

# Interaction of oxygen with the surface of vanadia catalysts

J. Słoczyński, R. Grabowski\*, A. Kozłowska, R. Tokarz-Sobieraj, M. Witko

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

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## Abstract

Kinetics of the re-oxidation of the H<sub>2</sub>-reduced or vacuum treated VO<sub>x</sub>/TiO<sub>2</sub> catalyst was studied. It was found that oxygen does not adsorb in the form of ad-atoms on the fully oxidized surface of the catalyst but re-oxidizes oxygen vacancies. On the basis of the surface potential measurements it was concluded that nucleophilic oxygen O<sub>(s)</sub><sup>2-</sup> is almost exclusively present above 550 K on the catalyst surface. The quantum-chemical calculations were supported by the experimental results. The implications of these results for the reaction mechanism of the oxidative dehydrogenation of propane are discussed.

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**Keywords:** Vanadia–titania catalyst; Reduction; Re-oxidation; Oxygen forms; Quantum-chemical calculations

## 1. Introduction

Vanadia oxides, especially dispersed on different supports, are active and selective catalysts of redox processes such as catalytic reduction of nitrous oxides [1], oxidation and oxidative dehydrogenation of hydrocarbons (ODH) [2]. One of the most important problems, which need to be explained for understanding the mechanism of the catalyst performance, is the comprehension of both the nature of active oxygen and the processes that change its concentration on the surface of the catalyst. Such processes comprise adsorption of oxygen and the reduction and re-oxidation reactions of the catalyst. These reactions were studied for the vanadium catalysts in relation to the Mars van Krevelen mechanism [3], steady state adsorption model (SSAM) [4] or their modifications [5], which were often proposed for the description of the ODH of hydrocarbons.

Investigation of the redox processes is usually performed with the aid of the dynamic TPR and TPO methods [6–8]. The TPR measurements using hydrogen as a reducing agent were reported for V<sub>2</sub>O<sub>5</sub> [9–13], V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> [13–19] and V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> + additives [20–22]. Several works presented results of investigations on the isothermal hydrogen reduction of V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> [23–25] and V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> + KHSO<sub>4</sub> [24]. In some cases, other reducing agents, such as CO [25], NH<sub>3</sub> [26–28],

propane [29] or propene [30], were used. The redox transformations of the vanadium species deposited on the surface of a single crystal of rutile were also investigated by cyclic voltammetry [31].

The reaction mechanisms proposed by some authors implied the existence of two forms of oxygen on the surface of the catalysts: (1) electrophilic oxygen species O<sub>2</sub><sup>-</sup> or O<sup>-</sup>, which are responsible for the combustion reaction of hydrocarbon, and (2) nucleophilic lattice oxygen O<sup>2-</sup>, which takes part in the formation of the products of the partial oxidation to aldehydes, alkenes, carboxylic acids [32]. The (1) is based on the observation, that the transition metal oxides, in which metals easily change the valence number and adsorb considerable amount of oxygen, are active in the processes of the total oxidation of hydrocarbons. There are transition metals like Ni, Co, Fe and Mn which form both moderately thermodynamically stable MeO and less stable oxides of the type Me<sub>2</sub>O<sub>3</sub>, and/or MeO<sub>2</sub>. Thorough discussion concerning the influence of oxygen chemisorption and the different forms of surface oxygen on the activity and selectivity of the catalyst in the oxidation of hydrocarbons can be found in the reviews [32,33]. Presence of the electrophilic oxygen on the surface of many oxide systems was confirmed by the ESR studies [34–36]. However, these studies were carried out at low temperatures and for low concentrations of oxygen to assure a good quality of the ESR spectra. Systematic studies of the oxygen adsorption have not been performed for the vanadia titania catalysts [2,37 and references therein] and there is no reliable data concerning thermally stable oxygen species O<sub>2</sub><sup>-</sup>

\* Corresponding author.

E-mail address: [ncgrabow@cyf-kr.edu.pl](mailto:ncgrabow@cyf-kr.edu.pl) (R. Grabowski).

and O<sup>-</sup> at temperatures close to the temperature of the catalytic reaction.

Theoretical and experimental studies of the oxygen adsorption and the surface reduction and re-oxidation of the vanadia catalysts were undertaken in this paper at the conditions close to that in which the ODH reaction is conducted. The obtained results were used in the discussion of the mechanism of the catalytic reaction.

## 2. Experimental

Pure and potassium promoted V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalysts (denoted further as VTiO and KVTiO) were the same as used in [38,39]. The catalysts were obtained by impregnation of the anatase support (tioxide, specific surface area 48 m<sup>2</sup>/g) with ammonium methavanadate solution at pH 6, followed by drying for 18 h at 120 °C and calcination in a stream of air at 450 °C for 5 h. Potassium was introduced by adding an appropriate amount of potassium nitrate to the methavanadate solution to obtain atomic ratio K/V of 0.1. The content of vanadium in the catalyst was 6.7 wt% corresponding to 1 monolayer of V<sub>2</sub>O<sub>5</sub>, calculated from the crystallographic data (1 monolayer of VO<sub>x</sub> contains 10 atoms of V per nm<sup>2</sup>). The XRD analysis showed the presence of the anatase phase only; no crystalline V<sub>2</sub>O<sub>5</sub> was observed.

The specific surface area of the catalysts was determined using the BET method with nitrogen as an adsorbate. The values of specific surface area of VTiO and KVTiO were 46.0 and 44.7 m<sup>2</sup>/g, respectively, they were thus smaller than that of the anatase.

A Sartorius vacuum microbalance S 3D-V attached to a standard vacuum line was employed to measure the reduction and oxidation rates. A considerable volume of the apparatus provided practically isobaric conditions. Prior to the reduction measurements, the samples were outgassed at room temperature at 0.1 Pa, then were heated in oxygen to an appropriate temperature and, after stabilization of the sample mass, were outgassed again. Such pretreatment of the sample ensured a clean and oxidized surface.

Mass changes on the reduction, recorded at 0.1 s intervals, were used for the calculation of the reduction degree. The measurements were conducted at 623 K and pressure ranges of 2–10 kPa. High purity hydrogen and oxygen (99.999) were used in the reduction and re-oxidation experiments. The rate of re-oxidation of the H<sub>2</sub>-reduced samples was determined after their outgassing at 623 K and 0.1 Pa for 1–2 h and cooling in vacuum to the temperature of a measurement. The uptake of oxygen was evaluated for the catalyst heated in oxygen at the temperature of the measurement and then outgassed for 1 h at 0.1 Pa to a constant mass (vacuum reduced surface). Additional experiments were done for the catalysts in which surface of vanadia was oxidized. In these cases oxygen from the gas phase was removed to the pressure of 1 Pa without further outgassing.

## 3. Theoretical modelling

The process of the interaction of an oxygen molecule with the vanadia catalyst was also investigated by theoretical calculations

using the DFT method and the cluster approach. Previous calculations (bulk and cluster) have shown [40–43] that the nature of electronic binding in the oxide and at its surface can be described reasonably by a cluster as large as V<sub>10</sub>O<sub>31</sub>H<sub>12</sub>. For modelling of the re-oxidation process, clusters without or with various types of oxygen vacancies were first considered. In the next step, the O<sub>2</sub> molecule was adsorbed (parallel and perpendicular to the surface) at the bare vanadium atoms and at the isolated mono-vacancies as well as at the homo and hetero di-vacancies. The adsorption sites and computed geometries of the adsorbed O<sub>2</sub> molecule are shown in Fig. 1, which represents the (0 1 0) surface.

To mimic the adsorption of oxygen at the full-oxidized surface (modelled in the calculations by the V<sub>10</sub>O<sub>31</sub>H<sub>12</sub> cluster), an O<sub>2</sub> molecule was adsorbed at the bare vanadium centres. On the contrary, the reduced surface was simulated by the V<sub>10</sub>O<sub>30</sub>H<sub>12</sub> and V<sub>10</sub>O<sub>29</sub>H<sub>12</sub> clusters with different types of oxygen mono- and di-vacancies. Isolated point defects were created at the surface by removing one surface oxygen atom from structurally different positions at the surface, namely by taking away O(1) terminal (vanadyl) oxygen, coordinated to one vanadium atom, or O(2) bridging oxygen, linked to two vanadium atoms, or O(3) oxygen that bridges three vanadium atoms in the surface (Fig. 1a). A more reduced (0 1 0)V<sub>2</sub>O<sub>5</sub> surface was considered by investigating the V<sub>10</sub>O<sub>29</sub>H<sub>12</sub> clusters with di-vacancies, that were obtained by removing two neighbouring surface oxygen atoms that are of the homo O(1)–O(1), O(2)–O(2), O(3)–O(3) or hetero O(1)–O(2), O(1)–O(3), O(2)–O(3) character in the sense of their coordination types (see Fig. 1b.). For each mono and di-vacancy a separated cluster was used in which the mono-vacancy or di-vacancies were created at the appropriate surface site/sites.

The calculations were carried out by means of ab initio DFT method [44,45] using the StoBe code [46]. The exchange correlation interactions were accounted for by the gradient corrected RPBE functional [47,48]. Kohn–Sham orbitals were represented by linear combinations of atomic orbitals using extended basis sets of contracted Gaussian-type orbitals (CGTO) of double zeta quality with polarization functions for transition metals [44,45]. All atoms except the saturated H atoms were optimized in the studied systems.

## 4. Results and discussion

### 4.1. Re-oxidation of the reduced catalysts

The effect of the H<sub>2</sub>-reduction of the vanadia–titania catalysts at 623 K is almost fully associated with the reduction of the vanadia phase. According to our experiments the stoichiometry of the vanadia catalyst reduction corresponds to the removal of one oxygen atom per vanadium in agreement with the literature data [15–17,19].

The catalysts previously reduced in hydrogen at 623 K to the reduction degree of 5–10% were reoxidized as described in Section 2. Fig. 2 illustrates changes in the re-oxidation degree of the VTiO and KVTiO catalysts at 523 and 623 K and a constant pressure of about 4.5 kPa. On the basis of the presented results, two conclusions can be formulated:

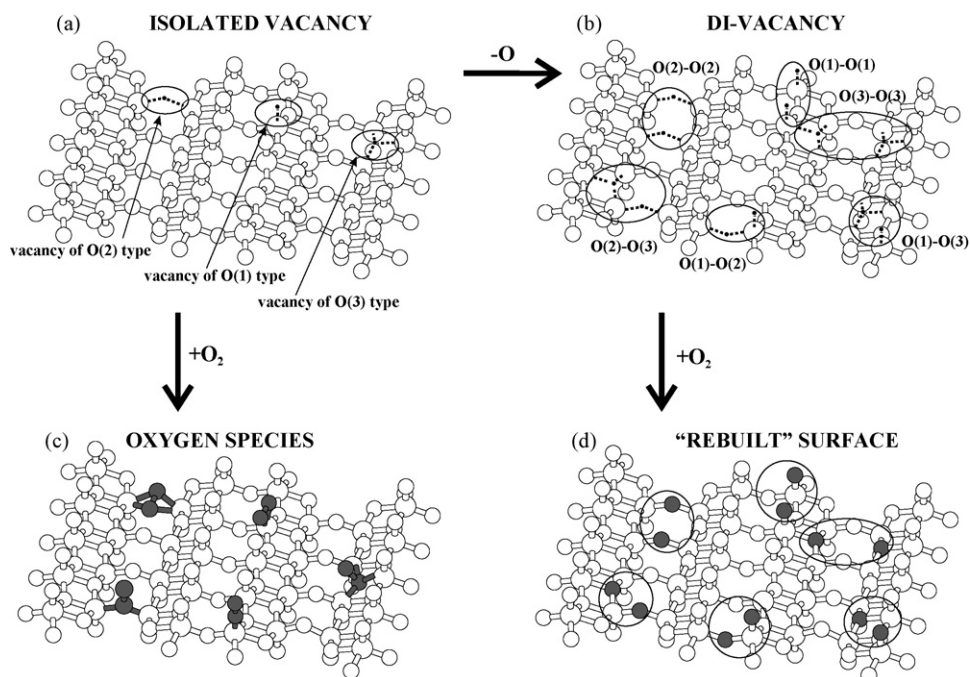


Fig. 1. Sketch of computed equilibrium geometries of an adsorbed  $O_2$  molecule at different monovacancies and di-vacancies sites of the  $V_2O_5$  (0 1 0) surfaces: (a) isolated point defects, (b) di-vacancies, (c) molecular oxygen adsorbs at different isolated vacancies, (d) molecular oxygen adsorbs at di-vacancies. Shaded balls show the  $O_2$  adsorbate species while the surface lattice is sketched by white balls.

- (a) The oxidation of the reduced catalyst occurs in two stages: after a quick reaction, lasting about 5–10 min, a slow process, taking several hours, follows.
- (b) The observed total increase of mass is always less than the mass loss during the reduction. The attained re-oxidation

degree of the samples is around 60–80% and is temperature dependent.

The results of the measurements indicate that the oxygen vacancies created in the vanadia phase are quickly reoxidized in

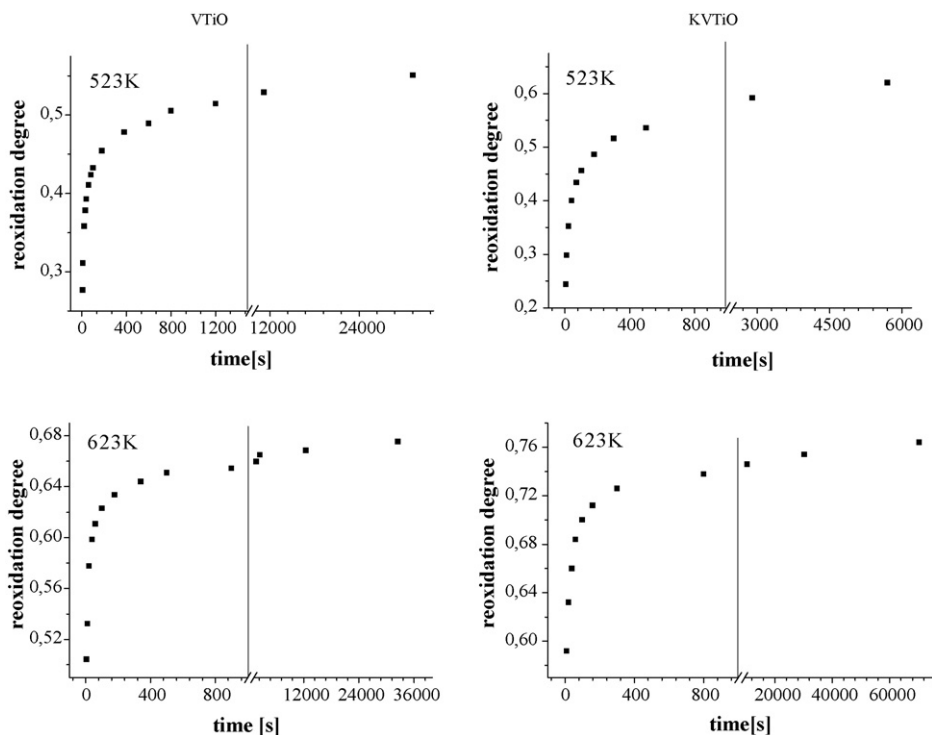


Fig. 2. Dependence of the re-oxidation degree of the reduced VTiO and KVTiO catalysts on time of oxidation. The starting degree of reduction was 5–10% in accordance with the stoichiometry  $O/V = 1$ . Perpendicular lines separate quick and slow stages of the re-oxidation. Oxygen pressure = 4.5 kPa.

the first stage of the reaction. Simultaneously, the re-oxidation measurements show that, during the re-oxidation, the number of the vacancies on the surface of the catalyst is less than indicated by the reduction degree of the stoichiometry  $O/V = 1$ . In the case of the catalysts containing greater amounts of the vanadia phase, when crystallites of  $V_2O_5$  are present, the surface of the samples can be depleted of oxygen vacancies during the reduction and the subsequent outgassing, because of an internal diffusion. This mechanism can be excluded in the case of the samples studied on account of a low content of vanadium oxide and its high dispersion. The reduction of the vanadia phase seems, however, to be accompanied by a slight reduction of the  $TiO_2$  carrier, pointing to a synergy in the system. In the  $VO_x/TiO_2$  system, additional oxygen vacancies can be formed in titania as a result of the substitution of  $V^{3+}$  for  $Ti^{4+}$ . The influence of the oxide additives on the formation of the  $O^{2-}$  vacancies in  $TiO_2$  was studied by Shannon [49]. It can be assumed that a part of the vacancies formed diffuse into the carrier, do not take part in the first stage of the reaction and are very slowly oxidized in the second stage of the reaction.

To describe quantitatively the quick stage of the catalyst re-oxidation, the degree of reaction  $\alpha$  must be calculated in relation to the number of the vacancies, which remain on the surface and are available for the quick oxidation. The following equation describes the process of the vacancy re-oxidation



Therefore, it was assumed that the rate of the process is

$$r = \frac{d\alpha}{dt} = k(1 - \alpha)^2, \quad p_{O_2} = \text{constant} \quad (2)$$

which gives, after integration and rearrangement

$$\frac{t}{\Delta m} = \frac{1}{k(\Delta m)_\infty} + \frac{t}{(\Delta m)_\infty} \quad (3)$$

where  $\alpha = \Delta m/(\Delta m)_\infty$ ,  $\Delta m$  is the mass increase corresponding to the re-oxidation after time  $t$  and  $(\Delta m)_\infty$  is the mass increase extrapolated for  $t \rightarrow \infty$ , which is the measure of the number of vacancies having the ability to reoxidize in the quick stage of the re-oxidation, whereas  $k$  is the rate constant of the reaction.

Quantities  $k$  and  $(\Delta m)_\infty$  were determined by fitting Eq. (3) to the experimental data using the least-squares method. The plots of  $\alpha(t)$  calculated on the basis of the determined parameters  $k$  and  $(\Delta m)_\infty$  are presented in Fig. 3.

The experimental data fulfill Eq. (2); the rate of the re-oxidation is proportional to the second power of the vacancy concentration, which indicates that the re-oxidation is connected with the dissociation of molecular oxygen according to Eq. (1). A broader discussion of this mechanism is given in Section 4.3.

#### 4.2. Measurements of the oxygen uptake

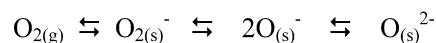
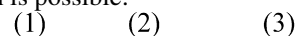
Indications of the microbalance were shifted by a value between 10 and 100 micrograms when oxygen had been introduced at the end of the outgassing under vacuum of the catalyst sample of 0.5 g. The shift was connected to the convection effects and was significant especially for low pressures (below

1–2 Torr). The shifts were determined in the blank tests carried out in the whole range of temperatures and pressures and have allowed to eliminate effects which were not associated with the oxygen uptake. The measurements of the oxygen uptake were repeated several times to obtain reliable results. The average values of the oxygen uptake under pressure of 3–5 kPa for samples evacuated for 1 h at 0.1 Pa are presented in Fig. 4. The results of the measurements for the potassium doped and undoped catalysts were the same in the limits of an error. Moreover, the oxygen uptake was fully reversible in the successive cycles of the adsorption–desorption. If the action of vacuum was very short, i.e. oxygen was only removed from gas phase and the surface of the catalyst was almost fully oxidized, the oxygen adsorption was not observed.

On the basis of the data in Fig. 4, one can calculate that the oxygen uptake is in the range  $(0.8\text{--}1.6) \times 10^{17}$  O atoms/m<sup>2</sup>, depending on the temperature. It is accepted for most metal oxides that the capacity of the oxygen monolayer is  $1 \times 10^{19}$  O atoms/m<sup>2</sup>. This value varies depending on the packing of oxygen atoms and on the oxide structure. The capacity of an oxygen monolayer for oxygen ions  $O^{2-}$  with the hexagonal close-packed structure and the radius of 1.4 Å, is taken as  $1.6 \times 10^{19}$  O atoms/m<sup>2</sup>. However, one can expect that packing of oxygen is looser in the vanadia catalysts, and therefore the lower value of the two was taken as a base of the calculation. Under this assumption, the observed values of the oxygen uptake represent 0.8–1.6% of the oxygen monolayer. The mechanism of the oxygen uptake will be discussed later in this paper.

#### 4.3. Nature of the surface oxygen species

The results described in the previous sections show that the oxygen adsorption leading to the formation of the ad-atoms does not occur on the completely oxidized surface of the vanadia catalysts. The oxygen uptake is observed only in the case when oxygen vacancies are formed on the surface of the vanadia phase as a result of the previous reduction or as a result of the action of vacuum at elevated temperatures. The vacancies formed are quickly replenished with oxygen from the gaseous phase at temperatures above 473 K. A priori, formation of the subsequent forms of oxygen is possible:



The present studies show that the rate of the catalyst oxidation above 473 K is proportional to the second power of the vacancy concentration, which indicates that molecular oxygen  $O_2$  dissociates, which eliminates the  $O_2^-$  form. The measurements of the surface potential have allowed deducing that other forms of the adsorbed oxygen take part in the surface oxidation. As it was shown by Grzybowska et al. [50], oxygen adsorption on the previously outgassed vanadia catalysts leads to an increase of the surface potential, which points to increasing negative charge on the vanadia catalyst surface. On the other hand, the outgassing of the vanadia–titania catalysts under high vacuum leads to a decrease of the surface potential because part of oxygen  $O_{(s)}^{2-}$  from the catalyst surface is liberated to the gas phase and the elec-

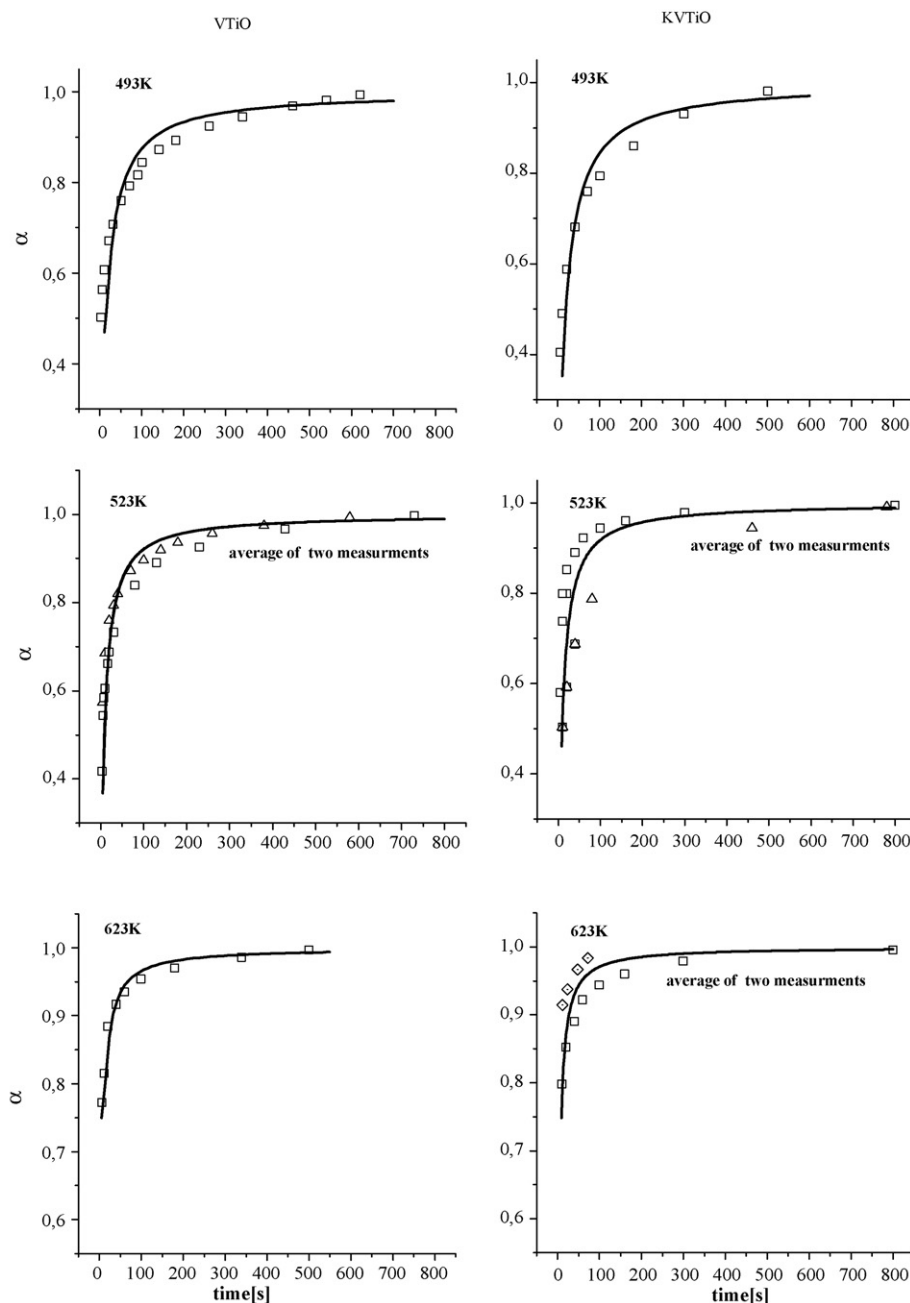


Fig. 3. Dependence of the re-oxidation degree for the reduced VTiO and KVTiO catalysts on time in the quick stage of the re-oxidation. Solid lines: fitted results obtained by solving Eq. (2). Oxygen pressure = 4.5 kPa.

trons are localized on the neighboring vanadium atoms, which leads to their reduction to  $V^{4+}$ . This process is reversible in the oxygen atmosphere and after the oxygen vacancies are filled, an increase of the surface potential is observed.

The measurements of the surface potential for the catalysts studied here were reported in our earlier paper [39], where also the experimental method is described. The oxygen uptake and changes of the surface potential for the same sample of the VTiO catalyst, previously outgassed in vacuum at 623 K, are shown in Fig. 4 as a function of temperature. The surface potential increases significantly up to 625 K and attains a constant value above this temperature (small changes which can be observed

are in limits of an error). The increase of the surface potential observed below 625 K (Fig. 4) can be explained by the increase of the oxygen concentration as well as the oxygen ionization i.e. transition from  $O^-$  to  $O^{2-}$ . However, as it was shown in [36], the incorporation of oxygen into external layers of the vanadia crystallites at higher temperatures of around 473 K, led to an immediate formation of the  $O^{2-}$  ions. The ESR signals characteristic of  $O^-$  or  $O_2^-$  are not observed at this temperature. The lattice oxygen  $O^{2-}$  is the most thermodynamically stable form of oxygen on the surface of the vanadia catalyst, therefore this form will not change at higher temperatures. Thus the stable surface potential at higher temperatures indicates that all

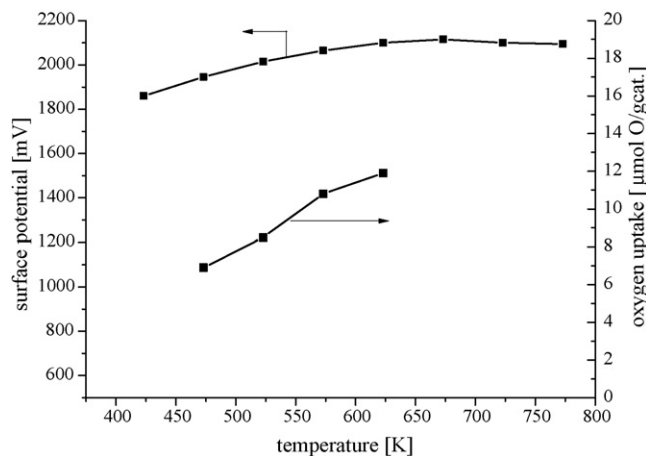


Fig. 4. Comparison of the temperature dependence of the surface potential and oxygen uptake for the VTiO catalysts. Oxygen pressure = 4.5 kPa. Changes of the surface potential were taken from [39].

vacancies which were formed by the action of vacuum at 623 K are filled with  $\text{O}^{2-}$ . Simultaneously, the correlation between the surface potential and the level of the oxygen uptake, which is observed below 550 K, suggests that mainly double charged oxygen is formed also in this range of temperatures and the changes in the surface potential can be explained by an increase of the concentration of  $\text{O}^{2-}$  on the surface of the catalyst.

Results of the studies on the kinetics of the re-oxidation of the reduced VTiO catalysts and on the oxygen uptake in relation to changes of the surface potential lead to the conclusion that the nucleophilic oxygen is the dominant form of oxygen on the surface of the catalyst in the range of temperatures, where the catalytic reactions of the hydrocarbon oxidation (500–600 K) occur. Such statement is confirmed by the energy diagram for the  $\text{O}^-$ ,  $\text{O}_2^-$  and  $\text{O}^{2-}$  surface forms in metal oxide systems [32]. The nucleophilic oxygen can be responsible both for the selective oxidation leading to the formation of the partial oxidation products as well as for the non-selective oxidation. The factor deciding about the selectivity is the way hydrocarbon interacts with the surface oxygen. In our earlier paper [51] concerning the kinetic model of the ODH of propane, it was suggested that, in the selective reaction, the molecule of propane interacted with one surface oxygen atom, while, in the combustion reaction, the attack of several oxygen  $\text{O}_{(s)}^{2-}$  atoms on the propane molecule was needed, resulting in the break of the C–C bonds. The experiments carried out in the anaerobic conditions (the transient experiments) have shown that, as the reduction degree increased, the selectivity to propene increased because the groups of several adjacent oxygen atoms  $\text{O}_{(s)}^{2-}$  were quickly depleted, which limited the combustion of propene. The observation has explained an increase of the selectivity to propene at the steady state condition with an increase of the redox potential of the feed mixture (increase of the propane/ $\text{O}_2$  ratio) as it shown in Fig. 5.

If the electrophilic oxygen  $\text{O}^-$  were responsible for the total oxidation of hydrocarbon then the selectivity of the ODH reaction would increase with the temperature due to the fact that the electrophilic forms of oxygen are unstable and their ionization is shifted to  $\text{O}^{2-}$  with the temperature. A typical situation is

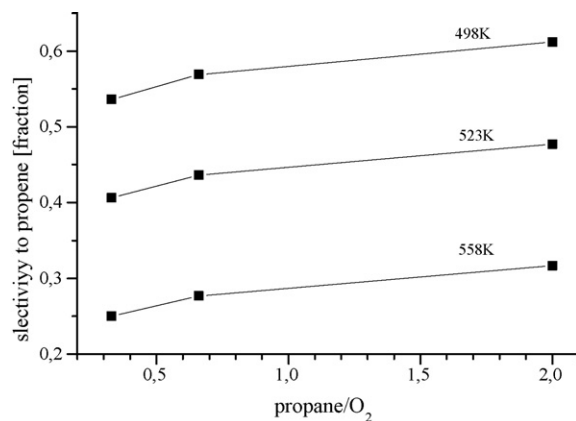


Fig. 5. Dependence of the selectivity to propene in the ODH propane reaction on the VTiO catalyst on the feed mixture redox potential. The propane/ $\text{O}_2$  ratios which are the measure of the redox potential of the feed mixture were taken from [52].

shown in Fig. 6 for two catalysts used in the ODH reaction. For the VTiO catalyst, the decrease of the selectivity with temperature is observed [52], which excludes the participation of the  $\text{O}^-$  form in the hydrocarbon combustion. It does not prevent the operation of such mechanism in the case of the other catalysts. As it is shown in Fig. 6, lower participation of the combustion reaction was observed for the VSiO catalyst [53] at higher temperatures. This dependency agrees with the results obtained by the EPR method [54], showing that the  $\text{O}^-$  ions have unusual thermal stability in this system.

#### 4.4. Theoretical modeling of the interaction of oxygen with vanadia surface

The results of calculations showed that the oxygen molecule does not adsorb at bare vanadium sites that are exposed at an “ideal” surface. An  $\text{O}_2$  molecule approaching the vanadium atom V(5), leads to its pulling out of the position above the bare vanadium center and to the formation of thermodynamically

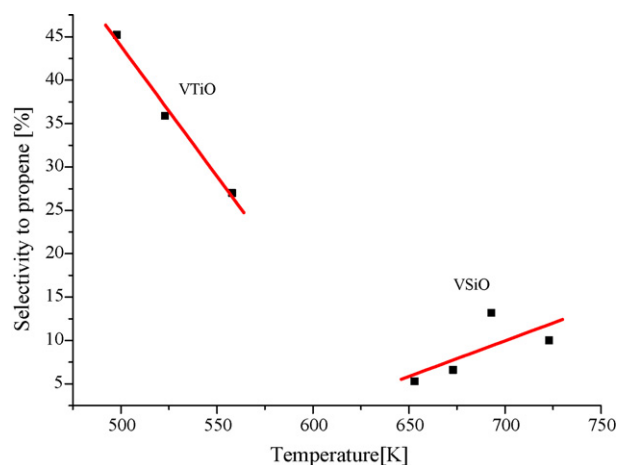


Fig. 6. Comparison of the temperature dependencies of the selectivity to propene for the VTiO and VSiO catalysts. The selectivities correspond to the 5% propane conversion.  $\text{O}_2$ /propane ratio in feed mixture was 1 and 2.75 for the VTiO and VSiO catalysts, respectively. Data were taken from [52,53].

cally unstable oxygen species at the surface. The binding energy is positive for both starting geometries of the adsorbed O<sub>2</sub> molecule and is 1.78 eV for the top-on geometry (where only one O atom of the di-oxygen molecule is bonded with a V atom) and 1.87 eV for the O<sub>2</sub> molecule adsorbed between two bare vanadium centers. Thus, the theoretical modeling has supported the experimental findings that the adsorption of oxygen does not take place at the completely oxidized (“ideal”) surface.

At a considerably reduced surface, which is modeled in the calculations by clusters with various types of vacancy dimmers, the adsorption of an oxygen molecule proceeds spontaneously; the gaseous oxygen dissociates without any barrier and replenishes the oxygen vacancy at the surface. As the result, the reduced surface is reconstructed and attains the ideal geometry (see Fig. 1). The adsorbed oxygen atoms acquire properties of surface oxygen sites, and no differences between them and the “real” surface oxygen sites can be observed. The adsorbed oxygen atoms form typical nucleophilic surface oxygen sites with charges that scale with their coordination: 0.3 for singly coordinated oxygen atoms, 0.7 for oxygen bonded two vanadium atoms and 0.9 for oxygen that link three vanadium centers. The binding energy of the O<sub>2</sub> molecule is close to 6 eV. Similarly to the experimental data, the theoretical results show that the re-oxidation of the reduced surface does not lead to the formation of the ad-atoms at the surface.

Additional oxygen atoms can appear at the reduced surface only as a result of the adsorption of molecular oxygen at isolated monovacancies that will be a result of a small scale reduction of the surface or its partial only re-oxidation. In such cases, molecular oxygen adsorbs at various isolated vacancies – (O(1), O(2), O(3)) – with different geometric orientations (e.g. perpendicular or parallel to the surface), shown in Fig. 1, where the parallel geometry is more stable than the perpendicular geometry.

Upon the stabilization at the surface, the oxygen species undergoes activation indicated by a weakened and stretched O–O bond. The O<sub>2</sub> bond length increases from 1.24 Å in the gas phase to 1.38–1.47 Å; the largest elongation is found for the adsorption of O<sub>2</sub> at vacancies formed at highly coordinated oxygen sites O(3). The increase of the bond length in the adsorbed oxygen molecule is associated with the weakening of the O–O bond. In contrast to the bond order characteristic of the free O<sub>2</sub> molecule (1.87), which indicates almost a double bond, bond orders of adsorbed oxygen species are close to 0.9 for all cases studied, suggesting single O–O bonds.

Oxygen molecule adsorbed at a vacancy assumes charge similar to that of the corresponding lattice oxygen at the undefected, ideal surface. This charge, which is characteristic of the lattice oxygen, is redistributed between the two oxygen atoms of the O<sub>2</sub> adsorbate providing two (instead of one) more electrophilic surface oxygen sites (defined by the Mulliken charges) as compared to the clean, undefected surface.

The activated oxygen molecule can undergo dissociation. Small, negative values of the binding energies (–1.46 eV for O<sub>2</sub> adsorption at O(1) vacancy, –1.27 eV for O<sub>2</sub> adsorption at O(2) vacancy, and 0.08 eV for O<sub>2</sub> adsorption at O(3) vacancy), corresponding to the removal of an oxygen atom from the O<sub>2</sub> adsorbate indicate the presence of active oxygen that can be eas-

ily released from the surface, especially at higher temperatures at which the catalytic reaction takes place.

To conclude it can be said that the degree of surface reduction affects essentially its re-oxidation mechanism. For a slight surface reduction, the re-oxidation process may lead to the formation of active electrophilic oxygen. However, the degree of surface reduction becomes significant in the reaction conditions and many neighboring vacancies are formed. Then, the re-oxidation reaction proceeds according to a different mechanism and does not lead to the formation of ad-atoms as in the case of monovacancies. Consequently, the oxygen molecule undergoes dissociation and refills vacancies leading to the non-defected structure of the surface.

## 5. Conclusions

1. Reduction of the vanadia phase both in hydrogen and under vacuum leads to the formation of oxygen vacancies.
2. The quick process of the vanadia phase re-oxidation is accompanied by a slow oxygen uptake connected with the oxidation of vacancies diffusing to the surface of the catalyst from the bulk TiO<sub>2</sub>.
3. In conditions of the catalytic ODH reaction, the re-oxidation of the vacancies by gaseous oxygen is associated with oxygen dissociation and leads to the formation of the nucleophilic forms O<sup>2-</sup>.
4. Oxygen does not adsorb on the oxidized surface of the catalyst with the formation of the ad-atoms. Conclusions 3 and 4 follow from the results of both theoretical modelling and experimental work.
5. Surface nucleophilic oxygen is probably responsible for the propene formation and the hydrocarbon combustion in the propane ODH reaction on the vanadia–titania catalyst.
6. Experimental and theoretical approaches are parallel and complementary methodologies that can lead to a deep understanding of chemical processes occurring at the catalyst surface.

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