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Activities of V–Ti–O Catalysts in the Ammoxidation of 3-Picoline

II. Acid–Base Properties and Infrared Spectra

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The acidity and basicity of prereduced V–Ti–O catalysts were measured by adsorption of NH_3 and CO_2. It was found that a high activity in the ammoxidation of 3-picoline corresponds to a relatively small amount of acidic sites. A catalyst selective in the formation of nicotinonitrile requires high concentrations of both acidic and basic sites. These results are discussed, and can be correlated if the acidity is considered to be a measure of the hydroxyl group concentration, and the basicity a measure of oxygen vacancies in the vicinity of V=O groups. Also, the infrared spectra of the prereduced catalysts were recorded. A new band was found at 995 cm^{-1}. The same band appeared in a homogeneous mixture of V_2O_5 and V_6O_{13}. It is proposed that this band can be assigned to V=O bonds in a reduced V_2O_5 phase with a number of disordered vacancies in the lattice, or a nonstoichiometric V_6O_{13} phase. The shift in frequency relative to that of $(V{=}O)^{3+}$ shows that these bonds are weaker, and probably also more active. The effect of TiO_2 is to increase the amount of V^{4+} in the vanadium oxide lattice. This is caused by dissolution of Ti^{4+} in the V_2O_5 melt during the catalyst preparation.

INTRODUCTION

Results concerning the ammoxidation of 3-picoline on prereduced V–Ti–O catalysts have been published (*1*). It was found that the activity as a function of the TiO_2 content had a maximum at 50–60 mole% TiO_2. The selectivity for nicotinonitrile exhibited a maximum at 10 mole% TiO_2, and minima at 0 and 30 mole% TiO_2. At higher TiO_2 contents, the selectivity increased continuously. The activity maximum was proposed to be a result of maximum contact between the vanadium and titanium phases. The variation of the selectivity was assumed to depend on the V^{4+}/Ti^{4+} ratio in the TiO_2 phase. However, it seemed necessary to obtain further information on the nature of the maxima and minima, in order to determine whether there were any characteristics to which the variations could be related. The methods used for this purpose were determination of the acidic and basic properties and infrared investigations of the catalysts. It was thought that valuable information could be obtained if the origin of the acidic and basic properties could be related to activities and selectivities. Results on the oxidation of butadiene and acetic acid on nonprereduced V_2O_5–TiO_2 catalysts have been discussed in more general terms with consideration of the acid–base properties (*2*). However, the conditions in the ammoxidation of 3-picoline are different, since there are three reactants, 3-picoline, oxygen, and ammonia. Also, the prereduced catalysts were different from nonprereduced ones, since V_6O_{13} was a major component. The infrared investigations were performed in order to determine whether the TiO_2 phase has any influence on the strength of the V=O bonds. It has been found that the presence of MoO_3 (*3*) and SnO_2 (*4, 5*) in vanadium catalysts weakens the V=O bond.

EXPERIMENTAL

1. Apparatus, analysis and activity, and selectivity measurements. The apparatus and the analytical procedures were the

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same as described earlier (*6*). The details of the activity and selectivity measurements were given in a previous article on ammoxidation of 3-picoline on V–Ti–O catalysts (*1*).

2. *Catalyst preparation.* The catalysts were prepared by heating V_2O_5 and TiO_2 (anatase) powders at 1150°C for 3 hr. The fused catalysts were divided into small particles. The 1.41–0.71 mm fraction was reduced in a hydrogen atmosphere at 450°C for 1 hr and then used in the activity measurements.

3. *Basicity and acidity measurements.* As a measure of the basicity and acidity of the catalysts, adsorption of CO_2 and NH_3 was used. The measurements were performed in an ordinary BET apparatus. Before adsorption, the samples were treated at 400°C and 13.3 mPa for 2 hr. The amount adsorbed at a pressure of 40 kPa was determined. The adsorption temperatures for CO_2 and NH_3 were 21 and 200°C, respectively. After this adsorption, the sample was pumped out for 30 min. Then the adsorption measurement was repeated. The amount of irreversibly adsorbed CO_2 and NH_3 was used as a measure of the basicity and the acidity, respectively. A similar procedure was used by Ai (*2, 7*).

4. *Recording of ir spectra.* The infrared spectra of the catalysts, V_2O_5, V_6O_{13}, and V_2O_4, were recorded on a Perkin–Elmer spectrophotometer 580B connected to a data station from the same manufacturer. The KBr disc method was used. The spectra were stored on disks and transferred to a Tektronix 4051 computer for evaluation.

RESULTS AND DISCUSSION

1. Catalyst Characterization

The initial composition of the prereduced catalysts was analyzed on a Philips X-ray diffraction instrument using a PW 1310/01/01 generator and Cu$K\alpha$ radiation. Diffraction patterns were recorded in the interval $10° \leq 2\theta \leq 60°$. The major phases which could be identified were V_2O_5, V_6O_{13}, V_2O_4, and the rutile phase of TiO_2. The number of visible lines of vanadium oxides diminished with increasing amount of TiO_2. For catalysts containing up to 50 mole% of TiO_2 a minimum of five V_2O_5 lines, seven V_6O_{13} lines, and three V_2O_4 lines could be identified. For the identification of V_6O_{13} the data given by Wilhelmi *et al.* (*8*) were used. The presence of V_2O_5, V_2O_4, and the rutile phase of TiO_2 was ascertained by comparison with ASTM data (*9*). The main diffraction lines used for the identification of the vanadium oxides are given in Table 1. For the catalyst containing 70 mole% TiO_2, four V_2O_5 lines, the two strongest V_6O_{13} lines having *d*-values of 3.51 and 3.32 Å, and the strongest V_2O_4 line, d = 3.20 Å, could be identified. In the catalyst with 90 mole% TiO_2 no vanadium oxides could be detected unless the catalyst particles were ground and analyzed as a powder. In this case, V_2O_5 could be found as a separate phase. The initial composition of the catalysts is given in Table 2.

Théobald *et al.* (*10*) have determined the structure of a monoclinic phase, $VO_2(B)$, which is neither the rutile phase nor the usual monoclinic one. There are only small differences between the X-ray diffraction patterns of $VO_2(B)$ and V_6O_{13}. The authors prepared $VO_2(B)$ by reduction of V_2O_5 in a hydrogen atmosphere between 210 and 400°C. Above 500°C, V_6O_{13} was formed. The V–Ti–O catalysts (*1*) studied in our

TABLE 1

Diffraction Lines Used for the Identification of Vanadium Oxides

V_2O_5		V_6O_{13}		V_2O_4	
(*hkl*)	*d*(Å)	(*hkl*)	*d*(Å)	(*hkl*)	*d*(Å)
200	5.76	200	5.85	011	3.20
001	4.38	002	4.98	$\bar{2}02$	2.43
101	4.09	110	3.51	$\bar{2}12$	2.14
110	3.41	003	3.32		
400	2.88	$40\bar{1}$	2.96		
		$31\bar{1}$	2.67		
		005	1.99		

TABLE 2

Relative Intensities (Percentage) of the Strongest X-Ray Reflection of the Phases in Unused Catalysts

Catalyst (mole% TiO_2)	Phases			
	V_2O_5	V_6O_{13}	V_2O_4	TiO_2
0	16	53	30	0
10	10	68	12	10
30	3	56	22	19
50	3	37	13	48
70	1	18	16	65
90	0	0	0	100
100	0	0	0	100

laboratory were prepared by reduction of V_2O_5 in a hydrogen atmosphere at 450°C. According to the X-ray diffraction patterns of the catalysts, the presence of V_6O_{13} was ascertained. The formation of $VO_2(B)$ was not observed. The typical $VO_2(B)$ lines (*10*) with the *d*-values 6.15, 3.08, and 2.05 Å were not found in any of the samples. Also, the strong line observed at $d = 3.32$ Å clearly distinguishes V_6O_{13} from $VO_2(B)$.

2. *Activities and Selectivities*

The initial reaction rate at 320°C and the selectivity for the formation of nicotinonitrile at 90% conversion are summarized in Table 3. These values correspond to the initial composition of the prereduced catalysts. It is seen that the activity has a maximum around 50–70 mole% TiO_2. The selectivity for nicotinonitrile has maxima at 10 mole% TiO_2 and 90 mole% TiO_2.

3. *Acidity of Catalysts*

The ammoxidation of 3-picoline to nicotinonitrile is usually carried out at a reaction temperature between 300 and 400°C. NH_3 is one of the reactants. Therefore the temperature for the measurement of NH_3 adsorption was chosen as high as possible, without having NH_3 oxidized to N_2 and H_2O by the lattice oxygen of the vanadium oxide. The temperature selected was 200°C. At this temperature, no oxidation of NH_3 could be observed, which seems to be in agreement with results obtained by others (*11, 12*). To better reflect the amount adsorbed at higher temperatures, the irreversible form of adsorbed NH_3 was chosen as a measure of the acidity.

Infrared studies of the adsorption of NH_3 on lower vanadium oxides have not been reported. It is well known that the transmittance of vanadium oxides is low, a fact which complicates infrared studies at low surface concentrations. This problem can be avoided by using supported samples, where the carrier has a higher transmittance and a high specific surface area. In this case, however, adsorption on the carrier can also occur (*13*). In the investigations of the prereduced V–Ti–O catalysts, it is most likely that the adsorption takes place on the vanadium oxide surface, because sintered pow-

TABLE 3

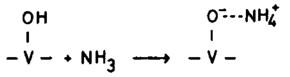
Initial Reaction Rate, Selectivity, Acidity, and Basicity[a]

Catalyst (mole% TiO_2)	Specific surface area (m^2/g)	r_0 ($\mu mole/m^2 \cdot min$)	Sel. (%) of nitrile	$(NH_3)_{irr}$ ($\mu mole/m^2$)	$(CO_2)_{irr}$ ($\mu mole/m^2$)
0	9.4	1.34	73.5	2.95	0.36
10	13.2	1.37	83	2.63	1.99
30	10.7	1.34	75.5	0.24	0.12
50	4.0	3.65	80	1.05	0.49
70	3.8	3.33	78.5	0.48	0.65
90	1.5	0.64	84.5	2.97	1.15

[a] Reaction parameters: Mole ratio air : 3-picoline : NH_3 : H_2O = 245 : 1 : 14 : 60. Temperature = 320°C. Pressure = 101 kPa.

der mixtures of V_2O_5 and TiO_2 in various ratios yield a higher vanadium content on the surface than the bulk composition (*14*). This is caused by the TiO_2 particles being embedded in a matrix of V_2O_5. It has been observed (*15–18*) that NH_3 on V_2O_5, below about 150°C, is adsorbed on Brønsted centers as NH_4^+ (ad). Belokopytov *et al.* (*19*) found that NH_3 is adsorbed on V_2O_5 both as NH_4^+ (ad) and as coordinatively linked NH_3. However, the ir spectra obtained by others (*15–17*) do not display any adsorption on Lewis centers. The adsorption of NH_3 at temperatures above 150°C is evidenced from the adsorption measurements on the prereduced V–Ti–O catalysts, and from the measurements by Ai (*2*) on nonprereduced V_2O_5–TiO_2 catalysts. Inomata *et al.* (*18*) mention that pulse chromatographic measurements of the adsorption on V_2O_5 revealed that NH_3 is strongly adsorbed at 150°C. They also observed that the quantity of NH_4^+ (ad) was not affected by oxidation or evacuation treatment at 400–500°C before the adsorption. This investigation clearly shows the existence of stable –OH groups on the V_2O_5 surface at those high temperatures which are of interest in the ammoxidation of 3-picoline. These groups can act as adsorption sites for NH_3 at high temperatures, even though the adsorbed quantity is too small to be detectable by infrared absorption because of the low transmittance of vanadium oxides.

From published results it is not possible to conclude whether or not NH_3 is adsorbed on –OH groups at 200°C and higher temperatures according to Scheme 1, or on oxygen vacancies. The results of the acidity measurements are collected in Table 3. It is obvious that catalysts with a high concentration of acidic sites, 0, 10, and 90 mole% TiO_2, also have a low activity. Furthermore, a high activity tends to correspond to a lower acidity. However, the relation in the interval 30–70 mole% TiO_2 is somewhat irregular. This clearly shows that other factors are also of importance, e.g., the oxygen bond strength and the concentration of active species. By considering the results, it seems clear that a high concentration of acidic sites effectively blocks active species. The concentration of active species can, however, vary independently of the concentration of acidic sites at medium and low acidities. The correlation between a high acidity and a low activity indicates that the measured acidity can be considered to be a measure of the –OH group concentration under ammoxidation conditions. The amount of adsorbed 3-picoline is low at a high concentration of –OH groups because these groups have no ability to adsorb 3-picoline.



$$\underset{|}{\overset{OH}{}}\;-V- + NH_3 \longrightarrow \overset{O^-\cdots NH_4^+}{\underset{}{|}}\;-V-$$

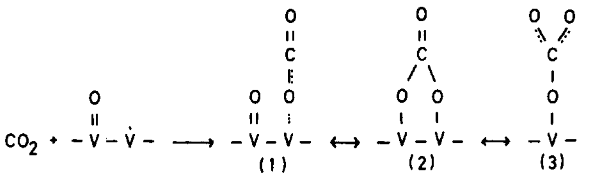
SCHEME 1

If the measured acidity were a measure of Lewis centers, it might be possible that these centers could act as adsorption sites for 3-picoline. This should result in the activity being high at a high surface acidity. The results given in Table 3 show the opposite. Evidence has been given (*20*) that 3-picoline is adsorbed on the oxide surface via the alkyl carbon and not via the ring or the nitrogen atom. This means that the adsorption probably takes place on a vanadyl group. Taking these facts into consideration, if the acidity were a measure of oxygen vacancies, a correlation should exist between selectivity and acidity. Such a correlation is not found.

The data given by Ai (*2*) on acidity and basicity of V_2O_5–TiO_2 catalysts differs considerably from those given in Table 3. This is due to differences in the preparation technique. The values in Table 3 refer to prereduced catalysts. The result of Ai concerns nonprereduced catalysts prepared by precipitation.

4. *Basicity of Catalysts*

Tha adsorption of CO_2 on the surface of oxides generally occurs in the form of carbonate-like species that reveal surface ba-



SCHEME 2

sicity. Hirota *et al.* (*21*) studied the exchange of oxygen between CO_2 and V_2O_5 at 370°C by using an isotope technique. Their results could be explained by assuming that CO_2 is dissociatively chemisorbed at a special site on the surface, composed of a vanadyl group and a vacant vanadium atom. These species were assumed to be easily convertible to other forms like a bridge type of adsorption and chemisorption of a CO_2 molecule on a surface oxygen atom. Fikis *et al.* (*22*) studied the same reaction at 400–500°C. They proposed a reaction scheme similar to that of Hirota *et al.* (*21*). The ESR spectra of a V_2O_5 crystal, which had been in contact with a mixture of CO and O_2 at temperatures above 400°C, were similar to those previously assigned to a V^{4+}–V^{5+} pair, accompanied by an oxygen defect (*23*). From these results, the adsorption at high temperatures can be illustrated according to Scheme 2.

During the prereduction of the V–Ti–O catalysts at 450°C, lower oxides and probably also oxygen defects were formed. These defects are surrounded by surface oxygen atoms. Therefore, surface sites exist which are similar to those proposed to be responsible for the adsorption of CO_2 (*21, 22*). Because these defects had already been created during the prereduction, it was thought that they could be measured by adsorbing CO_2 at a relatively low temperature after the samples had been outgassed. The initial amount of CO_2 adsorbed was, however, too high to possibly reflect the vacancy concentration. This could be due to the presence of physically adsorbed species. By choosing the amount of irreversibly adsorbed CO_2 at 21°C it was thought that this value better reflected the concentration of vacancies. The values are given in Table 3. It seems clear that the measured surface basicity can be correlated with the selectivity of formation of nicotinonitrile. This is also shown in Fig. 1. The correlation can be explained by assuming the basicity to be a measure of oxygen vacancies or some kind of diluted oxygen species, e.g., active oxygen atoms close to an oxygen defect. The existence of such species diminishes the possibility of complete oxidation to carbon oxides. This interpretation of CO_2 adsorption is in agreement with type (1) adsorption given in Scheme 2. The bridge type of adsorption can be excluded because no oxygen exchange between CO_2 and V_2O_5 occurs at 21°C. In accordance with the mechanism proposed for the decomposition of 2-propanol (*24*), it can be assumed that the vacancies can still play an active role in the ammoxidation reaction. This role involves the abstraction of hydrogen from the methyl group on 3-picoline. This can be supposed to be the first step in the mechanism of nicontinonitrile formation.

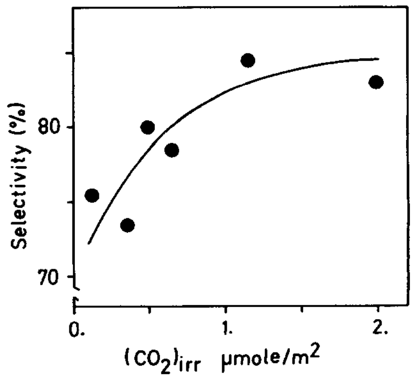


FIG. 1. Selectivity as a function of the basicity.

The existence of a correlation between the concentration of species with a vacancy and the selectivity of formation of nicotinonitrile is not quite expected. The role of ammonia also has to be considered in order to describe the system more completely. The ammoxidation reaction can be written:

$$(C_5H_4N)CH_3 + NH_3 + 3O \rightarrow (C_5H_4N)CN + 3H_2O$$

If 3-picoline is classified as an acid and ammonia and nicotinonitrile as bases, the reaction can be expressed as: Acid + Base → Base + Water. Brønsted acidic sites do not adsorb 3-picoline but can adsorb ammonia and nicotinonitrile. Basic sites can take part in the adsorption of 3-picoline but do not adsorb ammonia and nicotinonitrile. The acidity was measured by adsorbing ammonia. Nicotinonitrile is a weaker base than ammonia. Therefore the conclusion can be drawn that a selective catalyst should have a high concentration of both acidic and basic sites. This conclusion is strengthened by the results in Table 3, which show that the two most selective catalysts, containing 10 and 90 mole% TiO_2, also exhibit the highest concentration of both acidic and basic sites.

5. *Infrared Spectra of Pure Oxides*

The spectra of rutile TiO_2, the monoclinic form of V_2O_4, V_6O_{13}, and V_2O_5 are presented in Fig. 2. For a correct identification of V_2O_4 and V_6O_{13}, the X-ray diffraction patterns are also given. These patterns are in agreement with those given in the literature (*8*, *9*). The observed infrared bands are collected in Table 4.

The V_2O_5 spectrum between 250 and 1200 cm^{-1} shows seven peaks. The peak at 1023 cm^{-1} has been assigned to the stretching vibrations of the short double bond, $(V{=}O)^{3+}$ (*25*, *26*). A small peak can be observed at 968 cm^{-1}. This also seems to be the case in the V_2O_5 spectrum given by Fabbri and Baraldi (*27*). In other investigations it was not found (*25*, *26*). The nature of this peak has not been described in the literature. The band at 814 cm^{-1} has been attributed to V–O–V stretching vibrations (*25*, *26*). Bands in the range 400 to 600 cm^{-1} have been considered to be due to lattice vibrations (*26*) or V–O–V rocking vibrations (*22*). The nature of the peaks at 379 and 294 cm^{-1} is uncertain.

The infrared spectrum of V_6O_{13} has not been published previously. It has, however, been reported that V_6O_{13} shows bond stretching modes with a frequency of 900

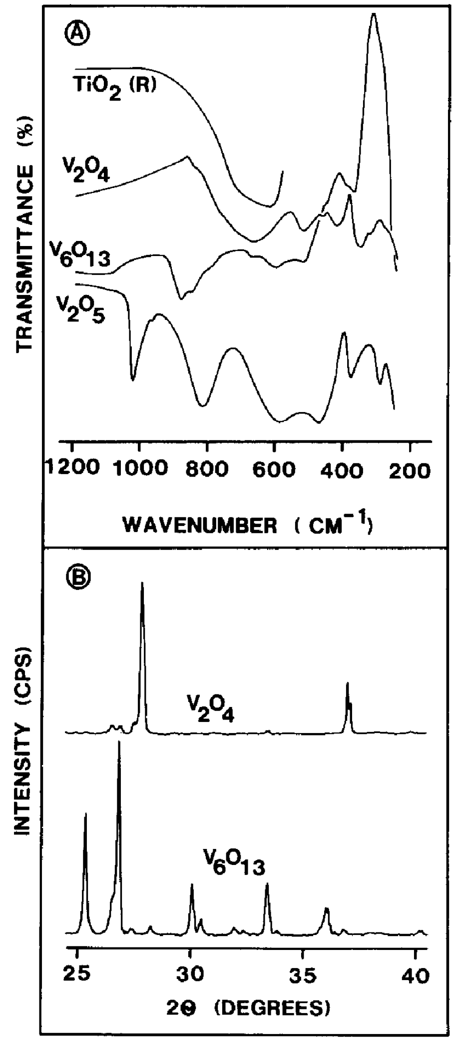


FIG. 2. (A) Infrared spectra of TiO_2 (rutile), V_2O_4, V_6O_{13}, and V_2O_5. (B) X-Ray diffraction patterns of V_2O_4 and V_6O_{13}.

TABLE 4

Infrared Band Maxima of V_2O_5, V_6O_{13}, and V_2O_4

Phase	Absorbance maximum (cm^{-1})	Intensity[a]
V_2O_5	1023	s
	968	w
	814	s
	590	s
	475	s
	379	m
	294	m
V_6O_{13}	885	s
	855	s
	795	m
	680	m
	595	m
	525	m
	470	w
	400	m
	380	m
V_2O_4	670	s
	527	m
	468	w
	425	m
	356	m
	320	w

[a] s, strong; w, weak; m, medium.

cm^{-1} (*28*). If the V_6O_{13} spectrum is compared with that of V_2O_5, it can be seen that there are similarities. The V_6O_{13} bands at 795–885, 470–680, and 380–400 cm^{-1} seem to correspond to the V_2O_5 peaks at 814, 475–590, and 379 cm^{-1}. The V_6O_{13} bands are composed of several peaks. The similarities in the spectra can be explained by the structural similarities between V_2O_5 and V_6O_{13}. The greater number of peaks in the V_6O_{13} spectrum can be understood since V_6O_{13} has three crystallographically different vanadium atoms and seven crystallographically different oxygen atoms, compared to V_2O_5 with three different oxygen atoms and all vanadium atoms the same (*8*). It is also obvious from the V_6O_{13} spectrum that peaks due to V═O bonds are absent. Peaks in the range 900–1100 cm^{-1} have been ascribed to stretching vibrations of Me═O bonds (*29*). The absence of pure V═O bonds in V_6O_{13} is documented by the charge distribution calculation performed by Dernier (*30*), showing that the greatest electron delocalization around a single V–O bond is 1.50 electrons.

In the preparation of the V_2O_4 sample, Merck V_2O_4 was heated at 400°C under vacuum and then cooled by keeping the sample tube at room temperature. The resulting V_2O_4 was the monoclinic form (*31*). The catalyst samples were cooled at the same temperature, and the V_2O_4 phase found in them at room temperature has monoclinic symmetry (Table 1). However, the structure of the V_2O_4 phase under the reaction conditions is uncertain. A monoclinic-to-tetragonal transition is known to occur at 340 K (*32*). Two other V_2O_4 phases, called VO_2(A) and VO_2(B), have been described (*33*). Important parameters determining the V_2O_4 structure are the temperature and the partial pressure of water. According to the phase diagram (*34*), it seems most likely that the V_2O_4 present under ammoxidation conditions has a rutile structure (tetragonal symmetry). The infrared spectrum of monoclinic V_2O_4 given in Fig. 2 agrees with the spectra obtained by others (*28, 35*). The broad band at 670 cm^{-1} has been proposed to be due to V–O–V stretching, and the peaks around 400–500 cm^{-1} to be due to lattice vibrations (*35*). The structure of the V_2O_4 samples investigated by Frederickson and Hausen (*25*) and Fabbri and Baraldi (*27*) is not mentioned, but the spectra given are not in agreement with that of monoclinic V_2O_4. The rutile structure of V_2O_4 was found to have no bands in the region 400–1200 cm^{-1} (*35*). Infrared spectra of VO_2(A) and VO_2(B) have been published (*34*).

6. *Infrared Spectra of Catalysts*

The infrared spectra of the prereduced V–Ti–O catalysts in the range 950–1050 cm^{-1} are shown in Fig. 3. The initial activity and selectivity of these catalysts are those values given in Table 3. It is obvious that a shoulder appears on the low wavenumber side of the V_2O_5 peak. No significant change in position of the V_2O_5 peak at 1023

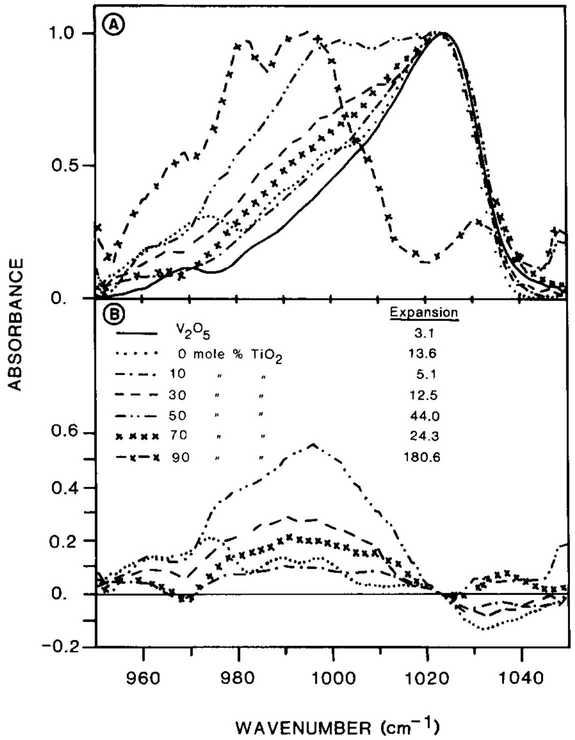


FIG. 3. (A) Infrared spectra of V_2O_5 and prereduced catalysts (1 mg sample). The strongest peak has been expanded to the absorbance equal to 1.0. (B) Resulting absorbance after subtraction of the V_2O_5 absorbance.

cm^{-1} can be observed, which is the case in the V_2O_5–MoO_3 (*3*) and the V_2O_5–SnO_2 (*4, 5*) systems. In Fig. 3A the absorbance maximum has been normalized to the value 1.0. The V_2O_5 spectrum was then subtracted, and the difference spectra obtained are presented in Fig. 3B. These spectra clearly show the existence of a band between 960 and 1020 cm^{-1} with a maximum around 995 cm^{-1}. The catalyst with 90 mole% TiO_2 also exhibits the same band, but no V_2O_5 peak. The only phases in the catalysts which could be identified by XRD were V_2O_5, V_6O_{13}, V_2O_4, and TiO_2, but according to Fig. 2 this band cannot be due to any of these phases.

The band at 995 cm^{-1} could not be observed in nonprereduced samples, and according to Fig. 3 it was also present in the catalyst with no TiO_2 phase. It has been shown that V_2O_5/V_6O_{13} boundaries are active and selective in the ammoxidation of 3-picoline (*1, 5, 6*). Therefore it was assumed that the band at 995 cm^{-1} can be due to such boundaries. For this reason, an attempt was made to prepare a sample with V_2O_5/V_6O_{13} boundaries. NH_4VO_3 was decomposed at 700°C in a nitrogen atmosphere. It has been found that V_2O_5 and V_6O_{13} are obtained when NH_4VO_3 is heated above 500°C in the presence of N_2 or H_2O (*36, 37*). The idea was that boundaries between V_2O_5 and V_6O_{13} should be formed in a detectable amount, because NH_3, which is a reducing agent, was evolved throughout the bulk of the material. As can be seen in Fig. 4B the product obtained was a mixture of V_2O_5 and V_6O_{13}. Figure 4A shows the infrared spectrum of the V_2O_5–V_6O_{13} mixture. By subtracting the V_2O_5 spectrum it is seen

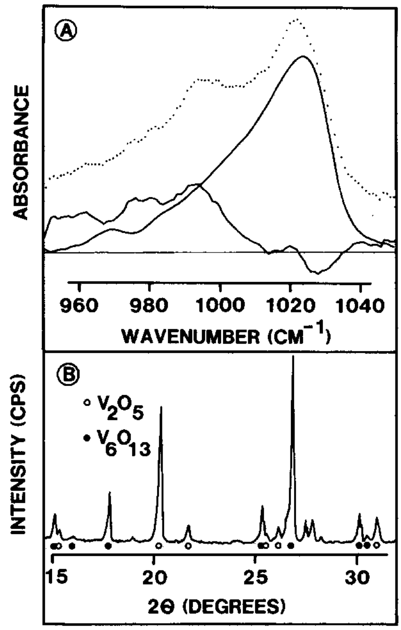
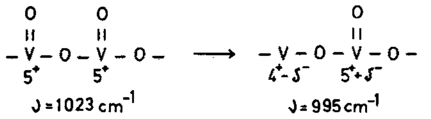


FIG. 4. (A) Infrared spectrum of NH_4VO_3 decomposed in a N_2 atmosphere at 700°C. (B) X-Ray diffraction pattern of the decomposition product.

that the difference spectrum contains the same band around 995 cm^{-1}, which was observed in the catalyst samples.

The nature of the boundaries between V_2O_5 and V_6O_{13} is not known. It has been demonstrated that sharp coherent V_2O_5/V_6O_{13} boundaries can be formed, because of a structural fit (*38*). Even though a crystallographic fit exists, it is possible that the boundary is not a sharp border but a transition region. Several oxides and defect structures with a composition between V_2O_5 and V_6O_{13} have been reported. In an electron microscopic investigation of the decomposition of V_2O_5, Tilley and Hyde (*39*) found two superstructures, 7-fold and 24-fold, of V_2O_5 at initial stages at low temperatures. Later on, a phase called VO_x could be observed. In samples annealed above 350°C, V_6O_{13} and V_3O_7 were assumed to be formed. The formation of V_2O_5 twin planes has also been observed in partly reduced V_2O_5 crystals (*40*). Waltersson *et al.* (*41*) have determined the structure of V_3O_7. Two crystallographically different V_4O_9 phases have been described. A V_4O_9 structure has been reported by Wilhelmi and Waltersson (*42*). However, calculations have indicated that the most likely composition of this phase is $V_4O_8(OH)$ (*43*). Another V_4O_9 phase has been observed by Théobald *et al.* (*44*). This phase was shown (*45*) to be identical with VO_x and a phase Q (*46*). A model of this structure was given, based on an ordered superlattice of oxygen vacancies in V_2O_5. A V_2O_5 structure with ordered oxygen vacancies was also proposed to give rise to 7-fold superlattice diffraction patterns (*39*). Théobald *et al.* (*47*) have given X-ray diffraction patterns of two V_6O_{13} phases, called C and D. It has been assumed (*48*) that these are identical with the V_6O_{13} structure, which has been refined by Wilhemi *et al.* (*8*).

The X-ray diffraction patterns of the catalysts did not agree with any of those given in the literature for oxides with a composition between V_2O_5 and V_6O_{13}. Except for the lines due to the phases given in Table 2, only a few additional weak lines were found. Their position varied from one sample to another. Also, the infrared difference spectrum shown in Fig. 3B was not identical with the spectra obtained for VO_2(A), VO_2(B), V_4O_9, or vanadium oxide hydrates (*34*). Under certain conditions, an ir band around 1000 cm^{-1} was found in V–Ti–O catalysts (*49*). The origin of this band was not established. In another investigation (*4*), it was found that a band around 1000 cm^{-1} appeared in melted V–Ti–O catalysts with a high TiO_2 content. This band was assigned to V_2O_4. However, the V_2O_4 reference spectrum given does not seem to agree with any other published V_2O_4 spectrum (*25, 27, 28, 34*). Bond *et al.* (*50*) have also given spectra of V–Ti–O catalysts. No additional band around 1000 cm^{-1} was observed in catalysts with a low sodium content. A peak at 1035 cm^{-1} due to monomeric $(V{=}O)^{3+}$ stretching vibrations in $VOCl_3$ has been reported (*51*). The stretching frequencies of $(V{=}O)^{2+}$ units in a number of



SCHEME 3

compounds have been found in the interval 955–978 cm^{-1} (*52*). No additional and reproducible X-ray lines were found in the catalyst samples, in spite of quite detectable infrared absorption at 995 cm^{-1}, which leads to the conclusion that this band can be due to a V_2O_5 phase with a number of disordered vacancies in the lattice or a nonstoichiometric V_6O_{13} phase. The shift of the V=O frequency from that for $(V{=}O)^{3+}$ toward that for $(V{=}O)^{2+}$ can thus be related to a decrease of $p_\pi - d_\pi$ oxygen–metal interactions and an increased electrostatic repulsion of the vanadium and oxygen species, as illustrated in Scheme 3 (*24, 53*).

The amount of V_2O_5 in prereduced catalysts relative to the amount before reduction is shown in Fig. 5. The calculation was performed by using X-ray data as well as ir data. The X-ray analysis refers to unground catalyst particles. The variance of both calculations is large, about ±50%. This can be expected because both methods are only semiquantitative. The results obtained by the two methods are different. The ir analysis gives information on the bulk composition, and the X-ray analysis on unground particles gives relatively more information on the surface layers. The conclusion is that the degree of reduction increases with the amount of TiO_2, and that V_2O_5 is the phase at the catalyst core. The composition of the vanadium oxide phase in the catalysts is presented in Fig. 6, which shows that the amount of V_2O_4 increases with the TiO_2 content. Kimizuka *et al.* (*28*) found that a relatively weak band appeared at about 1000 cm^{-1} in the ir spectrum of nonstoichiometric V_2O_4. It was assumed that this band may be caused by $(V{=}O)^{3+}$ stretching vibrations. Therefore, it seems possible that the new band observed at 995 cm^{-1} in the catalysts investigated is due to two defects: (i) a nonstoichiometric V_2O_5 or V_6O_{13} phase at low TiO_2 contents and (ii) an increasing amount of a nonstoichiometric V_2O_4 phase at higher TiO_2 concentrations. The weakening of the V=O bonds, if compared to those in pure V_2O_5, is in both cases caused by neighbouring V^{4+} ions. Due to the weakening of the V=O bond, the band at 995 cm^{-1} can be considered to be a measure of activity, provided all the species are situated on the surface. This is not completely the case, but because they are located at the outer parts of the catalysts, these oxygens may affect the catalytic activity. The relative amount per surface area was calculated. These values are plotted in Fig. 7, which shows that the amount increases with the TiO_2 content. In conjunc-

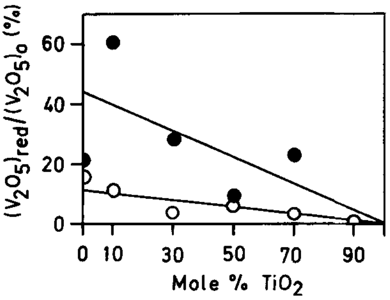


FIG. 5. Amount of V_2O_5 in prereduced catalysts relative to the amount before reduction. ○, from X-ray data; ●, from ir data.

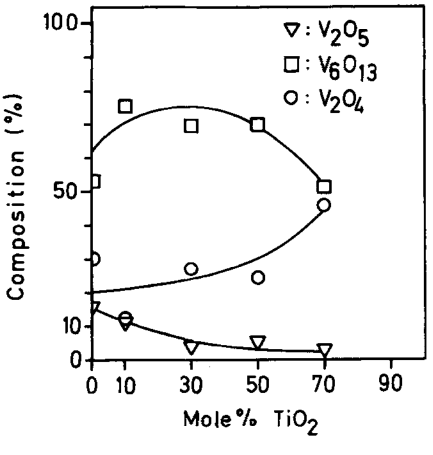


FIG. 6. Vanadium oxide composition in prereduced catalysts.

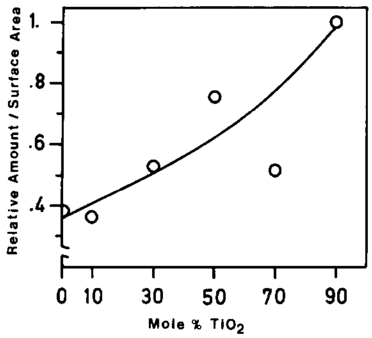


FIG. 7. Relative amount per surface area of V=O bonds at V_2O_5/V_6O_{13} boundaries as a function of mole% TiO_2.

tion with a low concentration of -OH groups on the surface, this can be essential for the increasing activity, which has been observed for a TiO_2 content up to 50 mole% (Table 3). The low activity of the 90 mole% TiO_2 catalyst depends on the high concentration of -OH groups on the surface. Another fact of importance is the possibility that the surface is not covered completely with vanadium oxides, thus exposing some of the TiO_2 phase. It has been found that TiO_2 with dissolved V^{4+} ions is selective but less active in the oxidation of butadiene (*50*).

7. *Catalytic Effect of* TiO_2

The catalytic effect of TiO_2 in vanadium oxide catalysts is well established. The origin of this effect depends on the method of preparation. It has been demonstrated that TiO_2 (anatase) increases the reduction rate of molten V_2O_5 in N_2 and O_2 atmospheres (*54*). Adamska *et al.* (*55*) found that TiO_2 (anatase) increases the rate of reduction with hydrogen at 540–620°C. Furthermore, TiO_2 (rutile) has been found to have an effect on the reduction rate of V_2O_5 (*50*). The oxygen loss started at about 900°C. The weight loss of V_2O_5–TiO_2 (anatase) mixtures observed in the solid state was explained as a result of topotactic reactions (*38*). From the references cited it may be concluded that the activation of the catalysts creates V^{4+} species, which therefore seem to be of great importance for the performance of the catalysts.

The band in the difference spectrum in Fig. 3B has the same position whether TiO_2 is present or not. Furthermore, the degree of reduction increases with the TiO_2 content (Figs. 5 and 6). These results can be explained by considering the work of Clauws and Vennik (*56, 57*), who found a defect in V_2O_5 crystals by studying the optical absorption. This defect was attributed to oxygen vacancies. The same near-infrared spectrum was obtained for TiO_2-promoted V_2O_5 crystals, but the intensity was greatly enhanced. This effect was explained by the incorporation of Ti^{4+} into V_2O_5, which was compensated by the creation of oxygen vacancies. A vanadium ion adjacent to the vacancy may localize an excess electron. This would lead to increased formation of V^{4+}. The catalysts used in this investigation were prepared by heating V_2O_5 and TiO_2 at 1150°C. At this high temperature Ti^{4+} is dissolved in the V_2O_5 melt and V^{4+} species are formed. These species weaken the V=O bonds due to increased electrostatic repulsion of the vanadium and oxygen ions, which was illustrated in Scheme 3. The amount of V^{4+} species probably increases with the TiO_2 content, since the contact area between the molten V_2O_5 and the TiO_2 particles increases. The increase in the amount of V^{4+}, as well as weak V=O groups, results in an increased degree of reduction during the H_2 treatment of the catalysts. This explains Figs. 5 and 6. It also to some extent explains the results plotted in Fig. 8, which shows the amount of irreversibly adsorbed CO_2 as a function of the TiO_2 content. The increase of $(CO_2)_{irr}$ from 0 to 10 mole% TiO_2 might be caused by an increase in the number of oxygen vacancies. The minimum at 30 mole% TiO_2 can be due to elimination of vacant sites by shear. It has been proposed (*58, 59*) that shear is likely to occur if the concentration of vacancies becomes too great. The final increase of $(CO_2)_{irr}$ from 30 to 90 mole% TiO_2 can then be considered to be due to an

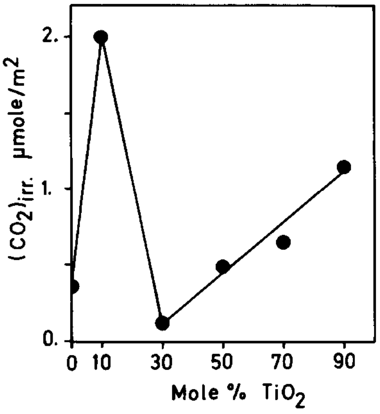


FIG. 8. Basicity as a function of the TiO_2 content.

increased concentration of vacancies in the shear structure.

CONCLUSIONS

The activity of the catalysts in the ammoxidation of 3-picoline is favored by the presence of active V_2O_5/V_6O_{13} boundaries, which are probably a region of a nonstoichiometric V_2O_5 or V_6O_{13} phase with V=O species adjacent to V^{4+} ions. The V=O bonds are weakened because of an increased electrostatic repulsion between the vanadium and oxygen species.

Active V=O groups are also selective if they are in the vicinity of hydroxyl groups and oxygen vacancies.

The promotional effect of TiO_2 is to increase the concentration of V^{4+}, which leads to an increased number of weak V=O bonds.

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