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TEMPERATURE-PROGRAMMED REDUCTION OF V_2O_5 AND COPRECIPITATED V_2O_5–TiO_2 BY HYDROGEN

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Abstract

Temperature-programmed reductions (TPR) with H_2 of both pure V_2O_5 and coprecipitated V_2O_5–TiO_2 systems with different titanium concentrations was performed. The original and the reduced samples following each TPR step were characterized by X-ray diffraction, Fourier transform infrared analysis and scanning electron microscopy.

Within the temperature range in which TPR analysis was carried out (100–600°C) the V_2O_5 phase was reduced in two or three steps, while no variation in the TiO_2 phase (anatase or rutile) was observed.

In the first reduction step only superficial reduction of the oxides was detected. In the following steps, the H_2 reacted with oxygen atoms of the V=O and V–O–V bonds. This led to important changes in the structure and morphology of the system.

The experimental evidence allowed the conclusion that titanium stabilizes certain phases of vanadium oxides in which vanadium appears as V(+4) or as a mixture of V(+4) and V(+5). Moreover, when moderate and high titanium concentrations were used, the reduction temperature of the bulk V_2O_5 decreased markedly.

Keywords: TPR, V_2O_5–TiO_2 system

Introduction

Both V_2O_5 and V_2O_5–TiO_2 systems, as well as other oxides of the transition metals, catalyze the selective oxidation of hydrocarbons. These processes take place according to the mechanism reported by Mars and Van Krevelen or that Hinshelwood [1].

Mars and Van Krevelen stated that the selective oxidation of hydrocarbons proceeds according to the following steps:

$$\text{REAGENT} + (\text{CATALYST})_{\text{OX}} \rightarrow \text{PRODUCT} + (\text{CATALYST})_{\text{RED}}$$

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$$(\mathrm{CATALYST})_{\mathrm{RED}} + \mathrm{O}_{2(g)} \rightarrow (\mathrm{CATALYST})_{\mathrm{OX}}$$

where the hydrocarbon adsorbed on the solid surface reacts with the oxygen atoms (oxide ions) of the crystalline network of the catalyst. Hence, it is important to know how easily the oxide ions of the solid can be removed (a property usually termed reducibility) in order to be able to explain the behavior of a given catalyst [2–4]. This property is studied by temperature-programmed reduction (TPR), one of the most widely used physicochemical techniques for the characterization of heterogeneous catalysts.

Studies on the TPR of pure V_2O_5, and also the influence of the addition of TiO_2 and the structural modifications exhibited by the reduced solids, are reported in the present article.

Experimental

Syntheses of the compounds

(A) V_2O_5

V_2O_5 was prepared by dissolving NH_4VO_3 (Mallinckrodt AR) in HCl (Merck PA), and further neutralizing this solution with NH_4OH (Merck PA) to $pH=5$. The precipitate was separated by decantation and washed with water to eliminate the NH_4Cl formed in the neutralization step. The solid thus obtained was then dried at 120°C and calcined at 500°C for 96 h.

(B) V_2O_5–TiO_2 solids

Five samples of V_2O_5–TiO_2 with titanium percentages ranging from 10 to 90% were synthesized. These solids were termed VT10, VT20, VT50, VT80 and VT90. All of them were obtained from $VOCl_3$ solutions, prepared as needed by dissolving NH_4VO_3 (Mallinckrodt AR) in concentrated HCl (Merck PA), and $TiOCl_2$, also prepared just prior to use by hydrolysis of $TiCl_4$ (Carlo Erba RPE). These solutions were mixed in the appropriate proportions and neutralized to $pH=6$ with NH_4OH (Merck PA) under continuous stirring and cooling. The precipitate was filtered off and washed as described for V_2O_5. It was also dried and calcined under the above-mentioned conditions.

In order to avoid bronze formation during all thermal treatments, either quartz or platinum laboratory materials were employed.

Temperature-programmed reduction

Figure 1 shows the flow chart corresponding to the equipment in which the reduction experiments were carried out. The flow rate of the feeding mixture (N_2–H_2) and the H_2 concentration can be varied independently of one another.

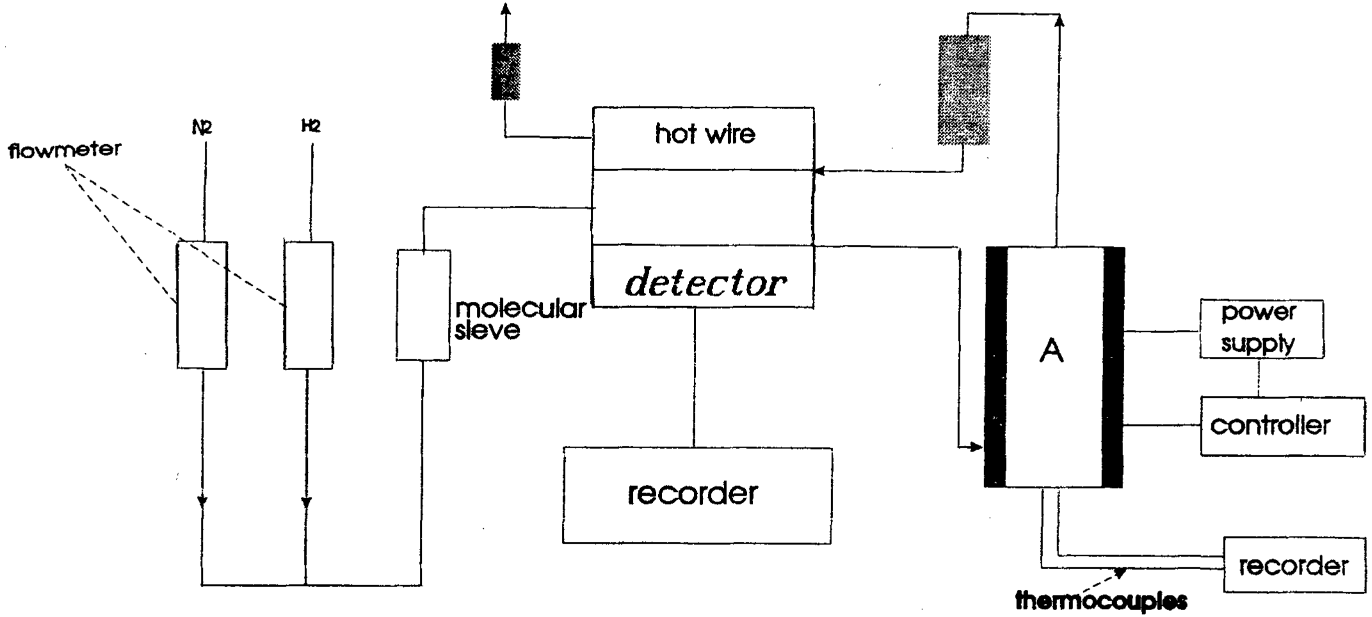

Fig. 1 Flow chart of experimental equipment

The mixtures of H_2 and N_2 passed through a column filled with a 5A molecular sieve. The gas stream leaving the reactor circulated through a trap cooled with liquid air, before passing through the catarometric detector (Gow Mac). In the present work, VT samples were reduced in a gas stream of 10% H_2 in N_2, with a total flow of 55 cm^3 min^{-1} and a heating rate of 5 deg·min^{-1}.

The operation variables, i.e. the flow rate of the mixture, the concentration of H_2, the amount of sample and the rate of heating, were set according to the criterion suggested by Monti and Baiker [5], who defined the characteristic number K as follows:

$$K=\frac{S_o}{V^*C_o}$$

where S_o is the initial amount of sample (mol), V is the total flow rate ($cm^3\,s^{-1}$) and C_o is the initial H_2 concentration (mol·cm^{-3}). According to Monti and Baker, the K values must be in the range 55–140 s for heating rates ranging from 0.1 to 0.3 deg·min^{-1}. The value K=83.0 s for the heating rate β= 5 deg·min^{-1} used in this paper is within the above band.

Reductions at temperatures programmed between 100 and 600°C were carried out on all samples as the first step of the study. Diagrams thus obtained are shown in Fig. 2. Reduction of TiO_2 (anatase or rutile) was not observed within this temperature range. The signal appearing in diagram G of Fig. 2, corresponds to TiO_2 dehydroxylation.

The next step consisted of tests involving stopping the reduction at the temperatures corresponding to each peak of the thermograms; the phases present were then characterized by different spectroscopic techniques.

Quantitative analysis

Concentrations of vanadium and titanium in the VT solids were determined by means of an EDAX Philips 505 microprobe. The equipment was calibrated with standards of V_2O_5 and TiO_2 of known concentrations. All samples were homogenized and coated with a very thin layer of conductive material by a sputtering technique. Results are shown in Table 1. These data were corroborated by volumetric chemical analysis [6] and by spectrophotometric analysis [7, 8].

X-ray diffraction analysis

XRD analysis of the samples was performed in the interval $15^\circ \leq 2\theta \leq 56^\circ$ by means of Philips Pw 1390 equipment. The spectra were recorded at 2000 cps unless specified otherwise.

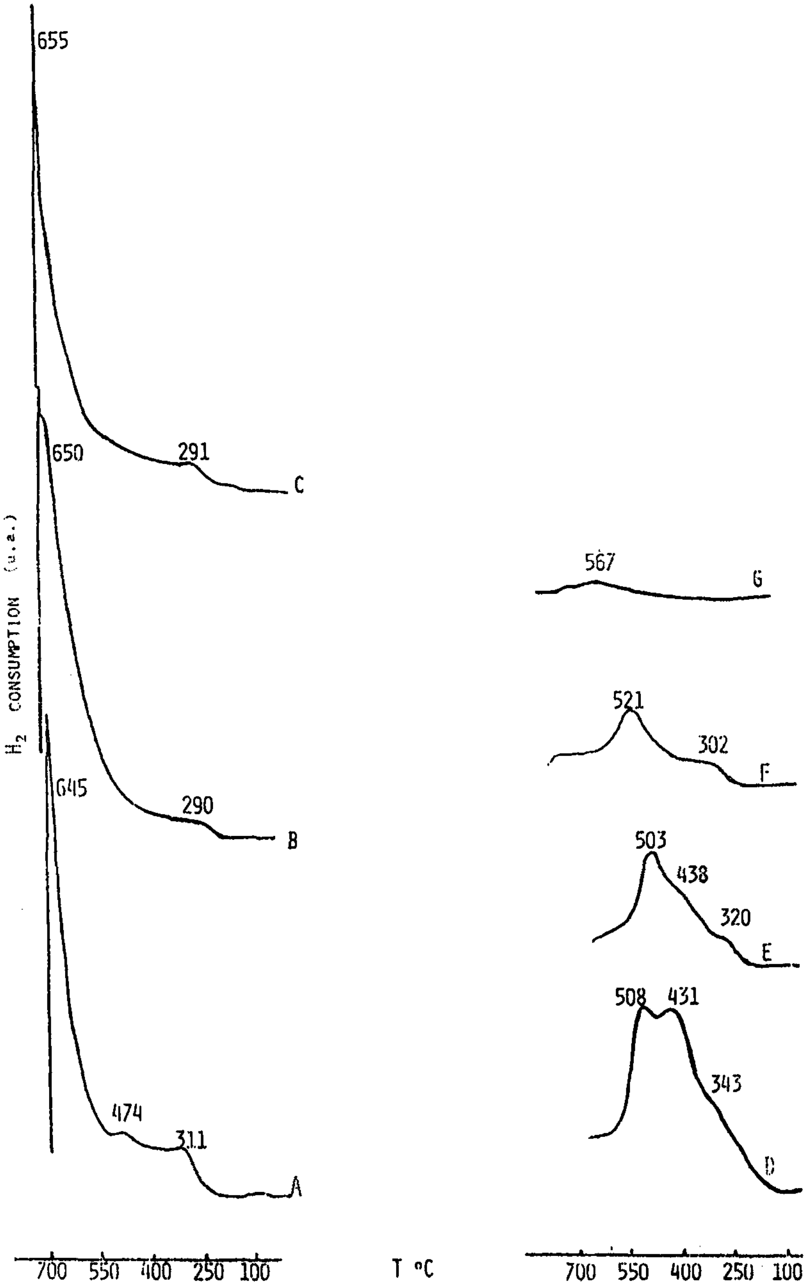

Fig. 2 Reduction profiles (TPR) measured for samples of (A) V_2O_5, (B) VT10, (C) VT20, (D) VT50, (E) VT80, (F) VT90 and (G) TiO_2. Conditions: heating rate, 5 deg/min; reducing gas mixture, 10% H_2 in N_2; gas flow rate, 55 cm^3(NTP) min^{-1}; sample mass variable

Table 1 Quantitative analysis of vanadium and titanium by EDAX microprobe in VT fresh samples

Sample	%W/W V_2O	%W/W TiO_2
VT10	90.0	9.9
VT20	86.9	13.1
VT50	57.6	42.4
VT80	27.9	72.0
VT90	14.2	85.8

The diagrams indicated that fresh samples were composed of well-crystallized orthorhombic V_2O_5 and TiO_2 (anatase and rutile). Comparison of the contributions of the (001), (110) and (400) planes of V_2O_5 are compared in Fig. 3.

As an example of the changes in the samples during the reduction tests, spectra of reduced V_2O_5 and VT50 are shown in Figs 4 and 5.

Infrared analysis

Samples were analyzed by IR spectroscopy on FTIR Bruker IFS 66 equipment. Comparisons between the spectra of fresh samples and those of corresponding reduced samples of V_2O_5 and VT50 can be seen in Figs 6 and 7. The positions of the IR bands of the V=O and V–O–V bonds as a function of the reducing temperature are listed in Table 3.

XRD and IR signals were identified according to the spectroscopic data reported by Frederickson *et al.* [10], Fabbri *et al.* [11], Theobald [12] and ASTM [13] for V_2O_5 and its reduced oxides. A thorough analysis allowed identification of the phases present in both fresh and reduced samples. It could also be established that the TiO_2 phases remained unchanged. Results can be observed in Table 2.

Scanning electron microscopy analysis

Fresh and reduced samples were analyzed with a Philips SEM 505 electronic microscope. Photographs 1,2 and 3, corresponding to samples of V_2O_5, VT10 and VT80, are the most representative ones. To facilitate comparison, every sample was analyzed at the same magnification (×2000).

Results and discussion

Figure 2 depicts the variation in H_2 consumption as a function of temperature in the different samples.

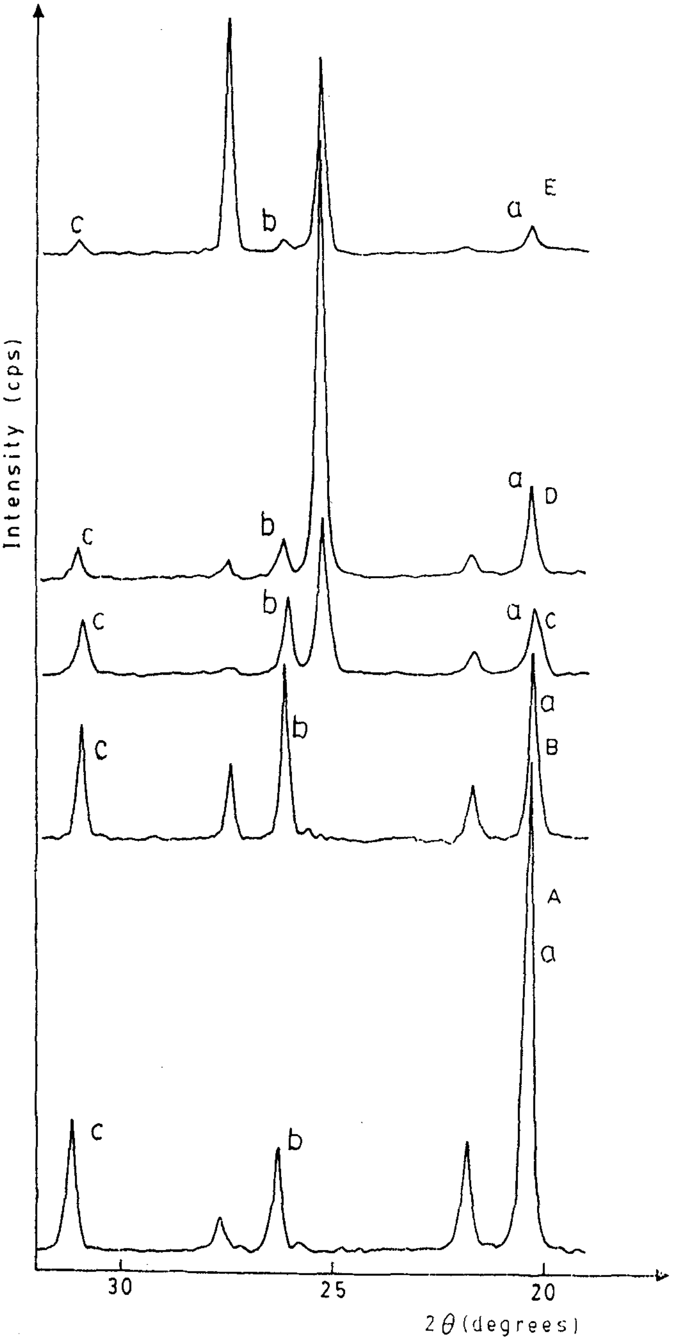

Fig. 3 Comparison of intensities of X-ray reflections (001), (110) and (400) of V_2O_5 phase of samples of (A) VT10, (B) VT20, (C) VT50, (D) VT80 and (E) VT90. a=(001), b=(110) and c=(400) planes

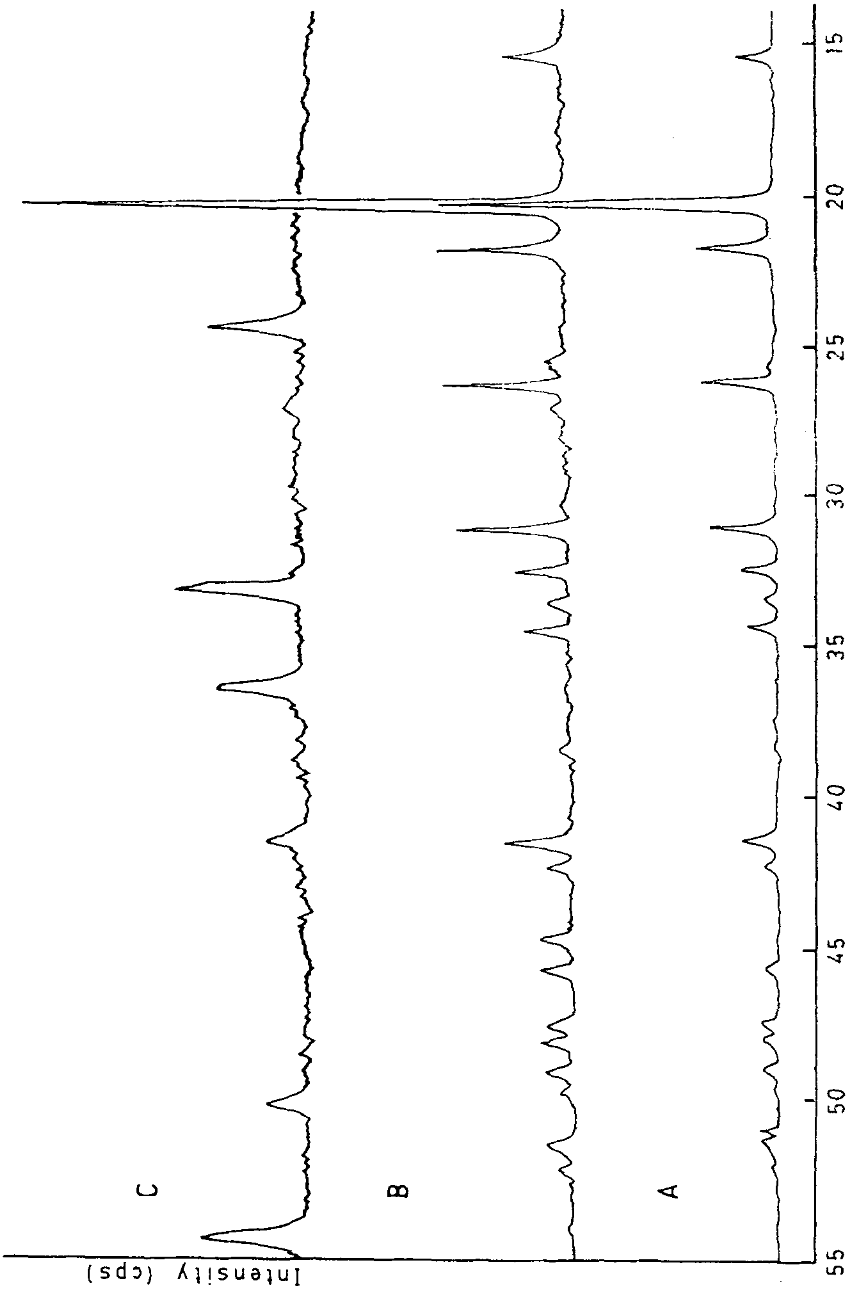

Fig. 4 Comparison of XRD patterns of sample of V_2O_5 reduced up to (A) 311°C, (4000 cps), (B) 474°C and (C) 645°C

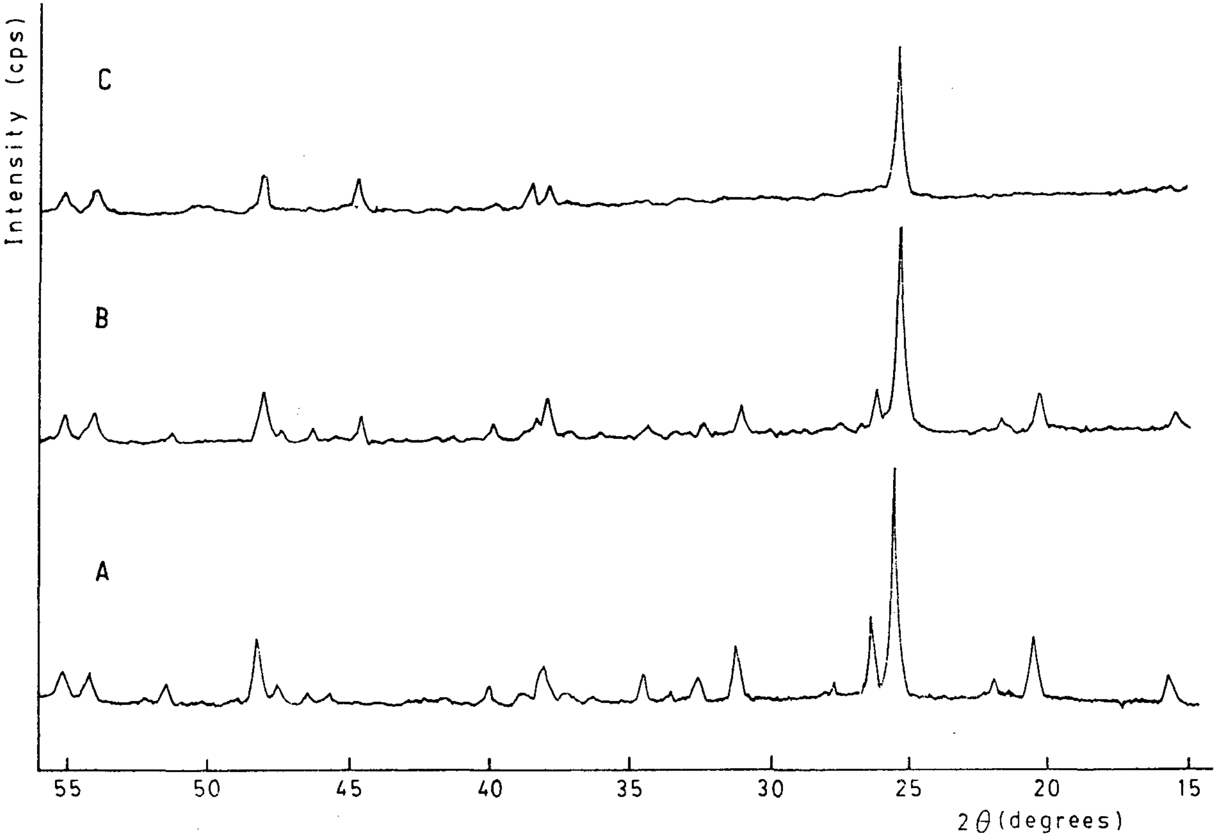

Fig. 5 Comparison of XRD patterns of VT50 reduced up to (A) 343°C, (B) 431°C and (C) 508°C

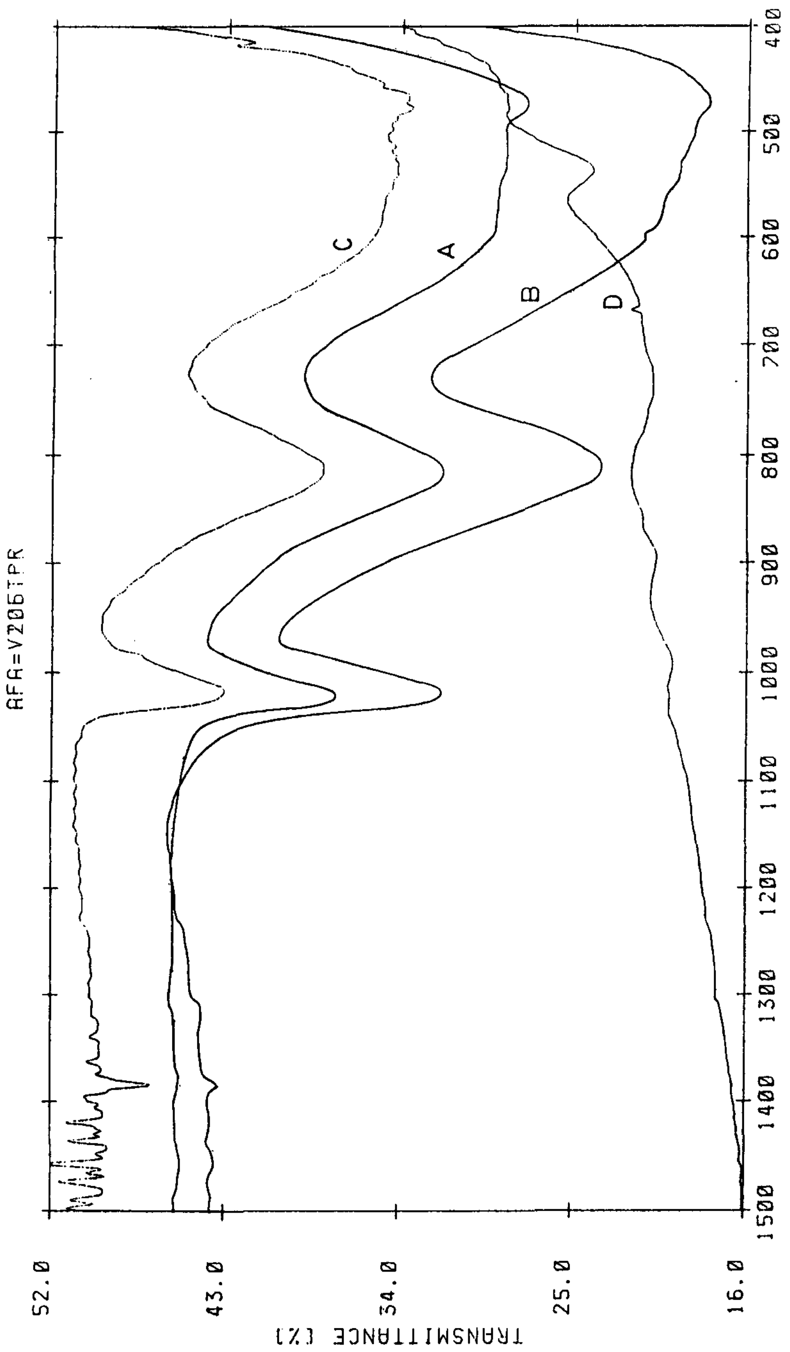

Fig. 6 Comparison of IR spectra of V_2O_5: (A) fresh, reduced up to (B) 311°C, (C) 474°C and (D) 645°C

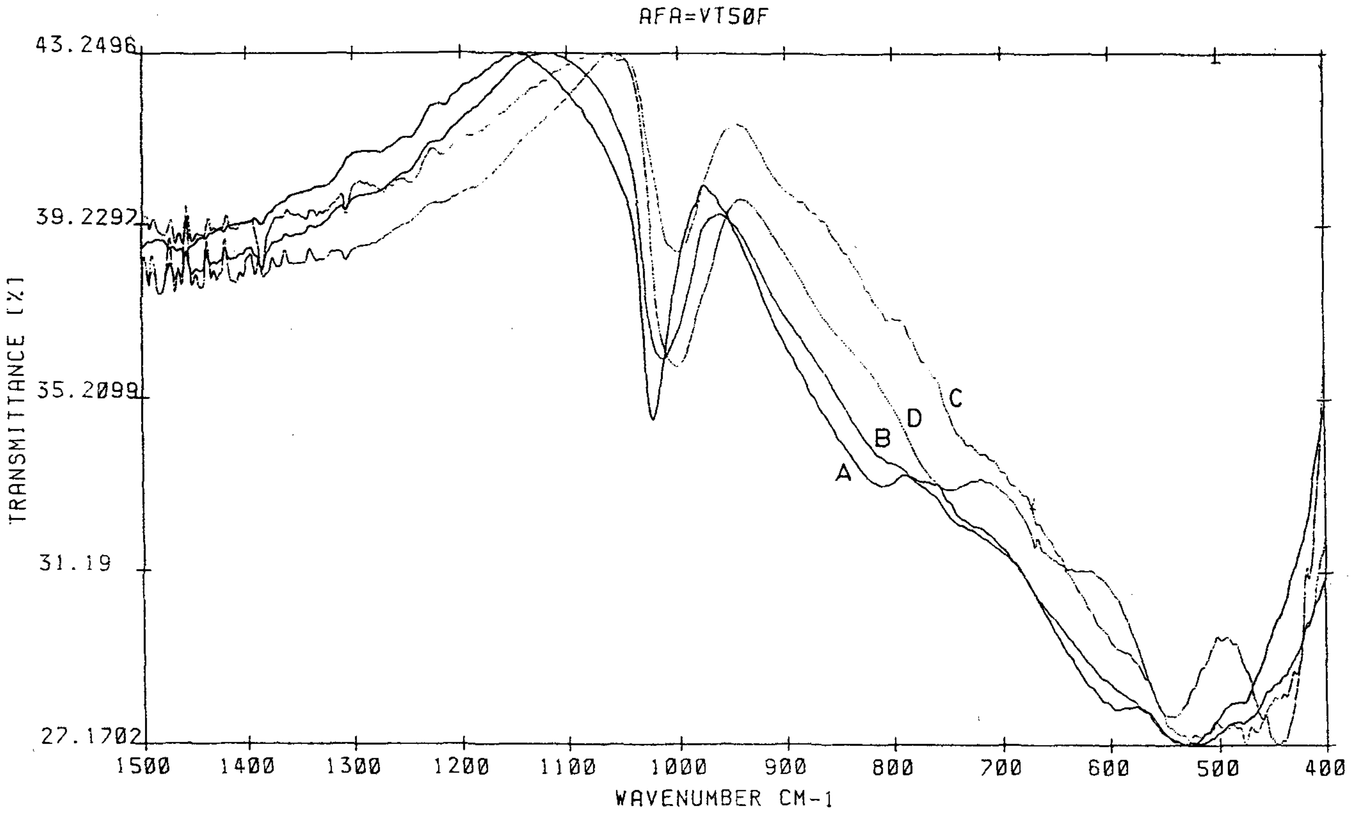

Fig. 7 Comparison of IR spectra of VT50: (A) fresh, reduced up to (B) 343°C, (C) 431°C and (D) 508°C

Table 2 Phases identified by X-ray diffraction and infrared spectroscopy in fresh and reduced samples

Sample	Fresh	Reduction temperatures/°C		
		T_1	T_2	T_3
		311°C	474°C	645°C
V_2O_5	V_2O_5	V_2O_5	V_2O_5,VO_2(B)	V_2O_3
		290°C	-	650°C
VT10	V_2O_5	V_2O_5		V_2O_5, V_2O_4
		291°C	-	655°C
VT20	V_2O_5	V_2O_5		V_2O_5, V_6O_{13}
		343°C	431°C	508°C
VT50	V_2O_5	V_2O_5	V_2O_5, V_2O_4, V_6O_{13} amorphous	V_2O_5,VO_2(B) amorphous
		320°C	438°C	503°C
VT80	V_2O_5	V_2O_5	V_2O_5,VO_2(B)	V_2O_5, low
		302°C	-	521°C
VT90	V_2O_5	V_2O_5		V_6O_{13}

Reduction of the systems V–Ti started at temperatures lower than (VT10 and VT20) or similar to (VT80 and VT90) that for V_2O_5, with the exception of VT50, to which a higher temperature corresponded (there was a difference of more than 30 deg). As far as crystallography is concerned, solids resulting from this first reduction step are identical to fresh samples. The major phase is V_2O_5 in both cases, as can be observed in Table 2. On the other hand, the IR signal corresponding to the V=O double bond showed no variation in either position or intensity as compared with the fresh sample (Table 3). However, it underwent a slight broadening.

Reduced V_2O_5, VT10 and VT20 samples did not display morphological differences from the fresh samples (Photographs 1A, 1B, 2A and 2B). They contained both plate- and needle-shaped particles, which is in accordance with the fact that their major XRD signal is the (001) plane the of V_2O_5 phase [10].

The most important crystallographic phase in the samples containing the highest titanium concentration (VT50, VT80 and VT90) (both in fresh samples and in those resulting from the first reduction) is anatase, the amount of V_2O_5 being low. Therefore, VT50, VT80 and VT90 appear not as plate formations, but as groups of small needles (corresponding to V_2O_5) and particles of granular shape, characteristic of TiO_2 (Photographs 3A and 3B).

Table 3 Infrared signals of V=O and V–O–V bands in both fresh samples and at different reducing steps

Sample	Temperature	Frequency/cm^{-1}	
		V=O	V–O–V
V_2O_5	Fresh	1020.8	816.4
	311	1019.5	810.0
	474	1015.6	815.0
	645	–	–
VT10	Fresh	1020.8	815.1
	290	1020.8	815.0
	650	1011.8	–
VT20	Fresh	1023.4	820.2
	291	1019.5	819.0
	655	1014.4	811.2
VT50	343	1023.4	810.0
	343	1014.4	815.1
	431	998.9	–
	508	1001.5	–
VT80	Fresh	1031.1	808.7
	320	1031.5	–
	438	1002.5	
	503	1000.2	–
VT90	Fresh	1031.1	–
	302	1029.3	–
	521	1011.8	–

The absence of important morphological changes in the first reduction was demonstrated by the small variation undergone by the specific surface of the solids. For example, that of the sample of VT80 changed from 6.0 $m^2 \cdot g^{-1}$ to 7 $m^2 \cdot g^{-1}$.

These results indicate that the first reduction signal involves reduction taking place only at the surface, with the subsequent energy variation of a small amount of exposed V=O, which leads to deformation of the IR band.

As can be inferred from the data in Table 2, samples of V_2O_5, VT10 and VT20 exhibit mostly reduced phases of vanadium in the bulk at approximately 650°C, whereas samples of VT50 and VT80 exhibit these phases at 430°C, and VT90 does so at 520°C. This behavior indicates that solids with high titanium content are more easily reduced, since the energy needed to remove oxygen from the crystalline oxide, network is lower. On the other hand, reduced tita-

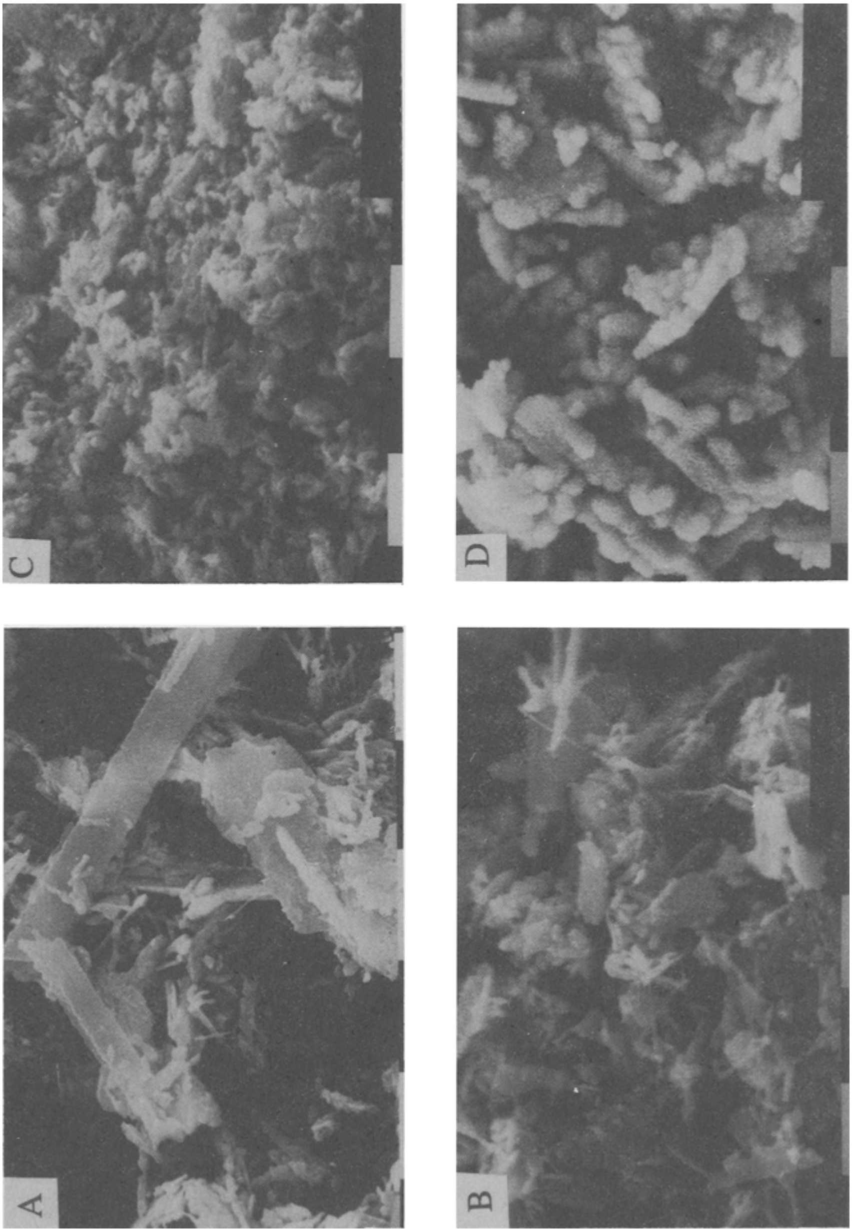

PHOTO 1 Scanning electron micrographs of V_2O_5, showing the corresponding surface morphologies: (A) fresh, reduced up to (B) 311°C, (C) 474°C and (D) 645°C

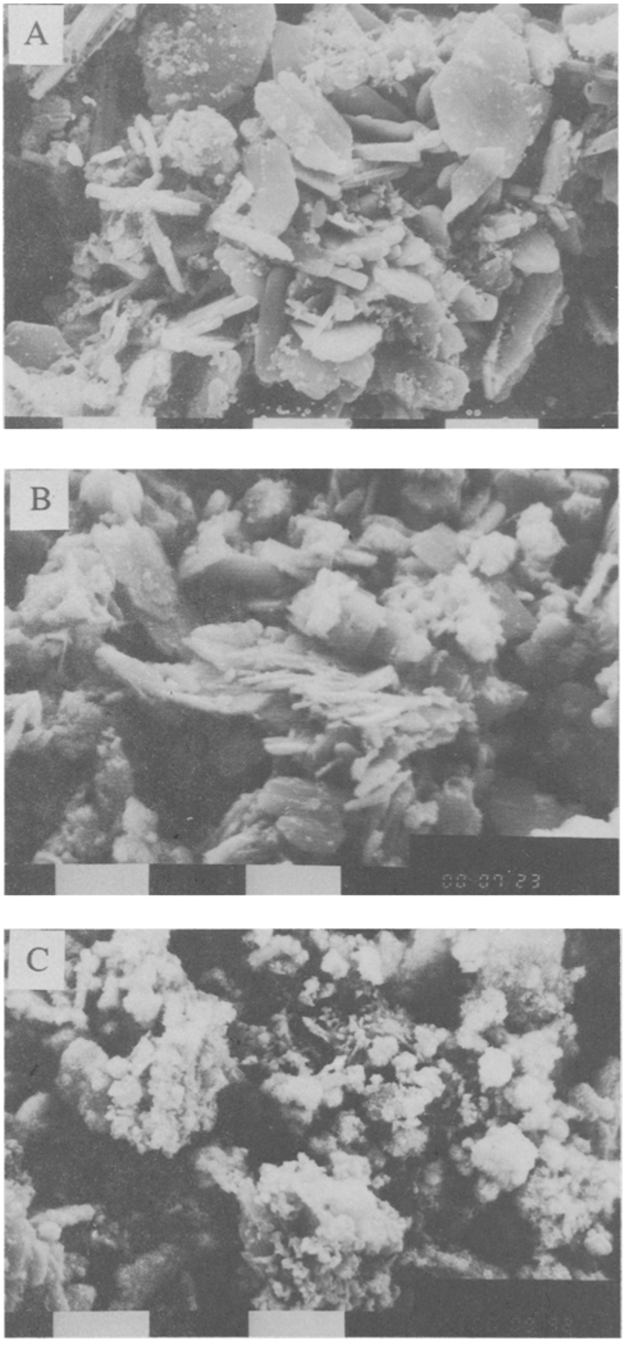

PHOTO 2 Scanning electron micrographs of VT10, showing the corresponding surface morphologies: (A) fresh, reduced up to (B) 290°C and (C) 650°C

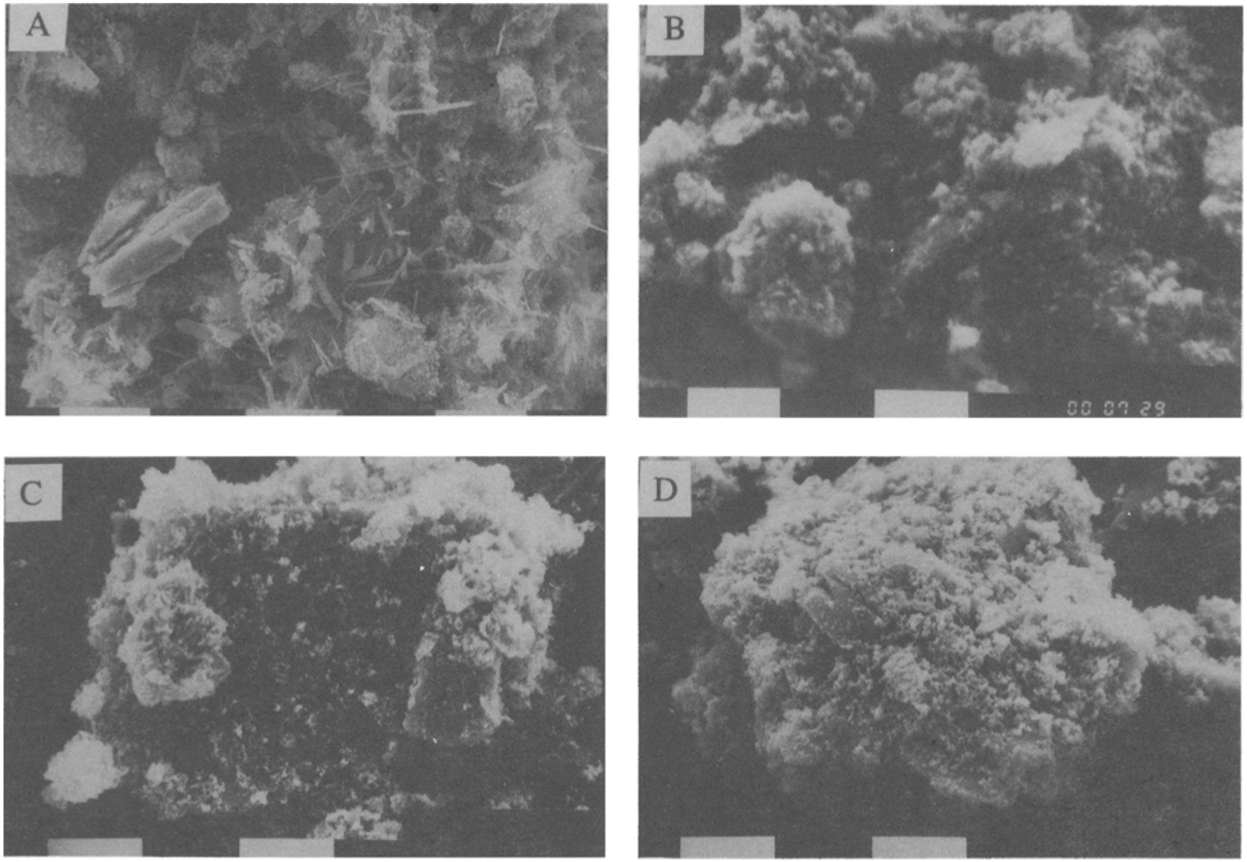

PHOTO 3 Scanning electron micrographs of VT80, showing the corresponding surface morphologies: (A) fresh, reduced up to (B) 320°C, (C) 438°C and (D) 503°C

nium-containing solids contain either oxides of vanadium(IV), or a mixture of vanadium(IV) and (V), but they are never reduced to V_2O_3, as is the cases with pure V_2O_5.

At the above-mentioned temperatures, the IR signal of the V=O bond was found at lower frequencies than the signals corresponding both to fresh solids and those arising from the first reduction. This shift indicates that the double bond was weaker, which is to be expected if it is taken into account that the average state of oxidation of the vanadium decreases as the samples are reduced at higher temperatures. Therefore, in the fresh solids there are $V^{+5}=O$ bonds of higher energy than the $V^{<+5}=O$ bonds of the reduced samples.

The V=O IR signal also exhibits a decreased intensity, which would suggest that the concentration of those species is also diminished in the reduced solids. Bearing in mind that the (001) plane of V_2O_5 ($2\theta = 20.3°$) contains the highest concentration of the V=O bonds of that phase [14], the conclusion drawn from the IR spectra is in accordance with the gradual decrease in intensity of the plane (001) signal undergone by all samples as the temperature of reduction increases (Figs 4 and 5).

From the second reduction step, the oxide ions of the V–O–V chains also started to react, as can be inferred from the gradual decrease in intensity of the IR band corresponding to this bond, until its disappearance in the last step of the TPR analysis (spectra in Figs 6 and 7). However, the VT20 sample exhibits exceptional behavior due to the fact that it does not lose the IR band of the V–O–V bond in the last reduction step.

As far as the morphology is concerned, the solids lose the plate formations, which seem to break down into smaller fractions, as can be seen in Photographs 1D, 2C and 3D.

Conclusions

The experimental evidence indicates that the reducibility of mixtures of the coprecipitated oxides V_2O_5–TiO_2 is mainly related to the crystalline structure and the morphology of their particles.

As the titanium concentration in the fresh series of vanadium-titanium oxides increases, the following changes occur.

(1) The concentration of V_2O_5 decreases. Then, both the contribution of the (001) plane of this phase (Fig. 3) and the concentration of the V=O species become ever smaller.

(2) The solids gradually lose the well-developed plate morphology characteristic of the (001) plane, changing to groups of small needles.

Only the surface V=O species are affected in the first reduction step. This fact will be verified by study of the surface oxidation states by XPS.

V_2O_5 and the V_2O_5–TiO_2 systems with low titanium concentrations exhibit mostly reduced phases at approximately 650°C. These samples have a high concentration of V=O bonds, whose electronic surroundings seem to be unaffected by the presence of titanium, since all of them are reduced at approximately the same temperature.

This situation is reversed for solids with higher titanium contents (VT50, VT80 and VT90). In these cases in which the titanium concentration is high, the electron acceptor effect, exerted on the V=O double bonds becomes important. As a result, these bonds become weaker and the energy needed for oxygen removal decreases, thereby making these samples more easily reducible.

As emphasized in the previous section, titanium stabilizes oxides of vanadium with oxidation state (IV) and mixtures of vanadium(IV) and (V). This could result from the formation of solid solutions between TiO_2 and these oxides, which are more stable than the crystalline structures.

As far as catalysis is concerned, theses observations are of interest when other studies too are taken into consideration. In these other studies on the partial oxidation of hydrocarbons with V_2O_5-containing catalysts, it is assumed that V=O is the active species in these reactions [15, 16]. On the other hand, Sachtler *et al.* have established that the catalytical activity of the oxides of the transition metals is parallel to the reducibility, whereas an antiparallel relationship exists between their selectivity and reducibility [4].

Taking this knowledge into account, it would be expected that solids with a high development of the (001) plane (which are not easily reducible) have a low activity, but can be very selective in the processes of partial oxidation of hydrocarbons. Solids reduced at lower temperatures would exhibit the reverse behavior.

Further studies on these assumptions will be performed by using these solids as catalysts in the partial oxidation of methanol.

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Zusammenfassung — Es wurde eine temperaturprogrammierte Reduktion (TPR) sowohl von reinem V_2O_5 als auch von kopräzipitierten V_2O_5–TiO_2 Systemen mit unterschiedlicher Titankonzentration in Wasserstoff durchgeführt. Die Ausgangsprobe und die reduzierten Proben nach jedem TRP-Schritt wurden mittels Röntgendiffraktion, Fourier-IR-Analyse und Scanning-Mikroskopie charakterisiert.

Innerhalb des Temperaturbereiches, in dem die TPR-Analyse durchgeführt wurde (100–600°C), wird die V_2O_5-Phase in zwei oder drei Schritten reduziert, während bei der TiO_2-Phase (Anatas oder Rutil) keine Veränderung beobachtet wird.

Im ersten Reduktionsschritt kann nur eine oberflächliche Reduktion der Oxide festgestellt werden. In den anschließenden Schritten reagiert H_2 mit den Sauerstoffatomen der V=O- und der V–O–V-Bindungen. Dies führt zu beträchtlichen Veränderungen bei Struktur und Morphologie des Systemes.

Experimentelle Beweise erlauben den Schluß, daß Titan gewisse Phasen von Vanadiumoxiden, in denen Vanadium als V(+4) oder als Gemisch aus V(+4) und V(+5) vorkommt, stabilisiert. Werden mäßige oder hohe Titankonzentrationen eingesetzt, wird die Temperatur für die Körperreduktion von V_2O_5 merklich herabgesetzt.