Studies on the V₂O₅-TiO₂ System

Part 3.—Monolayers of V₂O₅

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The catalytic behaviour of anatase- and rutile-vanadium monolayer-like catalysts has been studied in the dehydration of *N*-ethylformamide (NEF) in the presence of oxygen. The catalysts were prepared using two methods: grafting and impregnation. Physicochemical characterizations of the fresh and used samples were carried out using B.E.T. surface analysis and XRD, XPS and FTIR techniques.

The grafted samples are composed of the vanadium monolayer over the surface of anatase which undergoes sintering in the course of the catalytic reaction, probably forming V_6O_{13} . The vanadium monolayer formed on the anatase can protect it against the influence of the V_2O_5 crystals and may inhibit the anatase-into-rutile transformation during the calcination of catalysts. The impregnated samples are composed of fine grains of dispersed V_2O_5 in contact with the anatase grains. Calcination of these impregnated samples leads to the formation of a thin rutile-like layer on the surface of the anatase grains. The catalytic behaviour of these samples is similar to that of the V_2O_5 -TiO₂(rutile) catalysts.

There is no difference between the two rutile samples. Their catalytic properties seem to be a superposition of those found in pure rutile and V_2O_5 .

1. Introduction

In the previous papers of this series,^{1,2} N-ethylformamide (NEF) dehydration was studied using mechanical mixtures of TiO₂ (rutile or anatase) with V_2O_5 or V_6O_{13} as catalysts. The magnitude of the synergy between anatase or rutile and V_2O_5 was monitored as a function of the oxygen concentration in the feed, gas hourly space velocity (GHSV) and the thermal treatment of the samples.

It has been established that pure V_2O_5 undergoes reduction with the reaction mixture; the nature of the reduced vanadium oxide formed depends on the oxygen content in the feed. Compared with pure V_2O_5 , TiO₂(rutile) disadvantages the stabilization of vanadium in the +5 oxidation state, shifting the redox equilibrium of the vanadium oxides. Rutile promotes $V_2O_4(R)$ formation. On the contrary, in the presence of anatase V_2O_5 reduction stops at V_6O_{13} . V_6O_{13} is stabilized by anatase against further reduction or reoxidation with the reaction mixture. In addition, it was established that V_6O_{13} is the most selective phase in NEF dehydration. More reduced phases such as $V_2O_4(R)$ or $VO_2(B)$ are more active but less selective.

The cooperation between TiO_2 and V_2O_5 is proportional to the number of contacts between them. V_2O_5 reaches maximum contact with titanium oxide by its dispersion over the surface of the TiO_2 grains. The phenomenon of dispersion was observed for both the anatase and the rutile support.

The dispersion of V_2O_5 increases with the calcination of the oxides at high temperatures, bringing about a rise in the propiononitrile yield (the dehydration product). However, calcination at high temperatures can also lead to partial anatase-to-rutile transformation, which results in a decay of the catalytic properties.

In the first two papers, catalysts were prepared as mechanical mixtures of the two oxides, V_2O_5 and TiO_2 , prepared separately. This method was chosen in order to avoid any contamination between the oxides. It has also been shown that under certain catalytic conditions (reaction tempera-

ture = 623 K; O/N ratio = 0.8; GHSV = 400 h⁻¹), the difference in the catalytic behaviour of rutile and anatase mixtures is more pronounced. It seems to us that the intentional deposition of ions on the surface of TiO₂ enhances the phenomena observed with the mechanical mixtures and gives valuable information concerning the solid-state equilibrium of this system.

The aim of the present work is to determine the catalytic behaviour of anatase and rutile vanadium monolayer-like catalysts. The catalysts were prepared using two methods: grafting and impregnation with vanadium oxalate. The grafting technique allows for the production of a vanadium monolayer on anatase. Impregnation of anatase with vanadium oxalate results in the formation of very fine, dispersed V_2O_5 with a structure close to crystalline V_2O_5 , as determined by EXAFS and XANES.³ The study of these catalysts involved catalytic activity measurements and physicochemical characterization of the fresh and used samples. Both supports, anatase and rutile, were studied. As in the case of the mechanical mixtures, dehydration of NEF was used as a reaction test. Our objective was to compare the results obtained with the monolayer catalysts with the mechanical mixtures of vanadium with the rutile and anatase presented in the previous papers.

2. Experimental

2.1 Materials

TiO₂(anatase) ($S_{B.E.T.} = 46 \text{ m}^2 \text{ g}^{-1}$), denoted henceforth as A, Eurotitania 1 was supplied by Tioxide and VOCl₃ and nhexane by Fluka. The reagents used for the catalytic experiments were the same as in the previous paper.¹ TiO₂(rutile) ($S_{B.E.T.} = 6 \text{ m}^2 \text{ g}^{-1}$), denoted as R, was obtained by heating TiO₂A at 983, 1013, 1023 and 1033 K for 25 min at each temperature. Each heating was followed by an X-ray examination in order to determine whether the transformation of anatase into rutile was complete.

2.2 Sample Preparation

Based on the literature,⁴ we assumed that the amount of the vanadium reactant (VOCl₃ or vanadium oxalate) necessary

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to form a whole monolayer was 0.145 wt % per m² of the support. This assessment is based on a cross-sectional area of 'a V_2O_5 molecule' in cyrstalline $V_2O_5 = 0.105 \text{ nm}^{2.5}$ In fact, the real value is smaller, amounting to 0.1 wt % per m² ⁶ or 8.3 V atoms per nm²,⁷ which corresponds to 4.6 or 5.8 wt % for our TiO₂(anatase) and 0.7 or 0.9 wt % for our rutile samples, respectively. Therefore, the amount of the vanadium reactants taken for the preparation was sufficient to ensure the monolayer coverage of the support with vanadia.

The samples were denoted as follows: (A or R)VyX. A or R = anatase or rutile; $V = V_2O_5$; y = preparation method (g = grafting, i = impregnation); $X = V_2O_5$ amount loaded on a support (wt %). For example, RVg8.0 means 8.0 wt % of V_2O_5 was loaded on rutile using the grafting method.

Impregnation Method

Vanadium oxalate was used as vanadium source. Vanadium oxalate was obtained by dissolving 10 g of V_2O_5 in 30 g of molten oxalic acid and followed by cooling to room temperature. The resulting solid was dissolved in water and the solution was filtered. The water was evaporated under a pressure of *ca.* 20 hPa at 353 K.

To prepare samples by impregnation, the required amount of vanadium oxalate was dissolved in 100 cm^3 water. The solution was mixed with the support, anatase or rutile, and the water evaporated under a pressure of *ca*. 20 hPa and under continuous stirring. The residue was dried at 353 K for 16 h and then calcined in air at 673 K for 20 h.

Grafting Method

 $VOCl_3$ was used as vanadium source. It has been proven^{6,8} that the monolayer of V_2O_5 on TiO₂ is hydroxylated and thus it is possible to lay the second monolayer on the first one.

To prepare the first monolayer, 5 g of TiO_2 (rutile or anatase), dried at 413 K for 16 h, was placed in a one-neck flask, and the required amount of VOCl_3 in 100 cm³ of dry n-hexane was added. The solvent was evaporated under a pressure of *ca.* 20 hPa under continuous stirring and the residue was dried at 393 K for 16 h. The solid was calcined at 673 K for 20 h. The procedure was repeated in order to obtain the second monolayer. For both methods, the exact quantity of vanadia loaded on the support was determined by means of chemical analysis.

2.3 Characterization Techniques

Vanadium Content

To determine the vanadium content, each sample was treated with hot H_2SO_4 , diluted with water (1:4) and stirred for *ca*. 15 min. Samples containing TiO₂ were first heated in concentrated H_2SO_4 and then diluted with water. Under these conditions all vanadium was dissolved and was potentiometrically titrated with standardized Fe^{II} solution.

B.E.T., XRD and XPS

B.E.T., XRD and XPS measurements were carried out as described in ref. (1). The measurements were on mainly fresh catalysts but a few samples were also subjected, after the catalytic reaction, to a physicochemical investigation at room temperature, *i.e.* the samples were not protected from air contact.

FTIR Spectroscopy

All the IR spectra were taken with a Bruker IFS 48-IR FTIR spectrometer with a 4 cm⁻¹ resolution. The samples were diluted with KBr. Using the digital subtraction capability of the spectrometer, the support spectrum was subtracted from

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the sample spectra (to obtain only the spectrum of the vanadium oxide phase). The strong band below 700 cm⁻¹ could not be subtracted reliably and thus only the region above 700 cm⁻¹ was used in our final analysis.

Catalytic Activity

The catalytic activity measurements were carried out in a flow reactor as explained in ref. (1). Measurements of the activity as a function of time-on-stream and the oxygen-to-NEF (O/N) ratio were also carried out.

3. Results

3.1 Characterization

B.E.T. Surface Area

The B.E.T. surface area values for the fresh samples are gathered in table 1. Only the AVg4.4 sample, that corresponding to the monolayer coverage of anatase, has a surface area close to that of anatase. All the other samples are characterized by surface areas lower than expected. These differences are clearly seen when one compares the obtained values of surface area with the calculated surface area of the anatase fraction present in the studied samples (table 1).

XRD

The results are presented in table 1. Well crystallized V_2O_5 is present only in the fresh samples with a high vanadium content (AVi18.2 and AVi25.0). In the samples containing less V_2O_5 , only anatase was detected. The post-reaction X-ray examinations for all the samples do not provide any evidence of the presence of the well crystallized vanadium phases. For rutile samples, only rutile was detected.

FTIR Spectroscopy

Fig. 1 presents the FTIR spectra of the impregnated and grafted samples. For comparison, the V_2O_5 spectrum is also presented. Two large bands at 969 and 806 cm⁻¹ are present in the AVg4.4 spectrum, while only the 970 cm⁻¹ band is present in the AVi16.3 spectrum. With the increase in the V_2O_5 content in both the grafted and impregnated samples, additional bands at *ca*. 1020 and 850–860 cm⁻¹ appear. This is clearly seen in the AVi10 spectra [fig. 1(*e*) and (*f*)]. The spectrum (*e*), which is the difference between the AVi10 and anatase spectra, has three bands at 1020, 977 and 864 cm⁻¹, whereas in spectrum (*f*), being the subtraction result of AVi10 and AVi16.3, the 977 cm⁻¹ band disappears. Since the V_2O_5 content in the rutile samples is low, their FTIR spectra are not clear enough to give valuable information.

 Table 1. B.E.T. surface area and the phase composition of the impregnated (i) and grafted (g) anatase samples (fresh samples)

N.O. sentent	B.E.T .	V ray nhaaa	
(wt %)	sample	sample A in sample ^a	
		AVg	
4.4	43	44	Α
8.0	33	42	Α
		AVi	
6.3	38	43	Α
10.0	37	41	Α
18.2	32	38	A, V_2O_5
25.0	33.4	34.5	A, V_2O_5

^a B.E.T. surface area of anatase present in the sample calculated using $S_{B,E.T.} = 46 \text{ m}^2 \text{ g}^{-1}$. $S_{B,E.T.}$ of A in sample = {46[100 - V₂O₅ content (wt %)]}/100.

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(a)



Fig. 1. FTIR spectra of the anatase- V_2O_5 samples and the pure V_2O_5 . All the spectra of the anatase- V_2O_5 samples are the difference between the sample spectrum and that of anatase. (a) V_2O_5 ; (b) AVg4.4-4.31An; (c) AVg8.0-4.14An; (d) AVi6.3-1.09An; (e) AVi10.0-1.66An; (f) AVi10.0-1.57AVi6.3; (g) AVi18.2-1.42An; (h) AVi18.2-1.36AVi6.3. For example, (b) = AVg4.4-4.31An means that from the spectrum of the AVg4.4 sample, the spectrum of anatase (An), adjusted by the multiplying factor 4.31, was subtracted.

XPS

The values of the $V(2p_{3/2})$ binding energies and the V/Ti intensity ratios for the fresh and used catalysts are presented in table 2. It can be seen that for the fresh samples, the $V(2p_{3/2})$ binding energies have, within the limits of experimental error, the same values. After reaction, a decrease in the $V(2p_{3/2})$ binding energy for both rutile samples can be observed. No changes were observed for the anatase samples. After reaction, the V/Ti XPS intensity ratio decreases for the grafted anatase and for the impregnated rutile samples with a low vanadium content, *i.e.* AVg4.4 and RVi0.9. The amount of vanadium loaded in these samples corresponds to a monolayer.

The V/Ti ratio remains unchanged in the case of AVg8.0 after the reaction. For all the impregnated anatase samples, the V/Ti XPS ratio increases after the catalytic reaction. For the rutile loaded with a higher vanadium content (RVi1.8), the V/Ti XPS ratio also increases after reaction.

The intensity ratio of the XPS lines of vanadium (or titanium) in the fresh $(V_f; Ti_f)$ and used $(V_u; Ti_v)$ samples

 Table 2. XPS characterization of the grafted (g) anatase and impregnated (i) anatase and rutile samples

V ₂ O ₅ content (wt %)	B.E. ^a V(2	B.E. ^a V(2p _{3/2})/eV		V/Ti ^b		
	fresh	used	fresh	used	V_u/V_f^c	${\rm Ti_u}/{\rm Ti_f}^{\rm c}$
			AVg			
4.4	516.8	516.6	0.36	0.28	0.73	0.91
4.4 ^d	516.8	516.9	0.36	0.23	0.73	0.96
8.0	516.9	516.9	0.42	0.42	1.00	0.94
			AVi			
6.3	516.9	517.0	0.35	0.45	1.20	0.85
10.0	516.8	517.0	0.32	0.45	1.20	0.85
25.0	516.8	516.7	0.90	1.35	1.00	0.68
			RVi			
0.9	517.0	516.6	0.35	0.26	0.61	0.87
1.8	517.0	516.7	0.43	0.55	1.70	0.65

^a B.E. = binding energy. ^b V/Ti = V($2p_{3/2}$) to Ti($2p_{3/2}$) intensity ratio. ^c V_u/V_f and Ti_u/Ti_f represent the vanadium and titanium XPS intensity ratios of V($2p_{3/2}$) and Ti($2p_{3/2}$) lines for the used (u) and fresh (f) samples, respectively. The intensities were normalized to the O₁, peak. ^d After 3 h of the reaction.

were calculated to get an insight into the causes of the V/Ti XPS intensity ratio changes. When the V/Ti ratio decreases after catalytic reaction, the V_u/V_f ratio also decreases, while Ti_u/Ti_f remains practically unchanged (table 2). When V/Ti increases, an increase of the V_u/V_f and a decrease in the Ti_u/Ti_f are observed.

For the AVg8.0 sample, the V/Ti ratio does not vary in the course of the reaction and nor do the vanadium (V_u/V_f) and titanium (Ti_u/Ti_f) ratios. In the case of the AVi25.0 sample, the increase in the V/Ti ratio is not accompanied by an increase of V_u/V_f but only by a decrease in Ti_u/Ti_f .

3.2 Catalytic Activity Measurements

The catalytic activity measurements were carried out at 623 K. This was the lowest temperature at which the NEF conversions were lower than 100% for all the samples studied.

Activity as a Function of the Oxygen-to-NEF Ratio

Fig. 2 presents the NEF conversion and the propiononitrile and acetonitrile yields as a function of the oxygen-to-NEF (O/N) molar ratio at 623 K for the AVg4.4 and AVi10.0 samples. For both samples, at O/N ratio 0.8, the maximum of the propiononitrile yield and the minimum of the NEF conversion are observed, while the acetonitrile yield increases with the oxygen concentration. All subsequent catalytic reactions were carried out at an O/N ratio of 0.8.

Activity as a Function of Time-on-stream

Anatase Samples. Fig. 3 presents the NEF conversion and the propiononitrile yield as functions of time-on-stream for the impregnated and grafted anatase samples. The activities of both grafted samples are almost identical and they decrease slightly with time-on-stream [fig. 3(a)]. The initial activity of the impregnated samples is lower compared to that of the grafted ones and the decay of the NEF conversion with the time-on-stream is faster (and to a lower level).

There is a great difference in the time-dependence of the propionitrile yield of the grafted and impregnated samples [fig. 3(b)]. For the grafted samples, the yield values remain constant during the first 5 h of the reaction and then increase to values twice as high as the initial ones. For the impregnated samples the values of the propiononitrile yield increase

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Fig. 2. Conversion of NEF (C) and yields of propiononitrile (Y_p) and acetonitrile (Y_A) as functions of the oxygen-to-NEF (O/N) molar ratio at 623 K for the AVg4.4 and AVi10.0 samples. GHSV = 400 h⁻¹. AVg4.4: \Box , conversion; $\textcircled{\bullet}$, propiononitrile yield; \bigcirc , acetonitrile yield. AVi10.0: \blacksquare , conversion; \clubsuit , propiononitrile yield; \triangle , acetonitrile yield.

rapidly at the beginning of the reaction and after having reached a maximum, they decrease to a similar value for all the impregnated samples, which is only slightly higher than the values characteristic of the grafted ones.

The acetonitrile yields and their variations with time-onstream are very similar for all the grafted and impregnated samples. The variations of the acetonitrile yield with time-onstream are not as characteristic as the propiononitrile changes [fig. 3(c)].

Rutile Samples. Fig. 4 presents NEF conversion and the propiononitrile and acetonitrile yields as functions of timeon-stream for the grafted and impregnated rutile samples and for pure rutile.

The activity of the samples with lower V_2O_5 content (RVg0.8 and RVi0.9) is higher than that of the samples with higher amounts of loaded V_2O_5 (RVi1.8; RVg1.7) [fig. 4(a)]. Regarding the former catalysts, the NEF conversion drops abruptly at the very beginning of the reaction and remains constant thereafter. All vanadium-containing samples are less active than pure rutile.

The propiononitrile yield is high at the first stage of the reaction and it decreases with time-on-stream for all the samples studied [fig. 4(b)]. There is no essential difference between them and pure rutile in this respect.

The acetonitrile yield does not vary with time-on-stream for all the samples [fig. 4(c)]. However, the values of the yield are higher for those samples with a low V_2O_5 content. The yields for rutile are very poor and are not presented in the figure.

4. Discussion

4.1 Characterization of the Fresh Samples

The 4.4 wt % loaded on anatase by the grafting method corresponds to a monolayer coverage¹⁰ and the B.E.T. surface



Fig. 3. (a) Conversion of NEF (C) as a function of time-on-stream for the impregnated (open symbols) and grafted (closed symbols) anatase samples at 623 K. O/N ratio = 0.8 and GHSV = 400 h⁻¹. \bigoplus , AVg4.4; \blacktriangle , AVg8.0; \bigcirc , AVi6.3; \triangle , AVi10.0; ∇ , AVi18.2; \square , AVi25.0. (b) Yield of propiononitrile (Y_p) as a function of time-onstream for the impregnated (open symbols) and grafted (closed symbols) samples at 623 K. O/N ratio = 0.8 and GHSV = 400 h⁻¹. \bigoplus , AVg4.4; \bigstar , AVg8.0; \bigcirc , AVi6.3; \triangle , AVi10.0; ∇ , AVi18.2; \square , AVi25.0. (c) Yield of acetonitrile (Y_A) as a function of time-on-stream for the impregnated (open symbols) and grafted (closed symbols) samples at 623 K. O/N ratio = 0.8 and GHSV = 400 h⁻¹. \bigoplus , AVg4.4; \bigstar , AVg8.0; \bigcirc , AVi6.3; \triangle , AVi10.0; ∇ , AVi18.2; \square , AVi25.0. (c) Nield of acetonitrile (Y_A) as a function of time-on-stream for the impregnated (open symbols) and grafted (closed symbols) samples at 623 K. O/N ratio = 0.8 and GHSV = 400 h⁻¹. \bigoplus , AVg4.4; \bigstar , AVg8.0; \bigcirc , AVi6.3; \triangle , AVi10.0; ∇ , AVi18.2; \square , AVi25.0.



Fig. 4. (a) Conversion (C) of NEF as a function of time-on-stream for the grafted and impregnated samples and the pure rutile at 623 K. O/N ratio = 0.8 and GHSV = 400 h⁻¹. \blacklozenge , Rutile; \spadesuit , RVg1.7; \blacktriangle , RVg0.8; \bigcirc , RVi0.9; \diamondsuit , RVi1.8. (b) Yield of propiononitrile (Y_P) as a function of time-on-stream for the grafted and impregnated samples and the pure rutile at 623 K. O/N ratio = 0.8 and GHSV = 400 h⁻¹. \diamondsuit , Rutile; \spadesuit , RVg1.7; \bigstar , RVg0.8; \bigcirc , RVi0.9; \diamondsuit , RVi1.8. Yield of acetonitrile (Y_A) as a function of time-on-stream for the grafted and impregnated samples and the pure rutile at 623 K. O/N ratio = 0.8 and GHSV = 400 h⁻¹. \spadesuit , RVg1.7; \bigstar , RVg0.8; \bigcirc , RVi0.9; \diamondsuit , RVi1.8.

area is in good agreement with the calculated value (table 1). For higher V_2O_5 contents (8.0%) the B.E.T. surface area is much lower than expected. In the case of the impregnated samples, the B.E.T. surface area is lower than the calculated value even for samples with low V_2O_5 content (6.3%), close to monolayer coverage,⁷ which in our case is 5.8 wt % V_2O_5 . This indicates that V_2O_5 , loaded on anatase by the grafting method in amounts exceeding the monolayer coverage and by the impregnation method in all cases, is converted to V_2O_5 which blocks pores thus bringing about a decrease in the B.E.T. surface area. The IR studies confirm this picture.

In the FTIR spectrum of the AVg4.4 sample, the bands attributed to the monolayer phase⁹ (fig. 1) composed of the tetrahedral vanadium species are present.^{6,7,10} For higher V_2O_5 contents (8.0%) the additional bands at 1020 and 850 cm⁻¹, characteristic of V_2O_5 ,¹⁰ appear.

In the case of the impregnated samples, in the FTIR spectrum of the AVi6.3 sample only the broad 970 cm⁻¹ band is observed and on increasing the V_2O_5 loaded on anatase, additional bands appear indicating the formation of crystalline V_2O_5 . In the MoO₃-TiO₂(anatase) system,¹¹ a similar band at *ca.* 950 cm⁻¹ has been attributed to the polymeric octahedral molybdenum species. This would indicate that the vanadium monolayer composed of the tetrahedral vanadium species cannot be formed by the impregnation of anatase with vanadium oxalate. This is in agreement with the findings of Kozlowski.³ In the V_2O_5 -TiO₂(anatase) samples prepared by impregnation with vanadium oxalate, crystalline vanadium pentoxide was always found with EXAFS and XANES methods, even for loadings below the monolayer coverage.

4.2 Catalytic Activity and Post-reaction Characterization

The catalytic activity measurements provided further information concerning the nature of the vanadia-titania interactions. There is a great difference in the time dependence of the NEF conversion and the propiononitrile yield between the impregnated and grafted anatase samples.

Impregnated Anatase Samples

The impregnated samples are composed of the V_2O_5 and anatase grains. In such samples, heated at 673 K, we suppose that the polymorphic transformation of anatase into rutile takes place to an extent similar to that found in the AVA mechanical mixtures also heated at 673 K,² thus forming a thin rutile layer over the anatase particle surface. In fact, the time-dependence of the NEF conversion and propiononitrile yield supports this conclusion [fig. 3(a) and (b)]. A simultaneous influence of the rutile surface phase and anatase covered with a rutile layer on V_2O_5 is observed particularly well in the propiononitrile yield variations with time-onstream [fig. 3(b)]. The initial increase of the yields for the V_2O_5 -anatase mixtures,² is followed, after attaining the maximum, by a decrease as a result of the rutile action on vanadium pentoxide, which consists of the continuous reduction of V_2O_5 . The values of the maximal yields are proportional to the V_2O_5 amount loaded on anatase, *i.e.* in view of the result described in ref. (2), to the amount of V_6O_{13} formed in the course of the V₂O₅ reduction. In fact, these values agree very well with those obtained for the AVA mechanical mixtures² (fig. 5). The V_2O_5 dispersion on the impregnated anatase samples is higher than that found in the AVA mixtures, and during the reaction it further increases (table 2), which renders impossible the X-ray diffraction identification of the reduced vanadium oxides formed.

Grafted Anatase Samples

The grafted anatase samples exhibit high activities compared to pure anatase and practically do not deactivate in the course of the catalytic reaction [fig. 3(a)]. The timedependence of the propionitrile yield combined with the results of the XPS analysis of the fresh and the used samples reveals that the vanadium oxide monolayer is not stable under the catalytic conditions [fig. 3(b); table 2]. The decrease in the surface vanadium phase dispersion for the AVg4.4 sample, which is reflected in the decrease of the XPS V/Ti and V_u/V_f ratio (table 2), takes place in the course of the reaction and at the same time an increase in the propiononitrile yield is observed [fig. 3(b)]. As can be seen in table



Fig. 5. Comparison of the propiononitrile maximal yield taken from fig. 3(b) for the impregnated anatase samples with the propiononitrile yield characteristic of the AVA mechanical mixtures² plotted as a function of the V₂O₅ content. Reaction temperature = 623 K, O/N ratio = 0.8 and GHSV = 400 h⁻¹. \bullet , mechanical mixture²; \bullet , the maximal values of yield from fig. 3(b).

2, the decrease in the dispersion of the vanadium phase is complete after 3 h of reaction. Since the increase in the propiononitrile yield begins after more than 3 h of time-on-stream, the increase in the propiononitrile yield cannot only be related to the sintering of the surface vanadium phase. As has been demonstrated for the V_2O_5 -TiO₂(anatase) system,² this is V_6O_{13} which is formed and then stabilized on the anatase surface in the course of the NEF dehydration under the chosen catalytic conditions. Since the same conditions were applied in the present study, we relate the increase in the propiononitrile yield on time-on-stream to the formation of V₆O₁₃ from the vanadium monolayer. Consequently, the delay in this increase [fig. 3(b)] would be due to the formation of V_6O_{13} nuclei and the increase in the propiononitrile yield would start when V_6O_{13} crystallites begin to grow. In view of this interpretation, the increase of the propiononitrile yield could reflect the growth of V_6O_{13} crystallites.

The XPS intensity ratio does not vary under the influence of the catalytic mixture for AVg8.0 despite an increase of the propiononitrile yield similar to that of the monolayer catalyst [fig. 3(b); table 2]. It can be explained by the simultaneous sintering of the vanadium monolayer and the dispersion of the V_2O_5 crystals taking place in the course of the reaction, which as a result gives the unchanged V/Ti ratio.

The grafting method results in the formation of a vanadium monolayer over the anatase surface, which is composed of the bulk structure of anatase.⁷ According to Boehm¹² the unbalanced charges on the anatase surface are located on the OH⁻ groups. The model of the vanadium monolayer, advanced in ref. (7), suggests an almost perfect balance of local charges by the surface species. Such a monolayer is particularly stable and the calcination at 673 K does not affect its structure. The vanadium monolayer formed on the anatase surface can protect it against the influence of the V₂O₅ crystals and may inhibit the anatase-into-rutile transformation in the course of the calcination at 673 K. Indeed, the AVg8.0 sample composed of the vanadium monolayer and grains of crystalline V₂O₅ exhibits similar catalytic properties as the monolayer catalyst, i.e. there is no indication of the anatase-into-rutile transformation.

Grafted and Impregnated Rutile Samples

In the case of the rutile catalysts the catalytic experiments showed that there are no differences between the grafted and impregnated samples. Moreover, their catalytic properties under these particular conditions seem to be a superposition

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of those found for pure rutile and V_2O_5 . However, the XPS analysis revealed that the sintering of the vanadium phase, in the course of the catalytic reaction, is also seen for the impregnated sample with a low V_2O_5 content (RVi0.9) (table 2). When the amount of V_2O_5 loaded on rutile is higher (1.8 wt %), excess vanadium oxide, probably in the form of V_2O_5 crystallites, disperses in the course of the reaction, as in the case of the V_2O_5 -TiO₂(rutile) mechanical mixture.¹ The XPS studies showed that V_2O_5 undergoes reduction during the catalytic reaction (table 2).

FTIR Results

The 818 cm⁻¹ band, attributed to the deformation of V-O-V vibrations,¹⁰ in the V₂O₅ spectrum (fig. 1) shifts to a value of *ca*. 850 cm⁻¹ in the case of V₂O₅ loaded on anatase. This would indicate a strong interaction between anatase and V₂O₅. However, the value of 850 cm⁻¹ is closer to the value of 840 cm⁻¹ reported in ref. (1) for V₂O₅ than to 818 cm⁻¹. The reason for this divergence is not clear.

4.3 The Architecture of the Vanadium-Titania Catalysts

The physico-chemical characterization of the fresh and used samples combined with the catalytic measurements suggest the architecture schematically depicted in fig. 6.

The Impregnated V₂O₅ Anatase Catalyst

The impregnated V_2O_5 (anatase) samples are composed of vanadia clusters, for the samples with a low V_2O_5 content, and on increasing the V_2O_5 loaded on anatase, are composed of V_2O_5 crystallites of a crystallographically well defined structure (table 2, X-ray diffraction results). The rutile layer is formed during the calcination of the samples at the V_2O_5 -TiO₂ contacts. In the course of the catalytic reaction, V_2O_5 undergoes reduction giving reduced vanadium oxides characteristic (as is supposed) of the rutile influence on V_2O_5 .¹ The reduction is accompanied by an increase in the V_2O_5 dispersion. Due to the rutile phase present on anatase, the stabilization of V_6O_{13} , formed as a transient product of the reduction, by formation of a junction with anatase is not possible. As a result, further reduction of V_6O_{13} occurs,



Fig. 6. The architecture of the vanadia-anatase and -rutile monolayer-like catalyst, before and after the NEF dehydration. V_2O_{5-x} designates reduced vanadium oxide whose nature depends on the conditions of the catalytic reaction and V⁵⁺, fully oxidized vanadium layer.

which is manifested by a decrease in the propiononitrile yield similar to that of the V_2O_5 -rutile mixtures¹ [fig. 4(b)]. The XPS analysis, however, does not reveal any decrease in the $V(2p_{3/2})$ binding energy (table 2), indicating that the catalysts work at the fully oxidized state. A similar result has been found for the V_2O_5 -anatase mechanical mixtures.² It should be noted that, before the XPS analysis, the samples had been in contact with air which could influence the results of the measurements.

The Grafted V₂O₅-Anatase Catalyst

The grafted V_2O_5 -TiO₂(anatase) samples are composed of a vanadia monolayer on the anatase surface and, with increasing V_2O_5 contents, of V_2O_5 crystallites placed on top of the monolayer. The monolayer undergoes destruction in the course of the catalytic reaction forming crystallites of V_6O_{13} , covered with fully oxidized vanadium layers.

V₂O₅-Rutile Catalysts

The general image of the fresh grafted and impregnated V_2O_5 -TiO₂(rutile) samples is similar to that of the anatase grafted samples. However, their catalytic properties are similar to those characteristic of the V_2O_5 -TiO₂(rutile) mixtures.¹ This difference is easily understood if we take into account the XPS results showing that the grafted anatase catalysts work at the fully oxidized state, whereas the rutile catalysts work at the reduced state (table 2; fig. 6).

4.4 Final Remarks

A correlation between catalytic activity and physicochemical characterization of mechanical mixtures and impregnated or grafted V_2O_5 -TiO₂ samples shows that the dehydration of NEF is a useful method for monitoring physicochemical changes taking place on the surface of these catalysts, which cannot be satisfactorily followed using the usual physicochemical characterization methods. This particularly concerns the monolayer-type catalysts.

5. Conclusion

(1) V_2O_5 -TiO₂(anatase) samples prepared by the impregnation and grafting methods have different catalytic properties in NEF dehydration.

(2) The grafted samples are composed of the vanadium monolayer over the surface of anatase which undergoes sintering in the course of the catalytic reaction, probably forming V_6O_{13} .

(3) The impregnated samples are composed of the finely dispersed V_2O_5 in contact with the anatase grains. The calcination of these samples at 673 K induces the partial transformation of anatase into rutile, resulting in the formation of a thin rutile-like layer on the surface of the anatase grains. The catalytic behaviour of these samples is similar to that of the V_2O_5 -TiO₂(rutile) catalysts.

(4) The vanadium monolayer formed on the anatase surface can protect it against the influence of the V_2O_5 crystals and may inhibit the anatase-to-rutile transformation taking place in the course of the calcination at 673 K.

(5) There are no differences between the grafted and impregnated rutile samples in NEF dehydration. Their catalytic properties seem to be a superposition of those found for pure rutile and V_2O_5 .

6. General Remarks

The present studies have shown that the catalytic properties of the V_2O_5 -TiO₂ catalysts in NEF dehydration greatly depend on the state of dispersion of the vanadium phase over the TiO₂ surface and the thermal pretreatment of the catalysts. The evolution of the V_2O_5 dispersion and the catalytic properties of the vanadia-titania catalysts in the course of the reaction are characteristic of the polymorphic modification of TiO₂ present in catalysts and the method of preparation employed. Starting from ill dispersed (physical mixtures) or well dispersed (monolayer catalysts) V_2O_5 , the final V_2O_5 dispersion after catalytic reaction tends to reach a medium state between them under the particular conditions of NEF dehydration; the dispersion of V₂O₅ during the reaction is accompanied by a reduction. The type of reduced vanadium phase formed depends on the polymorphic modifications of TiO_2 and the O/N ratio and as a result of this dependence there is a difference in the catalytic behaviour of the V_2O_5 -TiO₂(anatase) and V_2O_5 -TiO₂(rutile) catalysts.

It is accepted that in the selective oxidation of hydrocarbons, *e.g.* o-xylene to phthalic anhydride, it is the vanadium monolayer on the surface of $TiO_2(anatase)$ which is the active and selective phase. The vanadium monolayer catalysts, when reduced or heated at high temperatures, lose their activity and selectivity. Our studies reveal that a destruction of the vanadium monolayer under the reducing conditions of NEF dehydration can take place in the course of the reaction. Calcination of the V_2O_5 -TiO₂(anatase) catalysts, even at moderate temperatures (673 K), initiates the anatase-into-rutile transformation, which is accompanied by a decay of their catalytic properties, whereas in untreated thermal physical mixtures this phenomenon is not observed.

Industrial catalysts usually contain excess V_2O_5 compared with the quantity needed to form one monolayer. In the present studies, it has been shown that the vanadium monolayer, formed by the grafting method, can protect the anatase surface against the influence of V_2O_5 crystals and, therefore, may inhibit the anatase-into-rutile transformation taking place during the calcination at elevated temperatures, and consequently prevent the decline of the catalytic properties. This is not the case for the catalysts prepared by the impregnation methods and calcined at 673 K. These catalysts should not be heated before a catalytic reaction.

As has been shown, NEF dehydration is very sensitive to the reduced state of the vanadium phase. Therefore, very small changes in the reductibility of the vanadia-titania catalysts, due to the polymorphic transformation of anatase-intorutile, result in well pronounced modifications of their catalytic properties.

Active and selective vanadia-titania catalysts in the selective oxidation of hydrocarbons, *e.g.* the oxidation of o-xylene to phthalic anhydride, are prepared by the impregnation of TiO₂(anatase) with vanadium salts, followed by calcination at elevated temperatures. The calcination of catalysts prepared in this manner does not influence their catalytic properties as it does in NEF dehydration. In the oxidation reaction, the vanadium phase operates in the oxidized state, which is apparently not influenced by the very fine rutile layer formed on the surface of the anatase grains in the course of the calcination to the same extent as in NEF dehydration. However, the nucleation and subsequent crystallization of the well crystallized rutile phase may take place from the rutile layer and can result in the shortening of the lifespan of the catalyst.

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