

# Oxidation catalysis—electronic theory revisited

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## Abstract

Transfer of electrons between reacting molecules and solid oxide catalysts is shown to be a much more complex phenomenon than assumed in the electronic theory of catalysis. Interface electron transfer requires matching energy and symmetry of frontier orbitals; therefore the energy levels of the reacting molecule must correspond to the region of high density of states of the solid. This can be achieved either by activation of adsorbing molecule or through generation of defects, introduction of dopants, or deposition of the active phase on a support to form oxide-monolayer-type catalysts. An example of the interaction of methane and  $V_2O_5$  with various defects is discussed. It is shown that the cleavage of the C–H bond in primary carbon proceeds by transfer of two electrons to the empty vanadium surface levels and formation of adsorbed alkoxy and surface hydroxyl species.

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## 1. Introduction

An organic molecule can react with oxygen along many possible consecutive and parallel reaction pathways, giving a number of different products [1–4]. The role of a catalyst is to accelerate only one of them, very often thermodynamically not the most favorable one, leading to the formation of the desired product. Such selectivity of action is the most important and characteristic feature of catalysts and makes possible the synthesis of products that would have never been formed in the absence of the catalyst because of other more rapidly proceeding competitive processes. Often a small modification of the composition of the catalyst or variation in the method of its preparation can modify its catalytic properties to such an extent that the direction of the reaction is changed and a new product may be formed, usually with high selectivity [5].

Oxidation processes may be viewed as reactions that consist in the abstraction of hydrogen atom(s) and addition of one or several oxygen atoms, resulting in products which differ in the ratios C/H and C/O. The reactions may start by activation of hydrocarbon or oxygen molecules. In heterogeneous catalytic processes activation of hydrocarbon

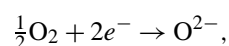
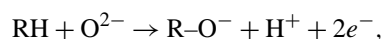
molecules through either homolytic C–H bond cleavage with the formation of radicals or heterolytic C–H bond cleavage at the acid–base pair of sites is usually considered. In the latter case two possibilities are taken into account: abstraction of hydrogen in the form of a proton and formation of an OH group and a carbanion fragment linked to a metal cation, or abstraction of a hydride ion and formation of an alkoxy group and a metal–hydride type complex [6,7]. However, experimental evidence has revealed the presence at oxide surfaces of only alkoxy and OH groups, hinting that both parts of the C–H bond become bonded to the surface oxygen atoms [7]. Depending on whether oxygen or the organic molecule is activated the reactions can be classified as electrophilic or nucleophilic oxidation processes [8,9]. They require the participation of different types of oxygen: in electrophilic oxidation  $O_2^*$ ,  $O_2^-$ , and  $O^-$  species [10] are involved, whereas in nucleophilic oxidation the lattice oxide  $O^{2-}$  ions perform the nucleophilic attack on the activated organic molecule [11]. The first class of processes lead under conditions of heterogeneous catalysis to total oxidation (combustion); the second class can be carried out with high chemo-, regio-, and stereo selectivity [12]. Depending on whether after activation of an organic molecule by abstraction of hydrogen to form an adsorbed alkoxy species the second hydrogen is abstracted from the  $\alpha$ -carbon or the  $\beta$ -carbon, an oxygenated molecule or an olefin is formed. Abstraction of a hydrogen atom from the olefin results in

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the formation of an allylic species or its homologues [13]. Further transformations, consisting in the abstraction of the second H atom and/or the addition of oxygen or an NH group, lead to formation of dienes, aldehydes, acids, or nitriles, respectively, all of great industrial importance [14].

Oxidation of organic molecules usually proceeds by the Mars–van Krevelen mechanism, in which the molecule is oxidized by the catalyst, which is then reoxidized by gas-phase oxygen. Thus, the catalyst must be characterized by facile change of the oxidation state of its cations. Since transition metal oxides belong to systems that may change the electronic states of metals in a wide spectrum, they are the components of all active and selective catalysts. The oxidation cycle thus involves two adsorbed redox couples,



of which the first injects electrons into the oxide catalyst, whereas the second one extracts them from the oxide.

The first attempts to understand the exchange of electrons between a solid catalyst and a reacting molecule were undertaken in the fifties and sixties of the twentieth century in the form of the electronic theory of catalysis, developed by Aigrain and Dugas [15], Weisz [16], Hauffe [17,18], Volkenstein [19], and others. They were attracted by the successes of solid-state theory, which they used to explain chemisorption and catalysis on the surfaces of semiconducting oxides. This theory was based on the general thermodynamic rules stating that depending on the relative position of the Fermi level in the solid and the redox level of the reacting molecule, electrons are transferred from the solid to the adsorbed molecule or vice versa. The appearance of the boundary layer at

the adsorbed molecules/solid oxide interface results in the bending of the energy bands of the solid until the Fermi level achieves the position of the redox level. It was postulated that the charge on the reacting molecule is the factor that influences the reaction pathway. This model rationalized a number of known effects, such as changes of conductivity observed during chemisorption or the influence of doping oxides with altrivalent ions on the catalytic activity [20,21].

The electronic theory of catalysis assumed that the solid surface is a continuum and the electron transfer depends only on the collective properties of the solid, which are expressed by the electrochemical potential (Fermi level). It did not take into account that the relative positions of the Fermi level and the redox level of the molecule determine conditions necessary but not sufficient for electron exchange. Namely, the injection of electrons from an adsorbed redox couple into a transition metal oxide of semiconducting properties can take place spontaneously only if the redox potential of this couple is situated above the Fermi level and above the bottom of the conductivity band. In contrast, the extraction of the electrons from the solid may occur only when the redox potential is located below the Fermi level and below the top of the valence band; see Fig. 1 [22]. The probability of these processes is a function of the density of states in the conductivity and valence bands, respectively, at the potentials corresponding to the redox potential of the adsorbed species. The relative positions of the energy levels in the solid and the redox potential of the reacting molecule may be adjusted by (a) formation of one or more oxide/oxide interfaces with such values of the contact potentials that the conductivity band will shift to the optimum position, (b) doping of the oxide with altrivalent ions, which will

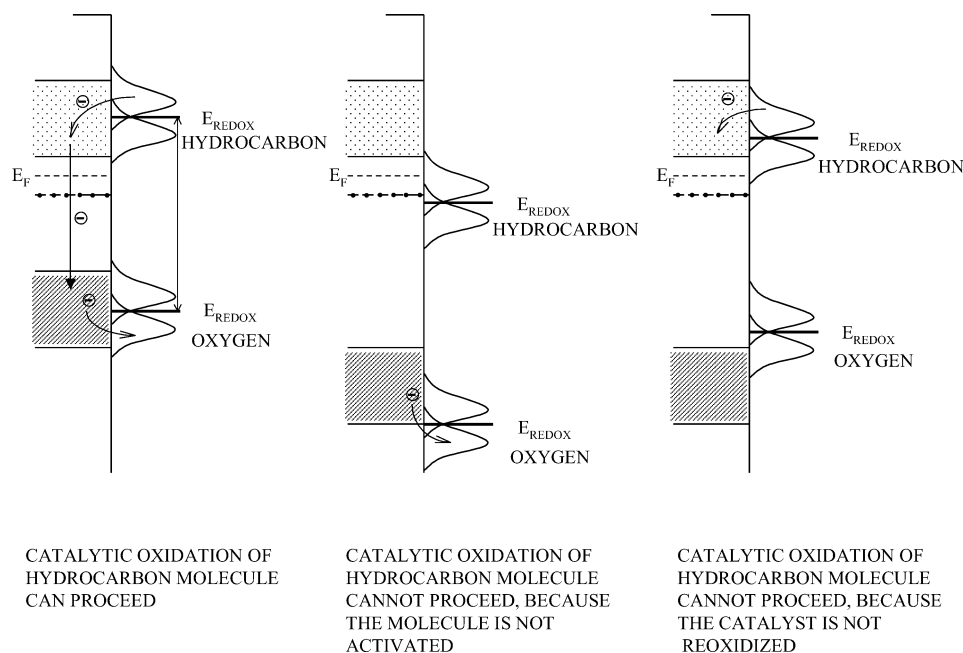


Fig. 1. Scheme of electron transfer across the adsorbate/oxide interface in the course of the heterogeneous catalytic oxidation of hydrocarbon molecules by gas phase oxygen.

shift the Fermi level, (c) generation of surface defects, which will create a broad distribution of surface electronic states mediating the exchange of electrons between the reacting adsorbed molecule and the surface of the oxide catalyst, or (d) application of an external potential. One should add that in the electronic theory no attention has been paid to the important role of the distribution of the electrons in the reacting molecule and the possibility that different orbitals participate in the interaction with the solid surface depending on the way the molecule becomes adsorbed.

The spectacular development of surface science techniques and theoretical computational methods in the past decades, together with the rapid growth of computer power, enables better understanding of the mechanism of electron transfer across a gas–solid interface and hence of the way an organic molecule reacts at the surface of a catalyst. Ample experimental evidence had indicated that catalytic transformations are local phenomena, in which active sites, composed of a transition metal ion and oxide ions that are present at the catalyst surface, are involved [23]. Moreover, it was soon understood that the surface of a solid oxide contains complex imperfections, which play the role of local surface donor or acceptor levels [24]. These levels, located usually in the band gap, may mediate the transfer of electrons between the solid and the adsorbed molecules. It became also clear that activity and selectivity in catalytic reactions are functions of many parameters characterizing the catalyst, the reactants, and the reactor [25]. Nevertheless, the transfer of electrons between the solid catalyst and the reactants remains one of the important factors, because the cleavage of the C–H bond, in which it is involved, is usually the rate-determining step of the oxidation process.

In the following the electronic properties of ideal as well as modified (by ionic surface vacancies and by doping with potassium as well as by support on titania)  $V_2O_5(010)$  surfaces are discussed. Further, the mechanism of electron transfer between organic molecules and solid catalysts is examined using results of quantum-chemical calculations,

which are performed for the interaction between methane and vanadium oxide (V), taken as an example of a transition oxide catalyst. Since it may be assumed that the first stage of the oxidation reaction, the cleavage of the C–H bond, is similar for all alkane molecules and the different reaction pathways observed are due to the differences in consecutive transformations of the resulting alkyl groups, methane is taken as the simplest representative of an alkane molecule for description of the cleavage of the C–H bond. The objective of present studies is to find the optimal adsorption sites for two fragments ( $CH_3$  and H radicals) at the vanadia surface; therefore preceding activation of the methane molecule is assumed. The results of calculations are compared with the results of electrocatalytic oxidation of catechol on an electrode composed of vanadium oxide supported on titania, which enable the demonstration that vanadium energy levels situated in the band gap of titania mediate electron transfer and make the oxidation reaction possible.

## 2. Quantum-chemical calculations

### 2.1. Ideal $V_2O_5(010)$ surface

To study the  $V_2O_5(010)$  surface a local cluster model ( $V_{10}O_{31}$ ) is used, based on the assumption that the chemical behavior of selected surface sites can be described by finite sections ( $V_{10}O_{31}$ ) cut out from the oxide surface, where dangling bonds are, for example, saturated by hydrogen atoms, leading to the  $V_{10}O_{31}H_{12}$  cluster (see Fig. 2), to obtain a neutral cut of the surface. Such sections, called surface clusters, are treated as fictitious molecules (with or without adsorbed molecules); therefore their electronic structure can be obtained from standard quantum chemical methods. In our case the DFT approach is applied [26–28], which in recent years has become the most successful method for studying the surfaces and bulks as well as the

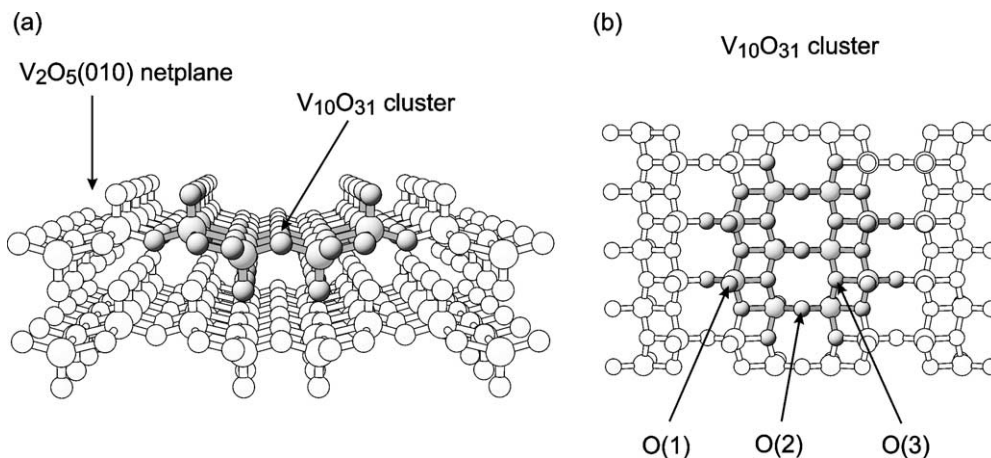


Fig. 2. Geometric structure of an orthorhombic bulk  $V_2O_5$ : (a) stacking (010) netplane where the selected  $V_{10}O_{31}$  cluster is marked, (b)  $V_2O_5(010)$  surface where  $V_{10}O_{31}$  cluster, as well as structurally different surface oxygen centers O(1), O(2), O(3), is marked. Vanadium and oxygen centers are shown as large and small balls, respectively, with connecting sticks indicating nearest neighbor relation.

interface interactions. The electronic structure of surface clusters is discussed by means of such parameters as atomic charges [29], bond orders [30], total energies, or densities of states (DOS). The reliability of the  $V_{10}O_{31}H_{10}$  cluster model is discussed elsewhere [31–37].

Vanadium pentoxide forms an orthorhombic-layer-type lattice [38]. The  $V_2O_5(010)$  surface [39] represents the preferred cleavage plane of the crystal; therefore its structure is mainly determined by surface local V–O bonding with almost no influence of the stacking crystal planes. There are three different (due to coordination number), oxygen centers accessible for incoming molecules (no steric hindrance) present at this surface: terminal (vanadyl) oxygen, O(1), coordinated to one vanadium atom through a short bond, and bridging oxygens, O(2)/O(3), coordinated to two or three vanadium atoms; see Fig. 2b. In addition, the surface exposes bare vanadium centers connected to bridging oxygen centers.

The detailed results of the calculations have been published elsewhere [31–37]; here only general conclusions are given. A comparison between the calculated atom charges and bond orders shows very close similarity between the one-layer ( $V_{10}O_{31}$ ) and two-layer ( $V_{20}O_{62}$ ) clusters [37], which confirms weak interlayer binding and a layer-type material. The charges of different oxygen centers scale with their coordination numbers and indicate that the bridging oxygen is more nucleophilic ( $q = -0.70/-0.87$  for O(2)/O(3)) than the terminal oxygen ( $q = -0.34$ ), which becomes important in view of the reactivity of the different sites with respect to surface chemical reactions. Atomic charges obtained from Mulliken analysis for both V and O centers are smaller than the formal valence charges, which indicates sizeable covalent contributions to interatomic binding inside the surface layers of  $V_2O_5(010)$ . The values of the bond orders suggest that terminal oxygen forms a very strong double bond, whereas all bridging oxygen sites are connected to their neighboring vanadium atoms by bonds weaker than single bonds. Altogether the bonding in the  $V_2O_5(010)$  surface is characterized as a mixture of ionic and covalent contributions.

The energetic distribution of the Kohn–Sham valence levels in the cluster can be described by the total density of states (DOS) with a possibility of its decomposition into partial (atom projected) densities, PDOS. Figure 3 shows DOS and PDOS for the  $V_{10}O_{31}H_{12}$  cluster (Fig. 3a), where the V contributions, as well as those from vanadyl and bridging oxygens, are included. The curves are smoothed by gaussian level broadening (FWHM of 0.8 eV). The energy region of the occupied level is separated from that of the empty levels by a thin vertical line. The total DOS in the region between  $-7$  and  $0$  eV shows a multippeak structure that agrees reasonably with the angle-resolved UPS experiment, see Fig. 3b [32,40]. The theoretical analysis assigns the most prominent central peak to terminal oxygen O(1) and two peripheral peaks at the top and bottom of the valence region to mixtures of vanadium with bridging oxygen atoms. The valence

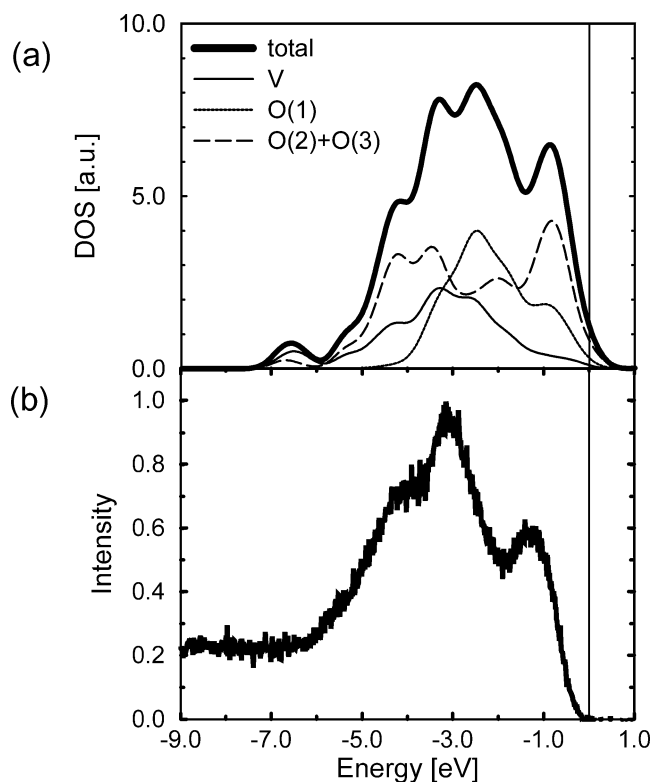


Fig. 3. (a) Total (DOS) and atom projected (PDOS) densities of states curves of the  $V_{10}O_{31}H_{12}$  cluster modeling the  $V_2O_5(010)$  surface. For further details see text. (b) Angle-resolved He-II ultraviolet photoemission spectrum of a  $V_2O_5(010)$  surface sample taken at normal incidence from Refs. [32,40].

and conduction bands (associated with the vanadium contribution) are isolated by an energy gap of about 2 eV.

## 2.2. Modified $V_2O_5(010)$ surface

Interaction of the surface with the incoming molecule requires fulfillment of simple quantum-chemical rules connected with bond formation. This means in particular that the energies of chemically active molecular orbitals (LUMO, HOMO) of the molecule should lie either below the top of valence bands or above the bottom of conduction bands of the surface orbitals. However, defects, dopants, etc. create additional local surface energy states, which may mediate the transfer of electrons. To secure the overlap the symmetry of interacting orbitals should also be the same. This requirement is easy to fulfill since the molecule can orient itself in a different way with respect to the surface.

### 2.2.1. Surface oxygen vacancies

Catalytic properties of all oxide-based catalysts depend strongly on their ability to provide surface oxygen as a reactant. Therefore, a theoretical study of chemical/catalytic properties of structurally different surface oxygen centers, as well as electronic/energetic properties of oxygen vacancies created due to oxidation reactions, can elucidate details of the reaction steps. Surface oxygen vacancies have

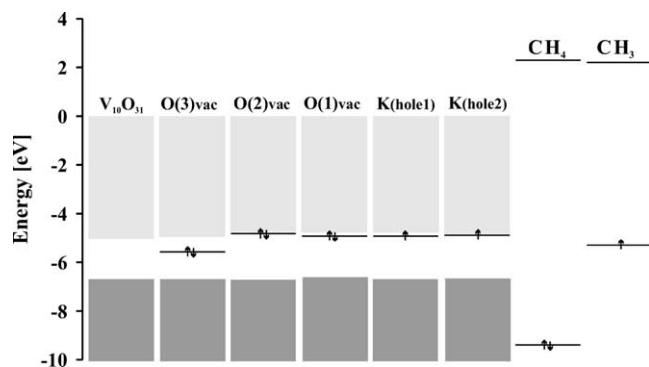


Fig. 4. Molecular energy diagram for the interaction of methane and  $\text{CH}_3$  radical with  $\text{V}_{10}\text{O}_{31}\text{H}_{12}$  cluster modeling ideal  $\text{V}_2\text{O}_5(010)$  surface (column denoted as  $\text{V}_{10}\text{O}_{31}$ ), with  $\text{V}_{10}\text{O}_{30}\text{H}_{12}$  cluster modeling the formation of O(3), O(2), and O(1) vacancies (columns denoted as O(3)vac, O(2)vac, and O(1)vac, respectively), as well as with  $\text{K}/\text{V}_{10}\text{O}_{31}\text{H}_{12}$  cluster modeling the adsorption of potassium at the  $\text{V}_2\text{O}_5(010)$  surface (columns denoted as K(hole1) and K(hole2)). Dark shaded columns refer to densely occupied energy levels (conduction bands) whereas light shaded columns to empty levels (valence bands) of the appropriate clusters. Local states occurring for modified surfaces are shown. For further details see text.

been studied for the  $\text{V}_2\text{O}_5(010)$  surface by ab initio DFT cluster calculations, where one of three structurally different surface oxygens was removed from the surface cluster and the electronic structure of the resulting cluster with vacancy ( $\text{V}_{10}\text{O}_{30}$ ) was re-evaluated [34–37]. The results of the calculations point out that oxygen is bound to its substrate environment very strongly (energy for vacancy formation ranges between 6.5 and 7.2 eV) and may not be removed in one single step during an oxidation reaction. However, pre-adsorbed atoms or molecules may weaken the surface binding of the oxygen and facilitate the oxidation process. Formation of surface oxygen vacancies leads to local relaxation and results in chemical reduction of the nearby metal sites. For cluster with vacancies the local occupied  $3d$  vanadium level appears above the  $\text{O}2sp$  valence region (see Fig. 4a), which substantiates the microscopic picture of chemical reduction of the metal sites observed also in photoemission experiments [41]. Formation of surface vacancies by removing O(2) or O(1) sites creates a local doubly occupied state that lies very near to the conduction band, whereas O(3) vacancies creates that state in the middle between the valence and conduction bands.

### 2.2.2. Alkali metal dopants

From experimental studies on oxidative dehydrogenation of propane it is known that potassium exhibits the strongest effect in increasing the selectivity of  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalysts. To study the dopant effect on the electronic/catalytic properties of  $\text{V}_2\text{O}_5(010)$  surface potassium is adsorbed at the  $\text{V}_{10}\text{O}_{31}\text{H}_{12}$  cluster. Results of ab initio DFT cluster calculations point out two places for potassium adsorption: the hole between four vanadyl O(1) oxygen sites—referred to as hole 1—and the hole between the bridging O(2) and O(3) oxygen sites—referred to as hole 2. Potassium is found to interact with the surface with relatively large energies ( $\sim 3.5$

and 2.8 eV/mol for hole 1 and hole 2, respectively). It is stabilized as a cation, donating one electron to the cluster. Adsorption of potassium results in the formation of a singly occupied local state of  $\text{V}3d$  character that lies close to the conduction band (see Fig. 4). After potassium is adsorbed, bonding of oxygen sites with vanadium becomes weakened, which makes surface oxygens more active. However, due to short-range effects the affected oxygen sites are at the same time sterically blocked by the adsorbed potassium.

### 2.2.3. $\text{V}_2\text{O}_5/\text{TiO}_2$ system

The properties of vanadium–oxygen clusters may be also modified by depositing them on oxide supports. Titanium oxide (IV) is the most commonly used support applied in many industrial processes. In order to study the support effect we have selected a  $\text{V}_2\text{O}_9/\text{Ti}_3\text{O}_{13}$  cluster (see Fig. 5) in which the support layer is larger than the supported one. We have limited the vanadia layer to a  $\text{V}_2\text{O}_9$  cluster, because the objective of our calculations was to compare isolated and supported clusters and to find influence of the support, which should be independent of the cluster size. Deposition of a  $\text{V}_2\text{O}_9$  cluster on a  $\text{Ti}_3\text{O}_{13}$  support changes only the nucleophilicity of the bridging oxygen ( $q_{\text{O}(2)}$ ) decreases from  $-0.63$  to  $-0.80$ ) and leads to weakening of the  $\text{V}-\text{O}(2)$  bonds, which results in more mobile/active O(2) oxygen.

The schematic band structure of  $\text{V}_2\text{O}_5/\text{TiO}_2$  as compared to  $\text{V}_2\text{O}_5$  and  $\text{TiO}_2$  is represented in Fig. 6. In addition, the modification of the band structure as the result of the formation of oxygen vacancies in the  $\text{V}_2\text{O}_9$  subcluster is also given. As expected, the valence band edge and the bottom of the conductivity band in the titanium cluster lie higher than those in the vanadium cluster. In the vanadia on titania cluster, vanadium levels are located in the band gap of the titanium oxide cluster. The oxygen vacancy level is situated at the bottom of the conductivity band in the  $\text{V}-\text{O}$  cluster, whereas it lies above the valence band for the  $\text{V}-\text{O}/\text{Ti}-\text{O}$  cluster.

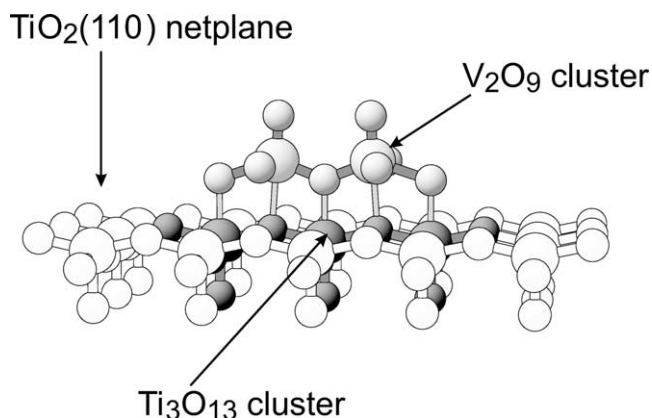


Fig. 5. Model for vanadia supported on titania. Geometric structure of  $\text{TiO}_2(110)$  netplane is given and the  $\text{V}_2\text{O}_9$  cluster used to mimic vanadia as well as  $\text{Ti}_3\text{O}_{13}$  cluster applied to model titania are marked. Vanadium and titanium centers are shown as large balls whereas oxygen centers are shown as small balls, with connecting sticks indicating nearest neighbor relation.

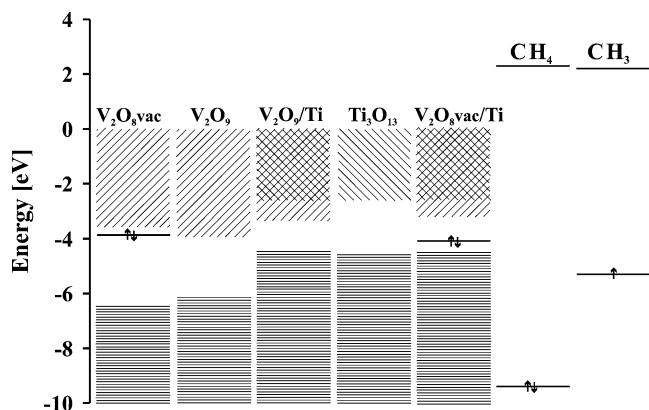


Fig. 6. Molecular energy diagram for the interaction of methane and  $\text{CH}_3$  radical with  $\text{V}_2\text{O}_5$ ,  $\text{TiO}_2$ , and  $\text{V}_2\text{O}_5$  supported on  $\text{TiO}_2$ . To model the  $\text{V}_2\text{O}_5(010)$  surface the  $\text{V}_2\text{O}_9\text{H}_8$  cluster (column denoted as  $\text{V}_2\text{O}_9$ ) is used. The same surface with a vacancy is modeled by  $\text{V}_2\text{O}_8\text{H}_9$  cluster (column denoted as  $\text{V}_2\text{O}_8$ ), vanadia supported on titania by the  $\text{V}_2\text{O}_9\text{H}_8/\text{Ti}_3\text{O}_{13}\text{H}_{14}$  cluster (column denoted as  $\text{V}_2\text{O}_9/\text{Ti}$ ), titania by the  $\text{Ti}_3\text{O}_{13}\text{H}_{14}$  cluster (column  $\text{Ti}_3\text{O}_{13}$ ), and formation of O(2) vacancy in  $\text{V}_2\text{O}_9$  cluster supported on titania by the  $\text{V}_2\text{O}_8\text{H}_8/\text{Ti}_3\text{O}_{13}\text{H}_{14}$  cluster (column  $\text{V}_2\text{O}_8\text{vac}/\text{Ti}$ ). Dark shaded columns refer to occupied energy levels whereas light shaded columns refer to empty levels of the cluster. Local states occurring for modified surface are shown. For further details see text.

### 3. Discussion

#### 3.1. Methane/ $\text{V}_2\text{O}_5(010)$ interaction

Figure 4 gives a simple molecular orbital diagram of methane interacting with a  $\text{V}_{10}\text{O}_{31}\text{H}_{12}$  cluster modeling the  $\text{V}_2\text{O}_5(010)$  surface. On the left side the valence and conduction bands of the ideal cluster, clusters with different oxygen vacancies, and clusters doped with potassium are schematically drawn, whereas the right side illustrates the HOMO and LUMO of  $\text{CH}_4$  and  $\text{CH}_3$  species.

It may be seen that the HOMO of methane is located in the energy range of the valence band of the solid; therefore no interaction can be expected. Its LUMO partner lies very high, so transfer of electrons from the solid would require very high energy. The energies of interacting systems may be made to match either by activation of the reacting molecule or by modification of the electronic structure of the solid surface. Activation of  $\text{CH}_4$  via cleavage of the C–H bond of methane results in the formation of  $\text{CH}_3$  and H radicals. The position of the SOMO of methyl species (located near the bottom of the conductivity band) enables facile transfer of one electron to the conductivity band of the solid. This will lead to the formation of  $\text{CH}_3^+$  species whose energy level is shifted downward and matches the occupied levels of the valence band. A bond may thus be formed between the HOMO of surface oxygen and the LUMO of methyl species, resulting in the formation of a surface methoxy group. The energy level of the hydrogen radical matches the conductivity band and electron transfer to the surface occurs with the formation of a surface OH group.

This is confirmed by ab initio DFT cluster calculations on  $\text{CH}_4$  interacting with a  $\text{V}_6\text{O}_{20}\text{H}_{10}$  cluster that models the  $\text{V}_2\text{O}_5(010)$  surface. A repulsive potential is found for a methane molecule approaching the surface irrespective of its orientation. Therefore, a priori activation of  $\text{CH}_4$  is assumed and the adsorption of isolated fragments ( $\text{CH}_3$  and H) is studied. The results of the calculations indicate that the  $\text{CH}_3$  fragment is preferentially adsorbed at the doubly coordinated oxygen site O(2) ( $E_b = 1.3$  eV), forming an O(2)–C bond ( $R_{\text{O}(2)\text{-C}} = 1.46$  Å), whereas the H radical becomes stabilized at the terminal oxygen ( $E_b = 2.25$  eV), leading to the typical O(1)–H bond ( $R_{\text{O}(1)\text{-H}} = 0.99$  Å); see Figs. 7a and 7b, case I. However, moving the fragments further apart lowers the total energy of the system (see Fig. 7b, case II) and indicates possible H and  $\text{CH}_3$  surface diffusion. Both fragments transfer electrons to the surface cluster, which results in the weakening of V–O surface bonds.

A general conclusion can thus be formulated that the cleavage of the C–H bond of primary carbon proceeds with the transfer of two electrons to the empty vanadium surface levels and the formation of adsorbed alkoxy and surface hydroxyl species as proposed in [22].

Generation of local energy levels in the band gap of the  $\text{V}_2\text{O}_5$  through formation of surface oxygen vacancies (local level doubly occupied) or doping with potassium (local level singly occupied) has a strong influence on the types of species that are formed as the result of the cleavage of the C–H bond, and hence the  $\text{CH}_3$ /surface interaction can be different. This is checked by simple calculations where the  $\text{V}_2\text{O}_9\text{H}_8$  cluster is taken as the model for the  $\text{V}_2\text{O}_5(010)$  surface and its interaction with the  $\text{CH}_3$  species is examined. Approaching the  $\text{CH}_3$  radical to doubly coordinated oxygen in a nondefected cluster results in the formation of an alkoxy group ( $R_{\text{O}(2)\text{-C}} = 1.42$  Å), where the distance of the carbon atom to the nearest vanadium  $R_{\text{V-C}} = 2.86$  Å. The adsorption energy  $E_b = 0.91$  eV is smaller than that obtained for a bigger  $\text{V}_6\text{O}_{20}\text{H}_{10}$  cluster, showing the dependence of the results on cluster size and the limitations of the cluster approach. Interaction of the methyl radical with the  $\text{V}_2\text{O}_8\text{H}_8$  cluster, which models the O(2) vacancy, gives an adsorption energy ( $E_b = 1.92$  eV) almost twice as large as for an ideal  $\text{V}_2\text{O}_9$  cluster. Here, the  $\text{CH}_3$  species approaches the surface more closely,  $R_{\text{V-C}} = 2.30$  Å, no alkoxy group is formed, and the surface becomes blocked by strongly bound chemisorbed species. This is in line with earlier calculations [42] performed for single V– $\text{O}_n$  pseudomolecules, which showed that a bare vanadium site has a tendency to bind a methyl group. The electron transfer, which is different in both cases (to the surface  $Q_{\text{CH}_3} = +0.26$  for the  $\text{V}_2\text{O}_9\text{H}_8$  cluster, and from the cluster  $Q_{\text{CH}_3} = -0.13$  for clusters with vacancies,  $\text{V}_2\text{O}_8\text{H}_8$ ), can be explained by using the simple molecular orbital diagram given in Fig. 6. The local doubly occupied state generated via formation of oxygen vacancies lies above the SOMO of  $\text{CH}_3$ , which enables the transfer of electrons into the organic species. The same electron trans-

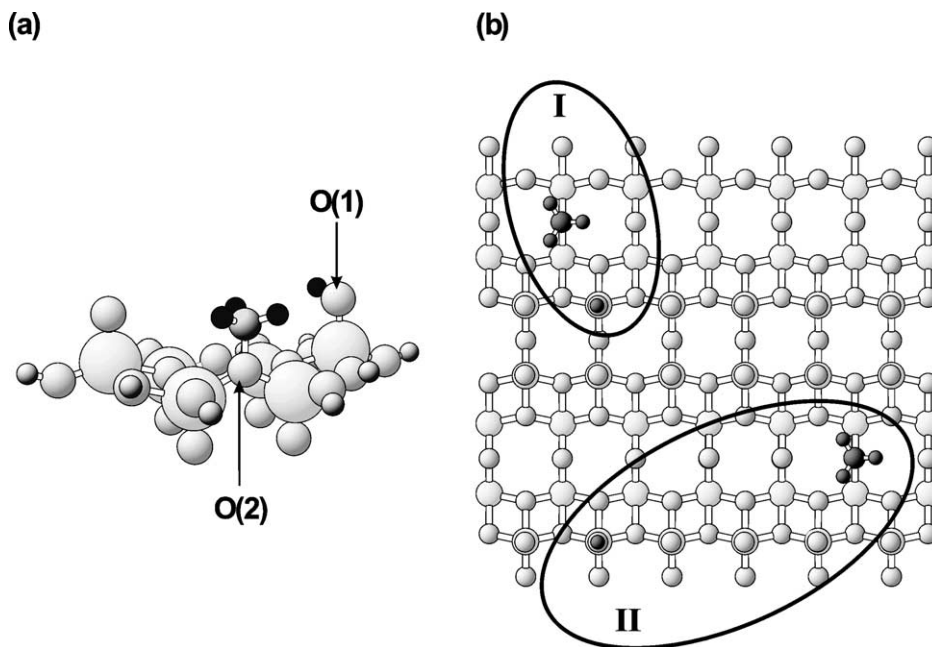


Fig. 7. (a) Interaction of  $V_6O_{20}H_{10}$  with isolated  $CH_3$  and H radicals obtained after  $CH_4$  activation by homolytic cleavage of the C–H bond. (b) Minimalization of total energy by moving apart the adsorbed species from (I) into (II) cases at the  $V_2O_5(010)$  surface. Vanadium and oxygen centers are shown as large and small balls, respectively, with connecting sticks indicating the nearest neighbor relation. Carbon and hydrogen atoms of  $CH_3$  and H radicals are marked as dark large and small balls, respectively.

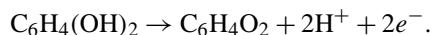
fer is expected to happen for the  $V_{10}O_{31}H_{12}$  cluster in the cases of O(2) and O(1) vacancies (see the relative position of levels in Fig. 4) as well as for clusters doped by potassium (see Fig. 4). Created local states mediate the electron transfer and decide on its direction.

In the case of a V–O/Ti–O cluster the energy level of the  $CH_3$  species lies in the region of the valence band of the solid and no transfer of electrons from the  $CH_3$  species to the solid, i.e., no oxidation of these species, could be expected. This is a result of the shift of the upper edge of the valence band of the  $Ti_3O_{13}$  cluster upward by about 2 eV in comparison with the  $V_2O_9$  cluster and the narrowing of the band gap to less than 2 eV. The experimental results give bandgaps of 3.0 eV for  $TiO_2$  and 2.2 eV for  $V_2O_5$ , the energy of the upper edge of the valence band being similar. This indicates that the cluster is too small to represent the changes of the properties of vanadia supported on titania, the results being very sensitive to the way saturation of the dangling bonds by hydrogen atoms is carried out. Nevertheless, the results presented in Fig. 6 indicate that deposition of vanadia on titania generates empty energy levels in the band gap of titania, which may mediate the transfer of electrons between the alkyl radical and the surface.

### 3.2. Comparison with electrocatalytic oxidation on $V_2O_5/TiO_2$ electrodes

The role of vanadium ions as sites involved as acceptor levels of electrons transferred from a reacting hydrocarbon molecule and responsible for its activation is corroborated by the results of electrocatalytic oxidation of catechol on

an electrode composed of  $TiO_2$  with supported vanadium ions. The cyclic voltammetric curve on such an electrode shows two redox levels corresponding to the reduction and oxidation of  $V^{5+}/V^{4+}$  and  $V^{4+}/V^{3+}$  couples, from which the positions of their redox levels in the band gap of  $TiO_2$  could be estimated [43] (see Fig. 8). When the cyclic voltammetric experiment is carried out in an aqueous solution containing  $1 \times 10^{-2}$  M catechol, a high current is observed in the anodic region of the curve due to the oxidation of catechol according to the reaction



In contrast, no current is observed in the absence of catechol in the solution. The oxidation and reduction currents may be taken as a direct measure of the rate of oxidation of catechol. Direct proportionality is found between the oxidation current, the reduction current, and the number of vanadium ions, as measured by the amount of charge passing through the electrode. This may be taken as evidence that surface vanadium ions are the active sites mediating the transfer of electrons. From the position of the reduction and oxidation extrema on the cyclic voltammetry curve registered during the oxidation of catechol, the redox potential of this reaction can be estimated and compared with surface energy levels generated by vanadium ions at the surface of the titania electrode, which are shown in Fig. 8. It may be seen that the redox potential corresponds to the  $V^{5+}/V^{4+}$  level at the surface of the electrode. In the flat band potential situation, when no external potential is applied the vanadium  $V^{5+}/V^{4+}$  ion level is occupied; thus no transfer of electrons from the oxidizing molecule can take place and no reaction is observed.

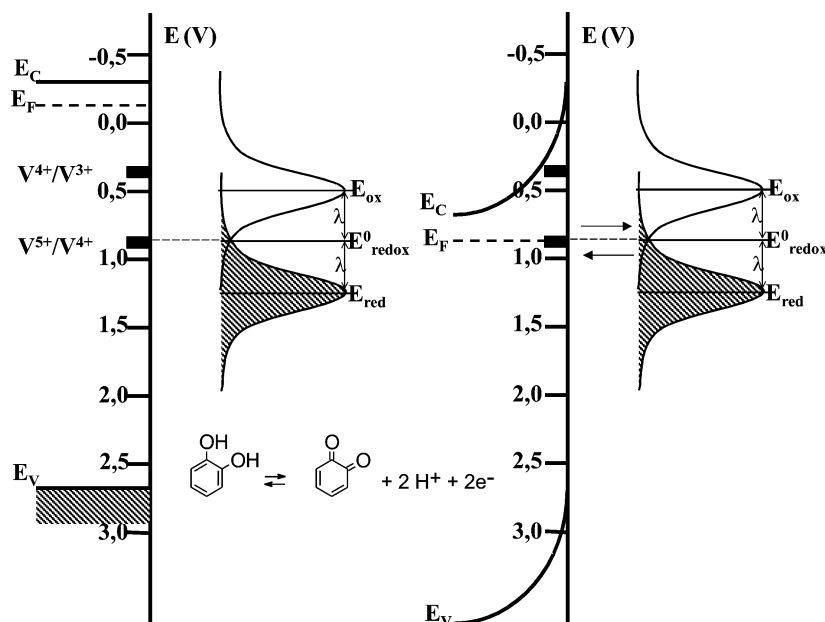


Fig. 8. Energetics of catechol oxidation on vanadium-doped  $\text{TiO}_2$  for the flat band potential (left part) and the applied external potential (right part).

When an external potential is applied, the energy levels of the solid become bent upwards, the Fermi level shifts below the  $\text{V}^{4+}/\text{V}^{3+}$  and  $\text{V}^{5+}/\text{V}^{4+}$  levels, and the electrons from these levels are moved into the conductivity band, leaving them in the vanadium 5+ state. Now these levels can mediate the transfer of electrons from the reacting molecules into the conductivity band of the solid and the oxidation reaction of catechol to *o*-chinon may take place.

$\text{TiO}_2$  is isomorphous with  $\text{VO}_2$ , so vanadium ions forming a solid solution in the lattice of titania will be strongly stabilized in the  $\text{V}^{4+}$  oxidation state and reduction to  $\text{V}^{3+}$  will not occur. The fact that it is observed in electrocatalytic experiments is due to charge compensation by protons, which may enter into the surface layer of the solid [44,45]. Also, the  $\text{V}^{5+}$  state would be unstable in the bulk but can be stabilized at the surface by adsorbing oxygen ions. This conclusion is corroborated by the observation that no redox transformation of vanadium ions can be seen on the voltammetric curve when the experiment is carried out in carefully dehydrated acetonitrile in which no protons are available. This points out to the possible role of hydrogen atoms abstracted in the course of the oxidation of hydrocarbon molecules, under the conditions of heterogeneous oxidation reactions. The hydrogen atoms at the surface of the oxide form OH groups, which may modify the electronic properties of the surface. Formation of stable surface hydroxyl groups has been confirmed by DFT calculations performed for adsorption of one and two hydrogens at structurally different surface oxygen sites, which are present at the  $\text{V}_2\text{O}_5(010)$  surface [37,38,40]. The influence of protons on the electronic state of the surface of an oxide catalyst in both electrocatalytic processes and heterogeneous oxidation reactions by gas-phase oxygen makes the comparison of the results legitimate.

#### 4. Conclusions

Hydrocarbon and oxygen molecules can react along many different reaction pathways, forming a complex network of consecutive and parallel elementary transformations. A catalyst should accelerate only those consecutive steps that transform the initial molecule into a desired product and hinder all other elementary steps leading to the formation of unwanted side-products. To this end the catalyst must be able to perform many functions [4,23]. A fundamental question emerges as to which parameters of the catalyst decide that the reacting system selects a given reaction pathway. A theoretical description by which one can try to answer this question is based on the concept of a potential energy surface. The minima on such a surface correspond to stable states of the system, i.e., to the reactants in the initial state and the products in the final state, whereas local minima account for intermediate products of the investigated reaction network and saddle points to the transition states. It should be remembered that different reaction pathways may be due either to the formation of different transition states or to different transformations of a given transition state. The construction of a potential energy surface for such a complex reaction network is a formidable task [46] and can be solved only by understanding each elementary transformation one by one. In the present paper we have discussed only the initial transformation consisting in the cleavage of the C–H bond in the hydrocarbon molecule. Each of the consecutive elementary transformations may require a transfer of electrons between the reacting molecules and the solid oxide catalysts, which is a much more complex phenomenon than assumed in the electronic theory of catalysis. For interface electron transfer, quantum chemical requirements of matching energy and symmetry of frontier orbitals must be fulfilled. However,



they can be adjusted; this may occur either by activation of adsorbing molecules or by modifying the electronic properties of the solid surface through generation of defects, introduction of dopants, or deposition of the active phase on a support to form oxide monolayer-type catalysts.

By proceeding step by step, potential energy surfaces for the whole network of reactions between different hydrocarbon molecules and oxygen will be constructed, opening the prospect of the molecular design of catalysts tailored to the needs of a required reaction. This will signify a change of the paradigm of catalysis.

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