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Structural Dynamics of a V_2O_5/SnO_2 Catalyst in the Ammoxidation of 3-Picoline

ARNE ANDERSSON

Department of Chemical Technology, Chemical Center, Lund Institute of Technology, P.O. Box 740, S-220 07 Lund 7, Sweden

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The influence of the reaction parameters on the conversion of 3-picoline and the yield of nicotinonitrile in the ammoxidation of 3-picoline on a V_2O_5/SnO_2 catalyst was studied. The highest yield of nicotinonitrile was 82%. This was obtained at 400°C, with a space velocity of 4000 h^{-1} and the following mole ratios: ammonia/3-picoline = 12, air/3-picoline = 210, and water vapour/3-picoline = 40. It was found that the composition of the surface of the catalyst depended strongly on the values of the reaction parameters. The dynamic structure of the catalyst surface was studied by determining the phases present by X-ray diffraction analysis and the average oxidation number of vanadium by titrimetric methods. These results were correlated, showing that catalysts with both V_2O_5 and V_6O_{13} were especially active and selective. The composition of the SnO_2 phase was analyzed and was found to be $V_{0.03}Sn_{0.97}O_2$, and did not depend on the reaction parameters. Infrared investigations showed that the role of SnO_2 was to weaken the short V=O bonds. This can probably be seen as a consequence of incorporation of Sn^{4+} in the V_2O_5 lattice.

I. INTRODUCTION

The ammoxidation of 3-picoline to nicotinonitrile is of industrial interest because of the possibility to transform the nitrile into nicotinamide by catalytic hydration. This two-step process gives a high yield of nicotinamide. In the first step it is possible to obtain a yield of nicotinonitrile of about 85–90% (*1*, *2*). The second step gives more than a 90% yield of nicotinamide (*3*, *4*). It is also possible to transform the nicotinonitrile into acid by hydrolysis (*5*). Both nicotinamide (vitamin B_3) and nicotinic acid are essential for the nutrition of human beings and animals, and they can be used as feed additives. Nicotinic acid can also be prepared by oxidation of 3-picoline by nitric acid or by oxidation with molecular oxygen (*6*), and nicotinamide can then be prepared from esters of nicotinic acid (*7*). However, by using the ammoxidation technique in combination with catalytic hydration or hydrolysis, the cost can be lowered and the production simplified.

V_2O_5-based catalysts are generally used in the ammoxidation and oxidation reactions of aromatic hydrocarbons. Other oxides can be added as promoters. SnO_2 is one of the promoters often mentioned in the patent literature (*8–10*).

The conditions in the ammoxidation of 3-picoline are both reductive and oxidative; i.e., the hydrocarbon consumes oxygen from the catalyst, which is then reoxidized. It can be expected that under the steady state conditions the catalyst will contain a certain amount of lower oxides formed by reduction of the originally charged catalyst. The degree of reduction will depend on the reaction parameters. Such phenomena have been described in the literature, for example in papers concerning the oxidation of *o*-xylene on a V_2O_5/SiC catalyst (*11*) and the oxidation of naphthalene on different vanadium oxides (*12*). Investigations of the structural dynamics of V_2O_5/SnO_2 catalysts in ammoxidation reactions have not previously been published, but it has been shown that the presence of lower vanadium oxides has a great effect on both the activity and the selectivity in the ammoxidation of 3-picoline (*13*, *14*).

The aim of this work was to study how

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the yield of nicotinonitrile depends on the reaction parameters in the ammoxidation of 3-picoline on a V_2O_5/SnO_2 catalyst. The intention was also to follow the changes of the catalyst composition when the reaction conditions were varied. The original charged catalyst composition was V_2O_5–$1.5SnO_2$, and the same catalyst has also been used with good results in the vapour phase oxidation of alkylpyridines (*6*).

II. METHODS

1. Apparatus

Air and ammonia were supplied from pressure cylinders. About 10% of the air stream passed through a 3-picoline evaporator. Water vapour could also be added to the reactant stream. The reactant mixture of 3-picoline, air, ammonia, and water entered the reactor, after which the product stream passed through condensers and absorbers. A detailed description of the apparatus is given elsewhere (*13*).

2. Analysis

The condensed mixture of the unreacted 3-picoline and the products, which mainly consisted of nicotinonitrile, pyridine, and a high-boiling fraction were analyzed by GLC (column; 1.5 m, 30% SE−30 + 1% TEA on A.W. Chromosorb W, 70°C). The carbon oxides formed were analyzed gravimetrically. A complete analytical procedure has been published (*13*).

3. Catalyst Preparation and Characterization

The catalyst was prepared by heating V_2O_5 and SnO_2 powders, mole ratio $V_2O_5 : SnO_2 = 1 : 1.5$, in crucibles in a high-temperature oven for 3 h at 1250°C. After a rapid cooling, the catalyst was divided into small particles and the 14–25 mesh (1.41–0.71 mm) fraction was collected and then used in the experiments.

Both unused catalysts as well as catalysts used under different conditions were characterized by various methods. The average oxidation number of vanadium was determined by titrimetric methods (*15*) using potassium permanganate and Mohr's salt.

X-Ray diffraction analysis of the phases present in the catalysts was carried out on a Philips X-ray diffraction instrument using a PW 1310/01/01 generator and Cu$K\alpha$ radiation.

Infrared spectra of the catalysts were recorded on a Perkin–Elmer 297 infrared spectrophotometer. The KBr disc method was used, 1–3 mg catalyst being added to 200 mg KBr.

SEM investigations were performed with a ISI-100A scanning electron microscope. Also, dot images of vanadium and tin were obtained by energy-dispersive X-ray analysis.

The surface areas of the catalysts were determined by the BET method using N_2 at liquid N_2 temperature. The area of the unused catalyst was 0.17 m^2/g, and it was not found to be different for used catalysts within the experimental errors.

4. Materials

The catalyst was prepared from V_2O_5 and SnO_2 supplied by Riedel-De Haën AG and Merck, respectively. They were of laboratory reagent purity. The 3-picoline used was from Merck–Schuchardt and contained 97% 3-picoline. Air and ammonia were commercially available gases and were used without further purification.

5. Operation

The experiments were carried out at atmospheric pressure in an integral glass reactor with an internal diameter of 2 cm. A thermocouple was positioned in the center of the reactor. The amount of catalyst varied between 2 and 14 cm^3 (4.4–30.7 g) and the studied temperature interval was 327–494°C. The flow of 3-picoline was practically constant at $2cm^3/min$ and the other flows varied as follows, air 196–728 cm^3/min, ammonia 3–48 cm^3/min, and water vapour 0–209 cm^3/min. The influence of mass transport phenomena was found to be negligible.

All the measurements were made under steady state conditions, which were obtained after a few hours' operation. Then the product stream was collected for 1 h and an integral analysis was made. The condition of steady state was checked regularly and the variation of each parameter was randomly made while keeping the other parameters constant. The best value obtained for each parameter was used in the further experiments.

III. RESULTS AND DISCUSSION

1. *Definitions*

Conversion (%) is defined as the fraction of 3-picoline converted into products × 100; yield (%) is the fraction of 3-picoline converted into a specific product × 100; selectivity (%) is the ratio of 3-picoline converted to a specific product to that totally converted × 100, and space velocity is the gaseous volume at 0°C and atmospheric pressure of the total feed per hour per unit volume of the catalyst bed.

2. *Nomenclature*

P_0: Partial pressure of air,
P_p: Partial pressure of 3-picoline,
P_N: Partial pressure of ammonia,
P_H: Partial pressure of water vapour,
T: Reaction temperature,
SV: Space velocity,
V: Linear inlet gas velocity at reactor temperature,
ON: Average oxidation number of vanadium.

3. *Effect of Temperature*

The variation of conversion and yields with temperature is shown in Fig. 1. The yield of nicotinonitrile passes through a maximum of 72% at 400°C. At higher temperatures the yield of the nitrile decreases and at the same time the yields of tar, carbon oxides, and hydrogen cyanide increase. Also, a few percent of pyridine was obtained at higher temperatures.

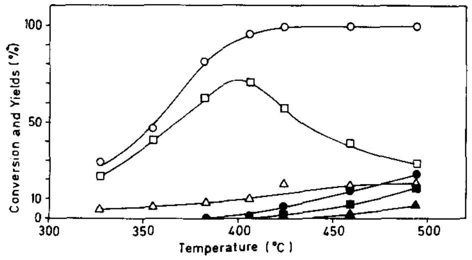

FIG. 1. Conversion and yields as a function of temperature. ○, conversion; □, yield of nicotinonitrile; △, yield of tar; ●, yield of carbon dioxide; ▲, yield of carbon monoxide; and ■, yield of hydrogen cyanide. $P_0/P_p = 213$, $P_N/P_p = 2.9$, $P_H/P_p = 44$, and $SV = 3786\ h^{-1}$.

4. *Effect of Mole Ratio Ammonia/3-Picoline*

Figure 2 shows the influence of the mole ratio ammonia/3-picoline. As can be seen the conversion is constant, but the yield of nicotinonitrile increases from 62 to 81% when the ratio increases from 1.6 to 10. At the same time the yields of tar and carbon dioxide decrease. At mole ratios higher than 10, the product distribution is constant.

5. *Effect of Space Velocity*

The conversion and the yields as a function of the space velocity are presented in Fig. 3. A maximum of 81% in the yield of nicotinonitrile is reached at space velocity 4000 h^{-1}. At a lower space velocity, 2800 h^{-1}, the yield of tar also passes through a maximum. The yields of carbon oxides

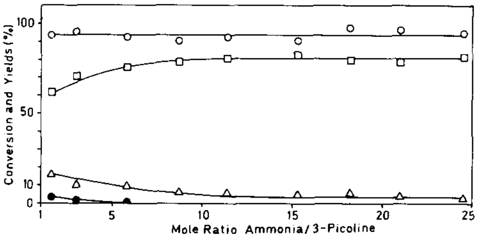

FIG. 2. Conversion and yields as a function of mole ratio ammonia/3-picoline. ○, conversion; □, yield of nicotinonitrile; △, yield of tar; and ●, yield of carbon dioxide. $T = 405°C$, $P_0/P_p = 213$, $P_H/P_p = 58$, and $SV = 3984\ h^{-1}$.

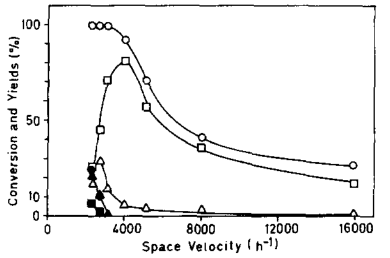

FIG. 3. Conversion and yields as a function of space velocity. ○, conversion; □, yield of nicotinonitrile; △, yield of tar; ●, yield of carbon dioxide; ▲, yield of carbon monoxide; and ■, yield of hydrogen cyanide. $T = 401°C$, $P_0/P_p = 219$, $P_N/P_p = 12$, and $P_H/P_p = 56$.

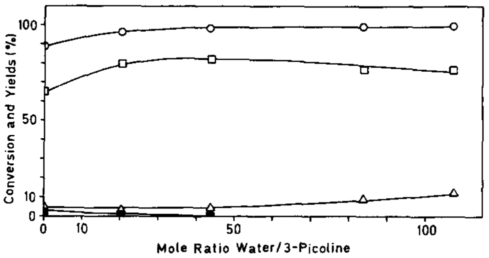

FIG. 5. Conversion and yields as a function of mole ratio water/3-picoline. ○, conversion; □, yield of nicotinonitrile; △, yield of tar; and ■, yield of hydrogen cyanide. $T = 403°C$; $P_0/P_p = 221$; $P_N/P_p = 12$, and $SV = 3870\ h^{-1}$.

increase considerably at lower space velocities. The conversion decreases continuously with increasing space velocity.

6. *Effect of Mole Ratio Air/3-Picoline*

From Fig. 4 it follows that the conversion increases with an increase in the mole ratio air/3-picoline. The yield of nicotinonitrile has a flat maximum of 81% between the mole ratios 200 and 300. At mole ratios above 300 the conversions to high-boiling components (tar) and carbon oxides increase. From the results it can be calculated that the selectivity of nicotinonitrile decreases from about 90% at mole ratio 97 to 67% at mole ratio 328.

7. *Effect of Mole Ratio Water/3-Picoline*

Figure 5 shows the effect of water vapour addition to the reactant stream. It seems that the conversion to nicotinonitrile reaches a maximum at a mole ratio of about 40. At high mole ratios the formation of tar increases. Smaller additions of water vapour cause a greater loss in the material balance than do additions greater than about 30 moles of water per mole 3-picoline. It seems possible that the presence of water vapour improves the condensation of unreacted 3-picoline as well as nicotinonitrile.

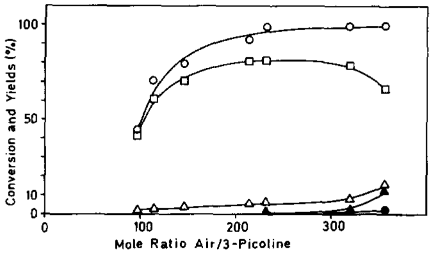

FIG. 4. Conversion and yields as a function of mole ratio air/3-picoline. ○, conversion; □, yield of nicotinonitrile; △, yield of tar; ●, yield of carbon dioxide; and ▲, yield of carbon monoxide. $T = 402°C$, $P_N/P_p = 12$, $P_H/P_p = 57$, and $SV = 4083\ h^{-1}$.

8. *X-Ray Diffraction Investigations of Catalysts*

It is important to investigate which phases are present in the catalysts at steady state conditions, as it has been shown that the formation of lower vanadium oxides affects both the activity and the selectivities (*13*, *14*). It should be noted that the reduced phases are probably located on the outer parts of the catalyst particles. ESCA, which is a more surface-sensitive method than X-ray diffraction, has been used to follow the reduction of a V_2O_5/SnO_2 catalyst in the oxidation of alkylpyridines (*16*). The results showed that the catalyst was reduced, but ESCA does not seem to be a suitable method to determine which lower vanadium oxides are formed. X-Ray diffraction is more suitable for this purpose.

The X-ray investigation of the unused catalyst showed the presence of V_2O_5 and SnO_2. The d values obtained agreed with ASTM data. No reduced phases could be detected. Table 1 presents the steady state

TABLE 1

X-Ray Investigation of Phases Present in Catalysts at Steady State

Expt. No.	Phases (Intensities[a])			
	SnO_2	V_2O_5	V_6O_{13}	V_2O_4
10	vs	vs	—	—
2	vs	vs	—	—
8				
(0–0.7 cm^3)	vs	vs	vw	—
(0.7–2 cm^3)	vs	vs	vw	—
16	vs	vs	vw	—
448	vs	vs	vw	—
449	vs	vs	vw	—
450				
(0–1 cm^3)	vs	vs	vw	vw
(1–2 cm^3)	vs	vs	vw	—

[a] vs: very strong; vw: very weak; —: not detectable.

composition of the first 2 cm^3 of catalysts at the reactor inlet under different experimental conditions. The results show that depending on the experimental parameters, some of the V_2O_5 phase was reduced to lower vanadium oxides. Five or six of the strongest V_6O_{13} lines given by Wilhelmi *et al.* (*17*) could be identified. The *d* values were (110) = 3.51, (003) = 3.32, $(40\bar{1})$ = 2.96, $(31\bar{1})$ = 2.67, $(60\bar{1})$ or (005) = 1.99 and (020) = 1.84 Å. When V_2O_4 (rutile) was present, two or three of the strongest lines according to ASTM data could be identified. No reduction of the SnO_2 phase was detected. A more detailed discussion of the importance of formation of V_6O_{13} and V_2O_4 will be given in the next section.

9. *Effect of Reaction Parameters on the Oxidation State of Vanadium*

The average oxidation number of vanadium was determined by titrimetric methods (*15*). This was 4.88 ± 0.01 for the freshly prepared catalyst, which shows that some V_2O_5 has been reduced during the preparation of the catalyst, even though no reduced phase could be detected by X-ray diffraction analysis. A similar reduction of V_2O_5 in the molten state has been observed (*18*).

Table 2 shows the effect of the reaction parameters on the average oxidation number of vanadium. Unless otherwise mentioned, the values of the oxidation number given are a mean value for the first 2 cm^3 of catalyst at the reactor inlet. The conver-

TABLE 2

Effect of Reaction Parameters on the Average Oxidation Number of Vanadium

Expt. No.	T (°C)	P_0/P_p (P_0 (kPa))	P_N/P_p (P_N (kPa))	P_H/P_p (P_H (kPa))	P_p (kPa)	V(cm/s)	ON	Conversion (%)	Yield (%)	Selectivity (%)
10	355	212 (82.6)	3.0 (1.11)	44 (17.1)	0.385	6.3	4.89	48	41	85
2	406	220 (82.3)	3.0 (1.11)	47 (17.5)	0.375	6.8	4.92	96	70	73
8	459	212 (82.7)	2.8 (1.11)	44 (17.1)	0.385	7.4	4.83 (0–0.7 cm^3) 4.91 (0.7–2 cm^3)	99.6	39	39
16	403	214 (76.1)	11 (3.95)	59 (21.0)	0.355	7.0	4.89	92	81	88
448	401	219 (77.0)	12 (4.26)	56 (19.7)	0.355	5.0	4.88	99.9	45	45
449	399	97 (57.4)	12 (7.09)	61 (36.2)	0.598	7.2	4.87	45	42	93
450	400	219 (95.6)	12 (5.27)	0 (0)	0.436	7.0	4.76 (0–1 cm^3) 4.91 (1–2 cm^3)	89	65	73

sions, yields, and selectivities of nicotinonitrile mentioned were obtained with 8 cm^3 of catalyst.

Experiments 10, 2, and 8 show the influence of increasing temperature. At 406°C, the oxidation number at steady state shows that the catalyst has been oxidized, as compared to the freshly prepared catalyst. On the contrary, at 459°C the first 0.7 cm^3 of the catalyst has a lower oxidation number than the unused catalyst. This reduction is in agreement with the X-ray data presented in Table 1, which shows that V_6O_{13} was formed at 459°C. The degree of reduction of the catalysts at steady state depends on the kinetics of the following two types of reaction

$$S_{ox} + R \rightarrow S_{red} + R\text{–}O, \qquad (1)$$

$$S_{red} + O_2 \rightarrow S_{ox}, \qquad (2)$$

where S_{ox} is a oxidized form of catalyst, S_{red} is a reduced form, R is a reactant consuming oxygen, and R–O is a product containing oxygen. Depending on the rate constants and the activation energies of the above reactions, the fact that the average oxidation number of vanadium varies with the temperature can be understood. This catalytic redox mechanism has also been observed in the oxidation of 2-methyl-5-ethylpyridine on a V_2O_5/TiO_2 catalyst (*19*). The increased oxygen consumption, which leads to the increased reduction of the catalyst, can also be followed in Fig. 1, where it is seen that the formation of carbon oxides strongly increases with the reaction temperature.

If the data in Tables 1 and 2 for Expts. 2 and 16 are compared it seems that an increase in the partial pressure of ammonia causes a small increase in the degree of reduction of the catalyst. Figure 2 shows that the conversion is constant over a wide range of partial pressures of ammonia, and that the yield of nicotinonitrile increases and the yield of tar decreases. The formation of carbon oxides is small. Thus it seems that the increased degree of vanadium in a lower oxidation state cannot be explained by a great increase in the oxygen consumption by the hydrocarbons. However, it is possible that the increased reduction can be caused by the oxidation of ammonia to nitrogen, which is known to occur on vanadium catalysts (*20*). On a V_2O_5/TiO_2 catalyst under the experimental conditions used in Expt. 16, the oxidation of ammonia to nitrogen was found to occur to a small extent (*21*). As can also be seen in Table 2 the selectivity of nicotinonitrile increases with the partial pressure of ammonia. This increase may partly be explained by the increased reduction, as it has been proposed that coherent boundaries between V_2O_5 and V_6O_{13} are especially selective in the ammoxidation of 3-picoline (*13, 14*). The amount of V_6O_{13} is greater in the catalyst being used in Expt. 16 than in the catalyst being used in Expt. 2, which agrees with the X-ray data presented in Table 1.

When different linear gas velocities are used, as has been the case in Expts. 448 and 16, it is seen that a lower velocity hardly affects the degree of reduction at the reactor inlet. This depends upon the fact that in the first parts of the catalyst bed the oxygen consumption is relatively small because nicotinonitrile is the main product. However, it can also be seen that at the reactor outlet (after 8 cm^3 of catalyst) the yield of nicotinonitrile is much lower at a lower gas velocity because of formation of carbon oxides, which are more oxygen-consuming reactions. These reactions, however, take place at lower parts of the catalyst bed and should cause a greater reduction of the catalyst, which cannot be noticed at the inlet.

If a comparison between Expts. 449 and 16 is made, it is seen that in the former the partial pressure of oxygen was lower and the partial pressures of the oxygen consuming components 3-picoline and ammonia were higher. The decrease in the partial pressure of oxygen gives a lower conversion (Table 2), which shows the importance of the partial pressure of oxygen on the reaction rates. In Expt. 449 the degree of reduction compared to Expt. 16 seems to have increased in spite of a lower conversion of 3-picoline. This can depend on an increase in the conversion of ammonia to nitrogen. But more interesting results are obtained if Expts. 10 and 449 are compared.

In both experiments the magnitude of the conversion was the same, but it can be concluded that an increase in the partial pressures of the oxygen-consuming components 3-picoline and ammonia cause a greater reduction of the catalyst and also an increase in the selectivity of nicotinonitrile. If it is assumed, in agreement with the X-ray data in Table 1, that the increase in the degree of reduction leads to an increase in the amount of coherent boundaries between V_2O_5 and V_6O_{13}, this supports earlier results (*13*, *14*) that the presence of both V_2O_5 and V_6O_{13} favourably affects the selectivity of nicotinonitrile.

Experiment 450 in Table 2 was performed without addition of water vapour to the reactant stream. If this experiment is compared with Expt. 16 it is seen that, in spite of the higher partial pressures of oxygen, ammonia, and 3-picoline used in Expt. 450, the total conversion and the selectivity of nicotinonitrile are lower than was the case in Expt. 16. Also, the degree of reduction of the vanadium in the catalyst was greater in the case without water vapour addition, especially in the first few cubic centimeters of the catalyst bed, which had become black. An explanation of these results could be that some of the vanadium is reduced to V_2O_4 (Table 1), which has been found to be inactive in the ammoxidation of 3-picoline (*13*). V_2O_4 has also been found to be inactive in the oxidation of *o*-xylene (*11*) and naphthalene (*22*). This can explain the lower conversion. The lower selectivity of nicotinonitrile can depend on the fact that the amount of coherent boundaries between V_2O_5 and V_6O_{13} decreases as some of the vanadium is reduced to V_2O_4. The V_2O_4 formed has a rutile structure and no coherent interface can occur between V_2O_5 or V_6O_{13} and V_2O_4 (*23*).

10. Investigations of the SnO_2 Phase

X-Ray investigations of the catalysts showed in all cases that the SnO_2 phase had not been reduced, but scanning of the lines in the back-reflection region showed that there was a small shift of the lines. This shift is shown in Fig. 6. The lines at 116.00 and 116.45° for pure SnO_2 are the α_1 and α_2 lines of the (501) plane and those at 130.54 and 131.16° are the α_1 and α_2 lines of the (521) plane. These values agree with data in the literature (*24*). The diffraction pattern of the unused catalyst shows a shift of the lines to 116.15, 116.57, 130.75, and 131.32°. The shift was the same for catalysts being used at different experimental conditions. This shift is caused by a change in the lattice parameters of the SnO_2 phase. This depends on some of the vanadium being dissolved in the SnO_2 phase, probably as V^{4+}. Sachtler *et al.* (*25*) used the ESR technique to show that the SnO_2 lattice is capable of dissolving tetravalent vanadium.

When the average oxidation number of vanadium was determined by the titrimetric methods, the catalysts were dissolved in sulfuric acid. It was observed that only the vanadium oxides were dissolved, and that the SnO_2 phase remained as a solid phase.

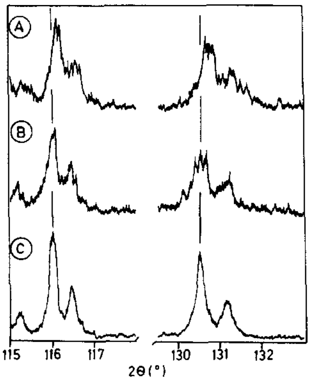

FIG. 6. Diffraction lines of SnO_2 in the back-reflection region. A, unused catalyst; B; mechanical mixture of $V_2O_5:SnO_2 = 1:1.5$; C, SnO_2 treated at 1250°C for 3 h.

After determination of the total amount of vanadium ions in the solution, it was found that there was a constant loss of vanadium. This loss is in agreement with the X-ray observations that some vanadium is dissolved in the SnO_2 phase. If it is assumed that the dissolved vanadium is present as V^{4+} and not dissolved in the sulfuric acid, the loss of vanadium can be calculated to 2.6%. The loss was the same for both freshly prepared catalyst and catalysts which had been used under different experimental conditions. From these results the composition of the SnO_2 phase can be written as $V_{0.03}Sn_{0.97}O_2$. This phase is surrounded by vanadium oxides of the compositions given in Tables 1 and 2.

11. Infrared Investigations of Catalysts

Figure 7 presents the ir spectra of SnO_2, V_2O_5, and the unused V_2O_5/SnO_2 catalyst. It is seen that there is no interference from SnO_2 in the interesting parts of the spectrum of the V_2O_5 phase. The V_2O_5 spectrum has peaks at 1025, 968, and 818 cm^{-1}. The peak at 1025 cm^{-1} is attributed to the stretching vibrations of the short V═O bond (*26–29*). The small peak at 968 cm^{-1} has been ascribed to the $V{=}^{18}O$ stretching bond (*30*). The broad band at 818 cm^{-1} is caused by the stretching vibrations of the longer V–O bonds (*26–28*). If the V_2O_5 spectrum is compared with spectrum C, of the unused catalyst, it can be seen that the peak at 1025 has shifted its position to 1020 cm^{-1}, and that the band at 818 cm^{-1} now appears at 822 cm^{-1}. Yoshida *et al.* (*29*) have observed a shift from 1025 to 1005 cm^{-1} in the V_2O_5/SnO_2 system, when the content of SnO_2 was more than 50 mole%. Also in the spectra of V_2O_5/SnO_2 catalysts obtained by Sachtler *et al.* (*25*) there seems to be a shift, because the peak mentioned appears at 1018 cm^{-1}. This is a lower frequency than that usually ascribed to the stretching vibrations of the V═O bond (*26–29*).

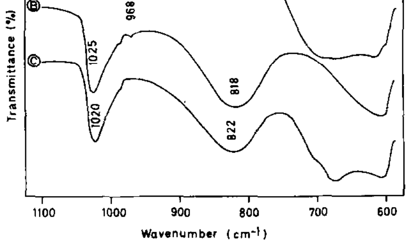

FIG. 7. Infrared spectra of A, SnO_2 treated at 1250°C for 3 h; B, V_2O_5; C, unused catalyst.

The shift of the peaks in the spectra of catalysts being used at different operational conditions agreed with the shifts obtained for the freshly prepared catalyst. No peaks due to lower vanadium oxides could be found. This seems to be in agreement with other observations (*25, 31*) that V_6O_{13}, which was present in the catalysts, has no peaks in the investigated interval of frequency.

The results obtained can be interpreted in terms of bond strengths. The shift of the peak at 1025 to 1020 cm^{-1} shows that the short V═O bonds in the V_2O_5/SnO_2 catalyst are weaker than those in pure V_2O_5, and the shift of the peak at 818 to 822 cm^{-1} is a result of a strengthening of the longer V–O–V bonds.

It has been shown (*18*) that V_2O_5 in the molten state loses oxygen and becomes substoichiometric. In the molten state, V_2O_5 can dissolve various ions. This dissolution affects the exchange of oxygen (*18*). It is possible that Sn^{4+} is dissolved in the substoichiometric V_2O_5 melt during the preparation of the catalysts. During the cooling Sn^{4+} can be incorporated in the V_2O_5 lattice or in a V_6O_{13} lattice. The weakening of the V═O bond can be seen as a consequence of this incorporation.

12. SEM Investigation of Catalyst

The catalyst was examined in a scanning electron microscope to obtain information about the surface structure (Fig. 8). It can be seen that the catalyst has a layer structure similar to that of V_2O_5. This structure is caused by the long $V–O_1$ distance (*32*).

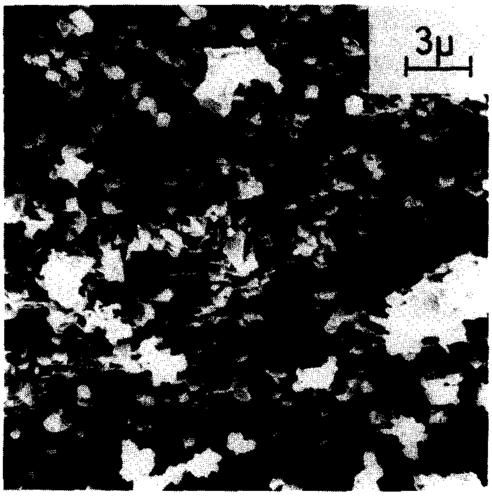

FIG. 8. V_2O_5/SnO_2 catalyst. Magnification 3000×.

Also, V_6O_{13} has a similar structure. This structure can be expected because during the preparation a mixture of V_2O_5 and SnO_2 was heated to 1250°C, where V_2O_5 was present as a melt and SnO_2 as a solid. At 1250°C some oxygen is lost (*18*). During the cooling of the mixture small amounts of lower vanadium oxides, probably V_6O_{13}, can be formed. The result is that the SnO_2 phase with incorporated V^{4+} is surrounded by a mixture of vanadium oxides. ESCA investigations of a V_2O_5/SnO_2 catalyst have shown that the surface concentration of V_2O_5 is higher than the stoichiometric bulk composition (*16*). When the solid catalyst is crushed, the phase boundaries between the different oxides are exposed. The importance of these boundaries was previously discussed.

The composition of the surface was also analyzed by energy dispersive X-ray analysis. The dot images of vanadium and tin are shown in Fig. 9. Vanadium and tin are seen to be highly interspersed, but they are still present as separate phases, which the X-ray diffraction patterns of the catalysts showed.

IV. CONCLUSIONS

The investigation of the influence of the reaction parameters on the yield of nicotinonitrile lead to the conclusion that the following conditions are suitable for an industrial production of nicotinonitrile on a $V_2O_5 : 1.5SnO_2$ catalyst:

temperature: 400°C,
mole ratio ammonia/3-picoline: 12,
mole ratio air/3-picoline: 210,
mole ratio water/3-picoline: 40,
space velocity: 4000 h^{-1}.

With these parameters the yield of nicotinonitrile is 82% and the conversion is 98%.

The studies of the composition of the catalyst revealed that the surface has a dynamic structure, which depends strongly on the partial pressures and the temperature. The effect of the SnO_2 is to weaken the V=O bonds and to increase the exchange of oxygen during the preparation of the catalyst. This leads to the formation of

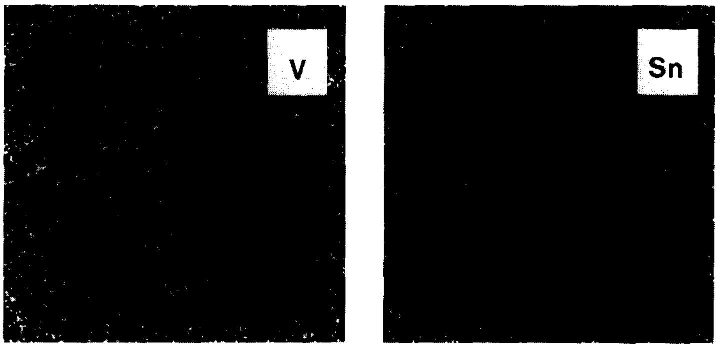

FIG. 9. Energy-dispersive X-ray analysis of vanadium and tin.

TABLE 3

Reaction Rates and Selectivities on some Vanadium Catalysts

Catalyst	r_0 (μmole/m^2 · s)	Selectivity (%)
V_2O_5	0.12[a]	61[a]
V_6O_{13}	0.25[a]	63[a]
V_2O_5 : 1.5SnO_2	1.30	84

[a] Obtained from data by Andersson and Lundin (*13*).

highly selective coherent boundaries between V_2O_5 and V_6O_{13}. The result of these effects is illustrated in Table 3, where the initial reaction rate (r_0) and the selectivity of nicotinonitrile obtained at the experimental conditions mentioned above are given for V_2O_5, V_6O_{13}, and the V_2O_5/SnO_2 catalyst. The high selectivity of the V_2O_5/SnO_2 catalyst is in agreement with observations that catalysts with both V_2O_5 and V_6O_{13}, which was the case in the V_2O_5/SnO_2 catalyst, are more selective than the oxides themselves (*13*, *14*). The high activity of the V_2O_5/SnO_2 catalyst confirm observations that oxygen can be removed easily from the boundary between V_2O_5 and a lower vanadium oxide (*33*).

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REFERENCES

1. British Patent 1 317 064 (1973).
2. Suvorov, B. V., Kagarlitskii, A. D., Afanas'eva, T. A., Lebedeva, O. B., Loiko, A. I., and Serazetdinova, V. A., *Khim. Geterosikl. Soedin.* **4**, 1024 (1969).
3. Japanese Patent 74 127 976 (1973).
4. German Patent 2 517 053 (1975).
5. German Patent 2 435 134 (1975).
6. Järås, S., and Lundin, S. T., *J. Appl. Chem. Biotechnol.* **27**, 499 (1977).
7. Beschke, H., Friedrich, H., Schaefer, H., and Schreyer, G., *Chem. Z.* **9**, 384 (1977).
8. USSR Patent 197 591 (1967).
9. U.S. Patent 3 925 447 (1975).
10. U.S. Patent 3 981 879 (1976).
11. Simard, G. L., Steger, J. F., Arnott, R. J., and Siegel, L. A., *Ind. Eng. Chem.* **47**, 1424 (1955).
12. Shaprinskaya, T. M., Korneichuk, G. P., and Stasevich, V. P., *Kinet. Katal.* **11**, 139 (1970).
13. Andersson, A., and Lundin, S. T., *J. Catal.* **58**, 383 (1979).
14. Andersson, A., and Lundin, S. T., *J. Catal.* **65**, 9 (1980).
15. Nakamura, M., Kawai, K., and Fujiwara, Y., *J. Catal.* **34**, 345 (1974).
16. Andersson, S. L. T., and Järås, S., *J. Catal.* **64**, 51 (1980).
17. Wilhelmi, K.-A., Waltersson, K., and Kihlborg, L., *Acta Chem. Scand.* **25**, 2675 (1971).
18. Desagher, S., Yu, L. T., and Buvet, R., *J. Chim. Phys.* **72**, 390 (1975).
19. Andersson, S. L. T., *J. Chem. Soc. Faraday Trans. I* **75**, 1356 (1979).
20. Il'chenko, N. I., and Golodets, G. I., *J. Catal.* **39**, 57 (1975).
21. Andersson, A., and Lundin, S. T., unpublished results.
22. Nishisaka, S., Takeyama, T., and Kioyama, T., *Shokubai* **8**, 302 (1966).
23. Vejux, A., and Courtine, P., *J. Solid State Chem.* **23**, 93 (1978).
24. "ASTM Powder Diffraction File," 3rd ed., No. 5-467. Joint Committee on Powder Diffraction Standards, Philadelphia, 1974.
25. Sachtler, W. M. H., Dorgelo, G. J. H., Fahrenfort, J., and Voorhoeve, R. J. H., *Recl. Trav. Chim. Pays-Bas* **89**, 460 (1970).
26. Koós, M. Hevesi, I., and Varga, A., *Acta Phys. Chem.* **19**, 29 (1973).
27. Fabbri, G., and Baraldi, P., *Anal. Chem.* **44**, 1325 (1972).
28. Frederickson, L. D., and Hausen, D. M., *Anal. Chem.* **35**, 818 (1963).
29. Yoshida, S., Murakami, T., and Tamara, K., *Bull. Inst. Chem. Res. Kyoto Univ.* **51**, 195 (1973).
30. Kera, Y., Teratani, S., and Hirota, K., *Bull. Chem. Soc. Japan* **40**, 2458 (1967).
31. Théobald, F., *Rev. Roum. Chim.* **23**, 887 (1978).
32. Bachmann, H. G., Ahmed, F. R., and Barnes, W. H., *Z. Kristallogr. Kristallgeometr. Kristallphys. Kristallchem.* **115**, 110 (1961).
33. Colpaert, M. N., Clauws, P., Fiermans, L., and Vennik, J., *Surface Sci.* **36**, 513 (1973).