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

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Ammoxidation of 3-picoline was studied on reduced V–Ti–O catalysts with V_6O_{13} as the major vanadium oxide. The results showed that the initial activity as a function of the TiO_2 content reached a maximum at 50–60 mole% TiO_2. It is proposed that there is maximum contact between the vanadium and titanium phases at this composition, which results in a weakening of the $(V{=}O)^{3+}$ surface bond. The selectivity of formation of nicotinonitrile exhibited a maximum of 83% at 10 mole% TiO_2 and minima of 73 and 75% at 0 and 30 mole% TiO_2, respectively. At higher TiO_2 concentrations the selectivity increased continuously to 83% at 90 mole% TiO_2. The variation of the selectivity of formation of nicotinonitrile depends on the V^{4+}/Ti^{4+} ratio in the TiO_2 phase. It was also found that the conversion and yields varied with the reaction time, which could be explained by the fact that reduced vanadium oxides were oxidized to V_2O_5 during the ammoxidation process. This oxidation leads to the formation of active and highly selective boundary surfaces between the TiO_2-promoted vanadium oxides V_6O_{13} and V_2O_5.

I. INTRODUCTION

Vanadium catalysts are generally used in ammoxidation processes. To these catalysts TiO_2 is often added as a promoter or a carrier (*1–3*). It has been found by ESR studies (*4*) that in V_2O_5–TiO_2 catalysts used in the oxidation of *o*-xylene, some of the vanadium atoms are dissolved in the rutile lattice. This incorporation leads to a loss of weight (*5, 6*), caused by the loss of oxygen. This loss of weight was found to occur simultaneously with a transformation of TiO_2 from the anatase to the rutile form. These reactions are activated by the structural similarities between some vanadium oxides and anatase (*7*).

The activities and selectivities of V_2O_5–TiO_2 catalysts with different compositions have in some cases been examined. The most active catalysts in the oxidation of *o*-xylene were found to contain 15 mole% V_2O_5 both in anatase and rutile catalysts (*5*). Other investigations of the oxidation of *o*-xylene (*8*) have shown that the selectivity for C_8-products has two maxima at 12.5 and 90 mole% TiO_2. A minimum was obtained at 35 mole% TiO_2. The activity as a function of the composition had a maximum at 65 mole% TiO_2. Similar results appeared in the oxidation of 1-butene (*9*). The reasons for the variation in activity and selectivity with catalyst composition in the V_2O_5–TiO_2 system have not yet been clarified. It has been proposed (*5*) that maximum contact between V_2O_5 and TiO_2 particles leads to maximum activity. The promoting role of TiO_2 has been suggested to consist of stabilizing vanadium in its lower oxidation states by forming solid solutions in the rutile lattice (*4*). We have previously reported (*10*) that V_6O_{13} was more active and selective in the ammoxidation of 3-picoline than both V_2O_5 and V_2O_4, and that catalysts containing both V_2O_5 and V_6O_{13} were more selective than pure V_6O_{13}, which might be explained by active boundary surfaces. Therefore it seemed to be of interest to investigate the promoting effects of TiO_2 in prereduced V_2O_5–TiO_2 catalysts containing V_6O_{13} as a major component.

II. METHODS

1. Apparatus and analysis. The apparatus and product analysis used in this work were the same as described elsewhere (*10*).

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2. Catalyst preparation and characterization. The catalysts were prepared by heating V_2O_5 and TiO_2 (anatase) powders in a quartz crucible in a high temperature oven for 3 hr at 1150°C. The fused catalysts were divided into small particles, the 14- to 25-mesh (1.41–0.71 mm) fraction was collected, and was then reduced in a hydrogen atmosphere for 1 hr at 450°C. The sample was shaken during the reduction to avoid composition gradients in the sample tube.

The unused catalysts were characterized by their specific surface areas, mean oxidation numbers of vanadium, and determination of the phases present by X-ray diffraction analysis.

The surface areas were determined by the BET method using N_2 at liquid N_2 temperature. The areas are shown in Fig. 1. The catalyst with 10 mole% TiO_2 had the largest area, 13.2 m^2/g, and pure TiO_2 catalyst the smallest one, 0.6 m^2/g.

The mean oxidation numbers of vanadium were estimated by titrimetric methods (*11*). The value was 4.5 for catalysts with 0 and 10 mole% TiO_2, 4.4 for catalysts with 30, 50, and 70 mole% TiO_2, and 4.3 for the 90 mole% TiO_2 catalyst.

X-Ray diffraction analysis was carried out on catalysts by a Philips X-ray diffraction instrument using a PW 1310/01/01 generator and Cu*Kα* radiation. The results of the investigations performed on undivided catalyst particles in a rotating sample holder are collected in Table 1. The results show that of the vanadium oxides, V_6O_{13} was the major phase. This was also confirmed by the typical bluish-black color. In catalysts containing 10, 30, and 50 mole% TiO_2 very small amounts of TiO_2 (anatase) could be detected. This was not the case in catalysts with 70 and 90 mole% TiO_2. Vanadium oxides could not be detected on the surface of the 90 mole% TiO_2 catalyst, probably because all the vanadium was incorporated in the TiO_2 (rutile) lattice. This has also been described by others (*6*), who suggest the formation of a compound $V_{0.04}Ti_{0.96}O_2$. If the 90 mole% TiO_2 catalyst was analyzed not as a particle but as a powder, V_2O_5 could also be found as a separate phase.

TABLE 1

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 (rutile)
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

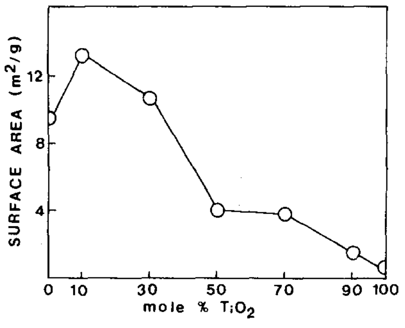

FIG. 1. Specific surface area as a function of mole% TiO_2.

3. Materials. The catalysts studied were prepared from V_2O_5 and TiO_2 supplied by Riedel-De Haën AG and Baker Chemical Co., respectively.

The 3-picoline used was from Merck-Schuchardt and contained 97% 3-picoline. Air, ammonia, and hydrogen were commercially available gases and were used without further purification.

4. Experimental. The experiments were performed at atmospheric pressure in a glass reactor with an internal diameter of 2 cm. A thermocouple was positioned in the center of the reactor. The bed depth of the catalyst was about 3 cm, and the inlet reaction mixture of 32 liters/hr contained 232–254 moles of air, 13–14 moles of ammonia, and 56–62 moles of water vapor for each mole of 3-picoline. The reaction was usually performed in the interval 300–400°C.

III. RESULTS

1. *Definitions*

Conversion (%) is defined as the fraction of 3-picoline converted into products ×100, yield (%) is the fraction of 3-picoline converted into a specific product ×100, and selectivity (%) is the ratio of 3-picoline converted to a specific product to that totally converted ×100.

2. *The Influence of the Reaction Time*

The conversion and the yields of nicotinonitrile, carbon oxides, and tar were analyzed as a function of the reaction time. 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 used only once.

Some of the results for the catalyst containing 30 mole% TiO_2 are shown in Fig. 2 at 307 and 385°C. The conversion decreased with the reaction time at the lower temperature. At the higher temperature the decrease was not so pronounced. The yield of nicotinonitrile also decreased strongly at temperatures around 300°C, but at temperatures above 350°C, on the contrary, the yield of nicotinonitrile increased with the reaction time. Concerning tar and carbon oxides, the yields decreased with reaction time at all temperatures investigated. The influence of the reaction time on conversion and yields was virtually the same for the catalysts containing 10, 30, 50, and 70 mole% TiO_2, and also for the catalyst without any TiO_2 (*10*). The yield of nicotinonitrile and the conversion on the catalyst with 90 mole% TiO_2 decreased with the reaction time at all temperatures between 305 and 525°C. The yields of tar and carbon oxides decreased slowly at temperatures below 400°C, and at higher temperatures these yields increased with the reaction time.

3. *Activities as a Function of the TiO_2 Content*

The specific surface areas of the catalysts varied with the TiO_2 content (Fig. 1). To compare the activities related to the initial composition of the catalysts, the rate constants at different temperatures were calculated from diagrams like Fig. 3, which were obtained by extrapolating the conversion and yields to zero reaction time. It was assumed that the complicated reaction scheme could be approximated by first-

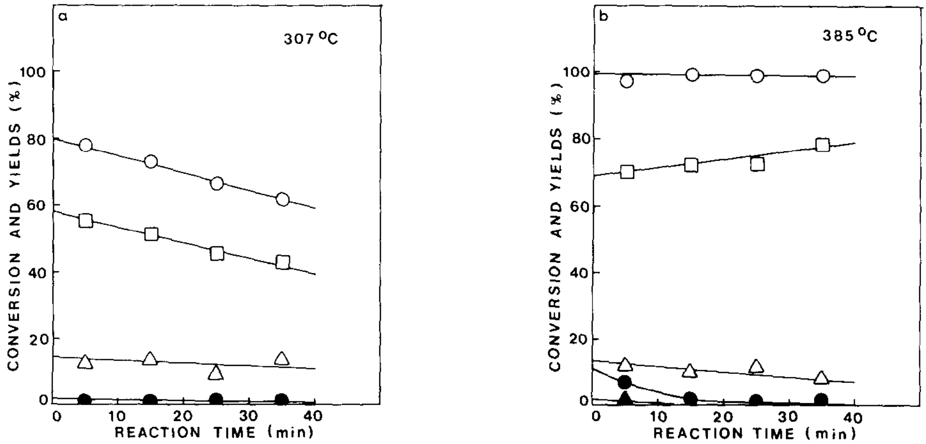

FIG. 2. Conversion and yields on 30 mole% TiO_2 catalyst as a function of reaction time at (a) 307 and (b) 385°C. ○, Conversion of 3-picoline; □, yield of nicotinonitrile; △, yield of tar; ●, yield of carbon dioxide; and ▲, yield of carbon monoxide.

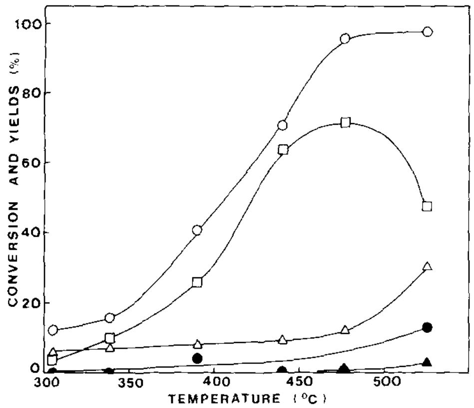

FIG. 3. Conversion and yields on 90 mole% TiO_2 catalyst as a function of temperature. ○, Conversion, □, yield of nicotinonitrile; △, yield of tar; ●, yield of carbon dioxide; and ▲, yield of carbon monoxide.

order reactions in a limited interval of temperature, where the main product was nicotinonitrile and only minor amounts of tar and practically no carbon oxides were formed. To see whether the approximation was reasonable, plots of the Arrhenius equation were made. It has been shown (*12*) that ammoxidation of 4-picoline on a vanadia catalyst can be expressed by first-order kinetics.

The material balance of the integral reactor could be written

$$\frac{A}{F_0} = \int_0^x \frac{dx}{-r}$$

where A = the catalyst surface area (m^2), F_0 = the inlet flow of 3-picoline (moles/min), r = reaction rate (moles/m^2, min), and x = total conversion. The following reactions were assumed.

$$(C_5H_4N)CH_3 + NH_3 + 1.5\ O_2 \rightarrow (C_5H_4N)CN + 3H_2O \quad (1)$$

$$(C_5H_4N)CH_3 + 1.5\ O_2 \rightarrow C_5H_5N + CO_2 + H_2O \quad (2)$$

$$(C_5H_4N)CH_3 + 5.75\ O_2 \rightarrow 6CO + NO_2 + 3.5H_2O \quad (3)$$

$$(C_5H_4N)CH_3 + 6.5\ O_2 \rightarrow HCN + 5CO_2 + 3H_2O \quad (4)$$

$$(C_5H_4N)CH_3 + 8.75\ O_2 \rightarrow 6CO_2 + NO_2 + 3.5H_2O \quad (5)$$

$$(C_5H_4N)CH_3 \rightarrow \text{tar} \quad (6)$$

If the conversions of 3-picoline in the different steps are denoted $x_1, x_2, \ldots, x_6$, the partial pressure of 3-picoline is $P_{3-p} = P_0(1 - x)(1 + a + b + c + d + \epsilon)^{-1}$ atm where a, b, c, and d are moles of ammonia, oxygen, nitrogen, and water, respectively, relative to one mole of 3-picoline in the inlet flow, P_0 is the total pressure, and ϵ is a function of $x_1, x_2, \ldots, x_6$. In this case $\epsilon \ll (1 + a + b + c + d)$. If the consumption of 3-picoline is written $r = -k \cdot C_{3-p}$, the rate constant obtained from the material balance is

$$k = \frac{F_0RT(1 + a + b + c + d)}{P_0A \ln(1 - x)} \quad m^3\ min^{-1}\ m^{-2}$$

and the initial reaction rate can be written

$$r_0 = \frac{k \cdot P_0}{RT(1 + a + b + c + d)} \quad \text{moles } m^{-2}\ min^{-1}.$$

The Arrhenius equation for the different catalysts has been plotted in Fig. 4. The calculated apparent activation energies vary between 67 and 142 kJ/mole (Table 2), which seems to be of a reasonable magnitude (9). No correlations with the apparent activation energies of the different catalysts could be found. The initial reaction rates at 320 and 380°C, comprising the interesting temperature interval in the ammoxidation

TABLE 2

Apparent Activation Energies

Catalyst (mole% TiO_2)	E_a (kJ/mole)
0	138
10	126
30	67
50	142
70	92
90	71

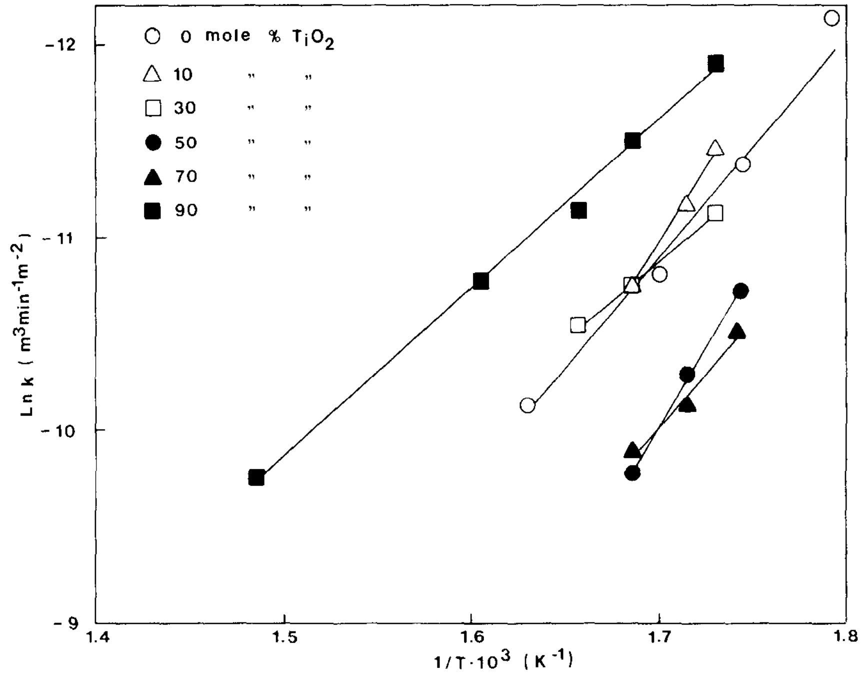

FIG. 4. Ln k as a function of $1/T$ for different V–Ti–O catalysts.

of 3-picoline, are shown in Fig. 5. It is obvious that the activity has a maximum at 50–60 mole% TiO_2.

An average reaction rate could also be calculated from the data given in Table 3. It is possible to compare the average reaction rates of the different catalysts because the conversions were of the same magnitude, except in the 90 mole% TiO_2 case. The calculated reaction rate of this catalyst is too high to be comparable, because of the low conversion, but this does not change the principal shape of the curve in Fig. 5, showing the average reaction rate as a function of the catalyst composition. Also when average reaction rates are compared, it is found that the most active catalyst contains 50–60 mole% TiO_2.

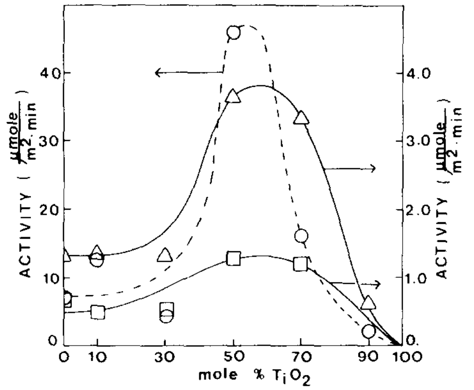

FIG. 5. Activities as a function of the TiO_2 content. △, Initial reaction rate at 320°C; □, average reaction rate at 320°C; and ○, initial reaction rate at 380°C.

4. Selectivities as a Function of the TiO_2 Content

Concerning the selectivity of nicotinonitrile on the different catalysts, it is of interest to compare them at a high conversion, the same ratios between the reactants and at the same temperature. Then, of course, the charged catalyst surface area will not be the same for the different catalysts. In Fig. 6 the selectivities of nicotinonitrile on catalysts with a given initial composition are compared at 90% conversion. The temperatures have varied somewhat, between 320 and 328°C. The selectivity varied between

TABLE 3

Calculated Average Reaction Rates (r_m) at 320°C

Catalyst (mole% TiO_2)	Charged catalyst surface area (m^2)	Conversion (%)	r_m (μmole/m^2 · min)
0	97.9	90	0.69
10	142.5	91	0.48
30	118.8	89.5	0.56
50	49.1	83	1.26
70	52.7	86.5	1.22
90	13.7	12	0.65
100	—	Inactive	0

73 and 83%, with a maximum at 10 mole% TiO_2 and a minimum at 30 mole% TiO_2. At larger TiO_2 contents, the selectivity increased continuously.

5. *Composition of Used Catalysts*

Used catalysts were examined by X-ray diffraction analysis. It was found that no new phases were created in the catalysts during the ammoxidation, but that reduced vanadium oxides were oxidized. The average vanadium oxidation number in catalysts, which had been used at 360°C for 40 min, was determined by the titrimetric method. The oxidation number had increased from 4.5 to 4.6 for catalysts with 0 and 10 mole% TiO_2, from 4.4 to 4.5 for catalysts with 30, 50, and 70 mole% TiO_2, and from 4.3 to 4.5 for the 90 mole% TiO_2 catalyst.

DISCUSSION

It is known that V_2O_5 is not soluble in TiO_2 (*13*), but that V^{4+} can be incorporated in the TiO_2 lattice (*4*, *6*, *14*). This means that in the catalysts investigated containing TiO_2, some V^{4+} is incorporated in the rutile lattice. The ratio V^{4+}/Ti^{4+} has been reported to depend on the V_2O_5 content (*5*, *15*). It has also been suggested (*6*) that about 8% w/w V_2O_5 becomes incorporated as V^{4+} in the rutile lattice, through the formation of $V_{0.04}Ti_{0.96}O_2$.

The results (Fig. 5) showed that the TiO_2 content had a great influence on the activity, which reached a maximum at 50–60 mole% TiO_2. It is possible that there is maximum contact between the V_6O_{13} and the TiO_2 phases at this composition, which could result in a weakening of the surface $(V{=}O)^{3+}$ bond. Another explanation could be that the catalyst is bifunctional, in which the V_6O_{13} phase and the TiO_2 phase with incorporated V^{4+} activate different steps in the mechanism. It is not probable that the TiO_2 phase with dissolved V^{4+} is especially active. This phase must dominate in the catalyst with 90 mole% TiO_2, but this catalyst was found to have low activity. The variation in the selectivity of formation of nicotinonitrile with the TiO_2 content (Fig. 6) can depend on the V^{4+}/Ti^{4+} ratio in the rutile phase, which varies with the vanadium oxide content (*5*, *15*).

The maxima and minima in activity and selectivity obtained as a function of the catalyst composition appear at essentially the same TiO_2 content as reported for the oxidation of *o*-xylene (*8*) and 1-butene (*9*) on nonprereduced V–Ti–O catalysts. This shows that TiO_2 affects V_2O_5 and V_6O_{13} in a similar way, probably by weakening the surface $(V{=}O)^{3+}$ bond.

From X-ray diffraction analysis and titrimetric estimations of the average oxidation number of vanadium in used catalysts, it follows that some V_6O_{13} is oxidized to V_2O_5 during the ammoxidation process. These changes in the composition of the catalysts were followed by

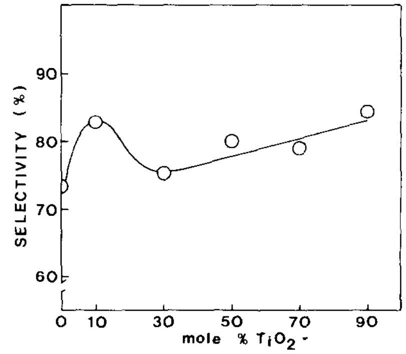

FIG. 6. The selectivity of nicotinonitrile as a function of the TiO_2 content.

the variation in the conversion and yields with the reaction time (Fig. 2). It has been proposed (*10*) that the results of low temperatures on a V_6O_{13} catalyst with no addition of TiO_2 can be explained by oxidation of the catalyst surface to V_2O_5, which is less active than V_6O_{13}. It was also found that the results at high temperatures, strongly increasing yield and selectivity of nicotinonitrile, cannot be explained by two separately acting phases, V_2O_5 and V_6O_{13}. These results were discussed in terms of formation of boundary surfaces between V_2O_5 and V_6O_{13}, which must be more active, and especially more selective, than any separate phase. As the dependence on conversion, yields and selectivities on the reaction time, and the temperature was essentially the same for the reduced vanadium catalysts with the addition of TiO_2 up to 70 mole%, as was found on the catalyst with no TiO_2 phase, it seems reasonable to suggest the same explanation for the results in this case, i.e., separately acting TiO_2-promoted V_2O_5 and TiO_2-promoted V_6O_{13} at low temperatures, and the formation of active and highly selective boundary surfaces between the TiO_2-promoted vanadium oxides at high temperatures. The results for the catalyst with 90 mole% TiO_2 were different in that the yield of nicotinonitrile decreased with the reaction time at all temperatures. An explanation for this can be that V_6O_{13} is present only as a thin layer on the TiO_2 phase, which has no bulk capacity for oxygen. This means that boundary surfaces between promoted V_2O_5 and promoted V_6O_{13} cannot be formed to any great extent, because of the limited transport of oxygen from the surface to the bulk.

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