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Mechanism of surface spreading in vanadia–titania system

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Spreading of vanadia over TiO_2 (anatase) supports of different specific surfaces has been investigated by XRD, XPS and ESR. It has been found that vanadia migration is favoured over well-developed anatase crystal planes. At 723 K spontaneous spreading takes place, controlled by diffusion of vanadium species through the vanadia monolayer. In reducing atmosphere an induction period is observed, possibly initiated by formation of a structurally modified titania surface layer. Amorphous vanadia is postulated as a transient form between crystalline V_2O_5 and the vanadia monolayer.

Keywords: vanadia–titania; surface spreading; solid/solid wetting; V_2O_5/TiO_2

1. Introduction

Supported oxides of transition metals, particularly of vanadium and molybdenum, are widely used as catalysts for various reactions. Dispersion of metal oxide constituting the active phase is one of the factors determining the catalyst performance. The so-called "monolayer" oxide catalysts are obtained when the amount of the active oxide deposited on the surface of the supporting oxide corresponds formally to a single bidimensional layer. Typically, this class of catalysts is prepared by impregnation of the support from an aqueous solution containing an appropriate compound of the transition metal to be supported, or by chemical vapour deposition using a volatile compound of this metal.

Solid state reactions offer an alternative route which permits to avoid many environmental problems associated with the catalyst manufacturing. The final result of a pretreatment of a mixture of one solid (active component) with another present in excess (support) depends on the reaction conditions. At relatively low temperature and limited chemical affinity and miscibility of reagents the minority oxide will accumulate at the surface of the other oxide and, when the appropriate surface free energy relation is fulfilled, will spread over this surface. At higher temperature and certain miscibility of the two oxide phases a surface solid solution may form resulting in modification of surface and electronic properties of the support. The experimental data concerning the spreading of different transition metal oxides on various oxide supports have been recently discussed in a review article [1], little, however, is known about the mechanistic aspects of surface migration. It seemed therefore of interest to examine factors influencing the efficiency of surface spreading in order to elucidate the mechanism of this process.

The titania supported vanadium oxide system chosen for investigation has long been extensively studied because of its use as catalyst for such important reactions as selective oxidation of *o*-xylene [2], ammoxidation of alkylaromatics [3] or selective reduction of NO by NH_3 [4]. Pentavalent vanadium oxide shows acidic properties and its chemical affinity to titania is negligible. In monolayer titania supported catalysts it retains its chemical identity and forms a bidimensional overlayer [5]. As the surface free energy of crystalline V_2O_5 amounts to $(8-9) \times 10^6$ J/cm^2 and that of titania to $(28-38) \times 10^6$ J/cm^2 [6] and the Tamman temperature of V_2O_5 is 642 K, spontaneous spreading of vanadia over the surface of titania takes place. This process is equivalent to the wetting of one solid by another induced by the forces of surface tension [7,8]. With sufficient amount of V_2O_5 one can expect spreading to continue until the completion of a thermodynamically stable overlayer. It should be emphasized that quite recent investigations showed the molecular structure of surface vanadium oxide at submonolayer coverage to be independent of the preparation method [9]. However, it has been also suggested that in real catalytic conditions, for the surface coverages close to one monolayer, most vanadium species exist as V(IV) incorporated into the surface layer of the titania support [10,11]. Formation of tetravalent vanadium and its incorporation into the crystal lattice of the titania support during catalytic reaction was observed also in earlier studies [2, p.130].

In the present work the role of such parameters as surface structure and morphology of the titania grains or composition of the gas phase, as well as the kinetics of surface migration have been studied in order to get some insight into the mechanism of spreading in anatase supported vanadium oxide system. Several anatase samples of different specific areas served as supports. Spreading of V_2O_5 was carried out in oxidizing or reducing atmospheres and was followed with X-ray diffraction, XPS, Raman and ESR spectroscopies.

2. Experimental

2.1. MATERIALS

TiO_2 (anatase) was prepared by hydrolysis with NH_3 aq. (1 : 1) of the $TiCl_4$ solution in water. The precipitate was washed with distilled water, dried at 393 K for 24 h, and, finally, calcined at 773 K for 1 h. In order to prepare samples with larger crystallites, the powder thus obtained was subjected to further heating at 773 and 813 K, lasting 70 h each. According to XRD analysis all samples consisted of anatase, with no detectable traces of rutile. The various anatase samples are further denoted AX, where A stands for anatase and X for the corresponding value of the BET surface area.

V_2O_5 was prepared by thermal decomposition of NH_4VO_3 (Merck) at 773 K for 5 h in a flow of air. Amorphous V_2O_5 was obtained by hydrolysis of $VOCl_3$.

2.2. TECHNIQUES

XRD analysis. X-ray diffraction patterns were recorded with a DRON 2 LOMO (USSR) apparatus using Cu Kα radiation. It was checked in the separate experiments, using KCl as an internal standard, that no sintering occurs at 723 K in either pure V_2O_5 or anatase support nor in some of their physical mixtures. The relative decrease of intensity of the (001) line of V_2O_5 was used to monitor the rate of vanadia spreading over anatase grains. In all calculations the most intense (101) line of TiO_2 (anatase) was chosen as the intensity reference for the V_2O_5 (001) line. Thus, the degree of the V_2O_5 spreading α was calculated according to the following formula:

$$\alpha = 1 - a\frac{I_{\mathrm{V}}}{I_{\mathrm{Ti}}},$$

where $a = I^0_{\mathrm{Ti}}/I^0_{\mathrm{V}}$, and $I^0_{\mathrm{V}}, I^0_{\mathrm{Ti}}, I_{\mathrm{V}}, I_{\mathrm{Ti}}$, are the intensities of the V_2O_5 (001) ($I^0_{\mathrm{V}}, I_{\mathrm{V}}$) and the anatase (101) ($I^0_{\mathrm{Ti}}, I_{\mathrm{Ti}}$) lines for the unheated and heated V_2O_5–TiO_2(anatase) mixtures respectively. Mean size of the TiO_2 grains was determined from the Scherrer equation [12], by measuring half-maximum width. Instrumental broadening was allowed for by Warren's equation [12].

XPS analysis. The X-ray photoelectron spectra were obtained with a VG ESCA-3 spectrometer using Al K_α of 1486.6 eV energy. The powder was deposited onto a stainless steel sample holder from cyclohexane–acetone (1 : 1) suspension and subsequently outgassed at room temperature. Spectra were calibrated against the C 1s 284.8 eV line. Analysis was based on the most intensive doublet of vanadium V $2p_{3/2,1/2}$, which partially overlaps with the $K\alpha_3$ and $K\alpha_4$ satellites of the oxygen O 1s peaks. Thus, it was necessary to subtract the satellites, their positions and intensities being assumed to be 9.7 eV, 7.3% and 11.7 eV, 3.1% from the O 1s peak, its binding energy taken as 529.6 eV. The spectra were accumulated and analysed with a computer, an appropriate programme being used for spectra deconvolution. Quantitative analysis of the surface composition was based on the effective cross section ratio calculated from the Scoffield and Wagner values, as described in ref. [8].

ESR analysis. The X-band ESR spectra were recorded at room temperature and at 77 K with a SE/X – Technical University Wroclaw spectrometer. DPPH and NMR-marker were used for the determination of *g* factors. Samples of approximately 50 mg were used for examination.

BET surface area. The specific surface area was determined from the nitrogen adsorption isotherm at 77 K, using the BET equation.

Raman spectroscopy. The in situ Raman spectra were collected with an Instrument SA equipped with a Spectra-Physics Ar^+ laser (model 171) by utilizing about 10–40 mW of the 514.5 nm line for excitation. Each sample consisted of ca. 200–300 mg of undiluted powder and was pressed into a thin wafer of about 2 mm. The wafer was placed into a stationary sample holder that was installed in an in situ cell equipped with an atmosphere control unit and an electric heating coil. The spectra were recorded for each sample: at room temperature under ambient air, at flowing dry air at elevate temperatures, and near room temperatures (323 K) after cooling. The spectral resolution was 2 cm^{-1}.

2.3. PROCEDURE

V_2O_5 and TiO_2 (anatase) powders were carefully mixed and ground in an agate mortar. The amount of V_2O_5 in each mixture corresponded to that required theoretically for the monolayer coverage of the anatase component (0.1 wt% V_2O_5/m^2 of the support [13]). Subsequently portions of the mechanical mixture were placed in a quartz tube and subjected to thermal treatment at 723 K, either in the flow of helium or in dry air (50 cm^3 min^{-1}, molecular sieve 5 Å), for increasing periods of time (up to 24 h). These samples are further denoted A*X*V*Y*, where A stands for anatase, *X* for its BET surface area, V for V_2O_5 and *Y* for vanadia content in the mechanical mixture. To check whether V_2O_5 crystallites spread over the already formed vanadia monolayer the surface of the A46 sample was saturated with vanadia deposit in the course of the vapour phase deposition of $VOCl_3$, calcined at 673 K for 20 h, and subsequently mixed with 4.4 wt% of V_2O_5. The sample was denoted A46V4.4i + V4.4.

3. Results

Table 1 summarizes experimental data on the BET surface area and the mean grain size of the prepared series of anatase supports. One can see that a decrease in the BET surface area achieved by prolonged heating is accompanied by a parallel increase of the mean grain size determined from the X-ray diffraction patterns. The data show that the chosen technique of sintering allows indeed to obtain the anatase support of different crystallite size. The V_2O_5 content required for the monolayer coverage, calculated for each anatase preparation, is also presented in table 1.

Fig. 1 shows the in situ Raman spectra of A46V4.6 mixture calcined in dry air. In the range 800–1100 cm^{-1} the Raman spectra exhibit two bands. The ca. 990 cm^{-1} band is characteristic of crystalline V_2O_5 and the one at ca. 1020 cm^{-1},

Table 1
Specific surface area and size of grains for the anatase samples and the V_2O_5

Sample	S_{BET} (m^2/g)	d_{XRD} (nm)	V_2O_5 content (%)
A101	101	12.9	10.0
A53	53	18.8	5.0
A46	46	25.0	4.6
A41	41	23.0	4.1

appearing at elevated temperatures, characterizes tetrahedrally coordinated vanadia species present on the surface of TiO_2 under non-aqueous conditions [13]. The presence of the latter is a direct indication that in the course of V_2O_5 spreading over titania surface vanadia monolayer is formed. This phenomenon is better reflected in fig. 2. The increase in the intensity of the 1020 cm^{-1} band is accompanied by the decrease of the 990 cm^{-1} band intensity which proves that spreading of V_2O_5 results in the formation of the vanadia monolayer.

The most vital information about the behaviour of V_2O_5/TiO_2 mixtures upon heating in air or in helium at 723 K stems from the XRD analysis and is gathered in

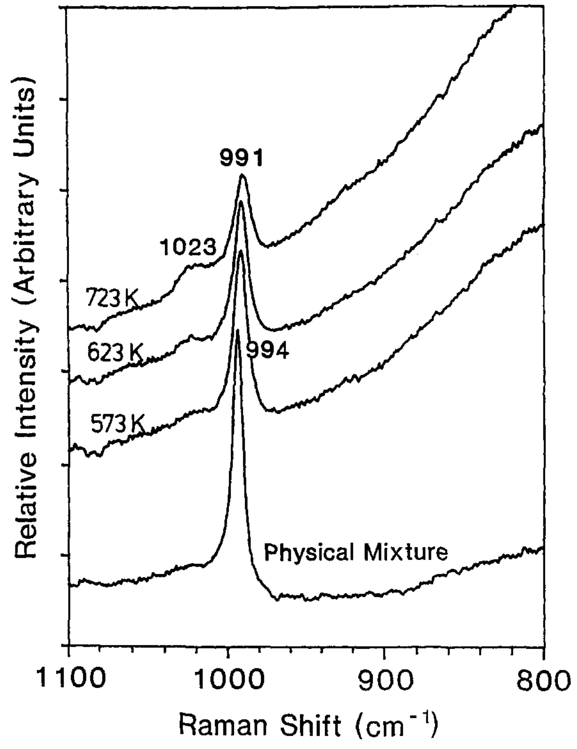

Fig. 1. In situ Raman spectra of the A46V4.6 physical mixture as a function of the calcination temperature. The sample was kept for 15 min at each temperature before recording the spectrum.

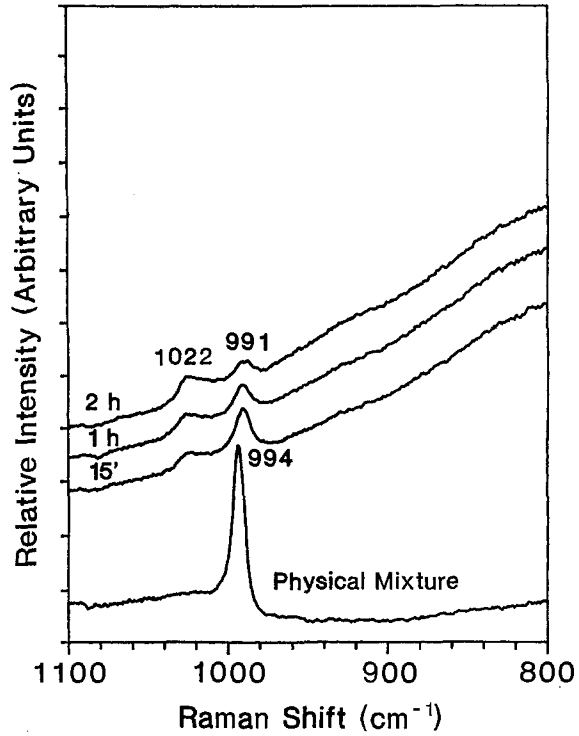

Fig. 2. In situ Raman spectra of the A46V4.6 physical mixture calcined at 723 K in dry air for different periods of time.

fig. 3. The degree α of disappearance of crystalline V_2O_5 as a function of time is taken to reflect the spreading of vanadia over the anatase surface. It can be seen that both the specific surface area of the support and the type of gas medium applied influence the process of spreading. The rate of spreading increases with decreasing specific surface area of the support, being unmeasurable for the A101V10 sample and maximum for the anatase of best available crystallinity. The spreading in helium atmosphere is less efficient as compared to the process occurring in the flow of air.

Fig. 4 gives the dependence of the extent of V_2O_5 disappearance (α) versus time, in parabolic law coordinates. A linear relationship can be observed for the experimental points. Such a dependence indicates a diffusion controlled process. However, if the parabolic law were to be obeyed ideally, the straight lines should cross the zero point. This is not the case. The graphs for the samples heated in air cross the ordinate axis at $\alpha \approx 10\%$, while for the helium treated sample the straight line crosses the abscissa.

Results of the XPS analysis of the A46V4.6 sample in which, according to XRD, a rapid spreading takes place, are gathered in table 2. The data present information on the physical mixture as received, as well as after heating for different per-

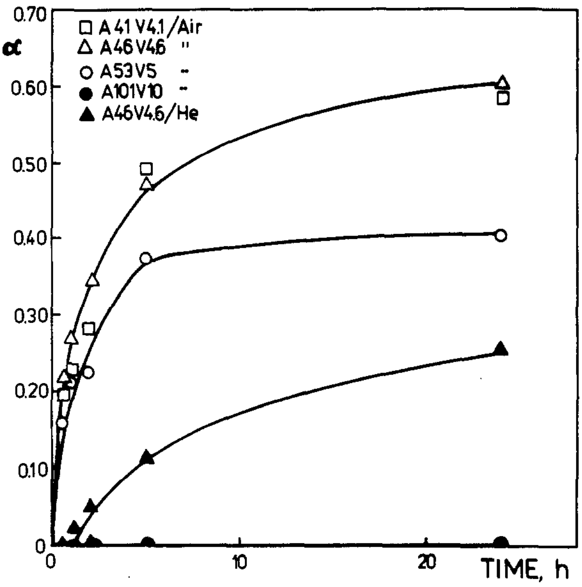

Fig. 3. The rate of V_2O_5 disappearance as a function of the calcination time in dry air or helium for anatase of different specific surface areas. Calcination temperature 723 K; anatase surface area in dry air: (●)101 m^2/g, (○) 52 m^2/g, (△)46 m^2/g, (□)41 m^2/g; in helium: (▲) 46 m^2/g.

iods of time in air and helium. The quantitative analysis for the surface V/(Ti + V) at% ratio confirms the picture provided by XRD. Indeed, the surface coverage with vanadium increases on heating at 723 K, the effect being more pronounced for treatment in air. The oxidation state of surface titanium ions, indicated

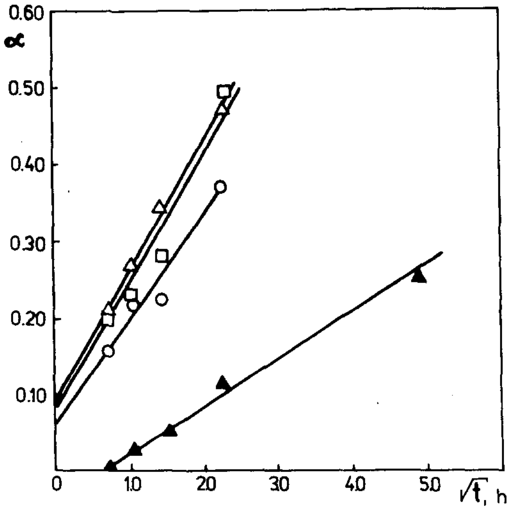

Fig. 4. Kinetic curves expressed in terms of the parabolic law. Symbols as in fig. 3.

Table 2
Binding energies of $Ti_{2p_{3/2}}$, $V_{2p_{3/2}}$ and atomic percentage of V for the A46V4.6 sample – unheated and heated at 723 K in different atmospheres

Sample A46V4.6	V/(Ti + V) (at%)	$Ti_{2p_{3/2}}$ (eV)	BE $V_{2p_{3/2}}$ (eV)
as received	4.7	459.3	517.2
air			
1 h	7.1	459.4	517.1
24 h	11.4	459.3	517.6
helium			
1 h	5.6	459.4	516.9
24 h	5.7	459.3	517.0

by the $Ti_{2p_{3/2}}$ electrons binding energy remains unchanged, irrespective of the treatment applied. The binding energies of $V_{2p_{3/2}}$ electrons are slightly lower for samples heated in helium, as compared to the untreated mixture, which could point to a partial reduction of vanadium. Prolonged heating in air leads to an increase in the $V_{2p_{2/3}}$ BE, indicating some further oxidation.

The XPS data from table 2 are plotted in fig. 5, together with the results for the A46V4.4i + V4.4 sample, being a mixture of V_2O_5 and titania previously covered with a monolayer of vanadia, subjected to annealing in air in a similar manner. For this sample, contrarily to the V_2O_5/TiO_2 mixture, there is no increase of the V/Ti atomic ratio after thermal treatment. In fact, initially a certain decrease in the V/Ti surface ratio is observed.

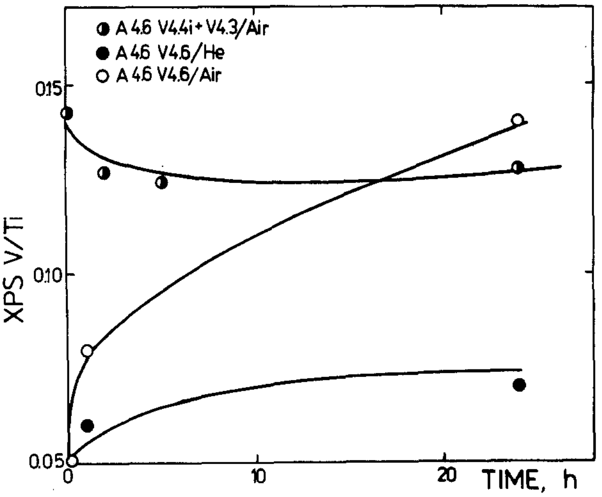

Fig. 5. Variation of the XPS V/Ti atomic ratio for the physical mixtures calcined at 723 K in dry air ((○) A46V4.6 and (◑) A46V4.4i + V4.3) and helium ((●) A46V4.6) as a function of the calcination time.

All investigated vanadium containing samples are ESR-active. The character of the observed signals depends on type and time of pretreatment.

All A46V4.6 samples heated in helium flow are dominated by a broad, structureless signal, centred around $g = 1.96$, similar to that observed in the initial mixture and due to the V_2O_5 component (fig. 6, solid line). A signal of this type has been reported earlier [14] for the polycrystalline, partially reduced vanadia, and is associated with V^{4+} ions in the V_2O_5 matrix. The lack of hyperfine structure, expected for the unpaired electron interacting with the ^{51}V nucleus (99.76% naturally abundant, $I = 7/2$), indicates close proximity of the responsible species, resulting in the dipolar broadening of the ESR line. The intensity of this absorption increases with time of sample pretreatment in helium indicating a progressing reduction. Beside this signal some traces of hyperfine splitting are visible in the spectra of helium treated samples indicating the presence of dispersed vanadium ions. The hfs structure becomes obvious after removal of the bulk vanadia component by dissolution in ammonia (fig. 6, dashed line). It shows that more than one vanadium species are present. The most intense signal is characterized by $g_{\perp} = 1.981$, $g_{\parallel} = 1.946$, $A_{\perp} = 6.46$ mT, and $A_{\parallel} = 17.61$ mT. The parameters of this signal fall in the range expected for $(V{=}O)^{2+}$ species in square pyramidal or distorted octahedral symmetry [15].

Spectra of all members of the air treated A46V4.6/air series differ considerably from those observed for the A46V4.6/helium samples. While in the latter the ESR signals are dominated by the broad structureless absorption, in the former distinct

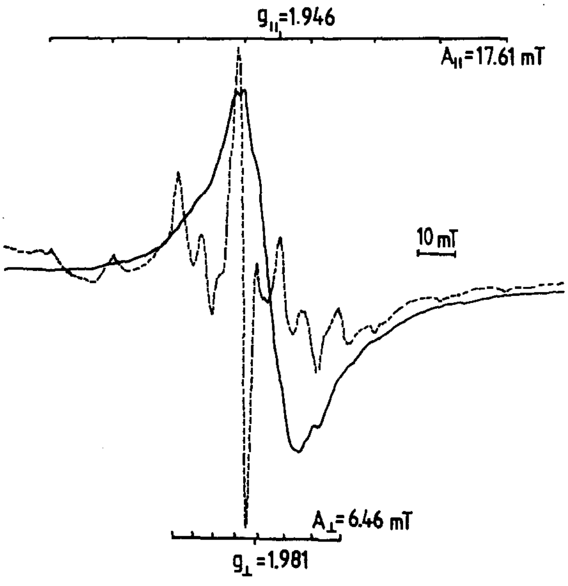

Fig. 6. The ESR spectra of A46V4.6 sample. Solid line: after calcination in helium at 723 K for 24 h, gain 2.5×10^3; dashed line: after subsequent dissolution of bulk vanadia in ammonia, gain 3.2×10^4.

signals with well resolved hyperfine structure, superimposed on the broad, structureless one appear.

In the initial stages of thermal treatment the signal shown in fig. 7a dominates. It is characterized by $g_\perp = 1.984, g_\parallel = 1.934, A_\perp = 6.76$ mT, and $A_\parallel = 16.94$ mT. The parameters of this signal differ from those observed for samples annealed in helium. On the other hand, they are very close to those observed for dispersed, octahedrally coordinated vanadyl ions present in the grafted vanadia–titania catalysts of the monolayer type [16]. On prolonged treatment this signal transforms into another one, of slightly different magnetic parameters $g_\perp = 1.986, g_\parallel = 1.933$, $A_\perp = 7.13$ mT, and $A_\parallel = 16.42$ mT (fig. 7b).

Brief vacuum treatment (5 min, 573 K) causes an overall increase of ESR signal intensity in both types of samples while in the pure V_2O_5 the ESR signal remains almost unchanged. The increase of intensity is particularly strong for the A46V4.6/air sample (order of magnitude) while in the A46V4.6/helium sample the signal is still comparable with that before treatment. Such behaviour indicates that upon thermal treatment of the vanadia–titania mixture the vanadia crystallites transform into an easily reducible phase, particularly abundant in samples annealed in air. The spectra show that in both types of samples, beside the broad background, new overlapping absorptions that can be assigned to dispersed $(V{=}O)^{2+}$ species in various surroundings appear. In the case of air treated samples it is possible to identify a contribution from the parallel hyperfine features of distinctly larger splitting ($A_\parallel = 19.53$ mT), similar to that found in the amorphous V_2O_5 (fig. 8). The appearance of the latter is clearly due to the interaction between the components of the V_2O_5–TiO_2 system, since this signal does not show in the pure vacuum treated V_2O_5 where the only detectable absorption remains the broad $g = 1.96$ line. It

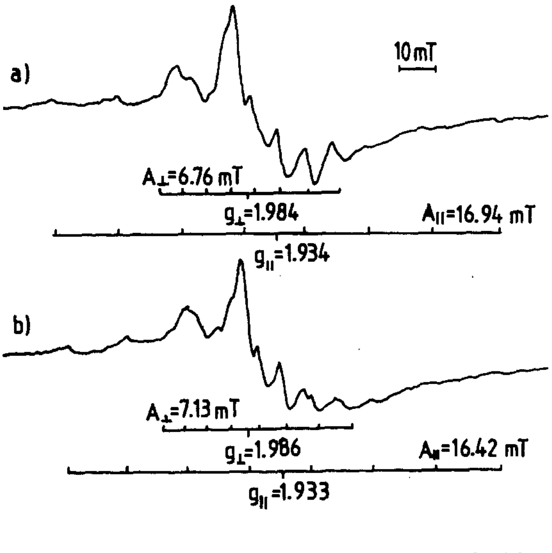

Fig. 7. The ESR spectra of A46V4.6 sample calcined in dry air at 723 K for 0.5 h (a) and 24 h (b).

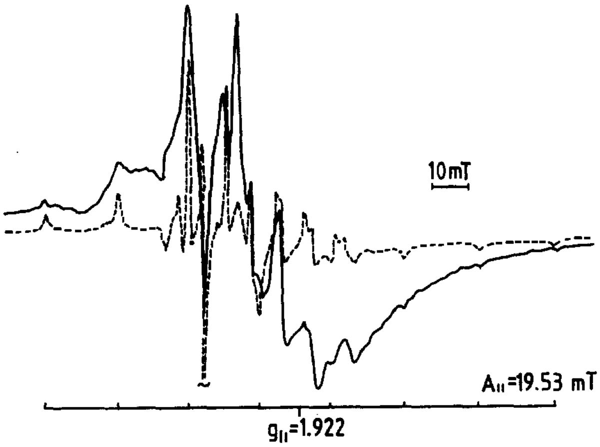

Fig. 8. The ESR spectra of A46V4.6 sample calcined in dry air at 723 K for 0.5 h and then reduced in vacuum at 573 K for 5 min (solid line), and amorphous V_2O_5 (dashed line).

may be taken as an indication that the easily reducible vanadium containing phase appearing in vanadia–titania samples upon annealing is of amorphous or poorly crystalline nature.

4. Discussion

The earlier published Raman results [9,17] on spreading of vanadia over titania indicate that the structure of surface vanadium species depends on the reaction conditions. It is argued that the calcination in a humid oxygen atmosphere results in the formation of polyvanadates whereas the thermal treatment in a dry O_2 leaves isolated tetrahedra. The latter species undergo hydration after exposure to humid atmosphere and produce a broad band at 990 cm^{-1}. This band may overlap with the sharp 990 cm^{-1} band characteristic of crystalline V_2O_5, therefore if moisture is present at ambient atmosphere during recording of the Raman spectra the absorption characteristic of the surface vanadium species may not be visible [9]. Present in situ Raman results confirm that under dry conditions spreading of vanadia over titania surface does occur. The formation of dehydrated tetrahedral surface vanadia species responsible for the 1020 cm^{-1} band is observed on the account of loss of the intensity of the 990 cm^{-1} band characteristic of crystalline V_2O_5.

It has been suggested that the rate of V_2O_5 migration over the TiO_2 surface depends on crystal size and morphology [17]. Since the difference in surface free energies is considered to be the driving force of vanadia spreading, one would expect that a decrease in crystallite size of TiO_2 should accelerate migration of V_2O_5 due to the excess surface energy of small crystals. However, in the present study an inverse dependence of the spreading phenomenon on crystallinity of titania is observed. This suggests that some other factor has also to be taken into consideration. It has been demonstrated by Haber et al. [18] that formation of surface vanadium complexes requires the anatase support to expose planes displaying a long-range crystalline order. The same authors have shown with aid of EXAFS that increase in the BET surface area of TiO_2 results in a progressive change from long-range order in external planes of crystallites to that characteristic of the amorphous oxide (fig. 1 in ref. [18]). In view of these findings the decrease of the rate of V_2O_5 spreading with increase of the titania surface area can be explained in terms of increasing difficulty in anchoring of vanadium complexes on progressively disordered TiO_2 surface.

Experiments checking on the influence of the surrounding atmosphere on the efficiency of spreading indicate that the redox properties of the gas phase are of principal importance for the process. In the oxidizing conditions a spontaneous spreading occurs at the very beginning of calcination, and then the process becomes diffusion-controlled (fig. 4). In helium, when surface reduction of V_2O_5 occurs, the spreading is inhibited (figs. 3 and 4). Although no data on surface energy of VO_2 have been published, its value must correlate with the oxide lattice energy and melting temperature. The latter is much higher for VO_2 (2240 K) than for V_2O_5 (963 K) and is comparable with that of TiO_2 (2123 K). Therefore the system of partially reduced vanadia and titania lacks the necessary driving force of different surface free energies.

An attempt to induce spreading of V_2O_5 over titania previously covered with a monolayer of vanadia (sample A46V4.4i + V4.4) failed completely, showing that in these conditions no migration of V_2O_5 is possible after the surface has been saturated with vanadium complexes (fig. 5). One may speculate that the surface free energy of TiO_2 covered with vanadia monolayer approaches that of vanadia itself, thus removing the driving force required for migration.

The ESR results also confirm that oxidizing atmosphere facilitates the vanadia spreading. In the air treated samples a quick decrease of the broad signal associated with the V_2O_5 component accompanied by the appearance of a well resolved spectrum of dispersed vanadyl ions is observed, while in the helium treated samples the broad absorption persists and obscures the signal from the dispersed vanadium species. The latter become clearly visible only after removal of unreacted vanadia by chemical dissolution and its ESR parameters are different. Important conclusions can be drawn from the observed differences in behaviour of samples subjected to vacuum reduction. Since well developed microcrystallites of V_2O_5 are resistant to the applied vacuum treatment, it is suggested that an amorphous or poorly crystalline vanadia phase formed upon annealing is responsible for the observed increase in signal intensities. Formation of this easily reducible phase is favoured in samples annealed in air, in which spreading occurs more readily. The appearance of ESR signal with $A_{\parallel}^{\triangleleft} = 19.53$ mT provides further indication that the transient form between the crystalline V_2O_5 and the vanadia monolayer may be amorphous V_2O_5 (fig. 8). It is worthwhile mentioning that the presence of amorphous vanadia in the V_2O_5/TiO_2 system annealed at 723 K has also been postulated on the basis of high resolution microscopic studies [19]. Present ESR data show also that depending on whether the atmosphere during annealing is oxidizing or reducing different types of ESR active vanadium species are formed. This suggests that in each case spreading occurs according to a different mechanism.

In view of the presented data we propose the following hypothetical mechanisms of surface spreading in the V_2O_5/TiO_2(anatase) system.

Under oxidizing conditions, at the very beginning of thermal treatment, the vanadia crystallites spread spontaneously over the TiO_2 surface, in the process that may be called a "hot plate" effect and which results in the amorphization of the vanadia structure. The driving force for this process is the difference in surface free energies of V_2O_5 and TiO_2. Afterwards, the spreading is controlled by diffusion. Since migration of vanadia over monolayer already formed is, in view of the data presented here, highly improbable, we propose that at this stage the spreading occurs by diffusion of defects, of the vacancy type, through the vanadia monolayer and their subsequent refilling with fresh vanadium ions at the interface between the monolayer and the "reactive" amorphous V_2O_5.

When annealing is conducted in the oxygen-free atmosphere of helium flow the surface of vanadia crystallites becomes reduced and the difference in the surface free energies of both components diminishes. As a result there is not enough driving force for spontaneous spreading. However, after some induction period spreading does occur albeit at a slower rate. We believe that the induction period is necessary for structural rearrangement at the titania surface, in the area of grain contacts with vanadia crystallites, to obtain structure which may accommodate vanadium ions and serve as a transporting medium enabling surface propagation of vanadium. This hypothesis is supported by findings of Kang and Bao [19] who, in a high resolution electron microscopic study, observed at the interface of V_2O_5/TiO_2(anatase) samples, pretreated in a similar manner as in the present work, appearance of an irregular lattice containing intergrown vanadia and titania fringes and forming a thin layer of a structure different from the parent matrices.

5. Conclusions

(1) V_2O_5 spreading over the titania surface is favoured on the well-developed anatase crystal planes.

(2) Under oxidizing conditions the spreading of V_2O_5 is initiated spontaneously at the V_2O_5/TiO_2 interface. Further migration of V_2O_5 is controlled by diffusion of defects through the vanadia monolayer and their reaction with the fresh vanadium ions at the "reactive" V_2O_5/monolayer interface and not by the migration of V_2O_5 over already formed vanadia monolayer.

(3) In absence of oxygen, under mildly reducing conditions (helium) the spreading of V_2O_5 is inhibited. It is postulated that in these conditions dispersion of vana-

dium occurs by diffusion through the structurally changed surface layer of titania whose nucleation is responsible for the observed period of induction.

(4) Amorphous V_2O_5 is suggested as a transient form between crystalline V_2O_5 and the vanadia monolayer.

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