Al_2O_3, respectively (N_2 adsorption at 77 K, 1 point method). XRD and electron diffraction analysis (during TEM) revealed the existence of only two crystalline phases in the VSb_5O_x catalyst $VSb_{1-x}O_{4-1.5x}$, (JCPDS no. 35-1485) and α-Sb_2O_4, (JCPDS no. 11-0694), the latter being the predominant phase. The VSb_5O_x(30 wt%)/Al_2O_3 showed only rare crystallinity. For this catalyst only α-Sb_2O_4 could be identified as crystalline bulk phase. Adsorption of pyridine studied by DRIFT spectroscopy showed that the VSb_5O_x catalyst exhibit Lewis acidic sites only (bands at 1440, 1486 and 1585 cm^{-1}), while for the alumina supported one also Brønsted sites (band at 1539 cm^{-1}) were observed.

2.2. Methods

Transient experiments in the vacuum were performed in the 'temporal-analysis-of-products'-reactor (TAP). Detailed descriptions of the equipment and operating conditions are given elsewhere [8]. Therefore, only information specific for the presented work is given below. During the transient experiments small gas pulses (10^{15}–10^{17} molecules/pulse) produced by two high speed valves enter a catalytic microreactor containing 150 to 250 mg catalyst. Transport of the molecules through the reactor occurs by diffusion processes under these conditions, because the reactor is kept in the vacuum. The responses to the inlet pulses at the reactor outlet are analyzed applying a quadrupole mass spectrometer. Intensity vs. time curves for specific m/e ratios (amu) were recorded. The substances were detected at the following amu values: 56 (acrolein), 53 (acrolein, acrylonitrile), 44 (N_2O, CO_2, C_3H_8), 43 (C_3H_8), 41 (C_3H_6, C_3H_8), 32 (O_2), 30 (NO, C_3H_6, C_3H_8) and 28 (CO_2, CO, N_2, N_2O, C_3H_8, C_3H_6). The contribution of different substances to a recorded response signal at one amu was calculated by experimentally determined fragmentation patterns of the pure substances. Applying the two pulse valves experiments were performed in which the catalyst was treated with two different gas pulses, which were sent in a time difference Δt over the catalyst. A detailed description of the applied conditions is reported in the results section. Experiments at steady state conditions were performed using a continuously opening valve allowing a gas flow of 4 ml/min over the catalyst under reduced pressure ($<$ 100 Torr). The TAP equipment was also used to perform temperature programmed desorption studies of ammonia (temperature range from 323 to 923 K, 15 K/min) on the mentioned catalysts, which were saturated with NH_3 at 323 K.

The adsorption structures of ammonia were investigated by means of DRIFT spectroscopic investigations. The catalyst (10–20 mg, powder) was first heated in the DRIFT cell in Ar to 823 K to remove loosely bonded species from the catalyst surface. Then the catalyst was cooled down to the temperature of the experiment and a stream of NH_3 (4% in Ar) was fed to the catalyst and DRIFT spectra were taken after 15 min up to no change in the spectra was observed.

3. Results

3.1. Interaction of pure NH_3 with catalysts

In order to investigate if adsorbed N-species are formed when NH_3 interacts with the V-Sb-O catalyst DRIFT spectroscopic studies for the adsorption of NH_3 on VSb_5O_x were performed. At temperatures below 623 K bands at 1408, 1440 and 1480 cm^{-1} indicating the presence of NH_4^+ and at 1625 cm^{-1} indicating the presence of coordinated NH_3 were observed. At higher temperatures only the band at 1625 cm^{-1} remained; identification of smaller bands in the 1440 cm^{-1} region at these temperatures was difficult, because of the increasing IR absorption caused by the catalyst itself. No indication for the presence of other NH_x-species was found.

When NH_3 is pulsed over the VSb_5O_x catalyst in the vacuum ($T = 673$ K; $m_{cat} = 150$ mg; $NH_3/He = 1{:}3$, 6.2×10^{16} molecules/pulse) reaction occurs on the catalyst. N_2 ($Y_{N_2} = 62\%$), NO ($Y_{NO} = 8\%$) and N_2O ($Y_{N_2O} = 23\%$) and water (not quantified) were detected as products. The same products are observed applying the catalyst modified with alumina. It should be mentioned that NO and/or N_2O was also observed at steady state conditions at reduced pressure when an ammoxidation feed gas ($C_3H_8/NH_3/O_2/Ne = 1{:}2.5{:}2.5{:}4$; $T = 650$ to 850 K) was fed to the catalyst. In that case the amounts could not be quantified, because of simultaneous production of CO_2.

TPD of ammonia over the VSb_5O_x catalyst exhibits as well the formation of NO and N_2O during heating in vacuum as can be seen in Fig. 1 which shows the thermal desorption curves for the masses 15, 28, 30 and 44. The curve for mass 15, which can be solely adapted to NH_3, indicates that NH_3 desorbs from the catalyst up to a temperature of 650 K. However, the curves of the masses 28, 30 and 44 reveal that part of the adsorbed NH_3 also desorbs being oxidized to N_2, N_2O and NO. The masses 12 and 14 (not shown in Fig. 1) as well as TPD spectra in the absence of ammonia reveal that the observed peak maxima for mass 28 ($T_{max} = 560$ K), 30 ($T_{max} = 600$ K) and 44 ($T_{max} = 560$ K) belong to N-species and not to CO or CO_2. However, the intensity increase of mass 44 and 28 above 800 K can be adapted to CO_2 formation, which is also observed in the absence of NH_3. Above 800 K the desorption of oxygen was also observed.

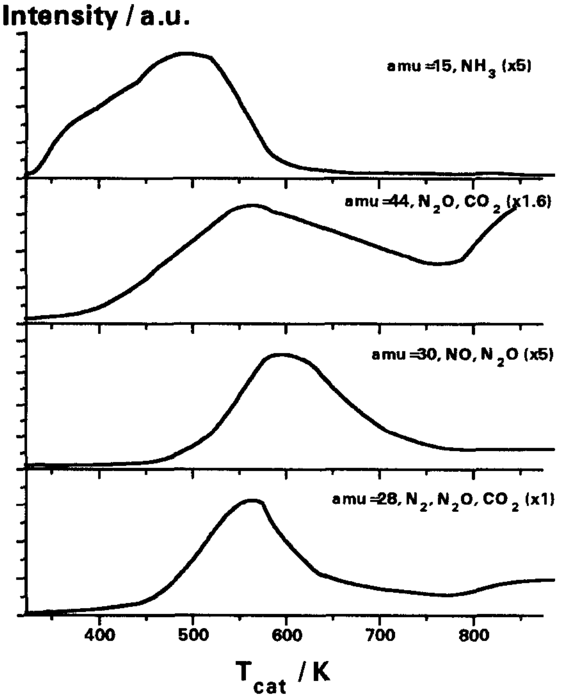

Fig. 1. Thermal desorption spectra of masses 15 (NH_3), 28 (N_2, N_2O, CO_2), 30 (NO, N_2O) and 44 (N_2O, CO_2) for a VSb_5O_x catalyst ($m_{cat} = 150$ mg; $T_{ads} = 323$ K; heating rate = 15 K min^{-1}).

In further transient experiments in the vacuum NO and N_2O were pulsed over the VSb_5O_x catalyst. No conversion could be observed at the

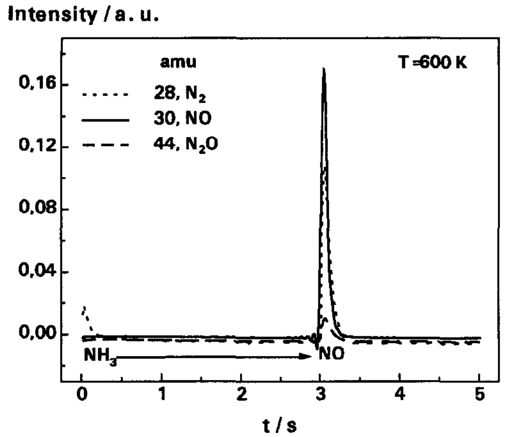

Fig. 2. Response signals for N_2, NO and N_2O when a VSb_5O_x catalyst was treated at 600 K with NH_3 first and subsequently with NO after a time difference of $\Delta t = 3$ s. (NH_3/He = 1:2; 6.3×10^{16} molecules/pulse; NO/Ne = 1:9; 3.2×10^{16} molecules/pulse; $m_{cat} = 150$ mg).

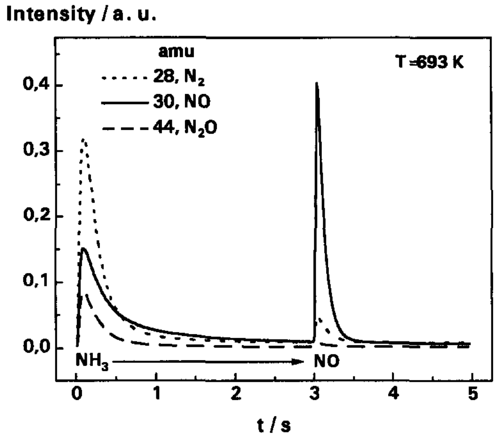

Fig. 3. Response signals for N_2, NO and N_2O when a VSb_5O_x catalyst was treated at 693 K with NH_3 first and subsequently with NO after a time difference of $\Delta t = 3$ s. (NH_3/He = 1:2; 6.3×10^{16} molecules/pulse; NO/Ne = 1:9; 3.2×10^{16} molecules/pulse; $m_{cat} = 150$ mg).

investigated temperature of 832 K. Also in mixtures together with propane no reaction occurred.

However, when pulsing first NH_3 over the VSb_5O_x catalyst subsequently followed by a pulse of NO ($T = 600$ K), the formation of N_2O and N_2 was observed in the response of the NO pulse (see Fig. 2). Increasing the temperature to 693 K the same qualitative behaviour was observed, however, the formation of N_2 and N_2O in the response to the NO pulse decreased, while the amount of N_2 (and NO) in the response to the NH_3 pulse increased (see Fig. 3).

3.2. Interaction of NH_3 with catalysts in the presence of C_3H_8 and oxygen

When C_3H_8 was pulsed in the vacuum over the VSb_5O_x(30 wt%)/Al_2O_3 catalyst in the presence of NH_3 and O_2, ACN ($Y_{ACN} = 1.0\%$), propene ($Y_{C_3H_6} = 15.5\%$) and CO_2 ($Y_{CO_2} = 1.7\%$) were observed as products in the mass spectrometer ($C_3H_8/NH_3/O_2/Ne$ = 1:2.5:2.5:4; 10^{16} molecules/pulse; $T_R = 823$ K). The conversion amounted to 18.2%. N_2 and NO were observed as by-products (not quantified).

When NH_3 was pulsed over the VSb_5O_x catalyst subsequently followed by a pulse of propane after a time difference Δt ACN was observed as product in the response to the propane pulse. The amount of ACN produced from propane decreases with increasing Δt (see Fig. 4). This indicates that only N-species with

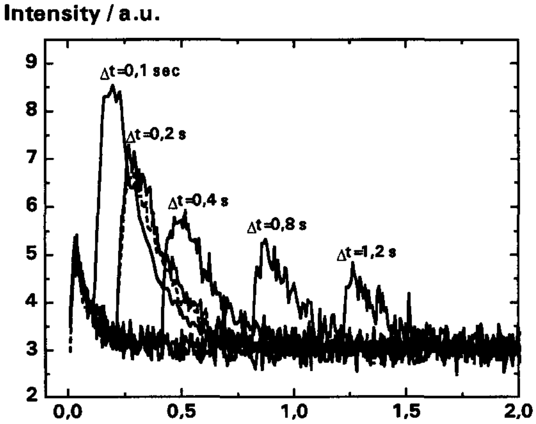

Fig. 4. Dependence of the amount of acrylonitrile observed in sequential pulses of: 1, NH_3 and 2, C_3H_8 on the time difference between pulses 1 and 2 over a VSb_5O_x catalyst. (NH_3/He = 1:3, pulse size: 4×10^{16} molecules/pulse; C_3H_8/Ne = 1:4, pulse size: 2×10^{16} molecules/pulse; $T_b = 450°C$, $m_{cat} = 250$ mg).

a limited surface life time (easily desorbing species, or fast unselectively reacting species) are involved in ACN formation. The half-time of these species is around 0.5 s for the VSb_5O_x and 5 s for the VSb_5O_x(30 wt%)/Al_2O_3 catalyst.

4. Discussion

From the results presented above it becomes obvious that several N-species are present on the catalyst even under ammoxidation reaction conditions which may contribute to the formation of selective and nonselective products. From the NH_3-DRIFTS, NH_3-TPD and transient vacuum investigations it is likely that these species are NH_3, NH_4^+, NO or N_2O.

4.1. Selective reaction pathway to acrylonitrile

The transient vacuum studies of sequential pulsing 1. NH_3 and 2. C_3H_8 reveal that short lived N-species are involved in the N insertion into propane. It can be assumed that these N-species formed from NH_3 either desorb or are unselectively converted with time. Since it was found that even at temperatures below 600 K ammonia is converted to NO, N_2O and N_2, products which are also observed under the reaction conditions of ammoxidation, it can be concluded that the loss of active N-species is caused by their oxidation to these products. It is therefore assumed that $NH_{3,ads}$ or NH_4^+, which were observed during the DRIFTS studies are most probably the N-species active in formation of acrylonitrile. This conclusion is in agreement with suggestions of Centi et al. [7] who observed NH_4^+-species during NH_3/C_3H_6 coadsorption on $(VO)_2P_2O_7$, which is also active in ammoxidation of propane, in the absence of gas phase oxygen. However, the authors concluded from their FT-IR experiments that NH_3 and/or NH_4^+ are dehydrogenated to NH_2^--species being active in formation of acrylonitrile producing propylamine as an intermediate. While we cannot exclude the formation of NH_2^- from the results presented above, the pathway via propylamine can be excluded on V-Sb-O catalysts under the applied conditions as is shown elsewhere [9].

4.2. Non-selective reaction pathway to N_2

The results reported above reveal that NO and N_2O are formed during interaction of NH_3 and during ammoxidation of propane under vacuum conditions on V-Sb-O catalysts. Their participation in the selective pathway was excluded, since they did not react with propane on the applied catalysts. Under atmospheric conditions these products, however, were not detected [3]. From our transient experiments it can be concluded that this is due to the fact that under atmospheric conditions, i.e. higher surface coverages of adsorbed ammonia, the NO and N_2O are converted to N_2 by adsorbed NH_3 or NH_4^+-species. This reaction may probably occur similar to the selective catalytic reduction of NO by NH_4^+ on V-OH sites (V_2O_5/TiO_2 catalyst) as suggested by Topsoe et al. [10]. However, this would suggest that the active N-species for the formation of acrylonitrile are also active in the non-selective oxidation of NH_3 to N_2. In fact, the decay of acrylonitrile with the life time of the NH_x-species is the same as for the formation of N_2, when stopping a continuous flow of NH_3 over the V-Sb-O catalyst (see Table 1),

Table 1
Dependence of the relative amount of acrylonitrile (ACN) and N_2 on a delay time dt after ammonia pulse or flow stop ($T = 823$ K)

dt (s)	Relative amount (%)	
	ACN	N_2
0	100	100
0.5	97	93
1.0	80	65
1.5	80	59
5.0	55	42
15.0	25	25
28.0	14	14

indicating that the NH_x-species are involved in both pathways.

5. Conclusions

Transient experiments in the vacuum reveal that NH_x-species with a short life time on the catalyst surface, most probably $NH_{3,ads}$ or NH_4^+, are involved in the formation of ACN and N_2 over V-Sb oxide catalysts. Active sites, which are formed by irreversible reaction of NH_3 with the catalyst, like Sb-NH-Sb centers, as were proposed by Grasselli et al. [6] for the ammoxidation of propene over Fe-Sb-oxides can therefore be excluded. The NH_x-species are also found to be the primary intermediates in the non selective oxidation of NH_3, which runs via subsequent formation of NO and/or N_2O to the final product N_2.

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