# Studies on the V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> System

Part 2.—TiO<sub>2</sub>(anatase)-V<sub>2</sub>O<sub>5</sub>

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Mechanical mixtures of separately prepared  $V_2O_5$ ,  $V_6O_{13}$  and anatase have been used as catalysts in the dehydration of *N*-ethylformamide (NEF) in the presence of oxygen. Catalytic activity was measured as a function of the gas hourly space velocity (GHSV), the oxygen-to-*N*-ethylformamide ratio (O/N), the temperature, the  $V_2O_5$  and  $V_6O_{13}$  contents and the surface area of  $V_2O_5$ . The characterization was carried out using B.E.T. surface analysis, XRD and XPS techniques.

It was concluded that there exists a cooperation between  $V_2O_5$  and anatase, which brings about the stabilization of  $V_6O_{13}$  by the anatase.  $V_6O_{13}$  is the most selective phase in NEF dehydration. The calcination of  $V_2O_5$ -anatase mechanical mixtures results in (i) an increase of the  $V_2O_5$  dispersion over the anatase surface, which brings about an increase of the selective product (propiononitrile), and (ii) partial anatase-into-rutile transformation, resulting in a decay of the catalytic properties. Under appropriate reaction conditions (temperature, O/N ratio) the anatase-into-rutile transformation does not take place.

## 1. Introduction

In the first paper of this series,<sup>1</sup> concerning the dehydration of N-ethylformamide on vanadia-rutile catalysts, it was shown that: (a) a synergetic effect exists between rutile and the  $V_2O_5$ ; (b) rutile disad vantages the stabilization of vanadia in an elevated oxidation state, promoting the formation of reduced phases; (c) the medium reduced vanadia oxides are less active but give higher propiononitrile yields than deeply reduced and fully oxidized vanadium oxides; (d) vanadium is dispersed on the surface of rutile.

This paper concerns the vanadia-anatase catalysts. A revision of the studies in the literature has been given in the first paper. However, some additional specific observations for the vanadia-anatase catalysts have been presented in recent years. A remarkable fit has been found to exist between structures of the cleavage plane (010) of  $V_2O_5$  and (001), (100)<sup>2</sup> and (011) planes of anatase.<sup>3</sup> Under the catalytic conditions, a reduction of  $V_2O_5$  to  $V_2O_4$  occurs while TiO<sub>2</sub>(anatase) remains unchanged since the temperature does not exceed 723 K. When the steady-state is reached under *o*-xylene and air the reduction stops near  $V_6O_{13}^4$  which is the phase of optimal structural fit with respect to anatase.<sup>3</sup>

The overall reduction degree of the supported vanadium phase has been presented in ref. (5). It has been found to be higher in the case of rutile than in that of anatase. However, after the o-xylene oxidation,<sup>6</sup> a vanadium oxidation state lower than +5 could not be detected by XPS in the V<sub>2</sub>O<sub>5</sub> anatase catalyst.

Another important aspect of the  $V_2O_5$ -TiO<sub>2</sub>(anatase) catalyst behaviour is the anatase-to-rutile transformation. When this occurs, the catalyst loses its activity and selectivity.<sup>5,6</sup> Such a transformation is promoted by  $V_2O_5$ .<sup>2</sup> Under N<sub>2</sub> at 873 K,  $V_2O_5$  is reduced topotactically to  $V_2O_4$  and a simultaneous transformation of anatase to rutile takes place.<sup>2</sup>

As in the first paper,<sup>1</sup> the dehydration of NEF as a test reaction was used. Similarly, mechanical mixtures of the separately prepared oxides were used as catalysts. The aim of our research programme was presented in the first paper; concerning the present work, our objectives are to study: (a) the nature of the phases which are active and selective in the dehydration of NEF; (b) the reductibility of the  $V_2O_5$  phase in the presence of anatase; (c) the changes in the dispersion of vanadium on the surface of anatase; (d) the anatase-to-rutile transformation promoted by the interaction of  $V_2O_5$  with the support; (e) the cooperation between anatase and  $V_2O_5$ . In order to facilitate the interpretation of the results observed for the anatase- $V_2O_5$  catalysts, some comparative studies were done for the anatase- $V_6O_{13}$  system.

The catalysts were prepared as mechanical mixtures of the separately prepared oxides and characterized by B.E.T. surface analysis, XRD and XPS. We have primarily characterized fresh catalysts. However, we have also studied a few samples that had been contacted with the reaction mixture in the flow apparatus used for the catalytic tests.<sup>1</sup> The experimental details are given in the first paper.<sup>1</sup>

TiO<sub>2</sub>(anatase) ( $S_{B,E,T} = 44 \text{ m}^2 \text{ g}^{-1}$ ), is denoted henceforth as A. Eurotitania was supplied by Tioxide for a cooperative study on TiO<sub>2</sub> by the Research Group on Catalysis of the Council of Europe (EUROCAT), and NH<sub>4</sub>VO<sub>3</sub> by UCB, Belgium; n-pentane was from Merck. The reagent for catalytic experiments was N-ethylformamide (99%) (Fluka); helium (99.995%) and oxygen (99.5%) were commercially available gases (Air Liquide, Belgium) and were used without further purification.

#### 2. Catalyst Preparation

 $V_2O_5$  was prepared as follows: 75 g citric acid and 31 g  $NH_4VO_3$  were dissolved in 750 cm<sup>3</sup> distilled water. The water was evacuated by continuous stirring under a pressure of *ca*. 20 hPa at 333 K. The residue was dried at 330 K for 3 h, and then calcined, first at 623 K for 18 h, and then at 673 K for 7 h. The resulting  $V_2O_5$  had a B.E.T. surface area of 10 m<sup>2</sup> g<sup>-1</sup> (high surface) and was denoted as  $V_2O_5H$ . When the first heating of the organic precursor was carried out at 603 K for 18 h and then at 673 K for 7 h, the low surface area (4 m<sup>2</sup> g<sup>-1</sup>)  $V_2O_5$  was obtained ( $V_2O_5L$ ).

 $V_6O_{13}$  was prepared by the reduction of  $V_2O_5$  in flowing  $H_2$  (30 cm<sup>3</sup> min<sup>-1</sup>), saturated with  $H_2O$  at 313 K ( $P_{(H_2O)} = 55.3$  Torr†), at 723 K for 3.5 h.<sup>7</sup> The X-ray diffraction pattern of the sample showed the *d*-spacings characteristic of  $V_6O_{13}^{8}$ 

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<sup>† 1</sup> Torr = 101 325/760 Pa.

and traces of  $V_2O_5$  estimated as corresponding to 2–3 wt %.

Mechanical mixtures of anatase and  $V_2O_5$  or anatase and  $V_6O_{13}$  were prepared by vigorous ultrasound mixing of the solid suspension in n-pentane, followed by evaporation under a pressure of *ca*. 20 hPa. The samples were then dried at 373 K for 16 h. The composition of each mixture is expressed as the mass ratio,  $M_R$ , which is the ratio of  $V_2O_5$  weight to the total weight of the sample  $(M_R = m(V_2O_5)/[m(V_2O_5) + m(TiO_2)])$ . The samples are denoted as A or RVXY, where A or R refer to anatase or rutile, V refers to  $V_2O_5$ , X is the type of  $V_2O_5$  used, H high surface or L low surface, and Y = mass ratio. AVH0.25 describes a mechanical mixture of anatase and  $V_2O_5H$  with  $M_R = 0.25$ . The samples containing  $V_6O_{13}$  are denoted as  $AV_6O_{13}Y$ , where the meaning of the symbols is as above.

## 3. Characterization Techniques

B.E.T. surface, XRD, XPS and catalytic activity measurements were carried out as described in the previous paper.<sup>1</sup> In principle, fresh catalysts were investigated. The physicochemical examination was, however, carried out for a few samples which had been brought into contact with the reaction mixture in the flow apparatus used for catalytic tests and then exposed to air at room temperature. The catalytic properties of the samples studied varied in the course of the catalytic reaction attaining steady-state after *ca*. 20 h. Therefore, the majority of the results presented were obtained after at least 20 h of the reaction.

The XRD identification of phases present in fresh and used samples was based on the data given in ref. (10) for anatase, rutile,  $V_2O_5$ ,  $V_2O_4(R)$  and  $V_4O_9$ , in ref. (8) for  $V_6O_{13}$ , and in ref. (11) for  $VO_2(B)$ .  $V_2O_4(R)$  is isostructural with  $TiO_2(rutile)$  and  $VO_2(B)$  with  $V_6O_{13}$ .<sup>11</sup>

The fraction of rutile in the system,  $X_{R}$ , was determined using:

$$X_{\rm R} = (1 + 0.794 I_{\rm a}/I_{\rm r})^{-1}$$

where  $I_a$  and  $I_r$  are the intensities of (101) and (110) reflections for anatase and rutile, respectively, in XRD patterns.<sup>9</sup>

#### 4. Results

#### 4.1 Catalytic Activity Measurements

## Catalytic Activity as a Function of Time-on-stream

Fig. 1 presents the conversion of NEF and yields of propiononitrile and acetonitrile as a function of time-on-stream for  $V_2O_5$ , TiO<sub>2</sub>(anatase) and their mechanical mixture with  $M_R = 0.5$  for the oxygen to NEF (O/N) molar ratio 0.8. This figure clearly shows the difference in the catalytic properties, in NEF dehydration, of pure anatase and  $V_2O_5$  and their mechanical mixture.

Anatase. The activity decreases progressively during the timeon-stream. The propiononitrile yield, after an initial increase, diminishes to a very low value.

 $V_2O_5$ . The activity does not vary during the catalytic reaction. Its initial value is lower compared with that of the two other samples, but after some hours the activity is of the same order as that of anatase. The propiononitrile yield abruptly drops with time. The acetonitrile yield is very low and does not change with time-on-stream.

AVH0.5. The activity of the mechanical mixtures is high at the beginning of the reaction and after a certain time it decreases, reaching a plateau after more than 20 h. Concurrently, the propiononitrile yield increases progressively, start-

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Fig. 1. (a) Conversion (C) of NEF and (b) yield of propiononitrile  $(Y_p)$  and acetonitrile  $(Y_A)$  as functions of time-on-stream for  $V_2O_5$ , TiO<sub>2</sub>(anatase) and their mechanical mixture with  $M_R = 0.5$  at 623 K for O/N ratio = 0.8 and GHSV = 400 h<sup>-1</sup>. Conversion and yield of propiononitrile:  $\blacklozenge$ , TiO<sub>2</sub>(anatase);  $\bigstar$ ,  $V_2O_5$ ;  $\blacklozenge$ , AVH0.5. Yield of acetonitrile:  $\triangle$ ,  $V_2O_5$ ;  $\bigcirc$ , AVH0.5.

ing from a lower level than that for  $V_2O_5$  and anatase and reaching, after 20 h, a higher constant value. The acetonitrile yield is low; it does not change with time-on-stream and is higher than that for  $V_2O_5$ .

#### Influence of Temperature

Fig. 2 illustrates the dependence of the NEF conversion and the yields of propiononitrile and acetonitrile on the reaction temperature for the AVH0.5 mixture. The maximum value of the propiononitrile yield is observed at 623 K. The conversion and the yield of acetonitrile rise when the temperature increases to 638 K, whereas the propiononitrile yield decreases at this high temperature. All other experiments were carried out at 623 K.

#### Influence of Oxygen Concentration and GHSV

Oxygen Concentration. In fig. 3, the NEF conversion and the propiononitrile and acetonitrile yields are presented as a function of the oxygen concentration for the AVH0.5 sample.



Fig. 2. Conversion (C) of NEF and yields of propiononitrile  $(Y_p)$  and acetonitrile  $(Y_A)$  as functions of the reaction temperature for the AVH0.5 mixture. O/N ratio = 0.8, GHSV = 400 h<sup>-1</sup>.  $\blacklozenge$ , conversion;  $\blacklozenge$ , yield of propiononitrile;  $\blacktriangle$ , yield of acetonitrile.



**Fig. 3.** Conversion (C) of NEF and yields of propiononitrile  $(Y_p)$  and acetonitrile  $(Y_A)$  as functions of the oxygen concentration in feed at GHSV = 400 h<sup>-1</sup> for the AVH0.5 mixture. The results of the XRD examination are also given.  $\triangle$ , Conversion;  $\bigcirc$ , yield of propiononitrile;  $\bigcirc$ , yield of acetonitrile.

A maximum in the propiononitrile yield is observed. It is obtained at an O/N ratio of 0.8 and corresponds to the minimum of the NEF conversion and a low value at the acetonitrile yield. For an O/N ratio of 2.0, high activity is observed as well as a maximum of the acetonitrile yield. The propiononitrile yield is low. A further increase of the O/N ratio causes a decrease in the propiononitrile and acetonitrile yields, but the conversion is still high. At very low O/N ratios a similar effect is observed, *i.e.* the yields of propiononitrile and acetonitrile are low and the NEF conversion is high.

GHSV. Some experiments were undertaken with a constant O/N ratio to study the influence of the GHSV. The results are presented in table 1. At an O/N ratio of 0.1, the increase of GHSV from 400 to 600  $h^{-1}$  leads to a decrease in the conversion and an increase in the propiononitrile yield. The acetonitrile yield is more or less constant. At an O/N ratio of 2.0, the increase of GHSV from 400 to 1600  $h^{-1}$  results in a decrease of the conversion, an increase in the propiononitrile yield and a decrease in the acetonitrile yield. At an O/N ratio of 3.0, when the GHSV increases from 400 to 1600  $h^{-1}$ , the conversion is always high and the propiononitrile remains more or less constant, whereas the acetonitrile yield increases.

#### Influence of V<sub>2</sub>O<sub>5</sub> Content and Surface Area of V<sub>2</sub>O<sub>5</sub>

The full range of  $V_2O_5$  content in mechanical mixtures was investigated. The studies were carried out (fig. 4) for  $V_2O_5$ samples of different surface areas ( $V_2O_5H$  with  $S_{B,E,T} = 10$  $m^2 g^{-1}$  and  $V_2O_5L$  with  $S_{B,E,T} = 4 m^2 g^{-1}$ ).

The synergetic effect is clearly observed in the whole range studied and for both  $V_2O_5$  types. The propiononitrile yield is greater than for the separated oxides. This effect is greater for samples with a larger surface area of  $V_2O_5$ . For  $V_2O_5H$  a maximum is observed at  $M_R = 0.5$ , whereas in the case of  $V_2O_5L$  the maximum was observed at 0.75. In addition, the values of the propiononitrile yield are lower for the AVL

**Table 1.** Conversion (C) of NEF and yields of propiononitrile  $(Y_p)$  and acetonitrile  $(Y_A)$  as functions of the GHSV<sup>a</sup>

| O/N | GHSV/h <sup>-1</sup> | C (%)      | Y <sub>P</sub> (%) | Y <sub>A</sub> (%) |
|-----|----------------------|------------|--------------------|--------------------|
| 0.1 | 400                  | ~100       | 2.0                | 2.5                |
| 0.1 | 600                  | 45         | 6.0                | 2.5                |
| 2.0 | 400                  | $\sim 100$ | 2.5                | 30.0               |
| 2.0 | 1600                 | 85.0       | 11.0               | 22.5               |
| 3.0 | 400                  | $\sim 100$ | 0.0                | 15.0               |
| 3.0 | 1600                 | $\sim 100$ | 2.0                | 37.0               |

<sup>a</sup> XRD results: O/N = 0.1,  $V_2O_4$  and O/N = 3.0,  $V_2O_5$ .



Fig. 4. Yield of propiononitrile  $(Y_p)$  as a function of the  $V_2O_5$  content in the mixture and the B.E.T. surface area. Reaction temperature = 623 K; O/N = ratio = 0.8;  $GHSV = 400 \text{ h}^{-1}$ . •,  $\text{TiO}_2(\text{anatase}) - V_2O_5H$  ( $S_{\text{B.E.T.}} = 10 \text{ m}^2 \text{ g}^{-1}$ );  $\blacktriangle$ ,  $\text{TiO}_2(\text{anatase}) - V_2O_5L$  ( $S_{\text{B.E.T.}} = 4 \text{ m}^2 \text{ g}^{-1}$ );  $\bigtriangleup$ , AVL mixtures calcined at 773 K for 3 h.

than for the AVH mixtures. However, these can be improved by calcination of the AVL (low surface of  $V_2O_5$ ) samples in air at 773 K for 3 h. In fig. 4, the open triangles represent the propiononitrile yields for the calcined AVL0.25 and AVL0.5 samples. It can be seen that the values are significantly higher than those characteristic of the uncalcined samples.

## Thermal Treatment of the V<sub>2</sub>O<sub>5</sub>H-containing Samples

The influence of the thermal treatment of the samples on their catalytic properties was investigated for the  $V_2O_5H$ -containing mixtures. Fig. 5 shows the yield of propiononitrile, the conversion of NEF and the yield of acetonitrile as functions of time-on-stream for the AVH0.25 sample calcined at 673 and 773 K for 3 h. For comparison, the results obtained for the uncalcined anatase- $V_2O_5$ , AVH0.25, and rutile- $V_2O_5$ , RVH0.25, samples are also presented.

**Propiononitrile Yields** [fig. 5(a)]. The calcined samples give the intermediate values for the propiononitrile yield lying between those for the uncalcined anatase and rutile mixtures. Their behaviour is dependent on the temperature of calcination.

The higher yields were observed for the sample calcined at higher temperatures. The shape of the curves for both calcined samples are similar. After the initial rise up to a maximum, reached after *ca.* 1 h, the propiononitrile yield decreases to the intermediate values lying between uncalcined AVH0.25 and RVH0.25.

Acetonitrile Yields [fig. 5(c)]. The acetonitrile yields for AVH0.25 (3 h at 773 K) are close to those of RVH0.25 and the AVH0.25 (3 h at 673 K) ones are close to those obtained for AVH0.25. At the beginning of the reaction on both calcined samples, the yield of acetonitrile decreases. For the sample calcined at high temperatures this decrease is more pronounced.

Conversion [fig. 5(b)]. The activity of the calcined samples lies between those for the calcined AVH0.25 and RVH0.25. The time-dependence of the conversion is similar for the calcined samples and the rutile mixtures but it differs for the uncalcined AVH0.25. In fact, after an initial (6 h) decrease the conversion becomes constant, whereas in the case of AVH0.25, the decrease in the NEF conversion is maintained. The conversion for AVH0.25 heated at 673 K for 3 h is higher than that for AVH0.25 heated at 773 K for 3 h. The values for the former are close to those obtained for  $V_2O_5$  (fig. 1).



Fig. 5. (a) Yield of propiononitrile  $(Y_p)$ , (b) conversion of NEF (C) and (c) yield of acetonitrile  $(Y_A)$  as functions of time-on-stream for the AVH0.25 mixture calcined at 673 and 773 K. The results obtained for the uncalcined AVH0.25 and RVH0.25 mixtures are also presented. Reaction temperature = 623 K, O/N ratio = 0.8 and GHSV = 400 h<sup>-1</sup>. Conversion of NEF and yield of propiononitrile:  $\blacksquare$ , AVH0.25;  $\blacklozenge$ , RVH0.25;  $\blacklozenge$ , AVH0.25 at 673 K;  $\blacktriangle$ , AVH0.25 at 773 K. Yield of acetonitrile:  $\Box$ , AVH0.25;  $\bigtriangledown$ , RVH0.25;  $\bigcirc$ , AVH0.25 at 673 K;  $\diamondsuit$ , AVH0.25 at 773 K.

## Mechanical Mixtures with V<sub>6</sub>O<sub>13</sub>

Fig. 6 gives the activity and the propiononitrile and acetonitrile yield changes with time-on-stream for  $V_6O_{13}$  and its mechanical mixtures with anatase ( $M_R = 0.25$  and 0.5).

Conversion. The activity of  $V_6O_{13}$  [fig. 6(*a*)] is much lower at the beginning of the reaction than that for anatase and  $V_6O_{13}$  mechanical mixtures. However, the mechanical mixtures give the same values after *ca*. 20 h of reaction. This time-dependence for the anatase and  $V_6O_{13}$  mixtures is similar to that for pure anatase (fig. 1).

Propiononitrile yield. The propiononitrile yield for  $V_6O_{13}$  [fig. 6(b)] is higher than for anatase and  $V_6O_{13}$  mixtures during the entire period of time-on-stream. In the case of the mixed catalysts, the dependence of the propiononitrile yield

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**Fig. 6.** (a) Conversion of NEF (C) and (b) yields of propiononitrile  $(Y_p)$  and acetonitrile  $(Y_A)$  as functions of time-on-stream for  $V_6O_{13}$  and its mechanical mixtures with anatase. Reaction temperature = 623 K, O/N ratio = 0.8 and GHSV = 400 h<sup>-1</sup>. Conversion of NEF and yield of propiononitrile:  $\blacklozenge$ ,  $V_6O_{13}$ ;  $\blacklozenge$ ,  $AV_6O_{13}0.25$ ;  $\blacktriangle$ ,  $AV_6O_{13}0.5$ . Yield of acetonitrile:  $\nabla$ ,  $V_6O_{13}$ ;  $\bigcirc$ ,  $AV_6O_{13}0.25$ ;  $\bigtriangleup$ ,  $AV_6O_{13}0.5$ .

on time suggests that their catalytic properties are a superposition of those characteristic of pure anatase and  $V_6O_{13}$ . The best selectivity towards propiononitrile in the steadystate for  $V_6O_{13}$  is 44%, for  $V_2O_5$  is 20%, and in the case of AVH0.25 is 37% (at the maximum observed in fig. 3).

Acetonitrile yield. The acetonitrile yield [fig. 6(b)] is independent of the amount of anatase mixed with  $V_6O_{13}$ ; it is lower than the propiononitrile yield.

#### 4.2 Characterisation

#### X-Ray Diffraction

Mechanical Mixtures,  $V_2O_5$  and Anatase. Table 2 gives the phase composition of the fresh and used mechanical mixtures and pure  $V_2O_5$  and anatase, for which the catalytic results are presented in fig. 4. For both types of mixture, *i.e.* anatase with  $V_2O_5H$  and  $V_2O_5L$ , only  $V_6O_{13}$  was identified after the reaction.

Table 2. Phase composition of the fresh and used AVH and AVL mechanical mixtures

|                |                                 | phase composition             |                            |  |
|----------------|---------------------------------|-------------------------------|----------------------------|--|
| M <sub>R</sub> |                                 | fresh                         | used"                      |  |
| 0              |                                 | Α                             | Α                          |  |
| 0.1            |                                 | A, V <sub>2</sub> O,          | $A, V_6O_{13}$             |  |
| 0.25           |                                 | A, V <sub>2</sub> O,          | $A, V_6O_{13}$             |  |
| 0.4            |                                 | A, V,O,                       | $A, V_6O_{13}$             |  |
| 0.5            |                                 | A, V,O,                       | $A, V_{6}O_{13}$           |  |
|                | V,O,H                           | A, V,O,                       | $A, VO_2(B)$               |  |
| 0.75           | 2 3                             | . 1 3                         | traces $\tilde{V}_6O_{13}$ |  |
|                | V <sub>2</sub> O <sub>2</sub> L | A, V,O,                       | $A, V_6O_{13}$             |  |
| 1.0            | 2 3                             | V <sub>2</sub> O <sub>5</sub> | $VO_2(B), V_6O_{13}$       |  |

" The catalytic results are presented in fig. 4.

Table 3. The results of the XRD examinations of the calcined  $TiO_2A-V_2O_5$  mechanical mixtures and  $V_6O_{13}$  and its mixtures with anatase

|   |                 | phase composition                                     |  |  |
|---|-----------------|---|--|--|
| sample  | $(T/K)/(t/h)^a$ | fresh   | used   |  |
| AVL0.25   | 773/3           | 9% R, 91% A,<br>V <sub>2</sub> O <sub>6</sub>         | 10% <b>R,9</b> 0% A                                      |  |
| AVL0.5  | 773/3           | 16% R, 84% A,<br>V <sub>2</sub> O <sub>6</sub>        | 16% R, 84% A   |  |
| AVH0.25   | 773/3           | 21% R, 79% A,<br>V <sub>2</sub> O <sub>6</sub>        | 20% R, 80% A,<br>V₄O₀                                    |  |
| AVH0.25   | 673/3           | A, $V_2O_5$   | $A, V_6O_{13},$<br>traces $VO_2(B)$                      |  |
| V <sub>6</sub> O <sub>13</sub>  |                 | $V_6O_{13}$ ,<br>traces $V_2O_5$                      | $V_6O_{13}, V_4O_9$                                      |  |
| AV <sub>6</sub> O <sub>13</sub> 0.25<br>AV <sub>6</sub> O <sub>13</sub> 0.5 |                 | A, $V_6O_{13}$<br>A, $V_6O_{13}$ ,<br>traces $V_2O_5$ | A, $V_6O_{13}$ , $VO_2(B)$<br>A, $V_6O_{13}$ , $VO_2(B)$ |  |

<sup>a</sup> T = thermal treatment temperature; t = time of treatment.

In the case of AVH0.75, the  $V_2O_5$  reduction does not stop at  $V_6O_{13}$  but goes on, partially, to  $VO_2(B)$ . Both  $V_6O_{13}$  and  $VO_2(B)$  were formed from pure  $V_2O_5$ , after the reaction. No change was observed for TiO<sub>2</sub>(anatase).

Influences of Oxygen Concentration on Phase Composition of Mechanical Mixtures. Fig. 3 presents the results of XRD examinations of used AVH mixtures. For the low oxygen concentrations  $V_2O_5$  was found to be converted, in the course of the catalytic reaction, to  $V_2O_4(R)$ , whereas under the medium O/N ratio  $V_6O_{13}$  appeared. The increase in the oxygen concentration stops the reduction of  $V_2O_5$ , this oxide also being present in the catalytic reaction.

Influence of Calcination Temperature of Mechanical Mixtures on their Phase Composition. The results of the XRD examinations of the calcined, fresh as well as used, anatase and  $V_2O_5$  mechanical mixtures are presented in table 3.

The calcination of the AVH and AVL mixtures at 773 K results in the partial transformation of anatase into rutile. In the AVH sample calcined at 673 K rutile is not detected with the XRD method. No vanadium phase was detected in the case of the used AVL mixtures. The thermal pretreatment of the AVH samples has a strong influence on the nature of the vanadium phase detected after the catalytic reaction:  $V_4O_9$  appears when a sample is calcined at 773 K, whereas  $V_6O_{13}$  and a small amount of  $VO_2(B)$  can be detected in a mixture pretreated at 673 K.

Mechanical Mixtures with  $V_6O_{13}$ . Table 3 also shows the results obtained for anatase and  $V_6O_{13}$  mechanical mixtures. Pure  $V_6O_{13}$  is partially reoxidized to  $V_4O_9$  and when mixed with anatase, is partially reduced to  $VO_2(B)$  in the course of the catalytic reaction.

 
 Table 4. The XPS results for some anatase and vanadium oxide mixtures

|                                      | V(2p <sub>3/2</sub> )B.E. <sup><i>a</i></sup> /eV |       | V/Ti <sup>b</sup> |      | <i>I</i> (Ti )/                          |                        |
|--------------------------------------|---|-------|-------------------|------|--|------------------------|
| sample                               | fresh   | used  | fresh             | used | <i>I</i> (Ti <sub>f</sub> ) <sup>c</sup> | $I(V_{\rm g})^{\rm c}$ |
| AVH0.25                              | 516.6   | 516.7 | 0.28              | 1.47 | 0.40                                     | 2.1                    |
| AVL0.25                              | 516.6   | 516.6 | 0.15              | 0.18 | 0.63                                     | 0.73                   |
| AVL0.25<br>773/3                     | 517.0   | 516.6 | 0.55              | 1.34 | 0.37                                     | 2.4                    |
| AV <sub>6</sub> O <sub>13</sub> 0.25 | 516.3   | 516.2 | 0.15              | 0.46 | 0.50                                     | 1.5                    |

<sup>a</sup> B.E. = binding energy; <sup>b</sup> V/Ti = V(2p<sub>3/2</sub>) to Ti(2p<sub>3/2</sub>) XPS intensity ratio; <sup>c</sup>  $I(Ti_f)$ ,  $I(Ti_u)$ ,  $I(V_f)$ ,  $I(V_u) = Ti(2p_{3/2})$  (Ti) and  $V(2p_{3/2})$  (V) XPS intensities for the fresh (f) and used (u) mixtures. The intensities were adjusted by the O<sub>1s</sub> intensity.

#### X-ray Photoelectron Spectroscopy

The results of the XPS examinations of a few anatase and vanadium oxide mechanical mixtures are presented in table 4. It is clear that values of the V( $2p_{3/2}$ ) binding energy for fresh and used catalysts AVH0.25 and AVL0.25 are characteristic of V<sup>5+</sup> in the V<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub> mixture.<sup>12</sup> For the calcined AVL sample, the V( $2p_{3/2}$ ) binding energy decreases under the influence of the reaction mixture, while in the case of the uncalcined AVL and AVH samples the V( $2p_{3/2}$ ) binding energy for the fresh and used AV<sub>6</sub>O<sub>13</sub>0.25 are the same and close to the values found in V<sub>6</sub>O<sub>13</sub>.<sup>12</sup> The V/Ti XPS intensity ratios increase after the reaction for the samples studied with the exception of AVL0.25. The *I*(Ti<sub>u</sub>)/*I*(Ti<sub>f</sub>) ratios decrease, while the *I*(V<sub>u</sub>)/*I*(V<sub>f</sub>) ones increase (with the exception of AVL0.25).

### 5. Discussion

### 5.1 The Stabilizing Role of Anatase

As in the case of rutile, our results show that a cooperation between anatase and vanadium oxide exists. Fig. 1 illustrates this phenomenon. Under the same catalytic conditions, anatase loses its catalytic activity and the propiononitrile yield, after the initial rise, decreases with the reaction time, as in the case of  $V_2O_5$ , but to a lesser extent. However, the dependence of the activity and propiononitrile yield on time for the AVH0.5 mechanical mixture is quite different: the activity is very high at the beginning of the reaction time and decreases, reaching a plateau with time; the propiononitrile yield increases progressively, starting from a value lower than for V<sub>2</sub>O<sub>5</sub> and anatase. As a result, the initial and final activities as well as the final propiononitrile yield of the mixed oxides are higher than those of the pure oxides that make up the mixture. The consequence of this cooperation seems to be the stabilization of  $V_6O_{13}$  by anatase, preventing a deeper reduction of  $V_2O_5$ . Some arguments confirm this hypothesis.

(1) Fig. 3 shows that the minimum catalytic activity and the maximum propiononitrile yield correspond to an O/N ratio of 0.8 for the AVH mixture. Under these conditions,  $V_2O_5$  is reduced to  $V_6O_{13}$ . When the oxygen content in the feed is lower,  $V_2O_5$  is reduced to  $V_2O_4(R)$ , whereas for the higher oxygen concentration, no reduction is observed. Comparing the propiononitrile yield at comparable compositions, it can be concluded that  $V_6O_{13}$  is the most selective phase in the dehydration of NEF.

(2) In fig. 4, the propiononitrile yield observed as a function of the V<sub>2</sub>O<sub>5</sub> content in the mixtures shows an important synergetic effect. The phase composition analysis of the used samples shows that  $V_6O_{13}$  was formed during the reaction (table 4). This type of anatase influence on  $V_2O_5$  is clearly observed in the whole V<sub>2</sub>O<sub>5</sub> concentration range. For the AVH mixtures, the propiononitrile yields are directly proportional to the  $V_2O_5$  concentration, in fact to that of  $V_6O_{13}$ , up to  $M_R = 0.5$ . In this zone the  $V_2O_5$  is in good contact with the large amount of  $TiO_2$ . The maximum synergetic effect is observed at  $M_{R} = 0.5$  and 0.75 for the AVH and AVL mechanical mixtures, respectively. In both cases,  $V_6O_{13}$  alone is observed after the catalytic test. These results indicate that the synergetic effect is proportional to the number of intergranular contacts between the oxides composing the mixtures.

(3) Under the reaction conditions applied, the  $V_2O_5$ -TiO<sub>2</sub>(anatase) samples give higher propiononitrile yields than the  $V_2O_5$ -TiO<sub>2</sub>(rutile) mixtures. In the case of the latter, two reduced phases were observed:  $V_6O_{13}$  and  $VO_2(B)$ ,<sup>1</sup> contrary to the case of the anatase  $V_2O_5$  mixtures where only  $V_6O_{13}$  was observed. We recall that  $VO_2(B)$  is the result of a deep reduction of  $V_6O_{13}$ .

This cooperation seems to explain the form of the curves presented in fig. 1. The plot of the propiononitrile yield vs. time-on-stream reflects the process of the  $V_2O_5$  reduction to  $V_6O_{13}$  for the AVH0.25 samples: under the same reaction conditions, the reduction of pure  $V_2O_5$  is faster and does not stop at  $V_6O_{13}$  but also yields  $VO_2(B)$ . In contrast to pure  $V_2O_5$ , anatase seems to stabilize the  $V_6O_{13}$  preventing its deeper reduction. The delay in the diminution of the conversion and the rise of the propiononitrile yield for the mixtures can be explained by the rate of nucleation of the  $V_6O_{13}$ phase.

The catalytic experiments carried out on  $V_6O_{13}$  confirm its good selectivity in the dehydration reaction (fig. 6). The best selectivities to propiononitrile at steady-state were 44% for  $V_6O_{13}$ , 20% for  $V_2O_5$  and 37% for AVH0.25, at the maximum observed in fig. 3.

In conclusion,  $V_6O_{13}$  seems to be the most selective phase in the vanadium oxide-TiO<sub>2</sub>(anatase) NEF dehydration. Within certain oxygen concentration limits, anatase stabilizes the  $V_6O_{13}$  phase, preventing its further reduction and reoxidation.

#### 5.2 Oxidation State of Vanadium

The XPS studies reveal that the surface layer of  $V_2O_5$  in the untreated mixtures contains  $V^{5+}$  ions after the reaction (table 4). The XRD analysis shows the presence of well crystallized  $V_6O_{13}$  (table 2). This indicates that the  $V_6O_{13}$  surface formed by the reduction of  $V_2O_5$  in contact with anatase, is in the oxidized state ( $V^{5+}$ ). The  $AV_6O_{13}0.25$  mechanical mixture shows a decrease of the  $V(2p_{3/2})$  binding energy. This corresponds to the vanadium with a valence state lower than +5, probably due to the presence of  $VO_2(B)$  on the surface (table 4). The XRD analysis shows the presence of a mixture of  $V_6O_{13}$  and  $VO_2(B)$  in the used catalyst (table 3). Small superficial nuclei of  $VO_2(B)$  are probably already present in the  $V_6O_{13}$  used to prepare the mechanical mixtures with anatase.

In the calcined AVL0.5 sample a decrease in  $V(2p_{3/2})$  binding energy after the reaction is observed, indicating the presence of vanadium ions at a valence state lower than +5. This is due to the rutile action on  $V_2O_5$ .<sup>1</sup>

#### 5.3 Effect of Temperature

The heating of the samples has two principal effects.

(1) There is an increase of the  $V_2O_5$  dispersion over the anatase surface, which is reflected in the increase of the V/Ti XPS intensity ratio. This increased  $V_2O_5$  dispersion over the anatase grains could be due to the wetting of TiO<sub>2</sub> with  $V_2O_5$ .<sup>13</sup> This dispersion increases with increasing temperatures. The dispersion leads to an increase in the contact between the oxides and, consequently, to an increase in the propiononitrile yield.

(2) There is also a partial transformation of anatase into rutile; according to the literature,<sup>2</sup>  $V_2O_5$  accelerates the anatase-into-rutile transformation. In addition, this transformation can already start at 723 K,<sup>3,14,15</sup> which explains why rutile is observed in the calcined sample at 773 K. As has been emphasized, the appearance of rutile aggravates catalytic properties, *i.e.* the values of the propiononitrile yield become lower than those of the pure anatase mixtures. In the light of these two effects, the results obtained with the calcined  $V_2O_5$ -TiO<sub>2</sub>(anatase) mixtures could be explained as follows.

#### AVL mixtures

The AVL mixtures calcined at 773 K for 3 h give higher propiononitrile yields than the uncalcined samples (fig. 4). The amount of anatase transformed to rutile in the calcined samples was less than 20%, and therefore the increase in the  $V_2O_5$  dispersion over the anatase was a prevailing effect compared to the anatase-rutile transformation, and it resulted in an increase of the propiononitrile yield compared with the uncalcined samples.

#### AVH0.25 Samples

The AVH0.25 sample calcined at 773 K was initially formed by anatase-rutile and  $V_2O_5$ . For the sample calcined at 673 K there is no indication of the formation of well crystallized rutile due to the calcination. XRD indicates that this sample, prior to the catalytic test, was composed of anatase and  $V_2O_5$ .

Literature shows, using the HREM techniques,<sup>14</sup> that heating the  $V_2O_5$ -TiO<sub>2</sub>(anatase) sample at 723 K for 4 h, results in the formation of a thin rutile-like layer on the surface of anatase. Therefore, we can assume that our samples calcined at 673 K also developed a layer of rutile on the surface, which was not detected by our XRD measurements. Otherwise, our results (table 4) indicate that the heating of the samples leads to an increase in the dispersion of vanadium on the surface of the TiO<sub>2</sub> and consequently, the evolution of the propiononitrile yield as a function of timeon-stream for the calcined samples seems to be a complex result of the simultaneous action of anatase and rutile on  $V_2O_5$  and an increase of the vanadium dispersion.

The results presented in fig. 5 seem to confirm this hypothesis. In particular: (i) the shape of the curves for the calcined samples are the same; (ii) the only samples which present a decrease in the propiononitrile yield are the calcined and rutile samples; (iii) the non-calcined sample shows an increase in the propiononitrile yield in the range of time studied, and, after the catalytic test, a rise in the dispersion of  $V_2O_5$ ; (iv) the reduced vanadium oxide ( $V_4O_9$ ) formed in the course of the catalytic reaction, for the sample at 773 K, is characteristic of rutile influences (table 3); (v) for the 673 K sample, traces of a reduced phase,  $VO_2(B)$ , were observed. This is also due to the influence of the rutile after calcination. We remark that for the non-calcined samples, no indication of formation of the reduced phases was observed.

Therefore, the shape of the curves for the calcined samples shown in fig. 5 can be explained as follows.

In the first 2 h the increase in the dispersion of vanadium occurred, succeeded by the reduction of  $V_2O_5$  to a selective reduced phase, probably  $V_6O_{13}$ . Both phenomena produce an increase in propiononitrile yield, and a decrease in conversion and acetonitrile yield.

Between 2 and 6 h the influence of the rutile formed during the calcination is more marked than in the first stage of the reaction. More reduced (and non-selective) phases, and probably the first nuclei of VO<sub>2</sub>(B) are formed. The propiononitrile yield decreases while at the same time, the acetonitrile yield increases weakly. We remark that when VO<sub>2</sub>(B) appeared together with V<sub>6</sub>O<sub>13</sub> in the mixture with TiO<sub>2</sub> (table 3), a lower propiononitrile yield<sup>1</sup> (fig. 6) was produced than for the mixture in which only V<sub>6</sub>O<sub>13</sub> was present (table 2, fig. 4). The nucleation of reduced phases is probably more marked in the samples calcined at 773 K because the drop is more pronounced in this sample.

After 6 h the reduced phases are already formed and the propiononitrile and acetonitrile yields do not change significantly. The fact that the sample calcined at 773 K presents a higher yield in propiononitrile can be explained by an increase in the dispersion of vanadium due to the temperature.

It appears that our results would allow us to speculate a little on the role played by a rutile-like layer on the surface of the anatase. If we accept, as has been discussed above, that



**Fig.** 1. The architecture of the anatase and rutile mixtures with  $V_2O_5$  before and after NEF dehydration.  $V_2O_{5-x}$  designates reduced vanadium oxide whose nature depends on the conditions of catalytic reaction.

samples calcined at 673 K also develop a layer of rutile on the surface, we could propose two characteristic features for this layer: (i) it does not have the properties of the well defined crystalline rutile bulk phase; (ii) it would probably partially mask the anatase influence on V<sub>2</sub>O<sub>5</sub>. Our suggestion is that the rutile layer does not affect the physicochemical properties of  $V_2O_5$ , but rather renders impossible the cooperation between  $TiO_2(anatase)$  and  $V_2O_5$ . Two observations seem to support this view: (i) the final propiononitrile yield is close to yields characteristic of  $V_2O_5$  (fig. 1); (ii) the vanadium oxide phase composition after reaction resembles that found in the pure V<sub>2</sub>O<sub>5</sub> samples. Therefore, anatase covered with a thin ill defined rutile layer preserves its activity but is not capable of affecting the nature of the vanadium oxide formed during the catalytic reaction. Obviously, this possibility needs to be investigated further.

## 5.4 V<sub>6</sub>O<sub>13</sub>-TiO<sub>2</sub>(anatase) Mixtures

The results obtained for these samples show that when independently prepared  $V_6O_{13}$  is mechanically mixed with anatase, a high propiononitrile yield is observed at the beginning of the reaction, but that with time-on-stream, it decreases strongly. The explanation is that, in these mechanical mixtures, the contact between the anatase and the  $V_6O_{13}$  is limited to physical contact alone. The  $V_6O_{13}$  undergoes a deeper reduction and anatase is not able to stabilize it. The dispersion of  $V_6O_{13}$  over the anatase surface by the wetting mechanism seems to be difficult and the literature shows that this mechanism is not observed in the anatase-reduced vanadium oxide system.<sup>17</sup>

On the contrary, the  $V_6O_{13}$  formed as a result of contacts between  $V_2O_5$  and anatase is better protected against a deeper reduction. In this case, anatase stabilizes the  $V_6O_{13}$ formed on its surface.

## 5.5 The Anatase--V<sub>2</sub>O<sub>5</sub> System

One can advance the following mode of cooperation between anatase and  $V_2O_5$  in the course of NEF dehydration.  $V_2O_5$ 

is dispersed over the anatase surface by a solid-solid wetting mechanism<sup>15,16</sup> and, at the same time,  $V_2O_5$  is reduced to  $V_6O_{13}$  with the organic reactants, which results in an increase of the propiononitrile yield.  $V_6O_{13}$  generated by the reduction of  $V_2O_5$  forms some sort of a junction with the anatase surface. Such a  $V_6O_{13}$ , bound to anatase, is more resistant to the influence of hydrocarbons and does not undergo further reduction, which results in a stable high propiononitrile yield. Probably as a result of the crystallographic fit between  $V_6O_{13}$  and anatase,<sup>2</sup> the bond between both oxides acts as an epitaxial function.

However, the calcination of vanadia-titania oxides at higher temperatures leads to polymorphic transformations of anatase into rutile. This transformation seems to be accelerated by the presence of vanadium. The formation of rutile prevents good cooperation between  $V_2O_5$  and the anatase, giving more reduced phases of vanadium which are less selective.

Fig. 7 presents, schematically, the architecture of the calcined and uncalcined  $V_2O_5$ -TiO<sub>2</sub>(anatase) and those after the catalytic reaction. Those for the  $V_2O_5$ -TiO<sub>2</sub>(rutile) sample are shown for comparison.

#### 6. Conclusions

It has been demonstrated that in the  $V_2O_5$ -TiO<sub>2</sub> system:

(1)  $V_2O_5$  is reduced in the course of the NEF dehydration and the  $V_6O_{13}$  phase is formed under appropriate reaction conditions (O/N ratio, temperature).

(2)  $V_6O_{13}$  is the most selective phase in the vanadium oxide-TiO<sub>2</sub>(anatase) system in NEF dehydration.

(3) The cooperation between  $V_2O_5$  and  $TiO_2(anatase)$  brings about the stabilization of  $V_6O_{13}$ , *i.e.*  $V_6O_{13}$  formed in contact with anatase is more resistant to reduction and reoxidation by the reaction mixture.

(4) The calcination of the  $TiO_2(anatase)$  and  $V_2O_5$  mechanical mixtures results in (a) an increase in the  $V_2O_5$  dispersion over the anatase surface, which brings about a rise in the propiononitrile yield, and (b) partial anatase-into-rutile transformation as a result of which a decay of the catalytic properties is observed.

(5) Under appropriate reaction conditions (temperature, O/N ratio), an increase of the  $V_2O_5$  dispersion over the anatase surface is observed. Under these conditions, the anatase-into-rutile transformation does not take place.

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