JOURNAL OF CATALYSIS **100**, 414–428 (1986)

A Combined Transient Response and Temperature-Programmed Desorption Technique Used in the Ammoxidation of 3-Picoline over a V_2O_5 Catalyst

ARNE ANDERSSON

Department of Chemical Technology, Chemical Center, Lund Institute of Technology,
P.O. Box 124, S-221 00 Lund, Sweden

Received May 2, 1985; revised January 23, 1986

The oxidation and ammoxidation of 3-picoline have been studied over a V_2O_5 catalyst using temperature-programmed desorption combined with studies of the transient responses to pulses of one of the reactants. The results obtained are related to the surface structure of the catalyst, deduced on the basis of metal–oxygen bond strength values. The mechanistic features that emerge are as follows. Some 3-picoline is adsorbed at partially reduced vanadium ions via the nitrogen atom. This picoline can either desorb unconverted or it can react with weakly bonded oxygen to afford both carbon oxides and 3-pyridinecarbaldehyde. It seems that the aldehyde formed can react with NH_3 to give nicotinamide. Some 3-picoline is immediately adsorbed in the form of partial degradation products. These products are further transformed into carbon oxides upon increasing the temperature. After abstraction of a methyl hydrogen atom 3-picoline becomes attached to a vanadyl oxygen species and then reacts with NH_3 to yield nicotinonitrile, although a dealkylation to produce pyridine also can occur. There are three different sites for the formation of nitrile. Most of the nitrile is formed in a reaction between chemisorbed 3-picoline and weakly adsorbed or gaseous NH_3. However, adsorbed NH_3 clearly takes part in the formation of nitrile at two other sites. In one case NH_3 is proposed to be adsorbed at a vanadyl oxygen vacancy. At the other site NH_3 is even more strongly adsorbed, probably in the form of either $—NH_2$ or $=NH$ groups, and there is a deficiency of oxygen associated with this site.

INTRODUCTION

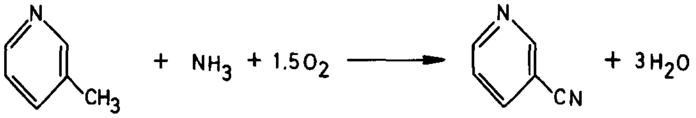
The technique of temperature-programmed desorption (TPD) accompanied by a chemical reaction has gained increased interest in recent years. It has been used to study the oxidation of various compounds on oxide surfaces (*1–9*).

The technique has recently been reviewed (*10*), and special emphasis has been placed on the theoretical approach in order to calculate kinetic and thermodynamic constants. However, one should be extremely careful using TPD experiments for such calculations. The effects of surface coverage and readsorption on curve shapes (*11*), as well as the effects of surface site energy distributions (*12*) and of mass transfer (*13, 14*) must be considered properly. In spite of these quantitative limitations, TPD investigations often give a sound base for qualitative conclusions.

Transient methods have frequently been used in the studies of catalytic processes (*15, 16*). The results obtained are usually so rich in data that they can give an essential contribution to the understanding of the reaction mechanisms.

In the present work the ammoxidation of 3-picoline to nicotinonitrile over a V_2O_5 catalyst was studied. This three-reactant system was investigated by a combined technique using TPD along with studies of the transient responses to pulses of one of the reactants. The pulses were injected both while keeping the temperature constant with time, and during a linear increase of the temperature. This technique was developed in a previous investigation of the ammoxidation of 3-picoline over a V_6O_{13}–V_2O_4

0021-9517/86 $3.00



catalyst, and was found to give an increased insight into the basic steps of the catalytic reactions (*17*). Therefore, this combined technique was used in this more extensive study of the ammoxidation on a V_2O_5 catalyst.

METHODS

Catalyst preparation. The catalyst was prepared by decomposition of NH_4VO_3 (Merck, p.A.) in a stream of air for 2 h at 400°C. According to the X-ray diffraction pattern, the catalyst was entirely composed of V_2O_5. The BET surface area of the catalyst was 10.9 m^2/g. Particles having a diameter between 0.1 and 0.4 mm were used in the experiments.

Experimental. One hundred milligrams of the V_2O_5 catalyst was packed in a stainless-steel tube with an internal diameter of 2 mm. The tube was placed in a temperature-programmable Pye 104 chromatographic oven, which via a heated capillary tube, was connected to a Finnigan 4021 automated quadrupole mass spectrometer system. Pulses of air and ammonia were injected into the catalyst bed by the use of a Valco 6-port valve. The volume of the sample loop was 1.01 cm^3. 3-Picoline was injected by a microliter syringe.

In a standard experiment the catalyst sample was first heated at 250°C in a stream of He (20 ml/min) for 30 min. Then pulses of 3-picoline (0.05 μl each) were injected at the same temperature until the surface was saturated. After a further 30 min in a stream of He, the temperature was raised linearly at 20°C/min from 250 to 500°C. The column was then kept at the final temperature for 10 min. All mass numbers from 20 to 250 were followed continuously. After this first standard TPD experiment the same catalyst sample could be used in additional experiments. In this case the catalyst bed was either immediately cooled down to 250°C, or first reoxidized by 10 pulses of air at 500°C before the cooling was started. After 15 min at 250°C, 3-picoline was readsorbed. The column was then allowed to stand for a further 30 min while maintaining a He stream before a second TPD was performed. Instead of carrying out the reoxidation at 500°C, the sample could be subjected to an air treatment at 250°C. Furthermore, transient responses to injections of either air or NH_3 both at 250°C and during TPD were registered.

Identification of desorption products was made using the instrument library and computer. The mass numbers selected to visualize the desorption curves of carbon monoxide, carbon dioxide, pyridine, 3-picoline, nicotinonitrile, 3-pyridinecarbaldehyde, and nicotinamide were 28, 44, 79, 93, 104, 107, and 122, respectively.

RESULTS AND DISCUSSION

1. The V_2O_5 Surface and the Adsorption of 3-Picoline

A theoretical model, the so-called oxidized surface state model of vanadium oxides, has previously been presented (*18*). In this model the bond strength concept of Pauling (*19*) has been extended to the treatment of vanadium oxide surfaces. The bond strength value, *s*, of the metal–oxygen bond was calculated using an empirical formula (*20*), $\log s = (1.791\text{-}d)/0.722$, where d is the vanadium–oxygen bond length. Ziółkowski has also used bond strength calculations to propose a model of active sites in the oxidation of propylene and *o*-xylene on brannerite-type vanadates (*21–23*). It has been proposed that the bond strength values are proportional to the bond energy of the metal–oxygen bond (*18, 21, 23*).

TABLE 1

Bond Distances and Bond Strengths of V_2O_5

	d (Å)	s (e^-)
1 × V—O(1)	2.785	0.04
1 × V=O(1)	1.585	1.93
2 × V—O(2)	1.878	0.76
1 × V—O(2)	2.021	0.48
1 × V—O(3)	1.780	1.04

Therefore, oxygen positions characterized by a relatively low bond strength value can be expected to be vacant, at least at high temperatures. It also seems reasonable to suggest that the bond strength value, or in principle the formal valence, can be used to identify electrophilic oxygen species. Moderate bond strength values could then be anticipated to be representative for bonds between vanadium and electrophilic oxygen. It follows that the bonds between vanadium and lattice oxygen (O^{2-}) must have high bond strength values.

The structure of V_2O_5 can be visualized to be built up from VO_6 octahedra. The vanadium–oxygen bond distances (*24*) are collected in Table 1, as are the bond strengths obtained using the empirical formula given above. From the surface model it follows that the O(1) species with bond strengths of 0.04 are weakly bonded. Thus, naked vanadium ions can be exposed at an adsorption temperature of 250°C. The O(2) and O(3) positions which have bond strength values between 0.48 and 1.04 are probably only partially occupied at this temperature. The bond strength values indicate that these oxygen species are electrophilic. Such oxygen species have been demonstrated to exist at temperatures up to about 370°C on vanadium oxides (*17, 25*). At higher temperatures these positions are probably empty. However, electrophilic oxygen species with very short lifetimes can still exist as a step in the oxygen transfer from the bulk to the gas phase.

When considering the planes parallel to the three crystallographic axes, it can be concluded after looking at Fig. 1 that the (010) plane of V_2O_5 exposes both V=O groups and V^{5+} ions. The (001) plane is covered with O(2) positions having bond strength values of 0.76. Looking at the (100) plane we find O(2) and O(3) positions with bond strengths of 0.48 and 1.04, respectively. These positions are localized at separate sheets.

In a previous work (*26*) on the adsorption of benzene, toluene, pyridine, and 3-picoline on V_2O_5 it was found that the amounts adsorbed at 250°C increased in the order benzene ≪ toluene < pyridine < 3-picoline. Furthermore, the relation T + P = MP was found to be valid, where T, P, and MP are the surface concentrations of toluene, pyridine, and picoline, respectively. It was argued that 3-picoline was adsorbed at the

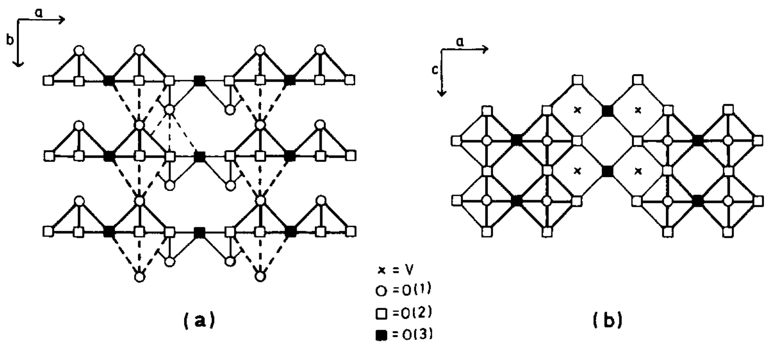


FIG. 1. Schematic presentation of the V_2O_5 structure. (a) (001) plane and (b) (010) plane.

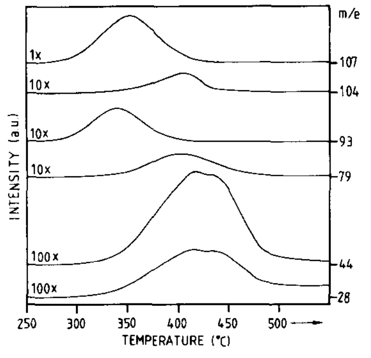


FIG. 2. TPD after air treatment at 500°C followed by adsorption of 3-picoline at 250°C (Expt 3). The linear heating rate was 20°C/min from 250 to 500°C.

surface mainly in two principally different ways. It could either be adsorbed via attachment of the nitrogen atom to partially reduced vanadium ions, or the methyl carbon atom could be attached to an oxygen species after an abstraction of hydrogen. By combining the results on V_2O_5 with those on V_6O_{13}, it was demonstrated that the amount that was adsorbed via the methyl carbon atom could be related to the concentration of vanadyl oxygen species. A consequence of the validity of the above equation was that the two types of adsorption must have occurred at different planes. These conclusions could be drawn since the adsorbed amounts of toluene, pyridine, and 3-picoline were of magnitudes which correspond to adsorption on regular planes, and not on surface irregularities, defects, corners, or edges. Thus, the naked V^{5+} ions on the (010) plane could not be involved in the adsorption of 3-picoline at the nitrogen atom. This was in agreement with the results of quantum chemical calculations, showing that the vanadium ions must be partially reduced for this type of adsorption to occur (*27*).

Electrophilic oxygen species have a high activity in catalytic reactions and are the main oxidizing species in the total oxidation of simple molecules (*28*). By consideration of bond strength values it was argued that the (100) and (001) planes of V_2O_5 accommodate such species. Indeed, the nonselective reactions in both the oxidation of *o*-xylene (*29*) and in the ammoxidation of 3-picoline (*30*) have been found to take place at such planes. In both cases the selective reaction was found to be related to the frequency of the (010) plane. Therefore, it seems reasonable to refer to the differing properties of the (100), (010), and (001) planes when discussing the results in the present work.

2. *Pretreatment Effects on TPD Curves*

Successive TPD experiments were carried out using the same catalyst sample. In all of the experiments the adsorption temperature was 250°C. The first TPD experiment was performed after degassing in He for 30 min both before and after adsorption of 3-picoline. Then TPD Experiment 2 was performed after the catalyst sample had been cooled down to 250°C and 3-picoline had been readsorbed. After Experiment 2, the catalyst sample was reoxidized at 500°C by passing 10 pulses of air through the bed. Then Experiment 3 was carried out after another readsorption at 250°C. This experiment was followed by a direct cooling to 250°C, a new readsorption and then TPD Experiment 4. The shape of the TPD curves and the positions of the curve maxima in the four experiments did not demonstrate any formation of new phases.

Typical TPD curves from Experiment 3 are shown in Fig. 2. It can be concluded that 3-pyridinecarbaldehyde (*m/e* = 107), nicotinonitrile (*m/e* = 104), unreacted 3-picoline (*m/e* = 93), pyridine (*m/e* = 79), CO_2 (*m/e* = 44), and CO (*m/e* = 28) were present. It is interesting to find the formation of nicotinonitrile even though no NH_3 had been injected. The reason must be that NH_3 had been adsorbed during the preparation of the catalyst, which was prepared by decomposing NH_4VO_3.

Relative mass number intensities as a function of the Experiment number are shown in Fig. 3. It was found that some of

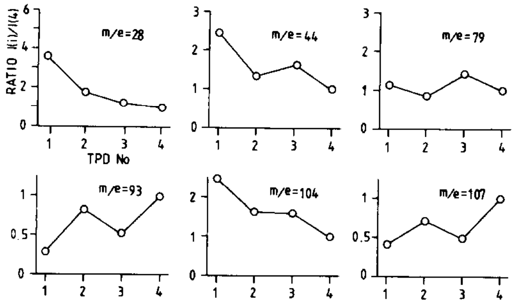


FIG. 3. Dependence of relative mass number intensity on the experiment number in successive TPD experiments. Expt 1: TPD after adsorption at 250°C. Expt 2: after Expt 1, readsorption at 250°C. Expt 3: after Expt 2, reoxidation at 500°C and then readsorption at 250°C. Expt 4: after Expt 3, readsorption at 250°C.

the picoline (m/e = 93) desorbed unconverted. This form of adsorbed picoline was probably bonded via the nitrogen atom to the type of cations (*17, 26*) which could be present at the (100) and (001) planes. Figure 3 shows that the amount which desorbed in unconverted form was relatively low in both the case of the freshly prepared catalyst and after reoxidation at 500°C. This was caused by the fact that the concentration of vacancies was low in these two cases. In addition to vacancies, the (100) and (001) planes can probably accommodate O^- species. These are almost completely absent at such a high temperature as was used in the reoxidation process (*17, 25, 28, 31*). However, the reoxidation at 500°C diminished the concentration of those vacancies in the bulk, which had been created in Experiments 1 and 2. This facilitated the replenishment of surface oxygen species by diffusion, and so increased the concentration of weakly bonded O^- species existing at the surface after cooling down to 250°C.

The variation of the relative amount of 3-pyridinecarbaldehyde (m/e = 107) desorbed was exactly the same as that for 3-picoline. It was found that the total amount of aldehyde formed was approximately one-tenth of the amount of picoline desorbed. An explanation for this behavior could be that after the adsorption of picoline via the nitrogen atom at, e.g., (100) or (001) planes, a reaction between the methyl group and oxygen occurred when increasing the temperature. This would mean that the formation of aldehyde was not preceded by an attachment of the methyl carbon atom to a vanadyl oxygen species, which was proposed in an earlier report (*32*).

Figure 3 shows that the variation with the Experiment number of the relative amount of pyridine (m/e = 79) formed was opposite to the variation of picoline and aldehyde. This indicates that a coordination of the nitrogen atom to a cation did not precede the formation of pyridine. Instead a chemisorption of the methyl carbon atom to an oxygen species after the abstraction of a hydrogen could have occurred. These steps were then followed by a dealkylation. It has been concluded that it is the vanadyl oxygen species which take part in this kind of chemisorption (*26*). Support for this opinion is given by the fact that the amount of pyridine formed was relatively large after reoxidation of the catalyst at 500°C. The concentration of O^{2-} species increased relative to the concentration of weakly bonded O^- species when the catalyst was oxidized at this high temperature.

The amount of nicotinonitrile (m/e = 104) formed decreased as a function of the Experiment number. Primarily, this was because the amount of adsorbed NH_3 was being depleted, since no NH_3 was readsorbed between the experiments. However, it is obvious that the reoxidation at 500°C had a beneficial effect on the formation of nitrile, which can be concluded from the existence of a plateau on the curve between Experiments 2 and 3. It therefore seems likely that vanadyl oxygen species took part in the formation of nitrile as they did in the formation of pyridine.

3. *Desorption of Carbon Oxides*

Figure 3 shows that the formation of CO

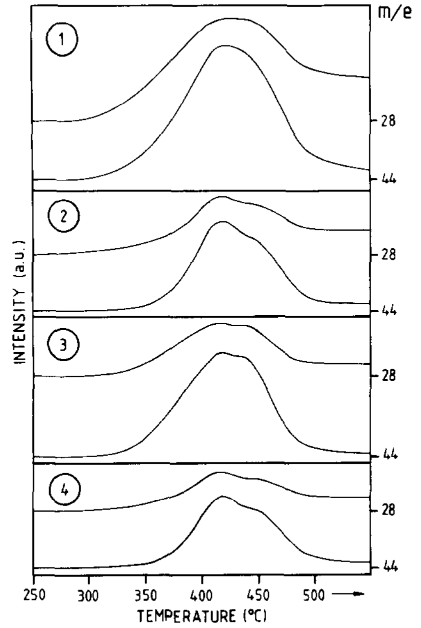


FIG. 4. Appearance of CO and CO_2 in Expts 1–4. Pretreatment conditions are given in the legend of Fig. 3.

($m/e = 28$) steadily decreased with the number of successive experiments. The variation of the relative amount of CO_2 (m/e = 44) was different. Like the formation of CO, the formation of CO_2 was initially high. However, the formation of CO_2 increased after having reoxidized the catalyst at 500°C (Experiment 3).

Figure 4 shows the appearance of carbon oxides in Experiments 1–4. It is of interest to note that the desorption curves of CO clearly lie above the baselines at 500°C. This deviation, due to diffusion of oxygen from the bulk to the surface, tends to decrease with the number of successive experiments performed. For CO_2 the deviation is relatively much smaller. In principle, this indicates that the formation of CO and CO_2 generally took place at different planes. CO was probably formed at the (100) and (001) planes. This can be inferred from the finding that the exchange of oxygen occurs more easily in the [100] and [001] directions than it does in the [010] direction (*33*). The decrease of deviation from baseline with an increased Experiment number could be due to an increase of the number of oxygen vacancies in the bulk, which slowed down the surface replenishment. On the other hand, the formation of CO_2 mainly took place at the (010) plane, which is in agreement with a relatively small deviation from baseline at 500°C due to the slow diffusion rate in the [010] direction. Further support for this conclusion comes from the finding that the amount of CO_2 formed increased after reoxidation at 500°C. This was due to an increase of the ratio of the concentrations of O^{2-} to O^- species at the surface. The CO_2 produced at the (010) plane was probably formed by the reaction of CO with vanadyl oxygen species. Support for this inference can be found in other published investigations (*34–36*). However, it is possible that some CO_2 can also be formed at planes which expose electrophilic oxygen species.

Figure 4 also shows that both CO and CO_2 desorbed as two peaks. The low-temperature peaks were comparatively larger when the concentration of oxygen vacancies at the surface could be expected to be high. Upon examination of Fig. 3, it can be proposed that this was due to the greater amount of 3-picoline which was adsorbed via the nitrogen atom in these cases. A substantial amount of this picoline could then consecutively be oxidized to carbon oxides at high temperatures. Compared to the origin of the high-temperature peaks, it therefore seems that the low temperature peaks originated from a degradation of nitrogen-bonded 3-picoline at planes having both relatively weaker bonded oxygen species as well as a relatively higher concentration of oxygen vacancies. However, the formation of carbon oxides corresponding to the high temperature peaks was not preceded by an adsorption to the nitrogen atom. In this case 3-picoline was immediately bonded to the surface in a degraded form and thus could not desorb intact. By consideration of Table 1 and Fig. 1 it seems that CO desorbing at low and high temperatures was formed at the (001) and (100) planes, respectively. The oxygen species of interest were respectively those with bond strength values of 0.76 and 1.04. CO formed at these planes could then be oxidized to CO_2 either by electrophilic oxygen species or by vanadyl oxygen species. Positions at the (100) plane with bond strength values of 0.46, which are localized at separate sheets, were probably largely vacant at 250°C. Some of the picoline which desorbed intact had probably been adsorbed at these vacancies.

TABLE 2

Effects of Air Pulses Injected at 250°C

m/e	A-250[a] (a.u.)	A-ref[b] (a.u.)	$\frac{A\text{-}250}{A\text{-ref}}$
28	1741	1556	1.12
44	2499	2502	1.00
79	44	51	0.86
93	44	65	0.68
104	33	33	1.00
107	4	7	0.57

[a] TPD areas after adsorption followed by two air pulses at 250°C.

[b] TPD areas after adsorption and without injection of air at 250°C.

4. *Effects of Oxygen at 250°C*

Two experiments are compared in this section. In both cases the catalysts had been used in a standard TPD experiment followed by reoxidation at 500°C and finally readsorption of 3-picoline at 250°C. In one experiment a TPD was performed immediately after degassing in He, while in the other experiment the TPD was started shortly after having injected two pulses of air into the He stream at 250°C. In connection with the air pulses small amounts of CO_2 were formed. The formation of CO could not be followed because N_2 in air contributed considerably to the intensity of mass number 28. The product distributions obtained in the two experiments are compared in Table 2. The amount of picoline desorbed was relatively smaller after air treatment at 250°C in comparison with the case where no air was admitted. Thus it seems that the amounts of carbon oxides formed by the injection of air came primarily from a combustion of 3-picoline adsorbed via the nitrogen atom. A relatively smaller decrease of the amount of pyridine formed was also observed. It has been previously concluded that pyridine is formed above 250°C by dealkylation of 3-picoline which has been adsorbed via the methyl carbon atom. However, some picoline was probably dealkylated immediately upon adsorption. The pyridine formed could then have readsorbed via the nitrogen atom and eventually have been combusted upon the injection of air. Additionally, the amount of aldehyde formed was lowered by air treatment. Aldehyde has been concluded to be formed by oxidation of nitrogen-bonded 3-picoline above 250°C. Therefore, the decrease of the amount of aldehyde desorbed can be seen as a consequence of the combustion of adsorbed picoline.

When comparing the amounts of carbon oxides formed in the two experiments under discussion, it is obvious that air admittance increased the amount of CO formed, while the amount of CO_2 was hardly affected. The reason could be that the oxidation at 250°C increased the concentration of weakly bonded oxygen species, which take part in the initial degradation of 3-picoline as well as in the subsequent oxidation to CO. On the contrary, the concentration of O^{2-} species, which participate in the oxidation of CO to CO_2, can be expected to have been the same in both experiments. This agrees with the observation that the amount of CO_2 formed was the same in the two experiments. Table 2 shows that the formation of nitrile was not influenced by oxidation at 250°C, a fact which indicates that the intermediate responsible for the formation of nitrile was stable and did not degradate in air at 250°C. This proves that the intermediate was located at planes not exposing O^- species.

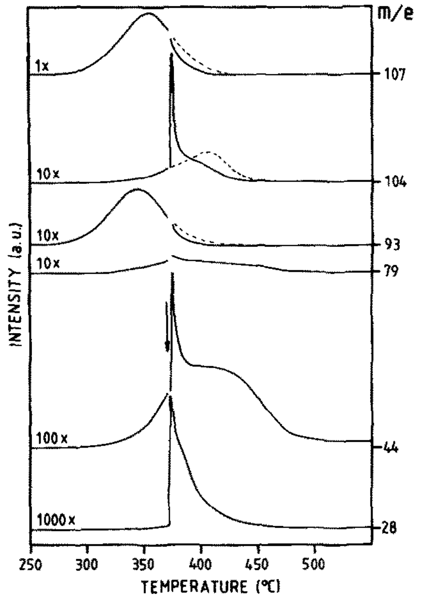


FIG. 5. TPD with injection (indicated by an arrow) of one pulse of air at 370°C. Pretreatment: A first TPD followed by oxidation at 250°C (10 × 1.01 ml of air) and then readsorption at 250°C.

5. *Responses to Oxygen Injected in the Course of TPD at 370°C*

A pulse of air was injected at 370°C during a TPD experiment. The amount of oxygen in the pulse was three times the stoichiometric amount needed for obtaining total combustion to carbon dioxide of all adsorbed picoline. The transient responses registered are shown in Fig. 5. There is a break in the curves due to omission of some initial pressure changes registered at the moment of injection. The dashed curves illustrate the desorption behavior in the case without air injection. When the catalyst is oxidized at 370°C we can expect an increase of the concentration of O^{2-} species, and a relatively smaller increase of the concentration of O^- species (*17, 25*). Figure 5 shows that both the amount of picoline and the amount of aldehyde desorbed per unit time decreased after the injection of oxygen in comparison with the case where no oxygen was admitted. At the same time a slight increase in the formation of CO_2 occurred. No conclusions about the formation of CO can be drawn directly because mass number 28 includes both CO formed as well as N_2 from the injected air.

The rate of the formation of nitrile increased considerably and rapidly when oxygen was admitted. However, the total area of nitrile formed did not increase in comparison with the case without injection. These results indicate that the diffusion of oxygen from the bulk to the surface was the rate-determining step for the formation of nitrile in the absence of gaseous oxygen.

6. *Effects of Preadsorption of NH_3*

In one experiment NH_3 was preadsorbed at 250°C prior to the adsorption of 3-picoline. It was observed that N_2 was formed upon the injection of NH_3. Studies of the oxidation of NH_3 on V_2O_5 have shown that predominantly N_2 is formed when the partial pressure of oxygen is low (*37–39*). When subsequently pulsing 3-picoline some preadsorbed NH_3 desorbed. This shows that NH_3 and 3-picoline could adsorb at the same sites.

Figure 6 shows the outlet responses of 3-picoline and nicotinonitrile registered when 3-picoline was injected at 250°C. In addition to the conversion to nitrile, less than 3% desorbed as carbon oxides. Figure 6 shows that most of the first pulse of 3-picoline was adsorbed. No nitrile was desorbed in connection with this pulse. However, nicotinonitrile was desorbed upon injection of a subsequent second pulse of 3-picoline. At the third pulse a much smaller amount of nicotinonitrile desorbed. It was observed

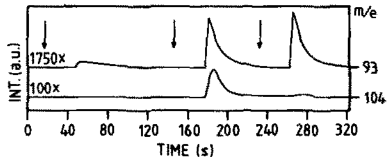


FIG. 6. Responses to 3 pulses of picoline injected (arrows) at 250°C. Pretreatment: A first TPD followed by reoxidation at 500°C and then injection of one pulse of $NH_3(g)$ at 250°C.

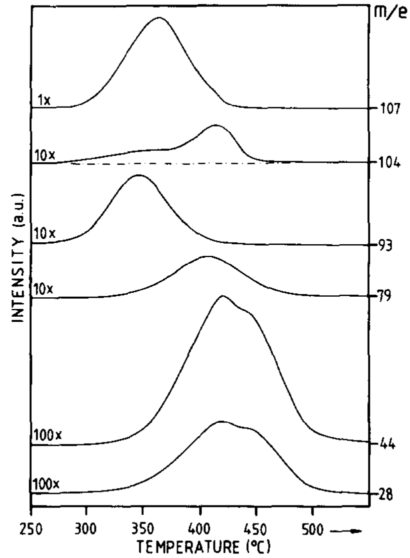


FIG. 7. TPD after one pulse of NH_3 followed by adsorption of 3-picoline at 250°C. Pretreatment: A first TPD followed by reoxidation at 500°C.

that no nitrile was formed at 250°C when 3-picoline was adsorbed on the freshly prepared catalyst. Hence it can be concluded that there was a second active site adsorbing NH_3 more weakly than the site at which NH_3 was adsorbed during the preparation of the catalyst at 400°C. The behavior of the nitrile curve presented in Fig. 6 can be explained as follows. Nitrile was formed after the first pulse of picoline. However, it was readsorbed at the surface. The second pulse of picoline caused the nitrile already formed to desorb because of competing adsorption, probably via a nitrogen atom. Finally, the nitrile desorbing after the third pulse of picoline had already been formed after the second injection. This peak was small due to the fact that almost all of the NH_3 present on this site had already reacted in connection with the first injection.

After the third injection, the catalyst sample was degassed in a stream of He for 30 min. Then the temperature was raised linearly. The TPD curves obtained are presented in Fig. 7. It is obvious that in addition to the nitrile peak usually obtained, a second peak of nicotinonitrile appeared at 360°C after NH_3 had been preadsorbed at 250°C. It cannot be excluded that this amount of nitrile was formed at the same type of site which produced the nitrile which desorbed after injection of the second and third picoline pulses. The reason it was not desorbed at these pulses might be that it had been readsorbed in a mode or at a type of site that did not allow a replacement by picoline to occur. Table 3 gives the peak areas calculated as well as a comparison to a similar experiment without any preadsorption of NH_3 at 250°C. The values in the table show that the nitrile peak with a maximum at 410°C was not affected by preadsorption of NH_3 at 250°C. This clearly shows that two active sites for the formation of nitrile have been discovered so far. Besides the appearance of two peaks of nitrile, only two other significant changes of desorbed quantities were observed in comparison with those of the reference experiment. Both the amount of unreacted 3-picoline desorbed and the amount of 3-pyridinecarbaldehyde formed were larger. This might be because the oxidation of NH_3 to N_2 consumed oxygen species, which resulted in a relatively large concentration of oxygen vacancies at the surface. 3-Picoline could then have been adsorbed at these vacancies via the nitrogen atom. The greater amount of aldehyde formed relative

TABLE 3

Effects of Adsorption of NH_3 at 250°C prior to Adsorption of 3-Picoline

m/e	*A*-NH[a] (a.u.)	*A*-ref[b] (a.u.)	$\frac{A\text{-NH}}{A\text{-ref}}$
28	1430	1556	0.92
44	2432	2502	0.97
79	55	51	1.08
93	88	65	1.35
104 (360°C)	16	0	∞
104 (410°C)	34	33	1.03
107	10	7	1.43

[a] TPD areas after preadsorption of NH_3 at 250°C.

[b] TPD areas without preadsorption of NH_3 at 250°C.

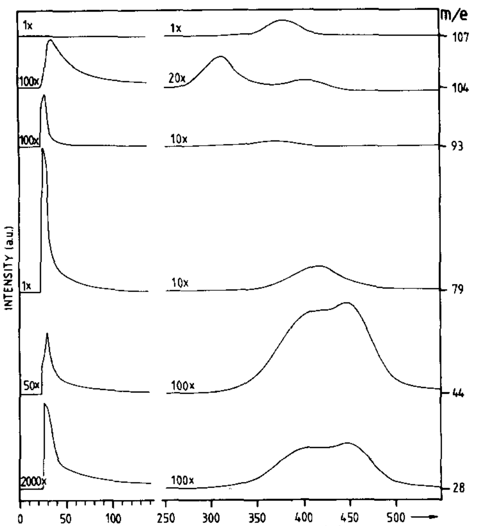


FIG. 8. Responses to one pulse of NH_3 ($t = 0$ sec) at 250°C and the subsequent TPD pattern. Pretreatment: A first TPD followed by reoxidation at 500°C and then readsorption of 3-picoline at 250°C.

to the reference experiment again demonstrates that aldehyde was formed from the picoline that was adsorbed via the nitrogen atom.

7. Responses to a Pulse of NH_3 at 250°C

After adsorption of 3-picoline a pulse of NH_3 was injected at 250°C. The transient responses as well as the desorption curves of the subsequent TPD experiment are shown in Fig. 8. Relatively large quantities of both nicotinonitrile and N_2 ($m/e = 28$) were formed upon injection. Desorption of 3-picoline, pyridine, and CO_2 also occurred upon injection. This shows that NH_3 could adsorb at the same sites, which are oxygen vacancies, as CO_2 and nitrogen-bonded picoline and pyridine. Both the pyridine and the CO_2 had been formed during the time that elapsed from adsorption of picoline to injection of NH_3.

The peak areas of the transient responses, the subsequent TPD curves and the reference experiment in which no NH_3 was injected are collected in Table 4. It can be seen that the amount of nitrile formed upon the injection of ammonia was considerably larger than the amount which was formed in the reference experiment. Two peak maxima were detected when the temperature was linearly raised (Fig. 8). The maximum at 310°C was probably caused by desorption of adsorbed nicotinonitrile which had been formed at 250°C. Indeed, the transient response of nitrile showed severe tailing, which indicates that readsorption occurred. It is interesting to observe that the area of the nitrile peak which appears at 410°C had not increased compared to the area of the corresponding peak in the reference experiment. This was observed in spite of the fact that when injecting NH_3 at 250°C an additional adsorption took place, which could be inferred from the simultaneous desorption of both pyridine, CO_2 and unreacted 3-picoline. These results again prove that the formation of nitrile occurred at planes which were structurally different from those at which picoline was adsorbed via attachment to the nitrogen atom. Furthermore, the amount of nitrile formed upon the injection of NH_3 was approximately ten times that formed when pulsing 3-picoline immediately after having preadsorbed NH_3 (Section 6). Murakami *et al.* (*40*) observed that in the ammoxidation of

TABLE 4

Effects of a Pulse of NH_3 Injected at 250°C after Adsorption of 3-Picoline

m/e	*A*-inj[a] (a.u.)	*A*-tpd[b] (a.u.)	Σ[c] (a.u.)	*A*-ref[d] (a.u.)
28	(3100)	1237	1237	1556
44	50	2090	2140	2502
79	2	36	38	51
93	43	10	53	65
104	177	79[e] 32[f]	288	33
107	0	1	1	7

[a] Areas of transient responses to a NH_3 pulse at 250°C.

[b] TPD areas obtained after the transient responses.

[c] $\Sigma = A\text{-inj} + A\text{-tpd}$.

[d] TPD areas without a NH_3 pulse at 250°C.

[e] Peak maximum at 310°C.

[f] Peak maximum at 410°C.

toluene over vanadium oxide catalysts benzonitrile was formed during the ammonia pulse rather than during the toluene pulse. We can therefore conclude that the nitrile, which was formed following the NH_3 pulse, was formed in a reaction between chemisorbed picoline and gaseous or weakly adsorbed NH_3 according to a Eley-Rideal mechanism. Such a mechanism has already been proposed in a previous work (*32*).

From Table 4 it can be calculated that the total amount (Σ) of nitrile formed had increased almost eightfold in comparison to the reference experiment. This amount corresponds to roughly 50% of the total amount of picoline adsorbed. However, the total amounts of carbon oxides had not decreased to an equivalent extent. This fact leads us to infer that the intermediate which took part in the nitrile formation was preferentially not oxidized to carbon oxides at high temperatures. Instead, it probably reacted to form coke and tarry products. Actually, on a V_2O_5 catalyst preferentially exposing the (010) plane, the selectivity for the formation of tar has been found to exceed the selectivities for the formation of carbon oxides (*30, 32*). Finally, the injection of NH_3 resulted in lower total amounts (Σ) of pyridine, picoline and aldehyde compared to the reference experiment. If the intermediate reacting to give pyridine was identical with that yielding nitrile the decrease in the amount of pyridine formed could be explained. The reason for the decrease in picoline and aldehyde could be that after being driven off by NH_3 some picoline was readsorbed at sites taking part in the nitrile formation.

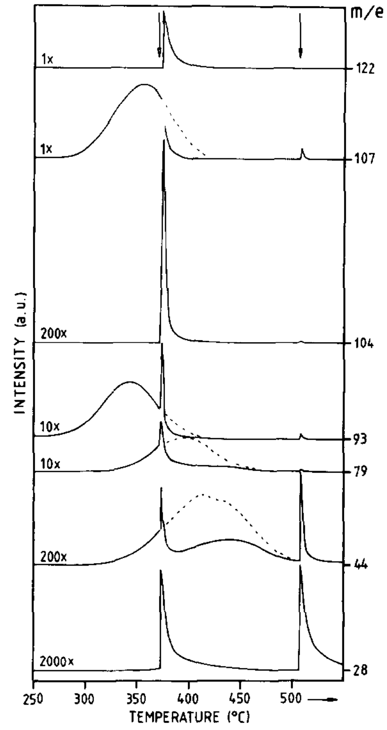


FIG. 9. TPD with pulses of NH_3 injected (arrows) at 370 and 500°C. Pretreatment: A first TPD followed by reoxidation at 500°C and then readsorption of 3-picoline at 250°C. Dashed lines illustrate the appearance without NH_3 injection.

8. *Responses to NH_3 Injected in the Course of TPD*

The responses to pulses of NH_3 injected in the course of a linear increase of temperature are shown in Fig. 9. Injection at 370°C led to the formation of nicotinonitrile and nicotinamide (*m/e* = 122). N_2 was also formed due to oxidation of NH_3. Pyridine, CO_2 and unreacted 3-picoline simultaneously desorbed. After an initial desorption of pyridine which had been previously created at a lower temperature, however, its desorption curve fell to the baseline. This again shows that the intermediates which reacted to nitrile and pyridine, respectively, could be identical. The desorption curve of CO_2 behaved in a similar manner. Of course, this was partly due to the formation of nitrile, which consumed probably vanadyl oxygen species (*30*). Such species competitively participated in the oxidation of CO to CO_2 as well (*34–36*). The formation of nitrile also prevented a combustion of the adsorbed intermediate. However, it was concluded in the previous section that this intermediate was not readily oxidized to yield carbon oxides. Therefore, the behavior of the CO_2 curve can be seen to be primarily a consequence of the

TABLE 5

Active Sites Participating in the Formation of Nitrile

Site	Reference	Status		Amount of nitrile formed	Availability of oxygen
		3-Picoline	NH_3		
1	Sections 2,5 Figs. 2,5	Chemisorbed	Strongly adsorbed	Small	Deficient
2	Section 6 Fig. 6	Chemisorbed	Adsorbed	Small	Good
3	Sections 7,8 Figs. 8,9	Chemisorbed	Gaseous or weakly adsorbed	Large	Good

fact that the formation of CO, and consequent formation of CO_2 from CO, were prevented. The reason might be that the oxidation of NH_3 consumed those oxygen species which could have participated in the formation of CO.

When injecting NH_3 the desorption curve of aldehyde rapidly sank to the baseline, which indicated a reaction between NH_3 and aldehyde. Amide was also formed during the NH_3 pulse. No formation of aldehyde occurred at 250°C and no amide was formed when NH_3 was introduced at this temperature (Fig. 8). It can tentatively be concluded that the formation of amide at 370°C was due to a reaction between aldehyde and NH_3. Both the formation of aldehyde and most of the adsorption of NH_3 have been shown to be localized at planes exposing oxygen vacancies as well as electrophilic oxygen species, e.g., (100) and (001) planes. Therefore, it does not seem that the formation of amide and nitrile were localized at identical crystal planes.

A pulse of NH_3 was also introduced at 500°C. Figure 9 shows that CO_2 which had been strongly adsorbed at the surface was desorbed. In addition to a large amount of N_2, additional small amounts of aldehyde, nitrile, picoline, and pyridine appeared in the product stream.

9. *Nature of Active Sites Participating in the Formation of Nicotinonitrile*

The present work has revealed the existence of three types of sites active for the formation of nicotinonitrile. The information obtained on the nature of these sites is collected in Table 5, which also refers to the appropriate sections.

It has been demonstrated that the amount of 3-picoline which is adsorbed via the methyl carbon atom can be related to the concentration of vanadyl oxygen species (*26*), and that the (010) plane of V_2O_5 is selective for the formation of nicotinonitrile (*30*). Therefore, it seems that Site 3 is typical for the (010) plane in general since large quantities of nitrile were obtained from this type of site. In Section 7 it was concluded that 3-picoline chemisorbed at Site 3 reacted with either gaseous or weakly adsorbed NH_3. Actually, each vanadyl oxygen species on the (010) plane has two V^{5+} ions in its immediate surroundings. If NH_3 adsorbs at these cations, it is probably only weakly adsorbed. This is inferred from quantum chemical calculations (*27*), which have shown that the adsorption of pyridine, a weaker base than NH_3, is not likely to occur at V^{5+} ions. The current experiments show that NH_3 could adsorb on the same partially reduced sites at which pyridine and 3-picoline were adsorbed by attachment to the nitrogen atom. The previous study (*26*) demonstrated that this kind of adsorption did not occur to a great extent at the (010) plane. In addition to V^{5+} ions, the (010) plane also exposes vanadium ions located at vanadyl oxygen vacancies. These can be formally considered as V^{3+} ions but their valence electrons might be delocalized to give V^{4+} ions. NH_3 can adsorb more strongly to these partially reduced vanadium ions than to V^{5+} ions, as is supported by the quantum chemical results referred to above. The concentration of vanadyl oxygen vacancies at the surface can be expected to be low, especially after reoxidation at 500°C. Such a vacancy is therefore surrounded by vanadyl oxygen species. The behavior of Site 2, Table 5, would fit very well with this sort of environment.

Site 1 differed from Site 2 in three respects. First, the supply of oxygen was worse at Site 1 than at Site 2. This was demonstrated by the results presented in Section 5 on the response to a pulse of oxygen injected at 370°C. Secondly, NH_3 was strongly adsorbed on Site 1 and adsorbed species were present even after the preparation of the catalyst at 400°C as well as after being heated to 500°C. On Site 2 ammonia species were not present at 400°C but existed after adsorption at 250°C (Section 6). Thirdly, almost all NH_3 at Site 2 reacted with the first pulse of picoline. However, reaction occurred at Site 1 in subsequent TPD experiments without readsorbing NH_3 between these experiments. The latter fact can be explained by a low coverage of 3-picoline due to a high activation energy for the adsorption. A high energy and a deficient oxygen supply might be a consequence of structural factors. It is possible that Site 1 is located at irregularities, corners, edges or planes of high indices.

Infrared studies of the adsorption of NH_3 on V_2O_5 have shown that NH_3 adsorbs in the form of either NH_4^+(ad) species (*41, 42*) or NH_3(ad) species (*42*). The NH_4^+(ad) species disappeared after outgassing at 120°C, and coordinately linked NH_3(ad) existed up to 250°C (*42*). In the ammoxidation of propylene on antimonates and bismuth molybdates the adsorption of NH_3 in the form of $=NH$ groups has been established (*43*). Such groups have not been found on vanadium oxides. However, on a V—Ti—O catalyst an infrared band at 1483 cm^{-1} has been tentatively assigned to $—NH_2$ species (*44*). Infrared investigations performed on the catalyst used in this work did not reveal any adsorbed ammonia species at 250°C or higher. Generally, the inability to detect ammonia species after treatment at high temperatures could be that the transmittance of pure V_2O_5 is low, which makes it difficult to detect adsorbed species in low concentrations. It is a fact that volumetric measurements have shown that a considerable amount of NH_3 is still adsorbed at 250°C at a relatively high pressure (*45*). The adsorbed ammonia species which react at Site 2 are probably coordinately linked NH_3(ad) species. On the other hand, NH_3 strongly adsorbed at Site 1 could be present in the form of either $—NH_2$ or $=NH$ groups, since in this case the adsorption occurred at a high temperature.

In a review Suvorov (*46*) has concluded that in both ammoxidation and oxidative ammonolysis nitriles are mainly formed via aldehydes as follows (Scheme 1);

$$RCH_3 + 2O \rightarrow RCHO + H_2O$$

$$RCHO + NH_3 + O \rightarrow RCONH_2 + H_2O$$

$$RCHO + O \rightarrow RCOOH$$

$$RCOOH + NH_3 \rightarrow RCONH_2 + H_2O$$

$$RCONH_2 \rightarrow RCN + H_2O$$

However, it is well known that amines dehydrogenate to form nitriles. Therefore, Suvorov suggested a second route as follows (Scheme 2);

$$RCH_3 + NH_3 + O \rightarrow RCH_2NH_2 + H_2O$$

$$RCH_2NH_2 + O \rightarrow RCHNH + H_2O$$

$$RCHNH + O \rightarrow RCN + H_2O$$

Either of these routes has been proposed to be valid both in the ammoxidation of 3-picoline (*32, 47*) and in the ammoxidation of toluene (*48*) and xylenes (*49, 50*). The results of the present investigation indicate that a substantial amount of nitrile is formed according to Scheme 2. Adsorption of 3-picoline takes place after abstraction of a hydrogen atom from the methyl group. After a second hydrogen abstraction the adsorbed radical reacts with NH_3 to form an amine complex, which is then easily dehydrogenated to give first an imine intermediate and then to afford the nitrile. All of these consecutive steps proceed without the necessity of desorption and readsorption of intermediate compounds. There were also indications that some amide was obtained by the reaction of aldehyde with NH_3. This is in line with Scheme 1. However, no information on the dehydration of amide to nitrile was obtained.

ACKNOWLEDGMENT

Financial support from the National Swedish Board for Technical Development (STU) is gratefully acknowledged.

REFERENCES

1. Danilova, A. A., Koval, L. M., and Kurina, L. N., *Russ. J. Phys. Chem.* **55,** 221 (1981).
2. Danilova, A. A., Koval, L. M.., and Kurina, L. N., *Russ. J. Phys. Chem.* **55,** 426 (1981).
3. Joly, J. P., Perrard, A., and Germain, J. E., *in* "Proceedings, 9th Iberoamerican Symposium on Catalysis," Vol. 2, p. 856. Soc. Iberoam. Catal., Lisbon, 1984.
4. Belokopytov, Yu. V., Grebennikov, Yu. N., Pyatnitskii, Yu. I., and Telyatnik, A. I., *React. Kinet. Catal. Lett.* **23,** 99 (1983).
5. Lucas, J., Vandervell, D., and Waugh, K. C., *J. Chem. Soc. Faraday Trans. 1* **77,** 15 (1981).
6. Lucas, J., Vandervell, D., and Waugh, K. C., *J. Chem. Soc. Faraday Trans. 1* **77,** 31 (1981).
7. Morselli, L., Trifirò, F., and Urban, L., *J. Catal.* **75,** 112 (1982).
8. Krenzke, L. D., Keulks, G. W., Sklyarov, A. V., Firsova, A. A., Kutirev, M. Yu., Margolis, L. Ya., and Krylov, O. V., *J. Catal.* **52,** 418 (1978).
9. Noller, H., and Ritter, G., *J. Chem. Soc. Faraday Trans. 1* **80,** 275 (1984).
10. Falconer, J. L., and Schwarz, J. A., *Catal. Rev. Sci. Eng.* **25,** 141 (1983).
11. Criado, J. M., Malet, P., Munuera, G., and Rives-Arnau, V., *J. Catal.* **75,** 428 (1982).
12. Britten, J. A., Travis, B. J., and Brown, L. F., *AIChE Symp. Ser.* **230,** 7 (1983).
13. Rieck, J. S., and Bell, A. T., *J. Catal.* **85,** 143 (1984).
14. Demmin, R. A., and Gorte, R. J., *J. Catal.* **90,** 32 (1984).
15. Bennett, C. O., *Catal. Rev. Sci. Eng.* **13,** 121 (1976).
16. Bennett, C. O., *in* "Catalysis under Transient Conditions" (A. T. Bell and L. L. Hegedus, Eds.), ACS Symp. Ser. 178, p. 1. Amer. Chem. Soc., Washington, D.C., 1982.
17. Andersson, A., Wallenberg, R., Lundin, S. T., and Bovin, J.-O., *in* "Proceedings, 8th International Congress on Catalysis," Vol. 5, p. 381. Verlag Chemie, Weinheim, 1984.
18. Andersson, A., *J. Solid State Chem.* **42,** 263 (1982).
19. Pauling, L., *J. Amer. Chem. Soc.* **51,** 1010 (1929).
20. Waltersson, K., *Chem. Commun. Univ. Stockholm* **7** (1976).
21. Ziółkowski, J., *J. Catal.* **81,** 311 (1983).
22. Ziółkowski, J., and Gasior, M., *J. Catal.* **84,** 74 (1983).
23. Ziółkowski, J., *J. Catal.* **84,** 317 (1983).
24. Bachmann, H. G., Ahmed, F. R., and Barnes, W. H., *Z. Kristallogr. Kristallgeom. Kristallphys. Kristallchem.* **115,** 110 (1961).
25. Grzybowska, B., Barbaux, V., and Bonnelle, J.-P., *J. Chem. Res. Miniprint* 0650 (1981).
26. Andersson, A., *in* "Studies in Surface Science and Catalysis" (M. Che and G. C. Bond, Eds.), Vol. 21, p. 381. Elsevier, Amsterdam, 1985.
27. Golender, L. O., and Shimanskaya, M. V., *React. Kinet. Catal. Lett.* **13,** 85 (1980).
28. Haber, J., *in* "Surface Properties and Catalysis by Non-Metals" (J. P. Bonnelle, B. Delmon, and E. Derouane, Eds.), NATO ASI Series, Ser. C, No. 105, p. 1. Reidel, Dordrecht, 1983.
29. Gasior, M., and Machej, T., *J. Catal.* **83,** 472 (1983).
30. Andersson, A., Bovin, J.-O., and Walter, P., *J. Catal.* **98,** 204 (1986).
31. Shvets, V. A., Vorotinzev, V. M., and Kazansky, V. B., *J. Catal.* **15,** 214 (1969).
32. Andersson, A., and Lundin, S. T., *J. Catal.* **58,** 383 (1979).
33. Kera, Y., and Hirota, K., *J. Phys. Chem.* **73,** 3973 (1969).
34. Hirota, K., Kera, Y., and Teratani, S., *J. Phys. Chem.* **72,** 3133 (1968).
35. Tarama, K., Yoshida, S., Ishida, S., and Kakioka, H., *Bull. Chem. Soc. Japan* **41,** 2840 (1968).
36. Kera, Y., *Bull. Chem. Soc. Japan* **52,** 888 (1979).
37. Ilchenko, N. I., and Golodets, G. I., *J. Catal.* **39,** 57 (1975).
38. Ilchenko, N. I., and Golodets, G. I., *J. Catal.* **39,** 73 (1975).
39. Kosaki, Y., Miyamoto, A., and Murakami, Y., *Bull. Chem. Soc. Japan* **52,** 617 (1979).
40. Murakami, Y., Niwa, M., Hattori, T., Osawa, S., Igushi, I., and Ando, H., *J. Catal.* **49,** 83 (1977).
41. Takagi-Kawai, M., Soma, M., Onishi, T., and Tamaru, K., *Canad. J. Chem.* **58,** 2132 (1980).

42. Belokopytov, Yu. V., Kholyavenko, K. M., and Gerei, S. V., *J. Catal.* **60,** 1 (1979).
43. Grasselli, R. K., Brazdil, J. F., and Burrington, J. D., *in* "Proceedings, 8th International Congress on Catalysis," Vol. 5, p. 369. Verlag Chemie, Weinheim, 1984.
44. Miyata, H., Nakagawa, Y., Ono, T., and Kubokawa, Y., *Chem. Lett.* **8,** 1141 (1983).
45. Ai, M., *Bull. Chem. Soc. Japan* **49,** 1328 (1976).
46. Suvorov, B. V., *Int. Chem. Eng.* **8,** 588 (1968).
47. Prasad, R., and Kar, A. K., *Ind. Eng. Chem. Process. Des. Dev.* **15,** 170 (1976).
48. Niwa, M., Ando, H., and Murakami, Y., *J. Catal.* **49,** 92 (1977).
49. Niwa, M., Ando, H., and Murakami, Y., *J. Catal.* **70,** 1 (1981).
50. Simon, G., and Germain, J.-E., *Bull. Chim. Fr.* **11–12,** 2617 (1975).