Catalysis Today 142 (2009) 100–113

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Fifty years of my romance with vanadium oxide catalysts

Jerzy Haber [*]

Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, ul. Niezapominajek 8, PL 30-239 Krakow, Poland

ARTICLE INFO

Article history:
Available online 7 January 2009

Keywords:
Vanadium oxide catalysts
Heterogeneous oxidation catalysis
Vanadium oxide monolayers
Redox properties of vanadium oxides

ABSTRACT

The fifties of XXth century were times when solid state physics and chemistry scored great successes both experimental and theoretical – transistors were discovered and the theory of electronic structure of solids made rapid progress. It was believed that this theory will permit the understanding of the mechanism of chemical reactions at metal and oxide surfaces and electronic theory of catalysis was developed. Vanadium oxides were a good example to be studied, because extremely rich chemistry of vanadium oxides and vanadium oxide based catalysts results from a number of different interrelated electronic and structural factors. These compounds have partially filled d-orbitals which are responsible for a wide variety of electronic, magnetic and catalytic properties. The phase diagram shows that vanadium atoms exist in different formal oxidation states, which vary from two to five. The easy conversion between oxides of different stoichiometry and formation of oxygen vacancies enables the oxide to function as catalyst in selective oxidation. Exposed to gas phase of sufficient redox potential reduction and reconstruction of the surface into V_6O_{13} phase may take place. Due to the anisotropy of crystallites different crystal planes have different adsorption properties and different catalytic active sites are present. Reducibility depends on the degree of dispersion. When deposited on other oxide supports their wetting is observed and surface migration from one support onto another one may take place depending on the surface free energy ratio. On exposure to water vapour, the vanadium monolayer transforms into polyanions. Depending on the type of support vanadium oxide shows various catalytic properties. The quantum-chemical calculations show that nonbonding d-orbitals of vanadium ions have the LUMO character and act as Lewis acid sites, whereas the lone electron pairs of bridging oxygen ions have the HOMO character and behave as Lewis basic sites. Cleavage along (1 0 0) planes leaves coordinatively unsaturated vanadium and oxygen ions which develop Brønsted acid–base interactions with reacting molecules and cause their heterolytic chemisorption. On the basis of the results collected in the last 50 years a book on physical chemistry of vanadium–oxygen system could be written.

Vanadium is a fascinating element. Its presence in the Mexican ores was discovered by Andreas Manuel del Rio in 1801, detected also in Swedish iron by Nils Gabriel Sefstrom in 1831 but identified as a new element and obtained in the elemental form by Henry Enfield Roscoe in 1869. Because of beautiful colours of its compounds it was named vanadis after the nickname of Freyja, in Scandinavian mythology the Goddess of beauty, love and fertility, whose characteristic attribute was a beautiful necklace, and who travelled in a carriage pulled by cats. When mineral beryl ($Be_3Al_2(SiO_3)_6$) contains trace amounts of vanadium, a crystal beautifully coloured green is formed called emerald, considered to be a very precious gemstone. The origin of the word "emerald" is said to be a Sanskrit word meaning "green". Vanadium gets the oxidation states +2, +3, +4 and +5, the compounds being characterized by different colours. A fascinating demonstration can illustrate the beauty of chemistry: starting from ammonium metavanadate (NH_4VO_3) yellow colour of VO_2^+ (+5 oxidation state) appears, on reduction VO_2^+ transforms into blue VO^{2+}, passing during the reaction through a green colour of the mixture, blue VO^{2+} is then reduced to green V^{3+}, followed by reduction to violet V^{2+}.

In the fifties the electronic theory of catalysis was developed based on successes of solid state physics [1,2]. The structure of a molecule, adsorbed at the surface of a solid with semiconducting properties, depends on the position of its redox potential relative to the position of the Fermi level, upper edge of the valence band and bottom of the conductivity band in the solid. The position of the Fermi level may be shifted by introduction of appropriate point defects. Many studies have been carried out to determine the type of defects formed in the crystal lattices of different oxides, the latter being widely applied in catalysts [3]. In our laboratories the thermodynamics of defects in ZnO, NiO, Cr_2O_3 and V_2O_5 were investigated. With Dr. Stoch we have found [4] that on heating V_2O_5 oxygen started to be released at 450 °C and at this temperature the changes of pressure continued for 110 h.

---

[*] Tel.: +48 12 6395152; fax: +48 12 4251923.
E-mail address: nchaber@cyf-kr.edu.pl.

0920-5861/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2008.11.007

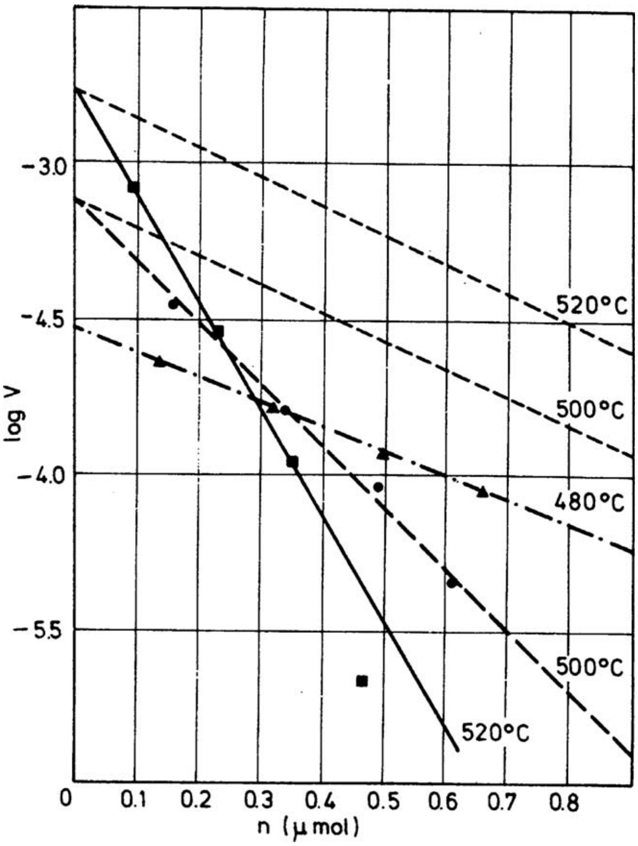

Fig. 1. Rate of oxygen uptake as a function of the amount of oxygen incorporated.

In other experiment the sample was outgassed for 40 min at 550 °C, cooled to 520 °C and oxygen was admitted in small doses. From the set of $p = f(t)$ curves the rate of oxygen adsorption at a given oxygen pressure could be calculated as a function of the amount of incorporated oxygen. Dependence of the oxygen uptake on the equilibrium pressure at different temperatures is shown in Fig. 1 [4]. The results clearly indicated that the evolution of oxygen observed on heating V_2O_5 above 450 °C should be ascribed to the shift of defect equilibria, as it is difficult to imagine that at such high temperatures adsorption of oxygen could last many hours. In the range of small degree of nonstoichiometry interaction between defects may be neglected and the dependence of the concentration $[d]$ of defects on oxygen pressure is given by the equation:

$$\log[d] = a + b\log[p]$$

Results presented in Fig. 1 permit to calculate the coefficients a and b

$$\log[d] = -2.06 - 0.507\log p$$

The value of 0.5 unambiguously points to the equilibrium

$$(1/2)O_2 + V_O = O_O$$

It may be thus concluded that the uptake of oxygen observed at temperature of the order of 500 °C is due to filling oxygen vacancies Vo in lattice of V_2O_5 and its rate may be expressed as

$$\frac{dp}{dt} = k p_{O_2} [V_O]^2$$

Catalysts, used in selective oxidation of o-xylene to phthalic anhydride are composed of vanadium ions supported on TiO_2 (anatase). The question arose which is the influence of the oxide matrix on the electronic state of vanadium ions. ESCA spectra obtained with V_2O_5, V_2O_5/TiO_2, $Ti_{1-x}V_xO_2$ indicated (Table 1) [5] that the BE of V $2p_{3/2}$ in V_2O_5 has the same value as that in V_2O_5/TiO_2, but after reduction it becomes shifted to lower value, similar to that in VO_2. It may be concluded that electronic structure of vanadium atoms deposited at the surface of TiO_2 remains unchanged in comparison with that in V_2O_5, but after annealing they diffuse into the lattice of TiO_2 where they assume the oxidation state four as in VO_2. The surface composition considerably differs from the bulk and strongly depends on the temperature of pretreatment. This is illustrated in Fig. 2 in which the ratio of intensities of the V $2p_{3/2}$ and Ti $2p_{3/2}$ peaks is plotted as a function of the temperature of annealing. It may be seen that on raising the temperature of annealing the surface becomes at first enriched in Ti ions, but above 500 °C a strong enrichment of the surface in V ions is observed [6]. We did not continue studying this problem.

In late seventies an idea was voiced that kinetic data from the reduction of metal oxides, deposited on supports, with gaseous reagents may be used to determine their surface area. Dr. Grzybowska-Swierkosz (now professor in our Institute) attempted to apply this method to a series of V_2O_5/TiO_2 samples of different vanadia content in the range of its concentration in which the catalytic properties of vanadia are ameliorated [7]. Results of their rate of reduction in hydrogen summarized in Table 2 clearly indicate that a marked increase of the reduction rate of V_2O_5 takes

Table 1
Binding energies of Ti $2p_{3/2}$, V $2p_{3/2}$ and O 1s electrons.

	Band position (eV)		
	Ti $2p_{3/2}$	V $2p_{3/2}$	O 1s
V_2O_5 [a]	–	517.7	530.8
V_2O_5 reduced	–	516.3	530.9
TiO_2 [b]	459.4	–	530.8
TiO_2 reduced	459.4	–	530.9
V_2O_5/TiO_2	459.4	517.7	530.8
$Ti/V/O_2$	459.4	518.5	531.0
$Ti/V/O_2$ reduced	459.4	518.8 517.2	531.0
VO_2 [c]	–	517.1	531.0

[a] Calibrated against C 1s (285.0 eV).

[b] Assumed as reference after M. Murata, K. Wahino, S. Ikeda, J. Electron. Spectrosc. Relat. Phenom. 6 (1975) 459.

[c] After C. Blaauw, F. Leenhouts, F. van der Woude, G.A. Sawatzky, J. Phys. Chem. Solid State Phys. 8 (1975) 459 and G.A. Sawatzky, E. Antonides, J. Phys. Coll. C4 37 (Suppl. 10) (1976) 117, with regard to BE O 1s = 531.0 eV, taken as the internal reference level.

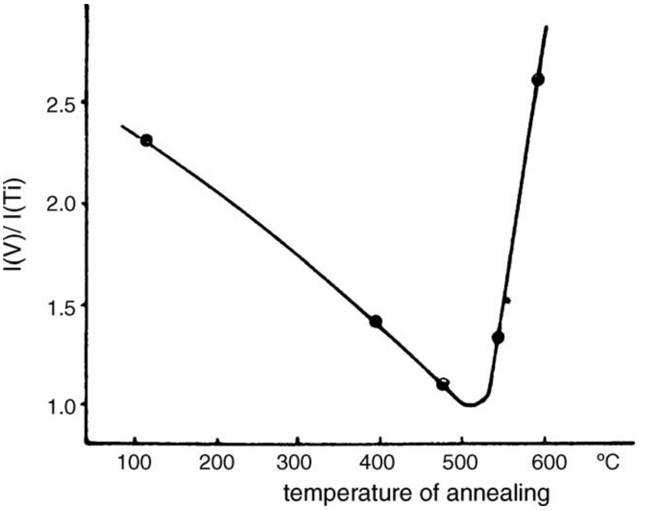

Fig. 2. The V $2p_{3/2}$/Ti $2p_{3/2}$ peak-to-peak ratio from XPS as a function of the temperature of annealing the V_2O_5–TiO_2 system.

Table 2
Reduction of the V_2O_5–TiO_2 system.

Sample	V_2O_5 (mol%)	E (kcal/mol)	K_s/K_4
TiO_2	0	–	–
V_2O_5–TiO_2	2	25.8	139
V_2O_5–TiO_2	5		66
V_2O_5–TiO_2	8	26.3	37
V_2O_5–TiO_2	10		23
V_2O_5–TiO_2	15	26.1	18.5
V_2O_5–TiO_2	20	25.6	17
V_2O_5	100	25.4	1

place when the latter is dispersed on the surface of TiO_2 which is not reducible. However, this rate is independent of the total content of vanadia. This observation has been attributed to the formation of a monolayer of V_2O_5 on the surface of TiO_2, which exhibits a much higher reduction rate than crystalline V_2O_5. A question was raised as to the oxidation state of vanadium ions, deposited at TiO_2 surface, in the course of catalytic oxidation of o-xylene. Dr. Gasior and Dr. Grzybowska-Swierkosz after a detailed study demonstrated [8] that the oxidation state of vanadium ions deposited at the surface of TiO_2 assumed in the reaction medium depends on its redox potential and the oxidation state of the fresh catalyst. When the oxidation state of vanadium ions in the initial catalyst is higher than that corresponding to the redox potential of reaction medium, reduction of surface vanadium will take place until an equilibrium is attained, when it is lower – surface vanadium ions will be oxidized (Fig. 3). The surface reconstruction of the V_2O_5/TiO_2 catalyst taking place in the course of the oxidation of o-xylene has a dramatic influence on the selectivity of the reaction. Changes of the selectivity to phthalic anhydride as function of the time of operation of the catalyst in the reactor are observed in the course of oxidation of o-xylene [9]. At first mainly total oxidation takes place, which then becomes slowly replaced by selective oxidation. In order to detect the surface reconstruction responsible for the change of the reaction pathway, Raman spectra were recorded of the catalyst in its initial state and after it has attained the high steady state selectivity [10]. Interaction with the reacting mixture resulted in the complete disappearance of the bands characteristic of V_2O_5 initially present in the sample. This is due to the reduction of V^{5+} ions to V^{4+} and V^{3+} ions, as indicated by the photoelectron spectra of V 2p electrons registered in the course reaction with the V_2O_5–TiO_2 catalyst [10]. A conclusion could thus have been drawn that the surface of V_2O_5 is active in total oxidation and only when its reconstruction into lower valent oxides takes place, the selectivity to partial oxidation products develop.

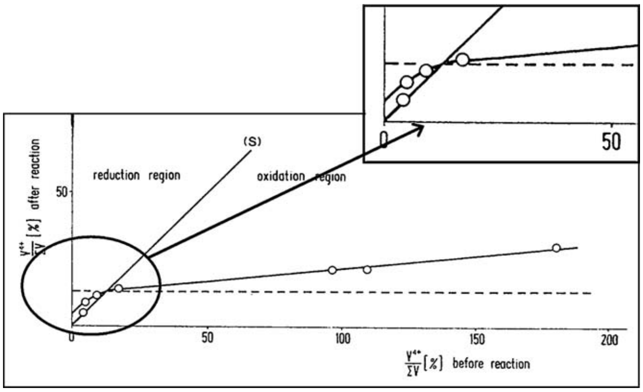

Fig. 3. Oxidation state of surface vanadium ions in V_2O_5/TiO_2 catalysts as function of the time-on-stream.

Thus, the observations made in seventies led us to the general conclusions that depending on the properties of the mixture of reactants of the catalytic reaction different phases may be formed at the surface of the catalyst, directing the reaction along different reaction pathways. The surface of the catalyst has a dynamic character and reconstructs depending on the properties of reactants of the catalytic reaction until it attains the structure and composition, corresponding to the given steady state conditions of the reaction. When these conditions are changed, the structure and composition of the catalyst surface changes also, modifying the activity and selectivity of the catalyst itself. This means that in the equation describing the rate of the reaction:

$$r = k \cdot f(p_1, p_2, \ldots, p_i)$$

it is not only the function f, which depends on the pressure of the reactants, but also the rate constant k:

$$k = f(p_1, p_2, \ldots, p_i)$$

Thus the conditions of the steady state influence the catalytic reaction not only directly through the kinetic parameters, but also by modifying the properties of the catalyst.

At the beginning of eighties an interesting question arose concerning the mechanism of processes taking place in the mixture of V_2O_5 and TiO_2 during preparation of V_2O_5–TiO_2 catalysts. The characteristic feature of solid state reactions consists in that they are localized at the interface between solid substrate and solid product, called the reaction interface [11]. In a powder mixture of two solids, the reaction interface is formed by intergranular contacts. If however, one of the solids migrates over the surface of crystallites of the second solid, the reaction interface may considerably increase in the first period of the reaction, resulting in its spontaneous acceleration. It is usually considered that migration of one solid over the surface of another solid results from surface diffusion of constituents of the lattice under the driving force of the difference of chemical potential. Taking into account the relatively high values of the lattice energy of the oxides one can – however – expect surface diffusion to be negligible in the temperature range usually applied in the preparation of oxide-on-carrier systems or in some solid state reactions in oxide systems. Thus we have advanced a hypothesis that an entirely different mechanism may be responsible for the rapid surface migration of solids, which we described as "wetting" of one solid by another solid. Such migration is due to the operation of the forces of surface tension in full analogy to those operating at the liquid/solid interface. In order to study this phenomenon a model system of V_2O_5 supported on two polymorphic modifications of TiO_2 – rutile and anatase – was selected [12], this system being known as an excellent catalyst in the oxidation of alkylbenzenes to aldehydes and anhydrides when anatase but not rutile is taken as a support. Pellets of V_2O_5, sintered at 958 K for 48 h were put on larger pellets of anatase and rutile, presintered at 1023 K for 48 h (Fig. 4a) [12]. The two sets were then placed in the electric oven and heated in air at 923 K for 48 h or at 823 K for 24 days. The V_2O_5 pellets were then separated from the support and small samples of the support, taken from the areas I and II of the pellets (see Fig. 4b) were analysed by X-ray diffraction, photoelectron and ESR spectroscopies. In order to obtain the concentration profiles in the subsurface layers, all samples were sputtered with argon ions for 5–15 min at the pressure of 10^{-6} Torr, voltage of 3 kV and ionic current of 20–26 μA. The ionic beam was directed at the angle of 45° to the surface of the sample. Fig. 5 shows the microphotographs of the pellets and their cross-sections after they have been heated at 923 K with V_2O_5 on top. One can see in Fig. 5a the black spot in the place where the V_2O_5 pellet was located on the anatase pellet and the cross-section reveals (Fig. 5b) that V_2O_5 penetrated along the grain boundaries into the pellet to a depth of about

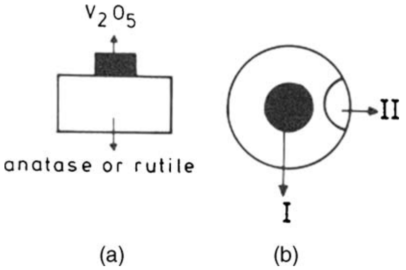

Fig. 4. Scheme of experiment: (a) arrangement of pellets in the course of heating and (b) areas of sampling from TiO_2 pellet after heating.

0.5 mm, the black colour resulting from the reduction of the vanadium ions to lower valence state in the course of sputtering. No traces of V_2O_5 were detected in the case of rutile pellet (Fig. 5c and d). In the photoelectron spectra of V 2p, O 1s and Ti 2p electrons of the sample of anatase, taken from the region of V_2O_5 migration, two doublets of V 2p electrons are visible hinting to the presence of two types of vanadium ions: V^{5+} ions in the coordination similar to that in V_2O_5 (form I) and V^{3+} ions in the environment strongly modified in comparison with pure vanadium compounds (form II). Changes of the total intensity of the V $2p_{3/2}$ peaks and of the Ti 2p peak with time of sputtering are shown in Fig. 6. The intensity of Ti 2p peak grows with sputtering time, whereas the total intensity of V 2p peaks decreases practically to zero after 20 min exposure to argon bombardment indicating that the thickness of vanadium oxide layer is of the order of several nm. Considerable increase of the intensity of the two forms of vanadium ions in the first period of sputtering is in line with the conclusion that the vanadium oxide layer enveloping the anatase grains is composed of two parts, form II of vanadium ions being in direct contact with TiO_2 and form I constituting the outer part.

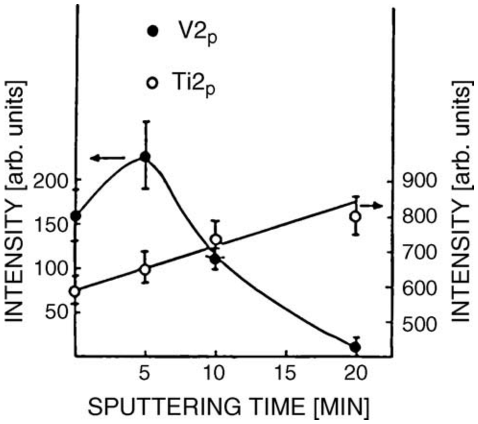

Fig. 6. Changes of the total intensity of V 2p and Ti 2p electron peaks with time of sputtering with argon ions.

Migration of vanadium oxides over the surface of anatase grains cannot be due just to the spreading under the influence of the concentration gradient, as in such case identical migration would have taken place over the surface of rutile, which is not the case. The only other driving force which may cause the spreading of V_2O_5 over the surface of anatase is the difference in surface free energy. A conclusion may thus be formulated that spreading of V_2O_5 over the surface of anatase is the manifestation of a general phenomenon, which we proposed to call wetting of one solid by another solid, fully analogous to wetting of solids by liquids. Such spreading will namely take place, if the surface tension of anatase, which is the measure of its cohesion energy is greater than the appropriate sum of the surface tension of V_2O_5, measuring its cohesion energy and the interfacial tension V_2O_5/anatase, equivalent to the energy of adhesion of these two solids (Fig. 7) [11]. The migration of V_2O_5 will continue until the film attains such

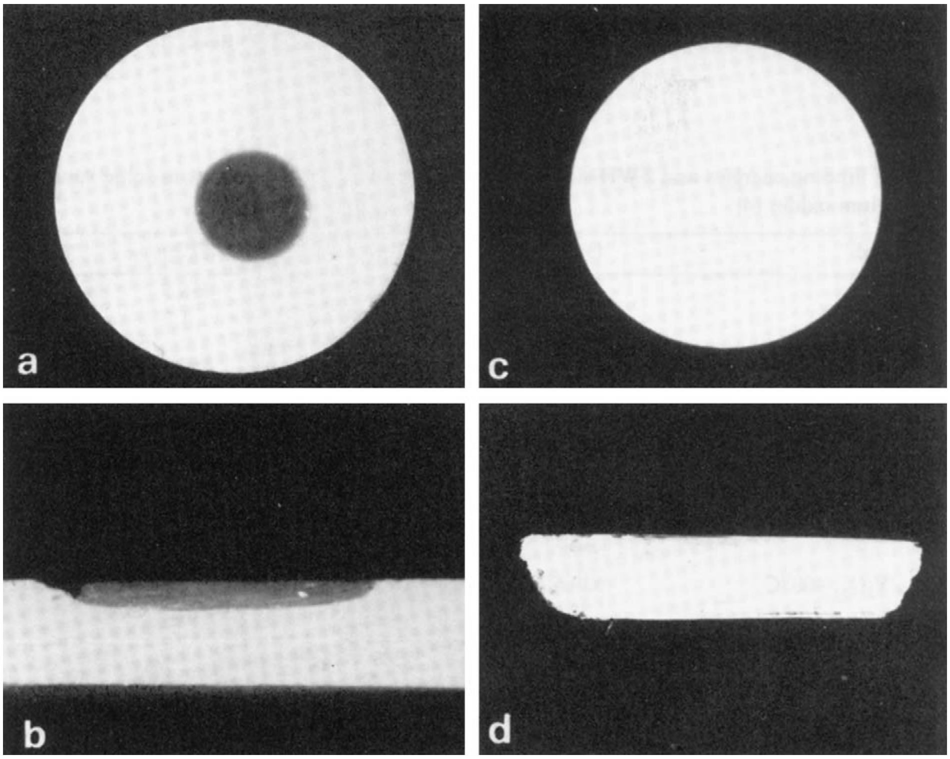

Fig. 5. Microphotographs of rutile and anatase pellets and their cross-sections after heating at 923 K with V_2O_5 on top: (a and c) top view of anatase and rutile pellets and (b and d) cross-section of anatase and rutile pellets.

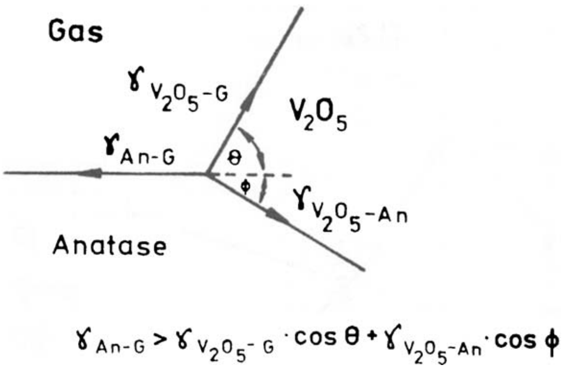

Fig. 7. Force diagram at V_2O_5–anatase interface.

Table 3
Occurrence of wetting in oxide systems.

Migrating oxide	Immobile oxide	Temperature (K)	Wetting
V_2O_5	TiO_2 anatase	823–923	+
V_2O_5	TiO_2 rutile	823–923	–
V_2O_5	ZrO_2 monoclinic	823–923	+
V_2O_5	SiO_2	923	–
V_2O_5	γ-Al_2O_3	923	+
V_2O_5	α-Al_2O_3	923	+
MoO_3	TiO_2 anatase	923	+
MoO_3	TiO_2 rutile	923	+
MoO_3	SiO_2	923	–
MoO_3	Co_3O_4	823	–
MoO_3	Mn_2O_3	823	+

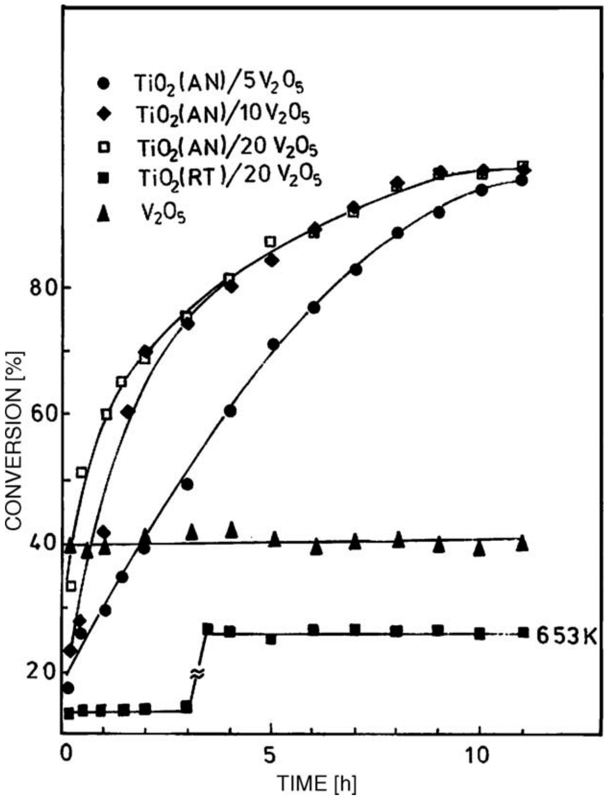

Fig. 8. Conversion of o-xylene on the gas phase oxidation at 633 K over V_2O_5 and its mechanical mixtures with anatase and rutile as a function of the time-on-stream.

thickness at which its surface free energy will not depend any more on the presence of TiO_2 support. Indeed, as discussed above, the outermost layers of the film show a behaviour similar to that of V_2O_5 at variance with the inner layers, whose properties are strongly modified by the interaction with TiO_2 support. Table 3 summarizes the interfacial relations in different oxide systems, containing V_2O_5. It may be seen that V_2O_5 is wetting not only anatase, but also ZrO_2 and both α and γ-Al_2O_3, whereas no wetting is observed in the case of SiO_2. The concept of wetting of solids by solids is now widely used to explain the behaviour of multicomponent oxide systems.

Wetting is responsible for the evolution of vanadium oxide catalysts in the course of the catalytic reaction. Gasior et al. investigated the catalytic properties of different mechanical mixtures of V_2O_5 and TiO_2 as function of the time-on-stream in the oxidation of o-xylene to phthalic anhydride [13]. Fig. 8 shows the conversion of o-xylene and Fig. 9 the selectivity to phthalic anhydride of such mechanical mixtures and pure V_2O_5 as function of the period of time they worked in the reactor. It may be seen that in the case of mixtures of V_2O_5 with anatase the conversion rapidly increases with the time-on-stream from a small initial value, corresponding approximately to the conversion on the amount of pure V_2O_5 contained in the mixture, to the very high conversion approaching 100%. This increase is due to the migration of V_2O_5 in the course of the reaction over the surface of anatase grains covering them with a thin layer. The rate of such migration should be proportional to the number of intergranular contacts between TiO_2 and V_2O_5 in the mechanical mixture. Indeed, the initial rates of the increase of conversion are proportional to the content of V_2O_5 in the mixture. In the case of samples of higher V_2O_5 content the intergranular contacts are so numerous that already after a short time-on-stream most of the surface of TiO_2 grains becomes covered by V_2O_5 and both samples show the same behaviour. Obviously all the curves level off when conversion of 100% is approached. The effect of the increase of conversion with time-on-stream is absent in the case of mechanical mixture of V_2O_5 with rutile and the conversion remains constant at the level corresponding approximately to the conversion on pure V_2O_5 in the amount present in the mixture. Even raising temperature to 653 K after 5 h of experiment did not change the behaviour and after a

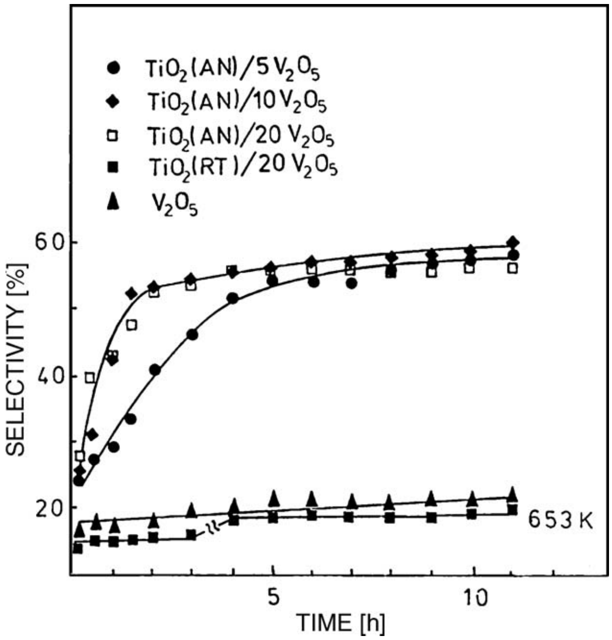

Fig. 9. Selectivity to phthalic anhydride in the gas phase oxidation of o-xylene at 633 K over V_2O_5 and its mechanical mixtures with anatase and rutile as a function of the time-on-stream.

jump of conversion due to the rise of temperature it remained constant during the rest of experiment. As seen from Fig. 9 in the case of mechanical mixture of V_2O_5 with anatase the selectivity to phthalic anhydride rapidly increases in first few hours of the reaction whereas the selectivity to products of total oxidation considerably decreases. This clearly indicates that not only spreading of V_2O_5 over the surface of anatase grains took place, increasing the conversion of o-xylene, but also the properties of the resulting V_2O_5 layer must have been changed so that total oxidation was considerably reduced.

It may be expected that in the case of transition metal oxides, which crystallize in lattices with anisotropic properties, a pronounced influence of geometry on the pathway of catalytic reaction will be observed. Gasior and Machej [14] have synthesized V_2O_5 preparations characterized by different crystal habits: from plate-like crystallites exposing mainly the (0 1 0) planes to needle-like crystallites, exposing mainly the (1 1 0) planes. They were characterized by a structural factor, defined as the ratio of intensity of the (0 1 0) X-ray reflection to the intensity of (1 1 0) reflection. They were able to show that the selectivity of o-xylene oxidation on these catalysts strongly depends of the structural factor (Fig. 10). On plate-like crystallites mainly selective oxidation of o-xylene to phthalic anhydride was observed, whereas on needle-like crystallites total oxidation took place. The difference in catalytic properties was related to the difference in adsorption as found by photoelectron spectroscopy. Fig. 11 shows the V 2p and O 1s photoelectron spectra of sample exposing (0 1 0) plane, and Fig. 12 the spectra of sample exposing (1 1 0) plane [15]. The spectrum from the (0 1 0) sample is composed of a simple V 2p doublet and O 1s simple line, remaining unchanged after sputtering. The V 2p doublet obtained from the (1 1 0) plane has the same parameters as those observed from the (0 1 0) plane, whereas a different picture is obtained in the range of BE values corresponding to O 1s electrons. Here a complex line appears which could be deconvoluted into two Gaussian lines: O_I corresponding to the BE of O 1s electrons 529.6 eV characteristic for the lattice oxygen ions of V_2O_5, and O_{II} corresponding to BE of 532.2 eV typical for OH groups in transition metal hydroxides. After sputtering the intensity of the O_{II} line decreases, whereas that of O_I line assigned to lattice oxygen increases. This indicates that the species responsible for the O_{II} line are the OH groups, located at the surface of the investigated crystals, screening the lattice oxygen ions. It may be thus concluded, that the (0 1 0) crystal plane of V_2O_5 is inert and remains bare, whereas the (1 1 0) plane adsorbs water molecules and becomes hydroxylated.

Kozlowski (now professor in our Institute) and Sobalik investigated the vanadia layers grafted on γ-alumina by IR spectroscopy of CO, CO_2 and NH_3 as probe molecules [16]. It has

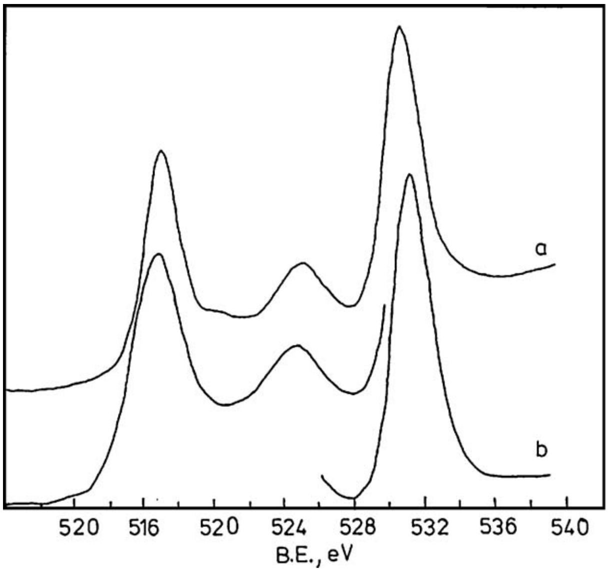

Fig. 11. V 2p and O 1s photoelectron spectra of sample A exposing the (0 1 0) plane: (a) as received and (b) after argon sputtering.

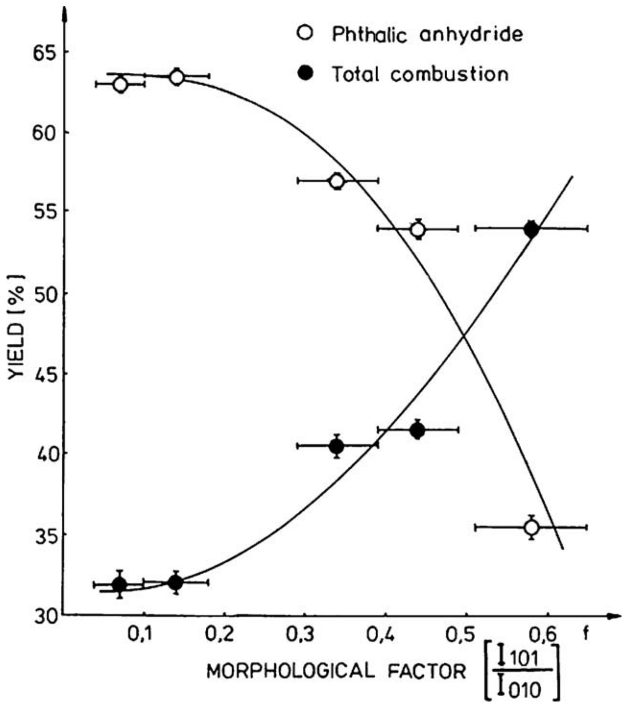

Fig. 10. Selectivities in oxidation of o-xylene on V_2O_5 as a function of the morphological factor.

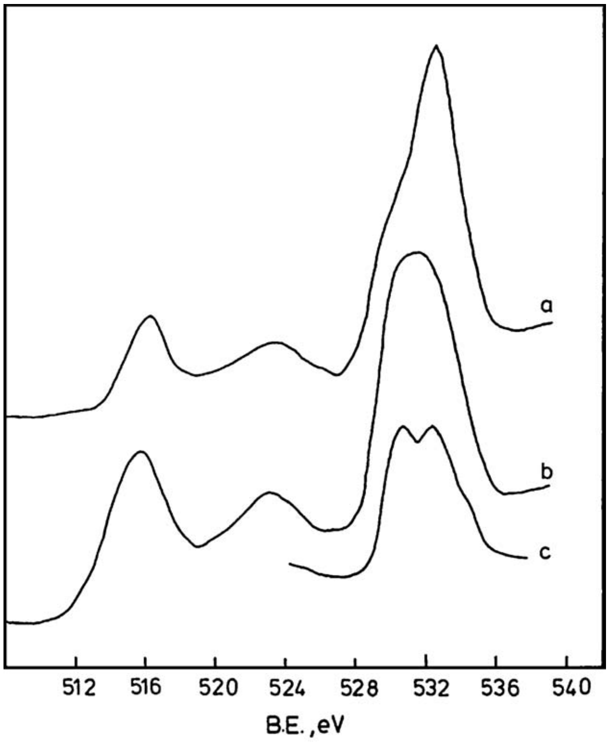

Fig. 12. V 2p and O 1s photoelectron spectra of sample B exposing the (1 0 0) plane: (a) as received, (b) after argon sputtering for 2 min and (c) for 5 min.

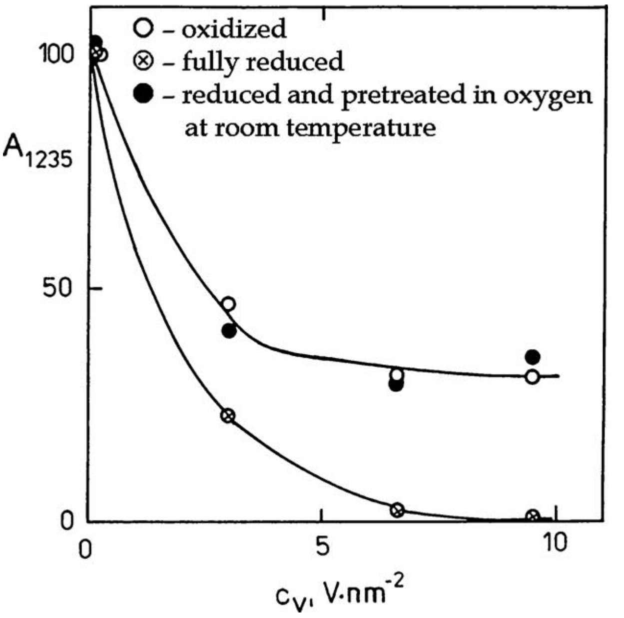

Fig. 13. Intensity of IR band (1235 cm^{-1}) of CO_2 adsorbed on vanadia–alumina catalysts as a function of the vanadia concentration. Band intensity measured for pure alumina is taken as 100%.

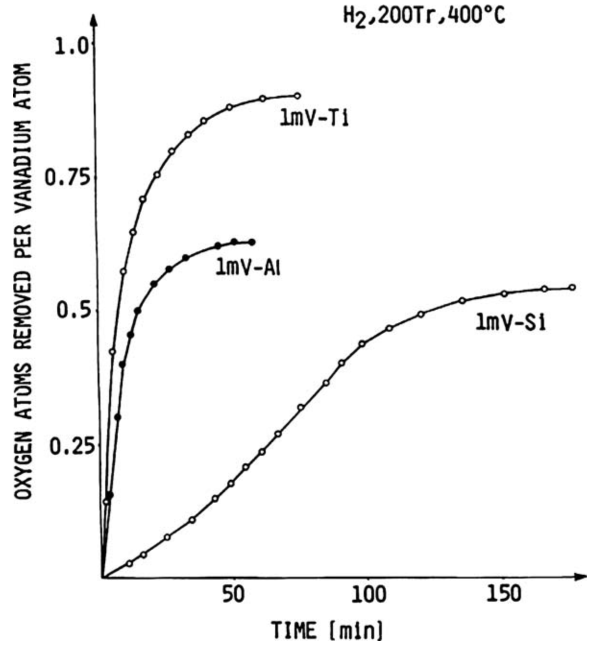

Fig. 15. Amount of oxygen removed from the monolayer samples as function of time of reduction with H_2 at 673 K.

been shown by Sobalik et al. that the basic OH groups of the γ-alumina surface interact selectively with CO_2, which leads to the formation of surface bicarbonate species. The species give rise to IR bands at about 1235, 1480 and 1640 cm^{-1} which can be used to monitor changes in the number of hydroxyl groups of the alumina support during the coverage with vanadium ions as well as during the subsequent reduction. With the low transmitting samples the measurements in this spectral region seem to be experimentally easier and even more specific than the direct measurements in the OH stretching region. On coverage of the support surface with vanadium the amount of basic hydroxyl groups on the alumina surface, as revealed by the intensity of the 1235 cm^{-1} band, decreases quickly (Fig. 13) so that no more groups are visible at vanadia coverage as low as 6.6 V atoms per nm^2. On subsequent reduction the surface hydroxyl groups can be partially restored. The reappearance of free alumina surface in the course of the reduction points to decrease of the dispersion of the surface vanadium phase, i.e. to coalescence of the reduced vanadium oxide monolayer into clusters (Fig. 14). Detailed studies of the reducibility of vanadia grafted at the surface of different supports revealed [17] that vanadia monolayer on anatase gives off stoichiometrically one oxygen atom for each vanadium polyhedron, whereas in the case of vanadium oxides supported on γ-alumina and SiO_2 only about 0.5 oxygen atom per vanadium ion can be removed on reduction (Fig. 15). The amount of vanadium which can be bound to the surface of anatase was found to be 8 V/nm^2. As to the geometry of the V–O species formed on the (0 1 0) plane of anatase, the simplest model would involve bonding of vanadium–oxygen ions to the surface through esterification with three hydroxyls. Vanadium would in this case occupy roughly a position which another Ti^{4+} would occupy, had the bulk structure continued. This should bring about almost perfect balance of the local charges rendering the vanadium complex particularly stable. Kozlowski [18] carried out also the EXAFS and XANES analysis which confirmed this model.

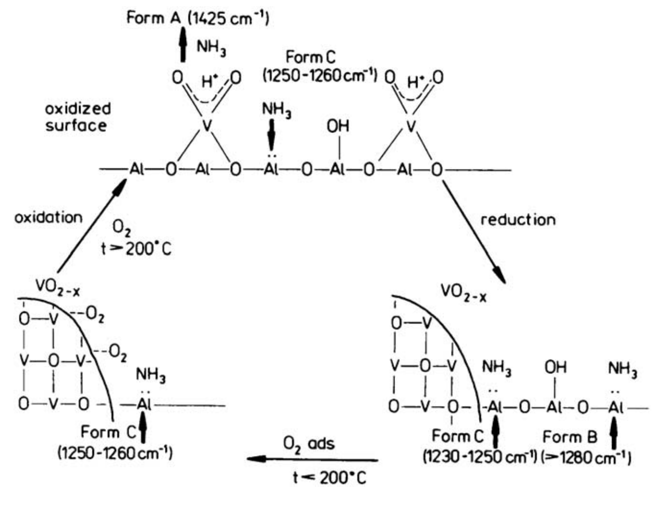

Fig. 14. Coalescence and spreading of vanadia supported on alumina on reduction and reoxidation.

Machej et al. [19] prepared a series of supported V_2O_5/TiO_2 catalysts using different preparation methods to determine the possible influence of the preparation procedures upon the final molecular structures of the catalysts and with the group of Prof. I.E. Wachs in Lehigh University it was found by means of ambient and in situ Raman spectroscopy that all the employed preparation methods lead to the same types of surface metal oxide species on the titania support (Fig. 16). The hydrated surface vanadium oxide species undergo, after heating in flowing dry air, reversible conversion into the dehydrated analogues (Fig. 17). The preparation methods appear to have no influence on the final vanadium oxide structures (Fig. 18).

A general conclusion may be formulated that the deposition of the overlayer of metal oxide proceeds by reaction with the surface hydroxyls of the high surface area oxide supports. The type of species deposited at submonolayer coverage is controlled by the point of zero charge of the support and corresponds to the species present in aqueous solution at the respective pH and concentration. It is independent of the method of synthesis. Chemistry of such overlayers may be understood in terms of the bidimensional hydrated surface phase. The heating of the active phase is the important factor, because it affects the presence of different metal oxide species: isolated oxy-ions, polymerized surface species and

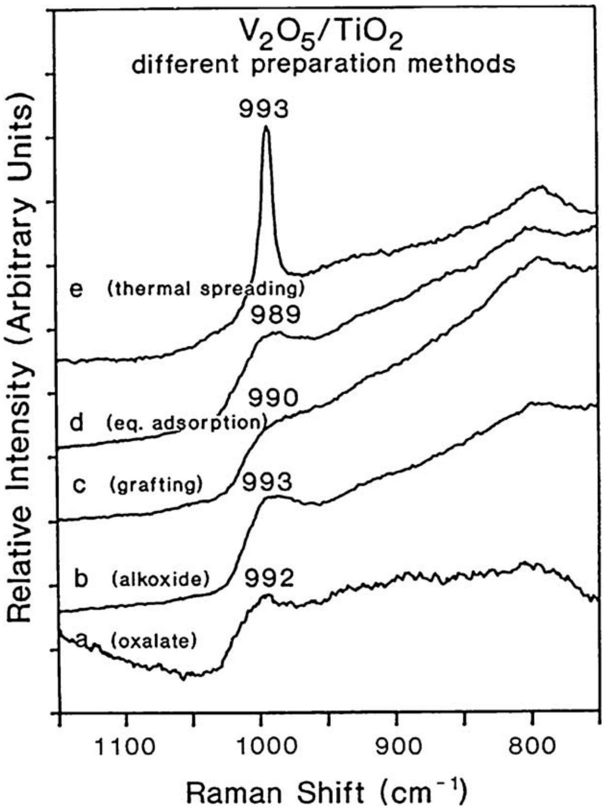

Fig. 16. Raman spectra of V_2O_5/TiO_2 catalysts prepared by different methods: (a) aqueous impregnation with vanadium oxalate, (b) incipient wetness impregnation with vanadium isopropoxide, (c) grafting with $VOCl_3$ in *n*-hexane, (d) equilibrium adsorption from ammonium metavanadate aqueous solution at pH 7.07, and (e) dry impregnation (thermal spreading) from a V_2O_5/TiO_2 physical mixture. V_2O_5 content 4.6 wt%, calcination temperature 773 K for 48 h.

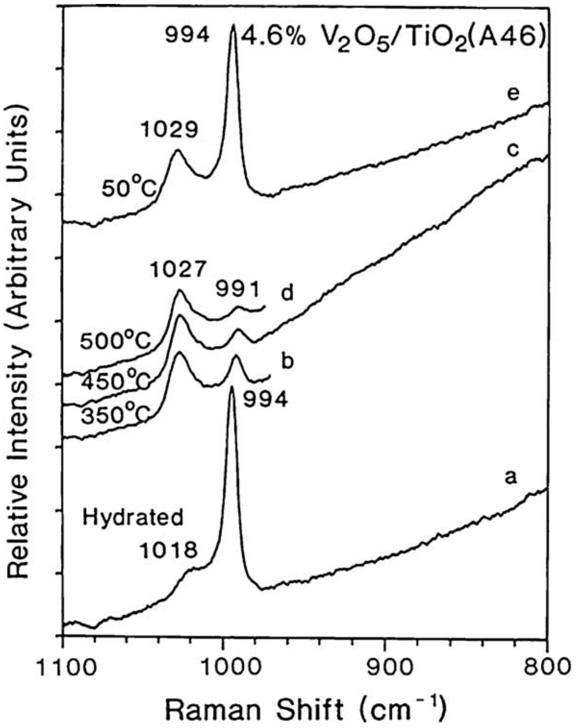

Fig. 17. In situ Raman spectra of the 4.6 wt% V_2O_5–anatase physical mixture preheated at 723 K for 5 h.

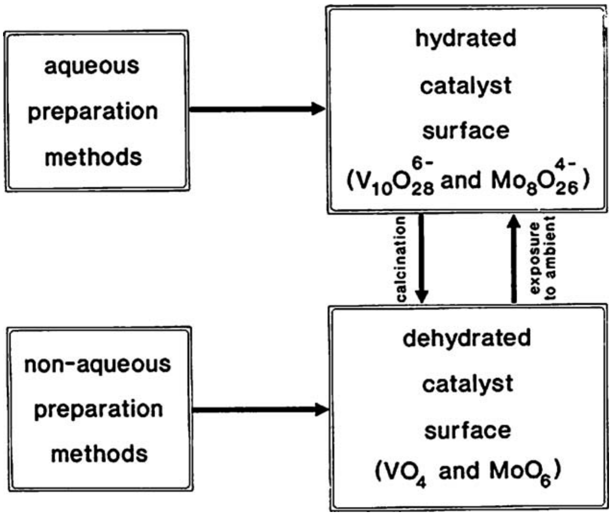

Fig. 18. Relationship between the different synthesis methods and the hydrated/dehydrated states of the catalyst surface.

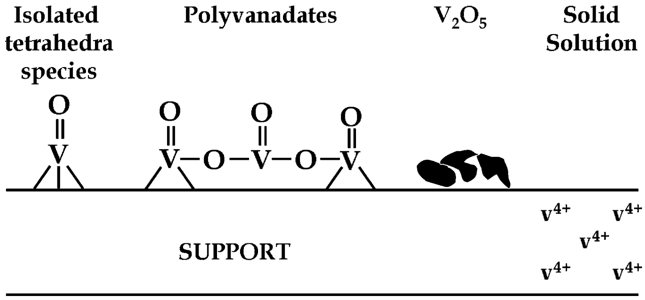

Fig. 19. Structure of the interface vanadium oxides/support.

crystalline phases. On calcination at moderate temperatures dehydration of the surface takes place, but at higher temperatures the molecularly dispersed metal oxide species may coalesce into larger crystallites and eventually form solid solutions. Various types of VO_x species observed on TiO_2–anatase support are shown in Fig. 19 [20].

Investigating by pulse method the catalytic activity of V_2O_5/TiO_2 catalysts in oxidation of o-xylene Grzybowska-Swierkosz and co-workers [21] found that with increasing number of o-xylene + oxygen pulses the conversion of o-xylene increases with a simultaneous decrease in the selectivity to phthalic anhydride due to the oxidation of the initial sample during the pulse experiment. In order to check whether reduction of samples affects their catalytic behaviour, one of the samples was subjected to the reducing pulses of o-xylene in nitrogen, after which its activity in the oxidation of o-xylene was checked again by injecting pulses of this hydrocarbon into the stream of air. The results shown in Fig. 20 clearly indicate that the selectivity to phthalic anhydride increases after the reducing pulses, but decreases again when pulses of o-xylene in air are injected onto the reduced sample. It may be concluded that adsorbed oxygen is responsible for total oxidation and it must be removed from the surface before high selectivity to o-xylene can be obtained with participation of lattice oxygen. This conclusion has been corroborated by Grzybowska-Swierkosz and co-workers [22] who in very elegant experiment measured the temperature dependence of work function of V_2O_5 and V_2O_5/TiO_2 after adsorption of controlled amount of oxygen, which permitted the calculation of the charge on surface oxygen ions. The results summarized in Table 4 clearly show that at temperatures lower

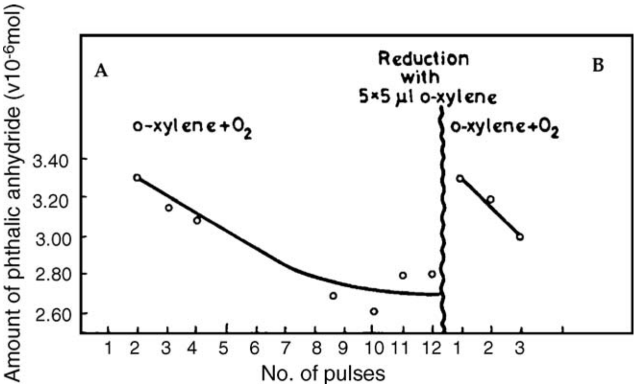

Fig. 20. Variations of the amount of phthalic anhydride with the number of pulses. (A) 2 ml pulses of o-xylene in air and (B) 2 ml pulses of o-xylene in air after reduction with 5× 5 ml pulses of o-xylene in nitrogen. $T = 623$ K.

than 653 K the surface is covered by reactive electrophilic O^- and O_2^-, whereas at temperatures higher than 653 K only nucleophilic O^{2-} species are present at the surface. It is well known that at temperatures lower than about 380 °C total oxidation of o-xylene takes place and only after reaching this temperature total oxidation disappears and selective oxidation to phthalic anhydride is suddenly triggered.

One of the most important catalytic gas phase oxidations of inorganic compounds is the oxidation of SO_2 to SO_3 in the production of sulphuric acid. Already in 1831 Phillips showed that platinum is a very good catalyst for this process and obtained the first patent in catalysis. In 1899 Maiers proved that V_2O_5 is even better catalyst. The first commercially successful vanadium catalyst was operated by BASF from 1920. The catalyst used today is composed of a mixture of V_2O_5 and K_2O, supported on kieselguhr. The main objective in the improvement of the vanadium catalyst were longer life and increased activity at lower temperatures. Although almost 100 years passed since the first industrial use of V_2O_5 as the catalyst for SO_2 oxidation, the mechanism of this process is not yet fully understood. Only in the forties it has been shown that the addition of alkali to vanadium oxide resulted in formation of a liquid melt supported on kieselguhr. Boreskov and co-workers found that the V_2O_5–K_2SO_4–SiO_2 system was approximately 20 times more active than the pure V_2O_5 over the temperature range of 713–773 K. The degree of reduction of the V_2O_5 to V^{4+} has been shown to have a direct connection with catalyst activity. It was also established that the rate of SO_2 oxidation was proportional to the liquid volume of the film less than 200 nm thick deposited on a nonporous support. The occurrence of the liquid phase has been a subject of long discussion. The phase diagram for the K_2SO_4–V_2O_5 has been examined and it was assumed that the activated catalyst is at least a four component mixture: K_2SO_4, SO_3, V^{IV} and V^{V}, the last two being compounds of complex composition. It was noteworthy that potassium salts are also used as promoting addition to the catalyst for the oxidation of o-xylene to phthalic anhydride, what led us to a hypothesis that the mechanism of its influence is similar. In the late seventies we were developing a scientific collaboration with Prof. G.K. Boreskov, then director of the Institute of Catalysis of the Academy of Sciences of USSR, who was one of the authorities in the industrial manufacturing of sulphuric acid [23,24]. With Dr. Ziolkowski (later professor in our Institute), we tried to explain the role of potassium in the oxidation on vanadium catalysts. Potassium vanadates of composition $K_2O{\cdot}nV_2O_5$ with $n = 3$–5, $K_2O{\cdot}5V_2O_5{\cdot}V_2O_4$ were synthesized, their structure was determined and their catalytic activity and selectivity in oxidation of o-xylene to phthalic anhydride were measured. In the conditions of the catalytic reaction the vanadates decompose to a nonstoichiometric compound of $3 < V/K < 4$ and V^{4+} content up to 10 at% with production of V_6O_{13}. Under the same reaction conditions pure V_6O_{13} is oxidized to V_2O_5. Thus the presence of potassium vanadates stabilizes the lower vanadium oxide V_6O_{13}, which may be considered to be the surface active phase of these catalysts [25].

As already discussed, in conditions of the usual pretreatment of supported transition metal oxides catalysts oxy-species are formed, whose structure and behaviour in elementary catalytic transformations are not yet fully understood, one of the difficulties being that oxygen ions of the transition metal–oxygen polyhedra are indistinguishable from those of the oxidic support. It seemed therefore interesting to investigate the behaviour of transition metal oxides dispersed on nonoxidic support in the hope that it will be possible to follow the fate of oxygen atoms from the different supported surface species. In collaboration with Prof. M. Wojciechowska and her group at the Poznan University magnesium fluoride was selected as the support because it is known to be fairly stable in different chemical environments and vanadium oxides were deposited. X-ray photoelectron spectra of all investigated samples of V_2O_5/MgF_2 in the ranges of binding energies (BE) of Mg 1s and F 1s electrons contained one symmetric peak, whereas all bands of O 1s electrons showed a composite structure. They could be deconvoluted into two peaks indicating that two different forms of oxygen are present in the samples: O_I at the BE of about 530 eV, which corresponds to lattice oxygen of V_2O_5 and O_{II} at about 532 eV characteristic for OH groups. As the O_I peak was absent from the spectrum of pure MgF_2 and its intensity was found to be proportional to the content of vanadium it may be assumed that this peak is related to the V_2O_5 deposited at the surface of MgF_2. As an example Fig. 21 illustrates the content of O_I oxygen as a function of the content of vanadium in MFV samples [26]. These samples were then examined as catalysts in a number of different reactions: dehydrogenation and dehydration of 2-propanol, cyclohexane dehydrogenation, cumene cracking, ammoxidation of toluene and reaction of nitrobenzene with ethylbenzene to form aniline and styrene. As an example Fig. 22 shows the yield of benzonitrile observed when pulses of toluene and ammonia were alternately passed over V_2O_5/MgF_2 catalysts of different composition [27]. Pure MgF_2 was completely inactive in this reaction. It may be seen that on increasing the load of V_2O_5 on MgF_2 the yield of benzonitrile rises and attains a plateau at 65% of yield. The amount of benzonitrile was gradually decreasing with the number of pulses but returned back to the initial value when the surface was reoxidized by pulses of air (curve 2 in Fig. 22). This

Table 4
Oxygen species at surfaces of various oxides.

Catalyst	Temperature range (K)	Oxygen species	Catalytic behaviour
Co_3O_4	293–423, 573–673	O_2^-, O^-	Total oxidation
V_2O_5 and V_2O_5/TiO_2	293–393, 533–653 653	O_2^-, O^- O^{2-}	Total oxidation Selective oxidation of alkyl aromatics
$Bi_2Mo_3O_{12}$	538–673	O^{2-}	Selective oxidation of olefins

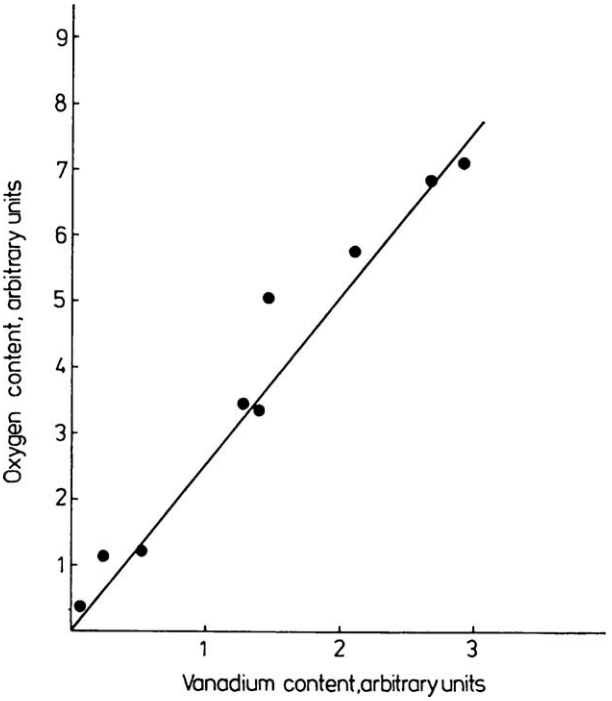

Fig. 21. Amount of O_I as determined from the intensity of O 1s peak at 529–530 eV as a function of the amount of vanadium estimated from at the intensity of the V $2p_{3/2}$ peak.

indicates that the decrease of the yield of benzonitrile in successive pulses of toluene and ammonia was due to the depletion of oxygen in the vanadium oxide monolayer. The activity of catalysts was considerably higher when pulses of oxygen were introduced alternately with pulses of toluene and ammonia (curve 3 in Fig. 22) so that yield of about 90% of benzonitrile was attained for catalysts with V/Mg ratio 0.1 or higher, i.e. when a monolayer coverage of V_2O_5 was formed. The results show also that it is the lattice oxygen which takes part in the reaction. It should be noted that the activity of pure V_2O_5 was low. After introduction of ammonia the band at 2240 cm^{-1} appears in the IR spectrum, which may be assigned to C≡N vibration, characteristic of benzonitrile, whereas the benzoic bands disappear completely and only the bands of aromatic ring at 1600 and 1500 cm^{-1} remain in the spectrum. As already mentioned our investigations of these catalysts showed that at low concentration of vanadium isolated VO_4 tetrahedra appear at the surface, which undergo polymerization to form chains of tetrahedra $(VO_3)_n$ of the metavanadate type or island of trigonal pyramids, when highest catalytic activity is observed. At higher concentrations polyvanadate species with octahedrally coordinated vanadium are deposited at the surface. The characteristic structural elements of metavanadate monolayer are with the bridging oxide ions playing the role of active sites at which oxygen is inserted into the hydrocarbon molecule in the oxidation reaction. By analogy to the bismuth molybdate catalysts, applied in ammoxidation of propene to acrylonitrile, which on interaction with ammonia exchange the surface oxide ions O^{2-} to NH^{2-} groups, which perform an electrophilic attack on the activated hydrocarbon molecule, it can be assumed that on interaction of ammonia with the surface of a monolayer of metavanadate the oxide ions may be exchanged to NH_2 groups, forming surface structural units of the type which may play the role of active sites in the ammoxidation of toluene.

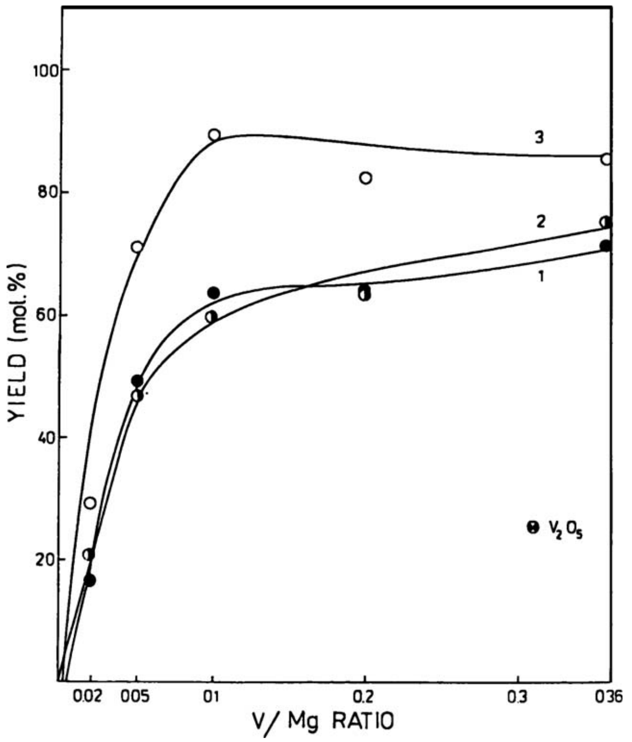

Fig. 22. Yield of benzonitrile in ammoxidation of toluene on V_2O_5–MgF_2 catalysts as a function of the V/Mg atomic ratio: (1) pulses of toluene followed by pulses of ammonia, (2) after addition pulses of air, and (3) oxygen.

Molecular oxygen is most commonly used as hydrogen acceptor, resulting in the formation of water. It seemed interesting to search for a catalyst, which will accelerate a process, in which hydrogen acceptor would be a compound giving some valuable product after hydrogenation, i.e. oxidative dehydrogenation would be coupled with catalytic hydrogenation.

Nitrobenzene was selected as hydrogen acceptor and the reaction

$$3C_6H_5C_2H_5 + C_6H_5NO_2 = 3C_6H_5C_2H_3 + C_6H_5NH_2 + H_2O$$

was studied. The system V_2O_5/MgF_2 turned out to be an active and selective catalyst, the yield of aniline being 90%. Fig. 23 shows [28] the yield of aniline obtained with a V_2O_5/MgF_2 catalyst with atomic ratio V:Mg equal to 0.1 (curve 1). It turned out that the addition of CdO stabilized the catalyst (curve 2) and addition of $KHSO_4$ prolonged its activity to 2.5 h (curve 3). These results showed that reaction of hydrogen transfer from ethylbenzene to nitrobenzene is catalysed by the coke deposited at the surface.

Maleic anhydride is an important product of chemical industry, with many different applications. Until the second half of XXth century it was produced by oxidation of benzene, however saturated hydrocarbons for use as petrochemical base materials to replace olefinic or aromatic feedstocks for selective heterogeneous oxidation reactions have by the end of XXth century received considerable attention due to the increasing price difference between the two raw materials and to the tighter emission control standards by environmental authorities. It was found that vanadyl pyrophosphate is an active and selective catalyst for gas phase oxidation of butane to maleic anhydride and many research groups started studying the mechanism of this reaction and method by which the properties of catalysts could be improved. Many studies were devoted to the search of elements, which would act as promoters, but elucidation of the mechanism, by which the introduction of these elements modifies the properties of catalysts were not fully understood. It seemed thus interesting to undertake investigations of various factors which could improve the performance of the catalyst. At that time a research group led by Dr. V.A. Zazhigalov worked in the Institute of

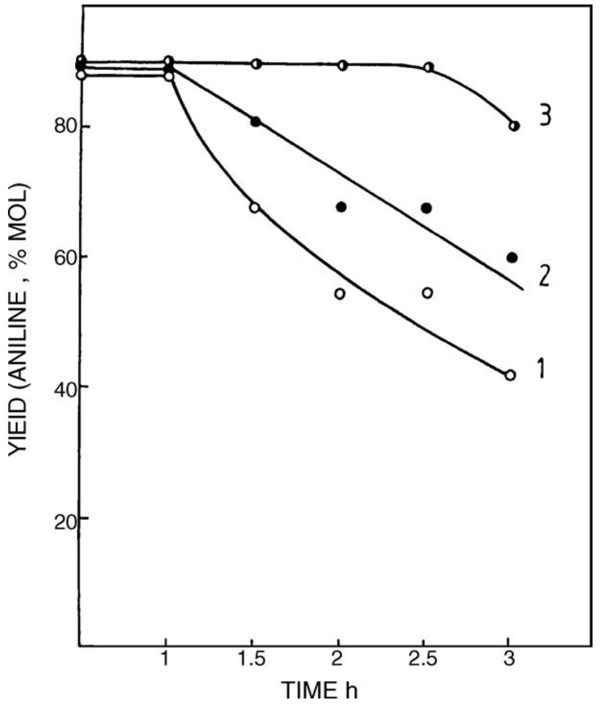

Fig. 23. Yield of aniline obtained in the reaction of nitrobenzene with ethylbenzene on V_2O_5–MgF_2 catalyst.

Physical Chemistry of the National Academy of Sciences of Ukraine in Kiev on the synthesis of compounds in the vanadium–phosphorus phase diagram. During a visit of Dr. Zazhigalov in our Institute it was agreed that a Polish-Ukrainian Laboratory of Catalysis will be organized to undertake the studies of the heterogeneous oxidation of alkanes with particular attention to vanadyl pyrophosphate, known to be the only active and selective catalyst for these processes. Synthesis of catalysts samples was carried out in Kiev, physical and chemical properties and kinetics of reactions were determined in Krakow, Dr. Stoch supervising the latter. It was found that incorporation of alkaline and alkaline earth metal additions at different concentrations to vanadyl pyrophosphate with P/V ratio equal to 1.07 and 1.20 leads to an increase of the effective negative charge on oxygen atoms, which is equivalent to the increase of nucleophilicity of surface and accelerates the rate of butane oxidation to maleic anhydride. A conclusion could be drawn [29] that catalytic activity in butane oxidation to maleic anhydride depends on the nucleophilicity of surface oxide ions (Fig. 24). Preliminary experiments hinted that catalytic activity of vanadyl pyrophosphate may be modified by supplying mechanical energy. Detailed investigations showed that milling in a planetary mill with 3000 rpm in air, ethanol or water suspension modifies the morphology of all vanadium-based catalysts with layer structure: vanadium oxide, V_2O_5/TiO_2 and vanadyl pyrophosphate catalysts. The mechanochemical treatment of the vanadyl pyrophosphate catalysts crushed the crystallites and slipped the layers along the cleavage planes causing a relative growth of the contribution of vanadyl plane (0 0 1) of $VOH{\cdot}PO_4{\cdot}0.5H_2O$ which transforms into the topologically similar (1 0 0) plane of $(VO)_2P_2O_7$ considered to be the active plane. A substantial increase of both activity in *n*-butane oxidation and selectivity towards maleic anhydride are observed (Table 5) [30]. The same effect is observed in the case of *n*-butene and benzene oxidation on V_2O_5 (Table 6) and *n*-butane and o-xylene oxidation on V_2O_5/TiO_2 (Table 7). Fig. 25 illustrates the dependence of the selectivity to maleic anhydride on the relative content of (0 1 0) plane in precursor [31]. In a similar way the mechanochemical treatment of the vanadyl pyrophosphate catalysts containing bismuth changes the sample morphology, favouring the formation of the vanadyl plane and provoking surface chemical reaction. The data obtained for $(VO)_2P_2O_7/BiPO_4$ and $(VO)_2P_2O_7/Bi_2O_3$ samples (Table 5) demonstrate that mechanochemistry is a new promising method for the introduction of promoters into the basic V–P–O composition [30]. We investigated also the possibility of regeneration of VPBiO

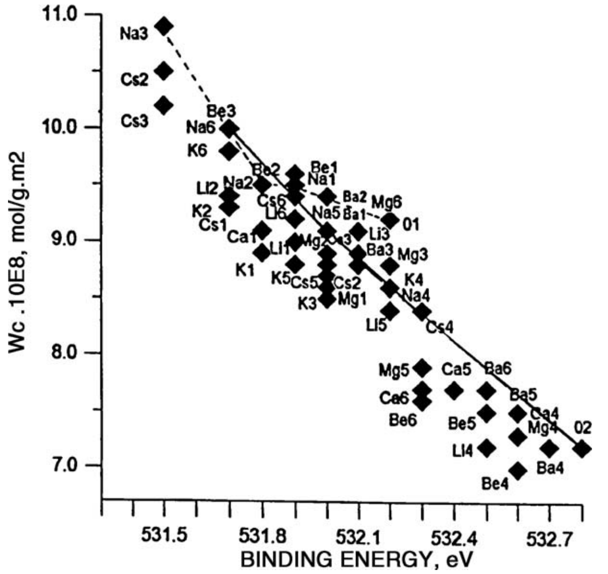

Fig. 24. The rate of *n*-butane oxidation on VPMeO catalyst in dependence on the surface basicity expressed by the binding energy of O 1s photoelectrons.

Table 5
Physico-chemical and catalytic properties of VPO/Bi catalysts after mechanochemical treatment.

Sample	TMCT (min)	Solvent	XRD $I_{(0\,1\,0)}/I_{(1\,1\,0)}$	XPS BE (eV)		P/V	Bi/V	Butane oxidation		
				O 1s	V 2p			X_{C4}	S_{MA}	Y_{MA}
VPO	0	–	0.74	531.7	517.5	1.43	–	73	67	49
VPBiO a	0	–	0.80	531.5	517.4	1.82	0.12	76	68	52
VPBiO b	2	Ethanol	1.03	531.6	517.4	1.95	0.16	77	70	54
VPBiO c	10	Ethanol	1.18	531.6	517.4	2.09	0.18	79	71	56
VPBiO d	10	Water	0.78	531.7	517.5	1.83	0.15	74	66	49
VPBiO f	10	–	0.76	–	–	–	–	71	65	46
VPO/Bi_2O_3 a	0	–	0.77	531.6	517.5	1.47	0.09	63	63	42
VPO/Bi_2O_3 b	10	Ethanol	1.16	531.7	517.6	2.02	0.02	83	72	60
VPO/$BiPO_4$ a	0		0.71	531.5	517.6	1.44	0.09	68	64	44
VPO/$BiPO_4$ b	10	Ethanol	1.15	531.4	517.2	1.96	0.03	88	74	65

Table 6
Influence of mechanochemical treatment in ethanol suspension on V_2O_5 properties.

TMCT (min)	S (m^2/g)	XRD $I_{(0\,1\,0)}/I_{(1\,1\,0)}$	XPS O 1s (eV)	XPS V 2p (eV)		n-Butene oxidation			Benzene oxidation		
				1	2	X	S_{MA}	Y_{MA}	X	S_{MA}	Y_{MA}
0	4.4	0.74	531.2	–	517.8	27.0	7.0	1.9	34.5	56.0	19.3
2	5.8	1.33	–								
10	5.6	2.15	531.2	516.6	517.8	34.0	9.5	3.2	53.5	64.0	34.2
20	8.0	4.07	–			45.5	12.6	9.5	–		
30	8.2	4.19	531.2	516.6	517.8	53.0	48.0	25.4	70.0	72.0	50.4

Table 7
Influence of mechanochemical treatment in ethanol on V_2O_5/TiO_2 properties.

TMCT (min)	XRD $I_{(0\,1\,0)}/I_{(1\,1\,0)}$	XPS BE (eV)			XPS V/Ti	n-Butane oxidation at 440 °C			o-xylene oxidation at 380 °C		
		O 1s	V 2p	Ti 2p		X_{C4}	S_{MA}	Y_{MA}	X_{C8}	S_{PhA}	Y_{PhA}
0	0.7	531.2	517.8	459.0	0.25	15.0	2.0	0.3	62.0	52.5	32.5
10	3.1	530.1	517.4	459.0	0.40	21.5	7.0	1.5	69.0	61.0	42.1
20	4.0	531.3	517.6	458.8	0.45	39.5	17.5	6.9	79.5	75.0	59.6
30	6.8	531.0	517.4	459.3	0.43	29.0	10.0	2.9	74.0	67.5	50.0

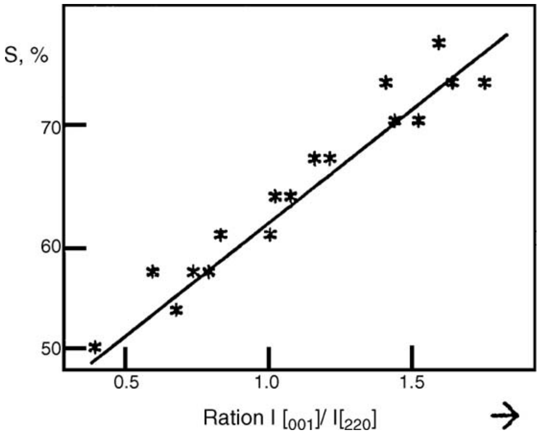

Fig. 25. Dependence of the selectivity to maleic anhydride on the relative exposure of the 0 1 0 plane in the precursor after mechanochemical treatment.

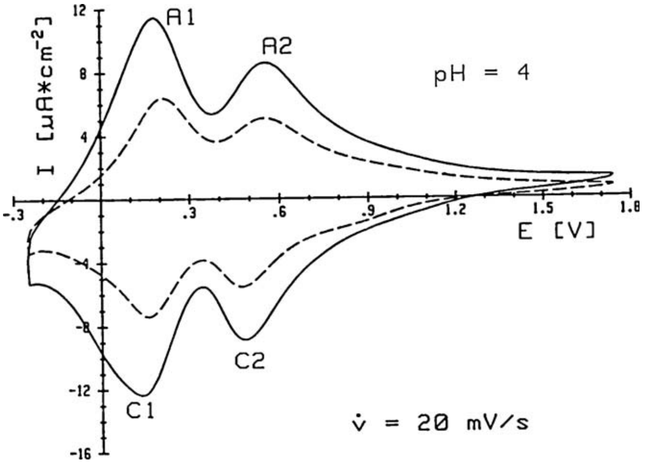

Fig. 26. Stationary voltammetric curves for the rutile electrode reduced in hydrogen and then heated for 1 h with V_2O_5 in argon atmosphere at 730 K.

catalysts deactivated during commercial use. We found that a combination of mechanochemical and barothermal treatment combined with addition of Bi_2O_3 or $BiPO_4$ and H_3PO_4 or P_2O_5 enable regeneration of used catalyst increasing the selectivity by 11–23% and restoring most of the initial catalytic activity.

Important information about the performance of vanadium ions as active sites of the V_2O_5/TiO_2 catalyst in the exchange of electrons in the course of oxidation reaction was obtained from the studies of electrocatalytic processes of oxidation of organic molecules, carried out together with Dr. Nowak (now a professor in our Institute). As an example exchange of electrons with catalysts composed of vanadia supported on titania will be discussed. Scanning tunnelling microscopy shows that heating in vacuum generates surface oxygen vacancies on the surface of the rutile monocrystal. By using cyclic voltammetric experiments it has been possible to show that these vacancies are active sites mediating the transfer of electrons in the oxidation of water and evolution of oxygen, the rate being proportional to the surface concentration of these vacancies. Vanadium ions deposited at the surface of rutile generate local energy levels below the conductivity band edge, whose energy position may be determined by cyclic voltammetry (Fig. 26) [32]. They mediate the electrocatalytic oxidation of many organic molecules [33], catechol being an example (Fig. 27), pure rutile surface being inactive. The rate of the oxidation reaction is proportional to the number of vanadium ions present at the surface (Fig. 28). V^{4+} ions diffuse into the subsurface layer and can be reduced to V^{3+} oxidation state due to charge compensation by protons incorporated into the surface layer, but only outermost vanadium ions can be oxidized to V^{5+} oxidation state as the result of chemisorption of oxygen. Thus, the position in the energy spectrum of the solid and the ability to change the valence state makes possible for vanadium ions to mediate the electron transfer between the reacting organic molecules and the catalyst and the oxidation of these molecules takes place, the catalyst mediating the flow of electrons from the organic molecule to dioxygen, which cannot take place directly.

In mid seventies the quantum-chemical methods were already developed to the extent which made possible to try the application of these methods to describe the mechanism of catalytic reactions. With Dr. Bocławik and Dr. Witko (now professors in our Institute) we applied these methods to elucidate the mechanism of activation of a hydrocarbon molecule by abstraction of hydrogen and the mechanism of insertion of oxygen into the activated molecule. At that period semiempirical MINDO method was used, but already valuable results concerning, e.g. oxidation of benzene to hydroquinone in the presence of V_2O_5 catalysts could be obtained, in agreement with the mechanism proposed by Waugh, corroborating also the linear dependence of the rate of benzene oxidation on the concentration of V^{4+} ions in V_2O_5–MoO_3 catalysts. By the end of XXth century the DFT method became generally used. The mechanism of oxidation of toluene to benzaldehyde [34] may

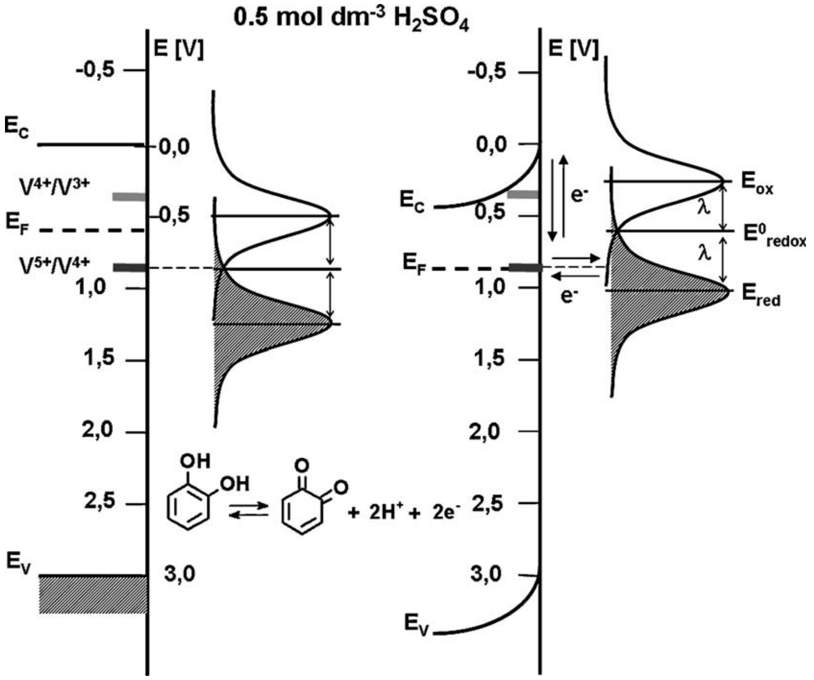

Fig. 27. Energy scheme of the oxidation of o-dihydroxybenzene on a rutile/Ti electrode doped with vanadium ions.

illustrate the possibilities of following step-by-step the catalytic transformation at the surface of V_2O_5 (Fig. 29). The interactions, which develop when toluene molecule is approached to a cluster of vanadium oxide, V_6O_{20}, taken as a model of the catalyst, were calculated. On approaching toluene molecule vertically end-on with the methyl group directed towards the cluster (Fig. 29a), the bonds between the bridging surface oxygen atoms and vanadium atoms in the cluster (Fig. 29b) are considerably weakened and surface oxygen atoms move above the surface of the cluster. The bonds are formed between these oxygen atoms and the methyl group with simultaneous abstraction of two hydrogen atoms, which form OH groups with other oxygen atoms of the cluster (Fig. 29c). Desorption of the benzaldehyde molecule follows, leaving two OH groups and an oxygen vacancy at the surface of the cluster (Fig. 29d). Different reaction pathway is followed when toluene molecule is approached to the cluster side-on. In this case strong interactions develop between all carbon atoms of the ring and the methyl group and oxygen atoms of the cluster already at the distance of 2A (Fig. 29e), resulting, on further approach, in complete destruction of the molecule and formation of coke or carbon oxides (Fig. 29f). Two important general conclusions may be formulated: (1) the reaction pathway is critically dependent on the orientation of the molecule approaching the surface, and (2) the surface undergoes reconstruction under the influence of the incoming molecule and adapts itself to the requirement of the reaction.

Let us now summarize the state of the art of catalysis by vanadium oxides. Special chemistry of vanadium oxides and

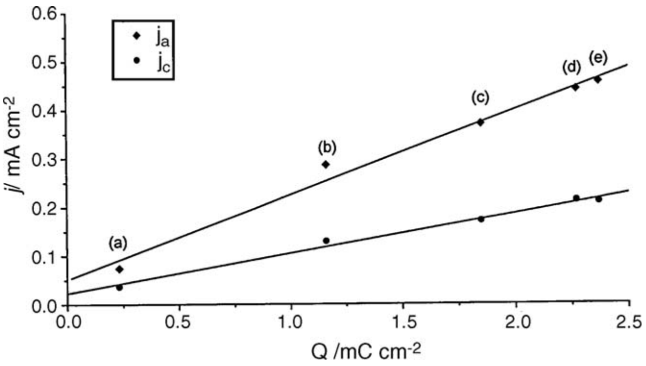

Fig. 28. Dependence of the current of o-dihydroxybenzene oxidation and reduction of the product of its oxidation on the amount of vanadium ions in the surface layer of the rutile/Ti electrode.

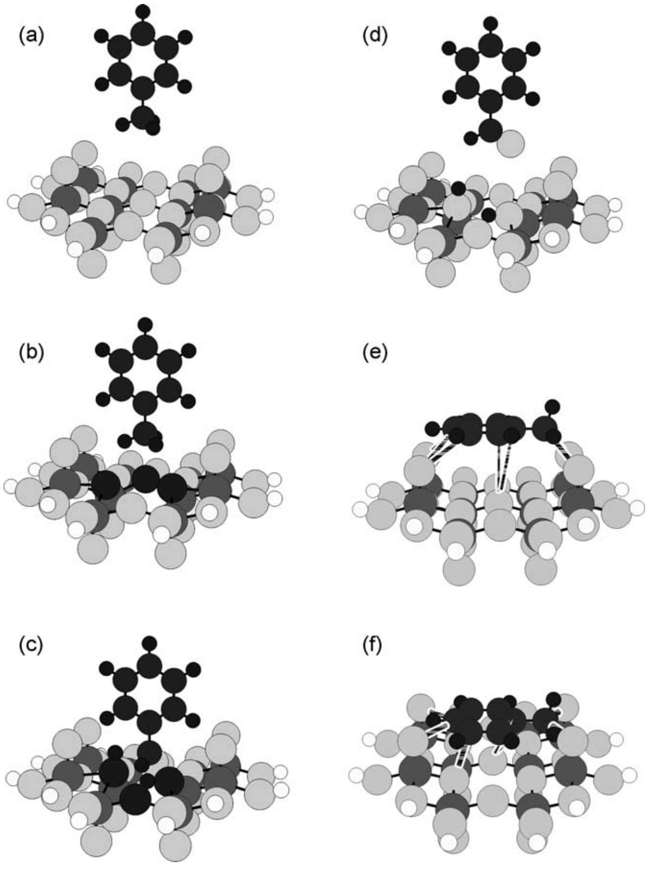

Fig. 29. Interaction of toluene with the surface of V_2O_5.

vanadium oxide based catalysts results from a number of different interrelated electronic and structural factors. First, these compounds have partially filled d-orbitals which are responsible for a wide variety of electronic, magnetic and catalytic properties. Vanadium atoms exist in different formal oxidation states which vary from two to five. This ability of vanadium atoms to possess multiple stable oxidation states results in the easy conversion between oxides of different stoichiometry by oxidation and reduction, which is the important factor for the oxide to function as catalyst in selective oxidation. Bulk vanadium oxide is a strong oxidant as indicated by the high negative value of the Gibbs free energy of the reduction equilibria:

$$V_6O_{13}(s) + O_2 = 3V_2O_5(s), \quad \Delta G^0 = -24.34\,\text{kcal/mol at } 600\,^\circ\text{C}$$

$$2V_2O_4 + O_2 = 2V_2O_5(s), \quad \Delta G^0 = -42.0\,\text{kcal/mol at } 600\,^\circ\text{C}$$

In the first step of reduction V_6O_{13} is formed which then transforms into V_2O_4.

When used as catalyst in oxidation of hydrocarbons total oxidation is the main reaction observed. The consecutive processes of reduction and oxidation in the course of catalytic reaction at the surface of crystalline V_2O_5 causes its amorphisation. In order to prepare a selective catalyst, vanadium oxides are either deposited at the surface of an oxide support, or reacted with other components to form appropriate compounds with required surface structure. The vanadia based systems are active and selective in various types of hydrocarbon oxidation reactions such as oxidative dehydrogenation of alkanes and olefins (V–Mg–O compounds, alkaline earth metal vanadates and systems containing $[VO_x]_n$ groups dispersed on basic oxide supports are used as catalysts), and reactions with formation of oxygenated products such as aldehydes, acids, anhydrides or their derivatives. In fact all heterogeneous oxide catalysts used in industrial processes for production of organic anhydrides and acids contain vanadium as the main component of the active phase. These are synthesis of maleic anhydride, previously from benzene (V–Mo–O catalysts) and presently from *n*-butane (V–P–O system), phthalic anhydride from o-xylene (V–Ti–O catalyst) and acrylic acid from acrolein (V–Mo–O system). The vanadia containing formulations turned also to be catalysts for oxidation of polycyclic aromatic hydrocarbons such as naphthalene, anthracene, phenanthrene and fluorine to dicarboxylic acids and quinones (V–Fe–O system) and for oxidation of methanol to methyl formate (V–Ti–O catalysts). Systems active in formation of acidic products contain usually elements forming oxides of more acidic character than vanadia as Mo, P or amphoteric oxides, whereas the oxidative dehydrogenation reactions require formulations in which the vanadium is accompanied by elements forming basic oxides as Mg or alkaline earth elements.

Under ambient conditions the structure of vanadium oxide dispersed at the surface of an oxide support closely follows the pentavalent vanadium ion behaviour in aqueous solutions, and consequently, the structure of the vanadium oxide species is controlled by the net surface pH at point of zero charge of the thin aqueous film on the oxide support and by surface concentration of vanadium and can be predicted from the corresponding aqueous chemistry. For the given support it is independent of the method of preparation. Under dehydrated conditions the behaviour of vanadium oxide depends on the relative values of surface free energy of vanadium oxide and the oxide support. When $(\Delta F)_{V_2O_5} < (\Delta F)_{\text{support}}$, phenomenon of wetting of the support by vanadium oxides operates and surface vanadia species spontaneously disperse over the surface of the support. As the surface free energy of the reduced vanadium oxides is higher than that of V_2O_5, the surface layer coalesce on reduction into larger particles and undergoes redispersion on subsequent oxidation. The common feature of all vanadia-based catalysts is the presence of V=O bonds, vanadium ions being surrounded by tetrahedral, octahedral or square pyramid arrangement of oxygen ions depending on the surface loading. Isolated V=O tetrahedra are formed when the concentration of vanadia at the support surface is low, or are joined through corners or edges, when loading is increased, forming chains of octahedral or bidimensional polymeric structures of monolayer type. In the case of isolated tetrahedra the terminal group V=O is linked with the support by V–O–Me bonds, where M represents the cation of the supporting oxide. In the case of higher loading the V–O–V bonds dominate at the surface. Quantum-chemical calculations show that the bridging oxygen V–O–V is most nucleophilic and is involved in the catalytic reaction. At still higher loading microcrystallites of V_2O_5 are formed. In solid solutions of vanadium ions in other oxides, or in compounds such as vanadyl pyrophosphate or magnesium vanadates the V=O polyhedra are separated by polyhedra containing other elements, e.g. P or Mg as central atoms and vanadium active sites become separated. As the V_2O_5 and its derivatives form anisotropic lattices, the catalytic properties show strong structure sensitivity. The active sites are present at (0 1 0) crystal planes [(1 0 0) planes in case of vanadyl pyrophosphate] containing V=O groups, which are cleavage planes. The exposure of these planes may be increased by mechanochemical treatment, which changes the morphology of catalyst crystallites enhancing thus the catalytic activity and selectivity. Mechanical milling may also increase the dispersion of vanadium oxide active phase on the support and accelerate the reactions of vanadium oxides with other components of the system.

References

[1] K. Hauffe, Adv. Catal. 7 (1955) 213.
[2] F.F. Wolkenstein, Adv. Catal. 9 (1957), 807, 818.
[3] A. Cimino, F.S. Stone, Adv. Catal. 47 (2002) 141.
[4] J. Haber, J. Stoch, M. Sawicka, React. Kinet. Catal. Lett. 5 (1976) 93.
[5] J. Haber, J. Stoch, React. Kinet. Catal. Lett. 9 (1978) 319.
[6] J. Haber, J. Stoch, in: K. Dyrek, J. Haber, J. Nowotny (Eds.), Reactivity of Solids, Elsevier, Amsterdam, 1982, p. 418.
[7] B. Dyakova, M. Mechandzijev, B. Grzybowska-Swierkosz, M. Gasior, J. Haber, Appl. Catal. 3 (1982) 255.
[8] M. Gasior, B. Grzybowska-Swierkosz, in: B. Grzybowska-Swierkosz, J. Haber (Eds.), Vanadia Catalysts for Processes of Oxidation of Aromatic Hydrocarbons, PWN, Warszawa, 1984, p. 133.
[9] M. Gasior, B. Grzybowska-Swierkosz, unpublished data.
[10] J. Haber, Izv. po Chimija 13 (1980) 65.
[11] J. Haber, Pure Appl. Chem. 56 (1984) 1663.
[12] J. Haber, T. Machej, T. Czeppe, Surf. Sci. 151 (1985) 301.
[13] M. Gasior, J. Haber, T. Machej, Appl. Catal. 33 (1987) 1.
[14] M. Gasior, T. Machej, J. Catal. 83 (1983) 472.
[15] M. Gasior, J. Haber, T. Machej, T. Czeppe, J. Mol. Catal. 43 (1988) 359.
[16] Z. Sobalik, R. Kozlowski, J. Haber, J. Catal. 127 (1991) 665.
[17] J. Haber, A. Kozlowska, R. Kozlowski, J. Catal. 102 (1986) 52.
[18] R. Kozlowski, P. Pettifer, J.M. Thomas, J. Phys. Chem. 87 (1983) 5176.
[19] T. Machej, J. Haber, A.M. Turek, I.E. Wachs, Appl. Catal. 70 (1991) 115.
[20] B. Grzybowska-Swierkosz, J. Haber, Catalysis, Annual Reports, Section C, vol. 11, The Royal Society of Chemistry, Cambridge, 1994, p. 395.
[21] R. Grabowski, B. Grzybowska-Swierkosz, J. Haber, J. Sloczynski, React. Kinet. Catal. Lett. 2 (1975) 81.
[22] J.M. Libre, Y. Barbaux, B. Grzybowska-Swierkosz, J.P. Bonnelle, React. Kinet. Catal. Lett. 20 (1982) 249.
[23] G.K. Boreskov, V.P. Pligunov, J. Appl. Chem. USSR 13 (1940) 653.
[24] G.K. Boreskov, in: J.R. Anderson, M. Boudart (Eds.), Catalysis—Science and Technology, vol. 3, Springer Verlag, New York, 1982, p. 124.
[25] M. Gasior, B. Grzybowska-Swierkosz, J. Haber, T. Machej, J. Ziolkowski, J. Catal. 58 (1979).
[26] J. Haber, J. Stoch, M. Wojciechowska, Surf. Interf. Anal. 15 (1990) 711.
[27] J. Haber, M. Wojciechowska, Catal. Lett. 10 (1991) 271.
[28] J. Haber, M. Wojciechowska, W. Gut, Bull. Polish Acad. Sci. Chem. 44 (1996) 55.
[29] V.A. Zazhigalov, J. Haber, J. Stoch, I.V. Bacherikova, G.A. Komashko, A.I. Pyatnitskaya, Appl. Catal. A 134 (1996) 225.
[30] V.A. Zazhigalov, J. Haber, J. Stoch, I.V. Bogatskaya, I.V. Bacherikova, Stud. Surf. Sci. Catal. 101B (1996) 1038.
[31] V.A. Zazhigalov, J. Haber, J. Stoch, A.I. Kharlamov, I.V. Bacherikova, I.K. Bogatskaya, Stud. Surf. Sci. Catal. 118 (1998) 385.
[32] J. Haber, P. Nowak, Top. Catal. 20 (2002) 75.
[33] P. Zurek, Ph.D. Thesis, ICSC PAS, Krakow, 2003.
[34] M. Witko, R. Tokarz, J. Haber, J. Mol. Catal. 82 (1993) 457.