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Activities of Vanadium Oxides in Ammoxidation of 3-Picoline

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Ammoxidation of 3-picoline to nicotinonitrile was studied on V_2O_5, V_6O_{13}, and V_2O_4 catalysts in a fixed-bed integral reactor. The activity studies showed that V_6O_{13} was the most active and selective catalyst of the pure oxides, with a maximum yield of 76% nicotinonitrile at 365°C. The maximum yield on V_2O_5 catalyst was 34%, and was obtained at a higher temperature, 458°C. V_2O_4 was found to be inactive under the conditions studied. The activities and selectivities of the oxides changed rapidly with reaction time when V_6O_{13} and V_2O_4 were studied. By means of X-ray diffraction and a titrimetric method, the average oxidation number of vanadium was determined, V_6O_{13} was both oxidized and reduced during the reaction; V_2O_4 was oxidized, while a relatively smaller reduction of V_2O_5 could be detected. The experiments showed that the V_6O_{13} catalyst used, with both V_2O_5 and V_6O_{13} phases present, was more selective than any of the pure oxides. This may be explained by active boundary surfaces. Also a mechanism of formation of nicotinonitrile is proposed, which includes a step in which an adsorbed aldehyde complex reacts with ammonia.

INTRODUCTION

Ammoxidation of 3-picoline to nicotinonitrile in the vapor phase is of interest because of the possibility of transforming the nitrile into nicotinic acid by hydrolysis (*1*, *2*) or to nicotinamide by catalytic hydration (*3*, *4*). Both nicotinic acid and its amide are considered to be parts of the vitamin B complex. Nicotinic acid can be made directly by vapor-phase oxidation of 3-picoline (*5*, *6*), but the yields are low compared to the ammoxidation process. A yield of 82% has been reported for the ammoxidation of 3-picoline (*7*). For the hydrolysis and catalytic hydration of the nitrile, yields of 93 to 95 and 100%, respectively, have been reported (*4*, *8*).

V_2O_5 is a widely used catalyst for oxidation reactions involving aromatic compounds, and it can also be used in the ammoxidation of these substances. It is known that the catalyst is reduced in the presence of reducing agents such as hydrocarbons (*9*, *10*) and ammonia (*11*). Both V_2O_4 and V_6O_{13} have been found in catalysts, initially charged as V_2O_5, after being used in the oxidation of *o*-oxylene (*9*). In the oxidation of naphthalene, it has been shown (*12*, *13*) that if the catalyst was charged as V_2O_4 or V_6O_{13}, it was oxidized by the oxygen present. Our experiments have shown that this is also true in the ammoxidation of 3-picoline. Activity studies of different vanadium oxides have not been reported for the ammoxidation of picolines, and those reported for naphthalene (*12–14*) include some discrepancies in the results. This is probably because activities in some cases are referred to a steady state, where the oxide compositions are no longer homogeneous. In the case of ammoxidation it has also been found that the activities of

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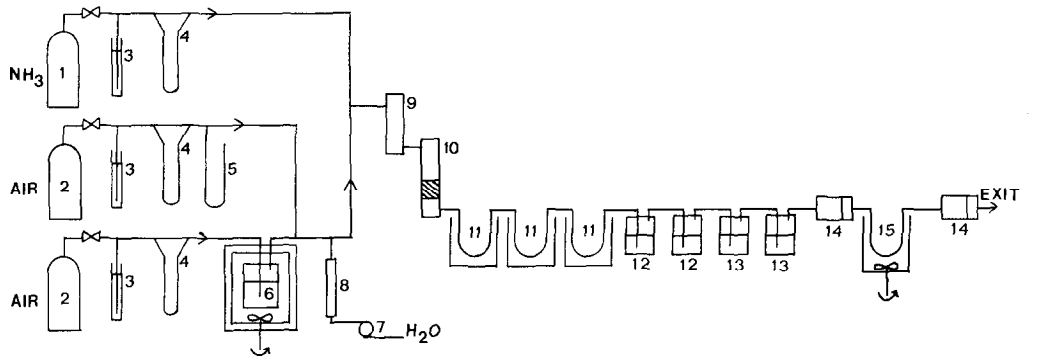
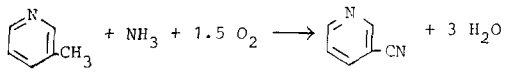


FIG. 1. Apparatus for investigation of ammoxidation of 3-picoline. 1, ammonia cylinder; 2, air cylinder; 3, bleed-off tube; 4, flowmeter; 5, manometer; 6, evaporator; 7, pump; 8, evaporator; 9, preheater; 10, reactor; 11, condenser; 12, water absorber; 13, H_2O_4 absorber; 14, Ascarite–Dehydrite; 15, I_2O_5.

V_2O_5 catalysts are favored by pretreatment with carbon monoxide (*15*).

The aim of this work was to determine the activity of V_2O_5, V_6O_{13}, and V_2O_4 in the ammoxidation of 3-picoline. The overall reaction is expressed by:



METHODS

Apparatus. The apparatus is shown in Fig. 1. Air and ammonia were supplied from pressure cylinders, and the flows were regulated by bleed-off tubes and measured on flowmeters. Some of the air passed through a 3-picoline evaporator. The mixture of air, 3-picoline, ammonia, and evaporated water was transported in heated tubes to a preheater before it entered the reactor. The main part of the nongaseous products and unreacted 3-picoline were condensed in three condensers, and the rest was absorbed in water absorbers. The temperatures in the condensers were −25, −65, and −75°C. Initially formed carbon dioxide was absorbed in tubes filled with Ascarite and Dehydrite. Carbon monoxide formed in the reactor was converted to carbon dioxide in a heated U-tube containing I_2O_5, after which the dioxide formed was absorbed on Ascarite–Dehydrite.

Analysis. The nongaseous products and unreacted 3-picoline were analyzed with a Varian 1200 gas chromatograph (column, 1.5 m; 30% SE-30 on A. W. Chromosorb W). To the column was added 1% TEA to prevent tailing (*16*). The oven temperature was 70°C, the carrier gas was nitrogen (20 ml/min), and 2-picoline was used as an internal standard. Carbon dioxide and carbon monoxide, which had first been converted to carbon dioxide, were analyzed by a gravimetric method using tubes filled with Ascarite and Dehydrite. The inlet content of 3-picoline was determined on a Perkin–Elmer F11 gas chromatograph. The 3-picoline was first totally combusted and then determined on the chromatograph as carbon dioxide (column, 2.3 m; silica gel). The oven temperature was 110°C, and the carrier gas was helium (21 ml/min).

The mean oxidation number of vanadium in the catalyst was determined by titrimetric methods (*17*). X-ray diffraction analysis was carried out by a Philips X-ray diffraction instrument using a PW 1310/01/01 generator and CuKα radiation.

SEM investigations of the catalysts were performed with a Jeol JSM-U3 scanning electron microscope.

Catalyst preparation. The V_2O_5 catalyst was prepared by heating V_2O_5 powder in a quartz crucible in a high temperature oven for 3 hr at 1150°C. The fused catalyst was divided into small particles, and the 14- to 25-mesh (1.41–0.71 mm) fraction was used in the experiments.

The V_2O_4 catalyst could not be prepared in the same way as the V_2O_5 catalyst because of its high melting point. The V_2O_4 catalyst used was prepared by heating appropriate mixtures of V_2O_5 and V_2O_3 powders in static vacuum at 800°C for 18 hr. The catalyst obtained was a powder with a rather homogeneous particle diameter of about 0.037 mm. The V_2O_3 powder used was obtained by reduction of V_2O_5 powder by hydrogen at 450°C for 20 hr.

Some preliminary experiments were carried out before the preparation of the V_6O_{13} catalyst. First we examined the composition of powders, which had been prepared by reduction of V_2O_5 powder in a hydrogen atmosphere at 450°C for different times. If the reduction time was 30 min, the powder obtained, according to X-ray analysis, consisted of V_2O_5 and V_6O_{13}. X-ray analysis showed that after a 1-hr reduction the powder was mainly V_6O_{13}; only a small percentage of V_2O_4 was indicated, and V_2O_3 could not be detected. If the reduction time was 2 hr, V_2O_3 also appeared. The V_6O_{13} catalyst which was used in the experiments was prepared from the previously mentioned V_2O_5 catalyst by reduction in a hydrogen atmosphere for 1 hr at 450°C. The sample was shaken during the preparation to avoid composition gradients caused by different locations in the sample tube. According to the preliminary experiments, the surface of the catalyst particles was now composed of V_6O_{13}.

TABLE 1

Relative Intensities of Phases in Unused Catalysts Obtained from X-ray Diffraction Analysis

Catalyst	Phases		
	V_2O_5	V_6O_{13}	V_2O_4
V_2O_5	10	0	0
V_6O_{13} catalyst surface	0.2	10	0.1
V_2O_4	0.2	0	10

TABLE 2

Average Oxidation Numbers of Vanadium in Unused Catalysts

Catalysts	V oxidation number
V_2O_5	4.98
V_6O_{13} catalyst surface	4.34
V_6O_{13} catalyst bulk	4.50
V_2O_4	4.10

After preparation, the various unused catalysts were examined by X-ray diffraction (Table 1). The surface of the V_6O_{13} catalyst contained only small amounts of V_2O_5 and V_2O_4. The analysis of the V_2O_4 catalyst showed two phases, V_2O_4 and V_2O_5. The investigations were carried out on undivided catalyst particles in a rotating sample holder.

The mean oxidation numbers of vanadium in different unused catalysts were estimated by titrimetric methods (Table 2). The value for the V_2O_4 catalyst was calculated to be 4.1. For the powder obtained after reduction of V_2O_5 powder at 450°C for 1 hr, the value was 4.34, which is in agreement with the value for V_6O_{13}. The average value of the oxidation number for all vanadium in the V_6O_{13} catalyst was found to be 4.5, due to the existence of a composition gradient in the catalyst particles. The phase is V_6O_{13} at the surface and both V_6O_{13} and V_2O_5 in the internal parts of the catalyst.

Materials. Air, ammonia, and hydrogen were commercially available gases and were fed from compressed gas cylinders. The vanadium pentoxide was supplied by Riedel-De Haën AG and was composed of 99.5% V_2O_5.

TABLE 3

Parameters Used in the Experiments

Catalysts	Mole ratio			A/F^a $\left(\frac{cm^2 \cdot sec}{mol}\right)$	T (°C)
	Air / 3-picoline	NH_3 / 3-picoline	H_2O / 3-picoline		
V_2O_5	240	13	60	110	300–516
V_6O_{13}	240	13	60	110	285–490
V_2O_4	240	13	60	110	350–500

[a] A = total surface area of the catalyst in the reactor.

Experimental. The experiments were carried out in an integral reactor. Each experiment was continued at constant temperature for 40 min, divided into four periods of 10 min. During each period the products and unreacted 3-picoline were collected in one sample, which was then analyzed. Each charge of catalyst was only used once.

The purpose of using catalysts in repeated 10-min periods followed by an integral analysis was that if the periods were short enough and repeated, in this case four times, it should be possible to obtain the activities for the pure oxides by extrapolation to zero time, even though the surface composition changed with reaction time.

For the different oxides used as catalysts, the temperature was varied while the other parameters were kept constant (Table 3).

RESULTS

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, and selectivity (%) is the ratio of 3-picoline converted to a specific product and totally converted × 100.

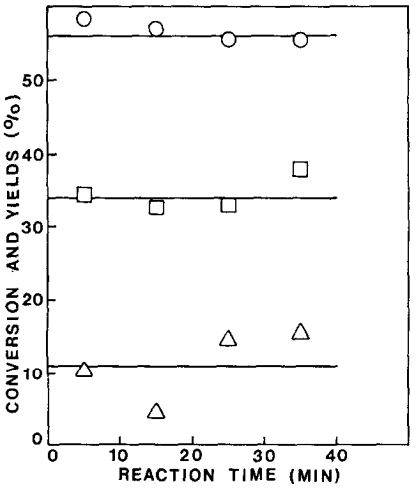


FIG. 2. Conversion and yields on V_2O_5 catalyst at 455°C as a function of reaction time. ○ = conversion of 3-picoline, □ = yield of nicotinonitrile, and △ = yield of tar.

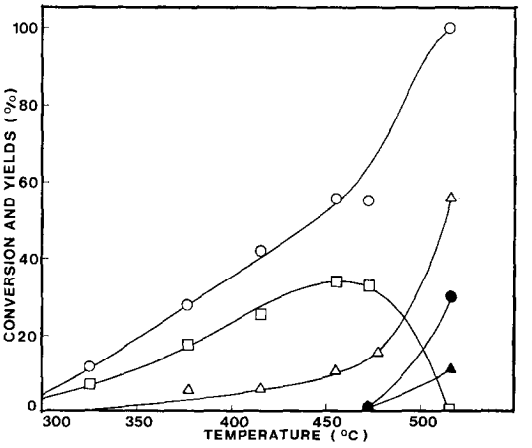


FIG. 3. Conversion and yields on V_2O_5 catalyst as a function of temperature. ○ = conversion, □ = yield of nicotinonitrile, △ = yield of tar, ● = yield of carbon dioxide, and ▲ = yield of carbon monoxide.

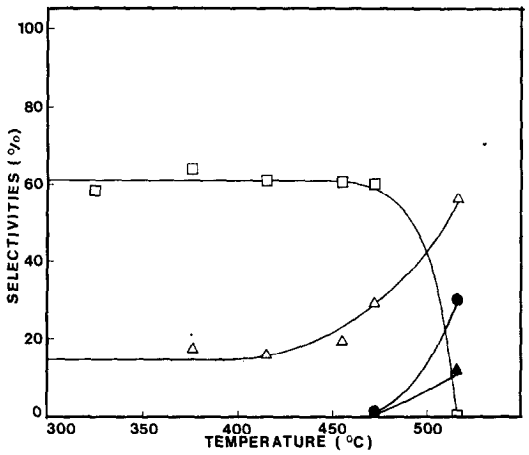


FIG. 4. Selectivities on V_2O_5 catalyst as a function of temperature. □ = selectivity of nicotinonitrile, △ = selectivity of tar, ● = selectivity of carbon dioxide, and ▲ = selectivity of carbon monoxide.

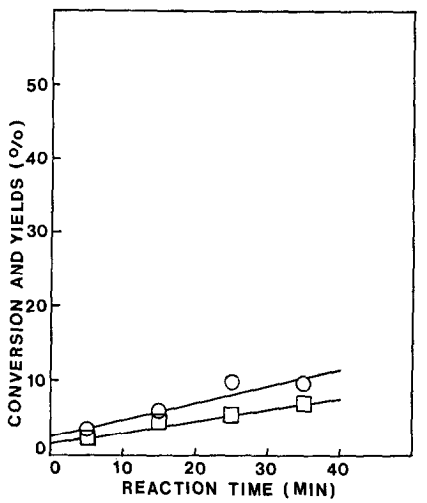


FIG. 5. Conversion and yield on V_2O_4 catalyst at 451°C as a function of reaction time. ○ = conversion of 3-picoline and □ = yield of nicotinonitrile.

Activity of V_2O_5. Figure 2 shows the conversion of 3-picoline and the yields of nicotinonitrile and tar at 455°C as a function of time. Carbon oxides were also formed in the experiments, but their yields are not shown as they were very low. As can be seen, both the conversion and the yields were constant during the time the catalyst was examined. The latter was the case for all the temperatures studied in the interval 300 to 516°C, allowing extrapolation of all results to zero time without difficulty.

In Fig. 3 the conversion and the yields of the V_2O_5 catalyst are shown as a function of the temperature. All the points in the figure were obtained by extrapolation in figures similar to Fig. 2. As can be seen, the conversion increased with temperature. The yield of nicotinonitrile had a maximum

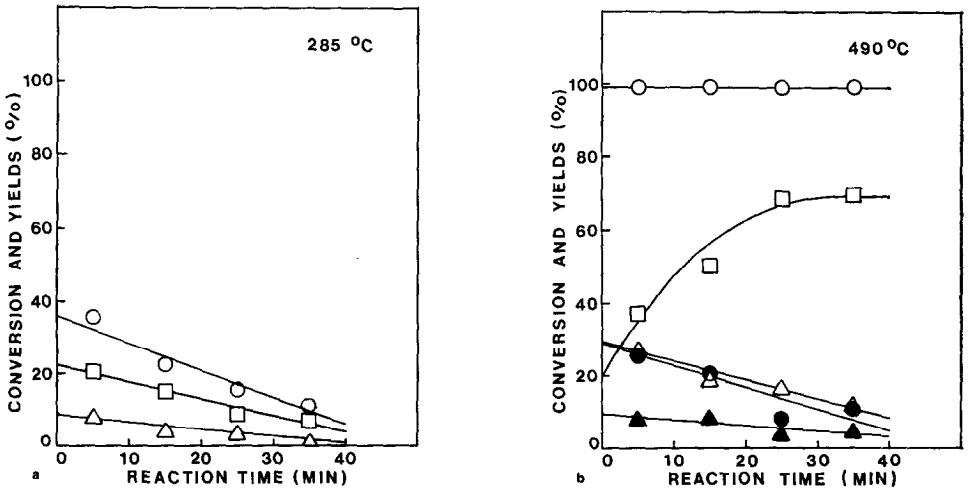


FIG. 6. Conversions and yields on V_6O_{13} catalyst as a function of reaction time at (a) 285 and (b) 490°C. ○ = conversion of 3-picoline, □ = yield of nicotinonitrile, △ = yield of tar, ● = yield of carbon dioxide, and ▲ = yield of carbon monoxide.

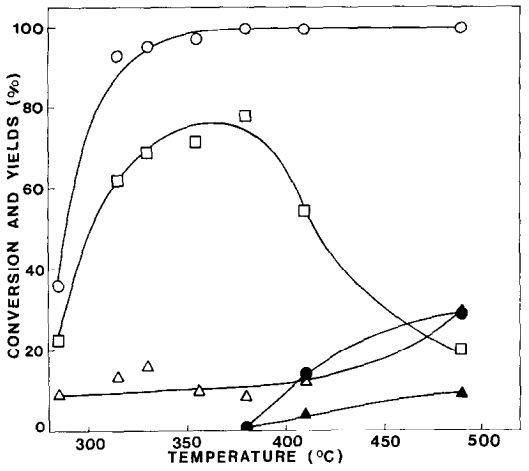


FIG. 7. Conversion and yields on V_6O_{13} catalyst as a function of temperature. ○ = conversion of 3-picoline, □ = yield of nicotinonitrile, △ = yield of tar, ● = yield of carbon dioxide, and ▲ = yield of carbon monoxide.

value 34%, at 458°C. The decrease in the yield of the nitrile at higher temperatures led to an increase in the yields of carbon oxides and tar.

As can be seen in Fig. 4 the selectivity of nicotinonitrile was constant, 61%, between 300 and 460°C. At higher temperatures the nitrile selectivity decreased. Titrimetric analysis of used V_2O_5 catalysts could not detect any change of the mean oxidation number of vanadium compared with unused catalysts. X-ray diffraction studies of used catalysts showed, however, that traces of V_6O_{13} had been formed.

Activity of V_2O_4. The conversion of 3-picoline and the yield of nicotinonitrile over the V_2O_4 catalyst are shown in Fig. 5 as a function time at 451°C. Fig. 5 shows that both the conversion and the yield increased with time.

The conversion and the yield which can be noticed after extrapolation to zero time depended on the V_2O_5 which was originally present in the unused catalyst (Tables 1 and 2). The results show that V_2O_4 was inactive, which can also be seen by comparison between Figs. 3 and 5. Figure 3 shows that the conversion over V_2O_5 was 54% at 451°C, and in Fig. 5 it can be seen, after extrapolation to zero time, that the conversion over the V_2O_4 catalyst at 451°C was 2.5%. This low conversion can be attributed to the small amount of V_2O_5 that was present in the unused catalyst. This was the case for all investigated temperatures between 350 and 500°C.

Used V_2O_4 catalysts were examined by X-ray diffraction. In catalysts used between 350 and 450°C only V_2O_4 and V_2O_5 could be seen in the diffraction patterns. In catalyst used at 500°C V_6O_{13} could also be detected. The ratios of the peaks with the highest intensities for this catalyst were $V_2O_5:V_2O_4 = 0.07$ and $V_6O_{13}:V_2O_4 = 0.15$. Titrimetric analysis showed that the average oxidation number for vanadium was 4.28 for the catalyst used at 510°C. The value for unused catalyst was 4.1.

Activity of V_6O_{13}. Figure 6 shows the conversion and the yields as a function of time for the lowest and the highest temperature in the inverval 285 to 490°C. It can be seen that the conversion and the yields of nitrile and tar decreased with time at 285°C. This was the case for all temperatures investigated up to about 350°C. At

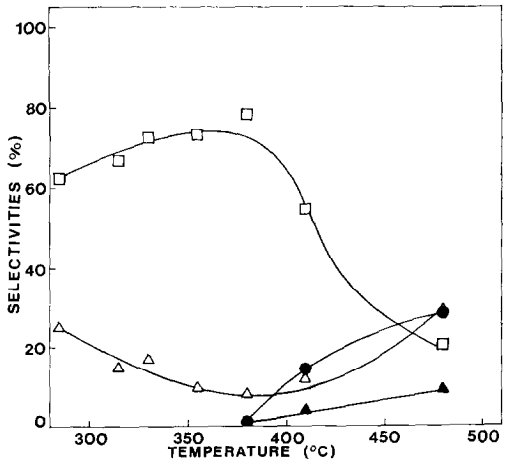


FIG. 8. Selectivities on V_6O_{13} catalyst as a function of temperature. □ = selectivity of nicotinonitrile, △ = selectivity of tar, ● = selectivity of carbon dioxide, and ▲ = selectivity of carbon monoxide.

higher temperatures the conversion still decreased with time, but the yield of the nitrile began to increase. The higher the temperature, the less significant became the decrease of the conversion and the more significant became the increase of the yield of the nitrile.

Through extrapolation of conversions and yields to zero time, values for the unchanged V_6O_{13} catalyst have been obtained (see Fig. 7). The yield of nitrile had a maximum, 76%, at 365°C. The selectivities are shown in Fig. 8. The nitrile reached a maximum selectivity of 74% at about 370°C. The selectivity of tar had a minimum at 390°C, probably because what is called tar was composed of more than one high boiling component, and the product distribution was dependent on the temperature.

After being used for 40 min, the X-ray diffraction patterns of the catalyst were registered, showing the presence of V_6O_{13} and V_2O_5. This was also the case when unused catalyst was analyzed. In the analysis of used catalysts very small amounts of V_2O_4 could also be noticed.

The average oxidation number of vanadium was also studied. The oxidation number had increased, especially after the catalysts had been used at higher temperatures. At 448°C the oxidation number had increased from 4.5 to 4.6 at the reactor inlet and from 4.5 to 4.7 at the outlet. At lower temperatures the increase was less.

SEM studies of catalysts. Both unused catalysts and those used in the ammoxidation of 3-picoline were examined. Figure 9a shows unused and Fig. 9b used V_2O_5 catalyst at a magnification of 3000×. It is possible to distinguish the layer structure of V_2O_5 caused by the long $V–O_1$ distance, which is 2.785 Å (*18*). No differences between used and unused catalyst could be noticed, as expected from our observations that the conversion and the yields did not change with time.

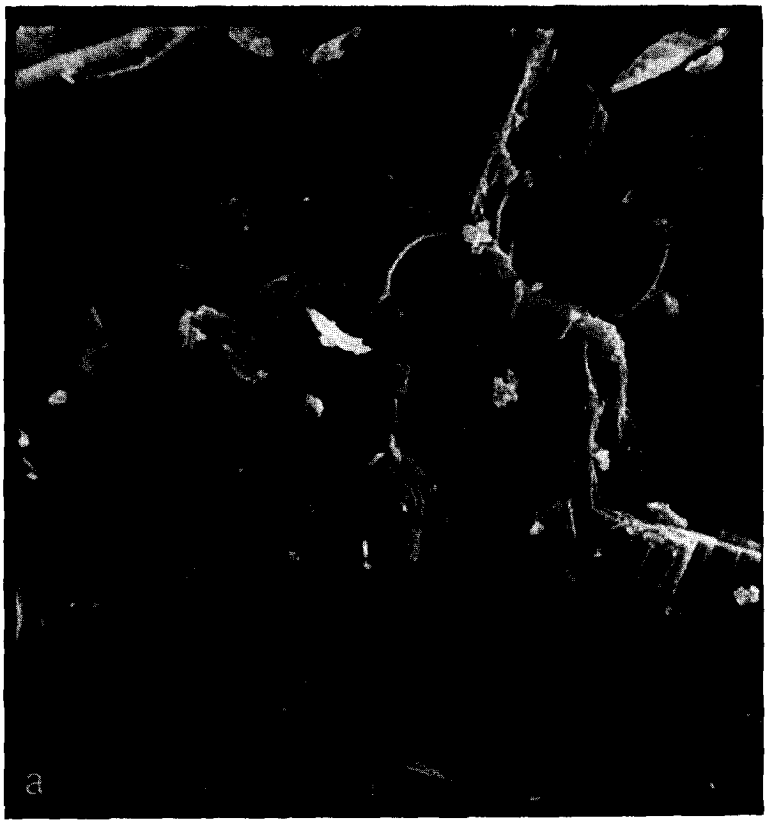
Figures 10a and b show unused and used V_2O_4 catalyst, 1000×. The rather homogeneous particle diameter can be seen on the pictures. From Fig. 10b it is apparent that some recrystallization had occurred on the surface during the use of the catalyst. This change of the structure is in agreement with the results, which showed that the catalyst was oxidized to higher oxides during the ammoxidation process.

Unused and used V_6O_{13} catalysts are shown in Figs. 11a and b, 1000×. We cannot see any striking differences between the two catalysts, but a layer structure similar to that in the V_2O_5 catalysts can be distinguished. It is also possible to see some nailing on the surface, which was not the case in the V_2O_5 catalysts.

DISCUSSION

The time dependence of conversions and yields. The results concerning the V_2O_5 catalyst showed that both the conversion and the yields were constant during the time the catalyst was used (Fig. 2). This indicates that V_2O_5 was the dominant phase during the experiments. This conclusion is supported by three other facts. First, the used and unused catalysts had the same color. If the catalyst had been permanently reduced to any great extent, the color would have changed from reddish brown to a darker color. Furthermore, the titrimetric method used to estimate the vanadium average oxidation number did not detect any change of the catalyst. Finally the X-ray diffraction analysis of used catalysts only showed traces of a newly formed phase, V_6O_{13}. The amount of V_6O_{13} formed was apparently too small to have a significant effect on conversions and yields.

In Fig. 5 it can be seen that the conversion and the yield of nicotinonitrile increased with time when V_2O_4 catalyst was used. As previously mentioned, titrimetric and X-ray investigations of used V_2O_4 showed that the catalyst was oxidized to



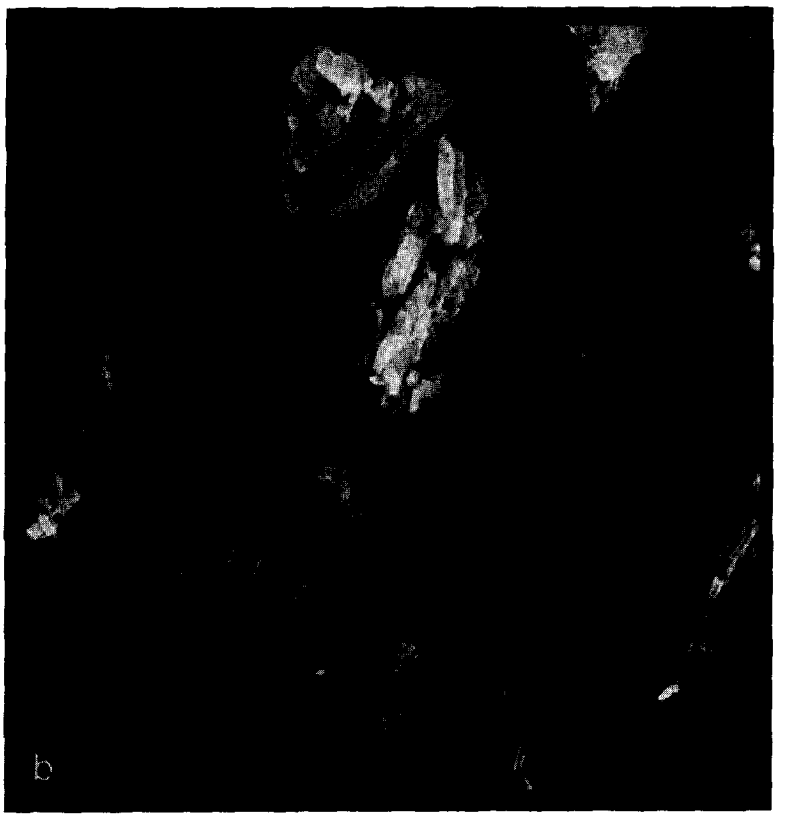


FIG. 9. V_2O_5 catalyst: a, unused; b, used catalyst. 3000×.

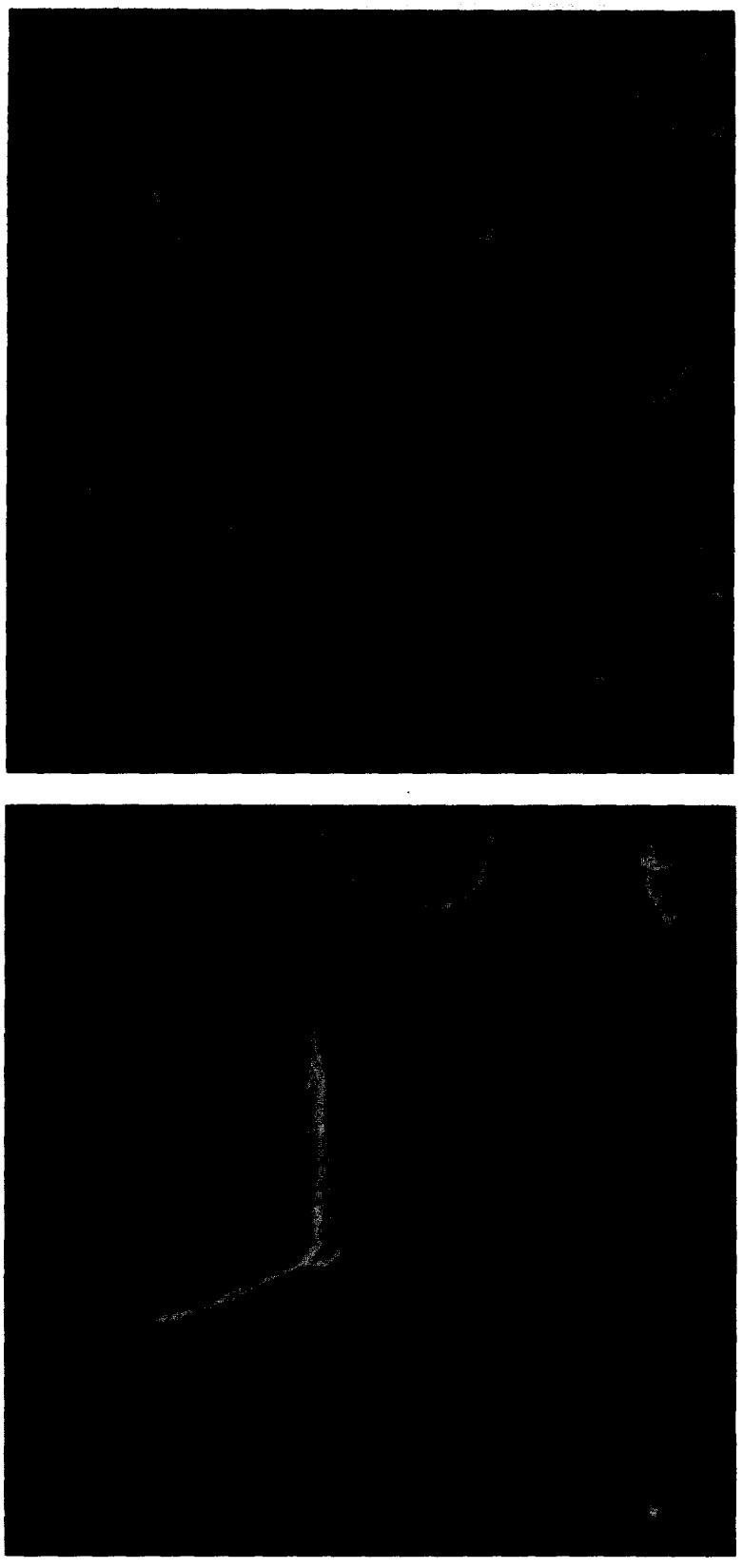


FIG. 10. V_2O_4 catalyst: a, unused; b, used catalyst. 1000×.

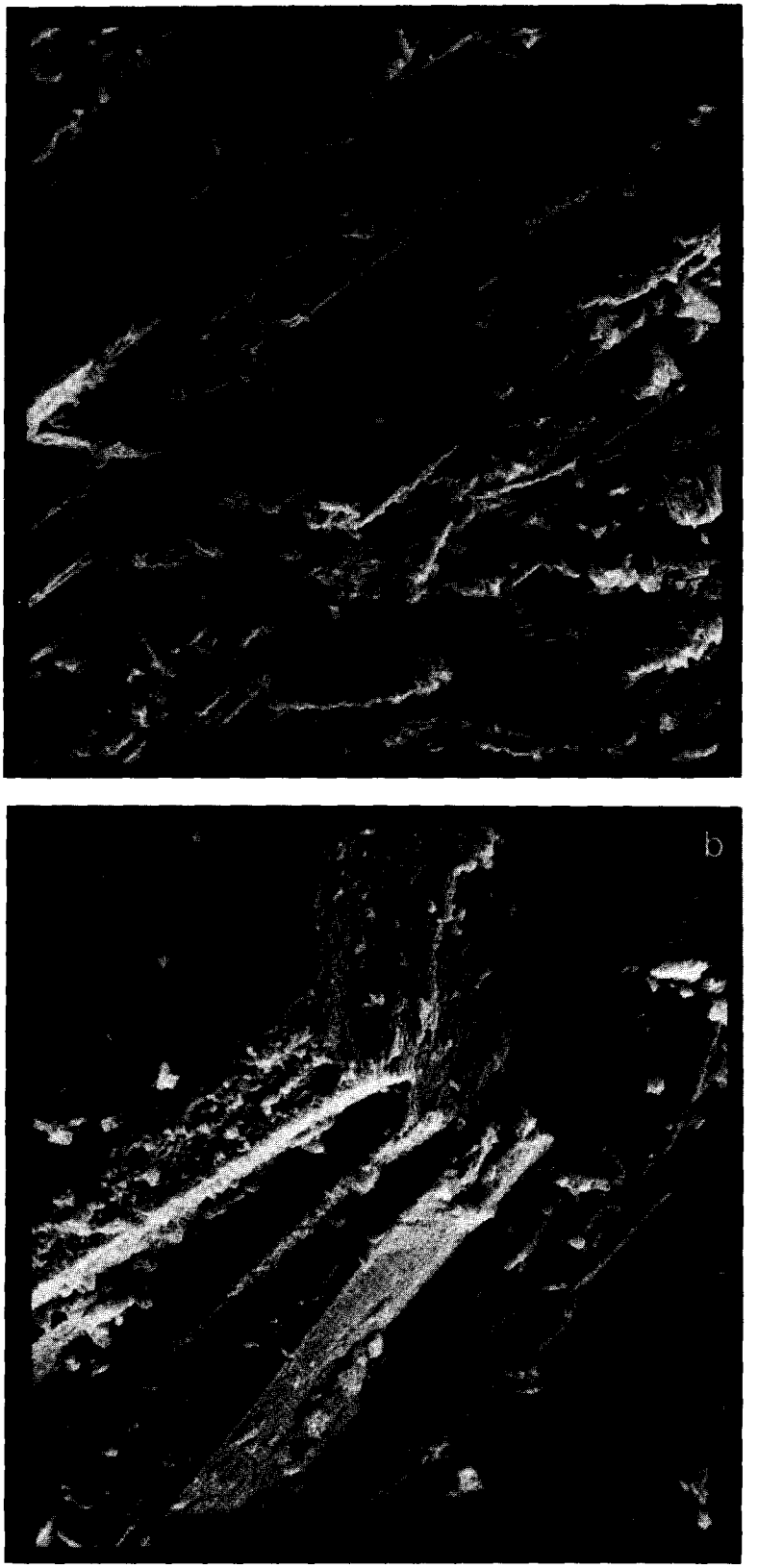


FIG. 11. V_6O_{13} catalyst: a, unused; b, used catalyst. 1000×.

V_2O_5 and V_6O_{13} during the reaction time. The appearance of higher oxides must be the explanation for the increasing conversion and yield. As is obvious from Figs. 3 and 7, both V_2O_5 and V_6O_{13} are active and selective. It was also found that V_2O_4 is inactive. The small initial conversion and yield seen in Fig. 5 can be attributed to the amount of V_2O_5 which was present in freshly prepared V_2O_4 catalyst. The selectivity at zero time calculated from Fig. 5 is 62%, which is in agreement with the selectivity achieved for pure V_2O_5 at conversions below 60% (Fig. 4). After

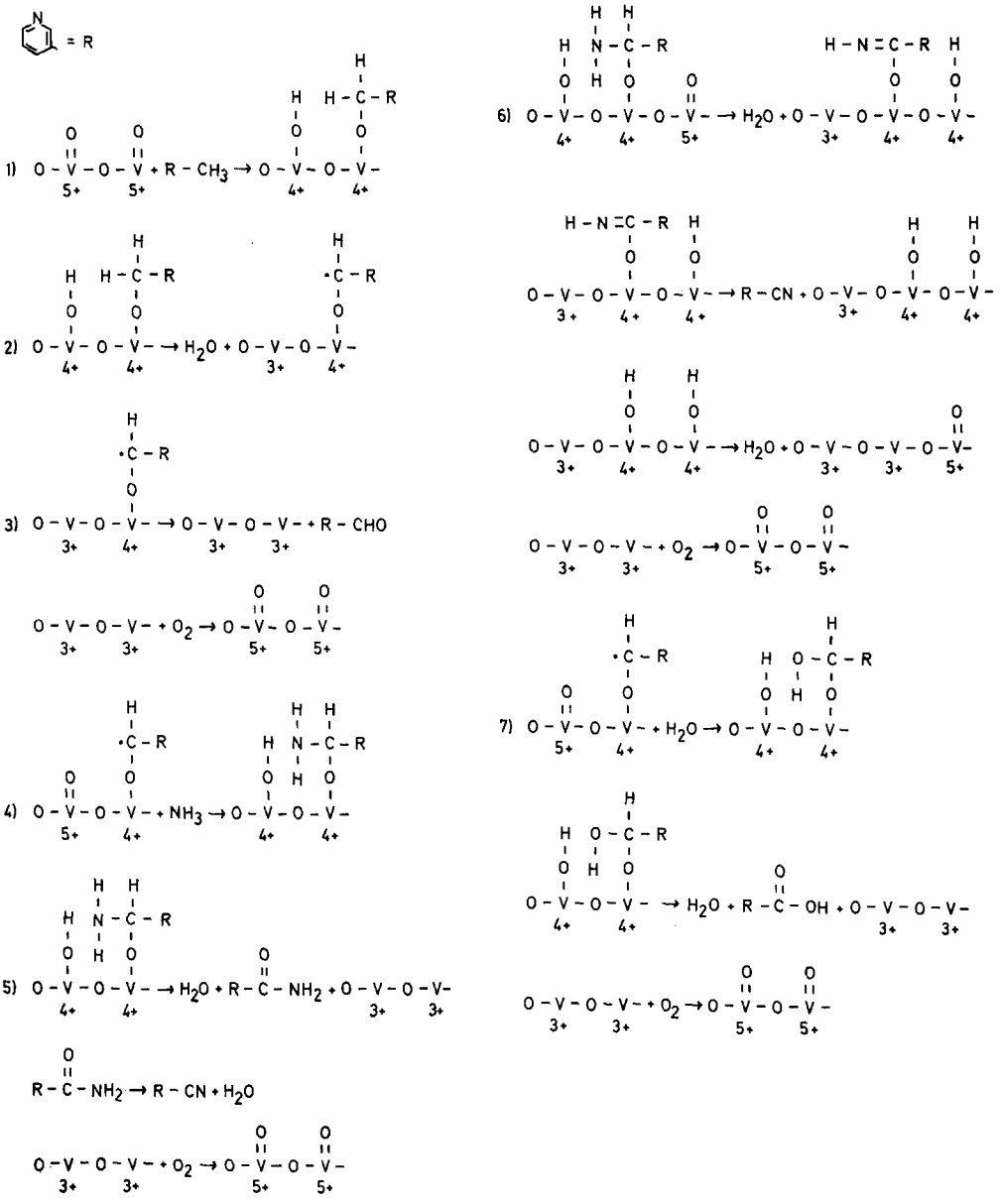


FIG. 12. Mechanism for ammoxidation of 3-picoline over V_2O_5 catalyst.

40 min the selectivity had increased somewhat (to 66%), which could depend on the increasing amount of V_6O_{13}.

In the case of the V_6O_{13} catalyst, the conversion decreased with the reaction time. This decrease was greater at low temperatures than at high temperatures. The selectivity as a function of reaction time was practically constant at 285°C, but it increased with the reaction time at higher temperatures. The increase became more apparent the higher the temperature. From X-ray investigations we know that during the reaction V_6O_{13} was both oxidized to V_2O_5 and to some extent also reduced to V_2O_4. This may explain the results at 285°C (Fig. 6a), as we found that both V_2O_5 and V_2O_4 have lower activity than V_6O_{13}. As can be calculated from Fig. 6a the selectivity of the nitrile was about 60% throughout the experiment. This could be expected as the selectivities of V_6O_{13} and V_2O_5 are about the same (60%) at this temperature (Figs. 4 and 8).

At higher temperatures, in the interval 300 to 400°C, where the selectivity of the V_2O_5 phase for the nitrile is lower than that of the V_6O_{13} phase (Figs. 4 and 8), a decrease in both activity and selectivity with the reaction time would be expected if the phase contributions were independent. At temperatures higher than 400°C, the selectivity of the V_2O_5 phase is higher than that of the V_6O_{13} phase, so at these temperatures a decrease of the activity and an increase of the selectivity would be expected. The results showed that the activity decreased, but the decrease was not so pronounced at the highest temperature. The measured increase of the selectivity for the nitrile is, however, remarkable. At 380°C, where the formation of carbon oxides was negligible, the selectivity increased from 79 to 93% during 40 min. At 490°C, where in the beginning the oxidation to carbon oxides was rather important, the selectivity increased with the reaction time from 21 to 70% (Fig. 6b). Thus the results at temperatures above 285°C cannot be explained only by independent phase contributions from the V_6O_{13}, V_2O_5, and V_2O_4 phases. An explanation of the results may be that the formation of new phases creates phase boundaries and that the extent of these boundaries increases with the temperature.

If these boundaries are active and more selective than the pure oxides, this will be in agreement with the results at high temperatures. As mentioned above, V_2O_5 was also formed at 285°C, and as is obvious from Fig. 6a it had a great influence on the change of the activity. However, at 285°C the results could be explained by independent phase contributions of the oxides regardless of phase boundaries. The reason for this may be that at low temperatures the phase boundary area is not so large because the V_2O_5 phase is mainly situated on the outer parts of the catalyst particles and the V_6O_{13} phase in the inner parts, while at high temperatures the oxygen mobility in the catalyst increases, which leads to a more even distribution between V_2O_5 and V_6O_{13} giving greater phase boundary area. This explanation is in agreement with the results obtained by Dyrek and Serwicka (*19*). They showed that reduced V_2O_5 was oxidized only in the surface layer at temperatures below 200°C. At 300°C the oxidation occurred also in the bulk. Our results propose a surface layer oxidation to a somewhat higher temperature (285°C), which can depend on the fact that during the ammoxidation both reduction and oxidation of the catalyst occur simultaneously.

Possible mechanism. When 3-picoline was ammoxidized the following main products were found: nicotinonitrile, tar, carbon dioxide, and carbon monoxide. Also small amounts of nicotinamide, pyridine, and nicotinic acid could be observed. We also found indications that the catalyst was both reduced and reoxidized during the reactions. These observations may be ex-

plained by the mechanism proposed in Fig. 12. In the first step is probably an abstraction of hydrogen (*20–22*) followed by adsorption of 3-picoline on the vanadium surface, which leads to a transformation of the $(V{=}O)^{3+}$ surface group to a $(V{-}O)^{2+}$ group. In step 2 a hydrogen atom on the methyl group reacts with a neighboring –OH group with formation of water. If there is no ammonia present the surface compound can be desorbed (step 3), which leads to formation of the aldehyde. But as we have found no aldehyde in our product analysis, it is possible that ammonia can react with the aldehyde complex before it has been desorbed (step 4). Step 5 suggests a hydrogen rearrangement causing formation of water and nicotinamide. The resulting amide then dehydrates to the nitrile and the catalyst surface is reoxidized. It would also be possible for the nitrile to be formed directly according to step 6. It is known (*20*) that water vapor among the reactants increases the selectivity for partial oxidation of organic compounds in the gas phase over oxide catalysts. Therefore it is possible that water, formed or supplied, is of importance in acid formation (step 7). Investigations (*21*) have shown that water vapor had no influence on the yield of nitrile in the ammoxidation of 3-picoline. This supports our opinion that water does not take part in the formation of nicotinonitrile. As ammonia has a greater nucleophilic character than water, this explains why the yield of the nitrile was high and the yield of the acid was low in spite of the fact that we had supplied water vapor to the reactants to prevent local overheating of the catalyst.

The small amounts of carbon oxides, which we obtained at lower temperatures, can depend on adsorption of 3-picoline via the pyridine ring. The pyridine which was formed probably arose from destruction of the aldehehyde complex formed in step 2. This destruction increases with temperature, which leads to an increase in the amount of carbon oxides formed from a ring opening of pyridine, which can occur after it has been adsorbed via the ring.

In the ammoxidation reaction high boiling compounds (tar) were also formed. This tar could be a polymer of the intermediate imine in step 6.

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