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Quantum-chemical description of the active sites for the selective oxidation of hydrocarbons

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Abstract

Different aspects of quantum chemical modelling of catalytic systems are discussed. Further, the electronic structure of various V_nO_m clusters representing the vanadium pentoxide (010) surface is studied and the reactivity of different surface oxygen sites with respect to adsorption of hydrogen as well as propylene is examined. Results of ab initio HF and DFT calculations are compared with those of the semiempirical INDO-type method. It is found that the different quantum chemical methods lead to the same qualitative results. Satisfactory convergence in cluster properties is achieved for clusters of ten vanadium atoms. The saturation of dangling bonds by hydrogen atoms does not influence the properties of the oxygen centers significantly. Among different oxygen centers the oxygens bridging two bare vanadium atoms are most negatively charged. Hydrogen binds to all inequivalent oxygen sites with the strongest binding occurring for oxygens bridging two vanadium atoms. INDO cluster studies for propylene adsorption/reaction on V_2O_5 (010) show that different approaches of the molecule to the surface yield different surface complexes which can then react to form different products.

Keywords: Quantum chemical calculations; Active sites; Selective oxidation of hydrocarbons

1. Introduction

An understanding of fundamental processes occurring on transition metal surfaces requires the characterization of the physical and chemical properties of the surface, information on the transition complex which is formed at the surface, and detailed insight into reactions between the adsorbates. The catalyst surface is the stage for various reactions including bond formation with the adsorbate, reconstruction of the surface, and penetration of the adsorbates into the surface. Studies on the transition complex derived from the adsorbed molecule and the surface atoms give information about bond making/breaking within the adsorbate as well as about changes in reactivity of bonds in the adsorbate. The results of such analyses allow us to determine which factors are responsible for the route of the reaction leading to the desired product. On the other hand, studies of the basic reaction between the reagents (adsorbates) show that both steric factor (i.e., the mutual orientation of the reacting molecules) and electronic factor (i.e., the activation of the reagent) contribute.

Recent developments in experimental techniques give access to a wide spectrum of information concerning the catalytic reaction on both atomic and electronic levels. In addition to experimental methods, various theoretical approaches (quantum chemical and/or solid state physics based) can be used as tools to study catalytic processes. These tools give fundamen-

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tal insight into the elementary steps of a reaction. Due to rapid advances in both the methodology and in the development in computers theoretical methods can now be applied successfully in parallel and complementary to experimental techniques. The nature of the catalytic reaction can be understood only by the synergy between experiment and theory.

The present paper focuses on the application of quantum chemistry to study active sites which are present at the surface of the vanadium pentoxide (010) surface. After a brief introduction into models used in the theoretical approach to catalysis the different geometrical and electronic approximations applied in the calculations are discussed. Next, systematic studies on models of different size using semiempirical, ab initio HF, and DFT methods are presented. The discussion concerning adsorption sites concentrates on results of Mulliken population analyses. Further, the adsorption of hydrogen at the structurally different oxygen sites is discussed. The results of such a probe reaction are compared with the adsorption/activation of the propylene molecule at the vanadium pentoxide (010) surface.

2. Theoretical approach to catalysis models

All theoretical treatments of catalytic systems are based on *models* which are, by definition, incomplete with respect to the real systems. The coexistence of various alternative or competing models for the same object follows from the fact that different models can reveal different aspects of a system [1]. Each model should fulfil some criteria including selfconsistency (agreement with basic principles accepted by science), simplicity (balance between transparency of the model and its completeness), stability (possibility of introducing some modifications to the model without destroying its internal structure), utility, and generality (prediction on some characteristics not explicitly stated or identification of some connections among distinct objects not evident during elaboration of the model).

In principle, each model requires three conceptional different ingredients. First, the geometric structure of the model system has to be defined. Second, the physics of the interaction between the chosen model geometry and the atoms neglected in the model has to be accounted for. Third, numerical approximations used to describe the physical interaction developing among the atoms have to be specified. Taking into account the different physical background of various mathematical methods the last two ingredients will be discussed together as the physical/chemical models.

2.1. Geometrical models

Based upon the size of the model which approximates the real catalytic system all models can be classified into *molecular models*, *cluster models*, and *slab / bulk models*.

In the molecular model one can study either the isolated molecule of the reactant or the isolated species formed by one atom/ion from the catalyst and the reagent. In the first case, the catalyst substrate is missing completely. However, the action of the catalyst may be allowed for by assuming the different electronic states of the reactants, their mutual orientation, or some deformation of the structure as the result of the interactions with the catalyst. In these studies standard quantum chemical methods, as used for standard chemical reactions, are applied. In the second case, the active center is included but its environment is missing. Here also quantum chemical methods can be used with the atom/ion of the catalyst treated as the reagent in the chemical reaction.

In the cluster model the substrate atoms are cut of the surface/bulk of the catalyst. Clusters can be chosen of different size and geometry, neutral or charged. The basis of the cluster model is the assumption of a localized interaction near the adsorption site thus neglecting long range interactions. Its possible drawback is the incorrect treatment of substrate atoms at the cluster periphery (problem of dangling bonds). This disadvantage manifests itself in the dependence of calculated results on the size and geometry of the cluster leading, in many systems, to slow convergence of the electronic properties with cluster size.

The slab/bulk model treats the catalysts substrate as an infinite system with periodic symmetry. In addition, the adsorbate molecules (reagents) have to be assumed in a 2-dimensional periodic arrangement on the surface (supercell geometry). These systems can be studied with electronic structure methods well known from the calculation of band structures in bulk solids based on density functional theory (DFT). The periodicity constraint may lead to artificially strong coupling between the adsorbate molecules which can be avoided by using very large supercells. However, the computational effort sets an upper limit to the cell sizes that can be treated numerically.

In studies concerning the heterogeneous catalysis all above types of models are applied. However, the cluster model and the slab model which approximate the real catalysts from the opposite directions are most commonly used.

2.2. *Physical / chemical models*

The quantum chemical methods used to treat catalytic systems can be classified into ab initio methods for a quantitative account of small model systems and semiempirical methods for obtaining qualitative trends in large model systems. Amongst the ab initio methods two approaches, the Hartree–Fock (HF) [2] and the Density Functional Theory (DFT) [3] approach, are commonly used.

In the HF approach [2] the exact Hamiltonian H of the system (for given nuclear positions) is used while the wave function is approximated by a finite set of Slater determinants built of one-electron functions (molecular orbitals). The variational principle for the expectation value of H defining the total energy leads to a set of one-electron equations (Hartree–Fock equations) for the orbitals which have to be solved to yield the electronic structure and derived properties.

The DFT approach [3] is based on the Hohenberg–Kohn theorem which states that the total energy of the ground state of a system is a functional of the electron density $\rho(r)$ and assumes its minimum for the exact $\rho(r)$ (variational principle). In the Kohn–Sham extension $\rho(r)$ is expressed by one-electron functions (Kohn–Sham orbitals) and the variational principle leads to a set of equations which are structurally identical to the Hartrre–Fock equations. However, the equations refer to a Hamiltonian whose form is not known. Therefore, further approximations in the Hamiltonian are needed to obtain the electronic structure and derived properties.

In both ab initio approaches the numerical application to clusters used for catalytic systems resorts to representing the orbitals by analytic basis sets (e.g., Gaussians). This yields highly accurate electronic states and potential energy surfaces with minima (characterizing reactants, intermediates, and products) and saddle points (describing transitions).

The various semiempirical methods [4] are based on the same formalism as the ab initio HF method. However, the electron integrals entering the variational equations (and calculated exactly in the ab initio technique) are approximated by experimental data or by fits to ab initio results. This procedure yields more approximate electronic states and potential energy surfaces compared to ab initio treatments but allows to deal computational with much larger systems.

3. Quantum-chemical calculations on V–O clusters

The (010) surface of vanadium pentoxide, V_2O_5, can be characterized as containing edge- and corner-sharing distorted square pyramids

[5,6]. It contains three types of structurally different oxygen centers, the vanadyl oxygen (coordinated to one vanadium atom), the oxygens bridging two vanadyl groups, and the oxygens bridging two bare vanadium centers (the latter two centers being coordinated to two or three vanadium atoms). The smallest cluster which models these three oxygen sites is V_2O_9 cluster of C_{2v} symmetry. It is built of two corner linked square pyramids (see Fig. 1a). The cluster has three dissimilar adsorption sites: site O(a) above a vanadyl group, site O(b) above the oxygen bridging two vanadyl units, and site O(c) above the oxygen bridging two vanadium atoms. In such a cluster cut out of the surface the problem of dangling bonds arises. Therefore, in addition to V_2O_9 cluster, the $V_2O_9H_8$ cluster is considered in which the dangling bonds of the peripheral oxygens are saturated by hydrogen atoms according to the number of the nearest vanadium neighbours (Fig. 1b). A comparison of the results obtained for these two clusters allows a discussion of the importance of the bond saturation (physical ingredient of the model). In addition, a set of different size clusters $V_2O_9H_8$, $V_{10}O_{31}H_{12}$, and $V_{16}O_{49}H_{18}$ (see Fig. 2) is considered. Each bigger cluster of this series includes the next nearest neighbours which are missing in the previous smaller cluster. Such a systematic study allows to discuss changes in the properties of the adsorption sites connected with the changes of the size and geometry of the cluster (geometrical ingredient of the model).

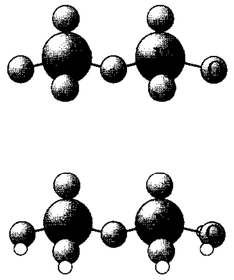

Fig. 1. Vanadium–oxygen clusters modelling the (010) V_2O_5 surface: (a) the unsaturated V_2O_9 cluster, and (b) the saturated by H atoms $V_2O_9H_8$ cluster. The biggest balls denote for V, the smaller for O, and the smallest ones for H atoms.

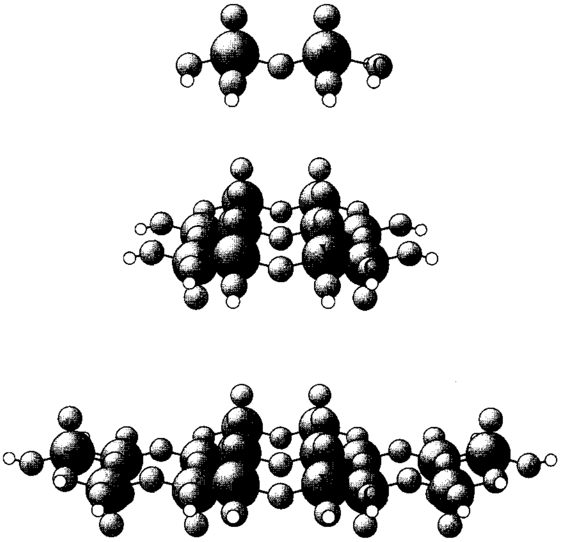

Fig. 2. Different vanadium–oxygen clusters chosen to model the (010) V_2O_5 surface: (a) $V_2O_9H_8$, (b) $V_{10}O_{31}H_{12}$, and (c) $V_{16}O_{49}H_{18}$ clusters. The biggest balls denote for V, the smaller for O, and the smallest ones for H atoms.

The studies are based on calculations using different quantum chemical methods (mathematical ingredient of the model).

In order to discuss the different ingredients of the models the following studies are carried out:

1. ab initio HF calculations for the V_2O_9 and $V_2O_9H_8$ clusters to study the saturation problem;
2. ZINDO, ab initio HF, and DFT calculations for $V_2O_9H_8$ cluster to study the influence of different electronic structure approaches;
3. ZINDO and DFT calculations for $V_2O_9H_8$, $V_{10}O_{31}H_{12}$, and $V_{16}O_{49}H_{18}$ clusters to discuss the geometrical aspect of the cluster model.

The electronic wave functions and derived properties of the clusters are determined using Gaussian basis sets (GTO) [7–9] and pseudopotential [10] in the HF approach, GTO [11] in the DFT treatment, and Slater type orbitals (STO) [12–14] in the ZINDO calculations.

Table 1 summarizes the results of Mulliken population analyses from the calculations mentioned above. The differences in the population analysis results of the V_2O_9 and $V_2O_9H_8$ clusters suggest that the saturation of the V_2O_9 cluster affects mostly the V and the bridging oxygens O(b,c) atoms. This is, however, somewhat misleading because both clusters are characterized by a different number of electrons. The result that saturation contributes only little is illustrated by the electrostatic potential contour maps which are shown in Fig. 3 for both clusters. Here the overall shape of the contours is found to be very similar for both V_2O_9 and $V_2O_9H_8$ clusters. This indicates the minor effect of the saturation.

Results of different quantum chemical treatments (HF, DFT, ZINDO) of the $V_2O_9H_8$ clusters yield the qualitative agreement. The vanadium atom is always positively charged and its charge varies between 0.98 and 1.22 depending on the method. All oxygen sites are negatively charged with the bridging oxygens being more negative than the vanadyl oxygens. The charge difference between the two types of oxygens is smallest in the ZINDO and largest in the HF approach. In general, the atom charges obtained from the DFT and ZINDO calculations are rather similar but somewhat different from the HF data. One possible origin of this discrepancy are differences in the basis sets used in the calculations.

The results of calculations on the $V_2O_9H_8$, $V_{10}O_{31}H_{12}$, and $V_{16}O_{49}H_{18}$ clusters performed with the DFT and ZINDO methods show that the cluster convergence is achieved for $V_{10}O_{31}H_{18}$ cluster. Other studies concerning the electronic structure of vanadium oxide clusters are summarized in [15–17].

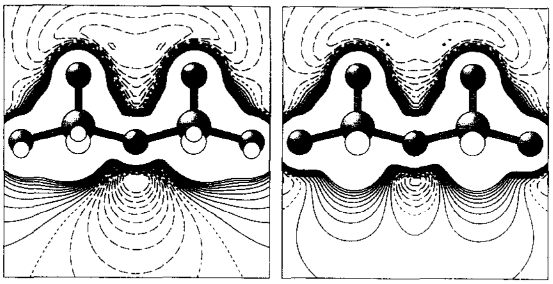

Fig. 3. Electrostatic potential contour maps obtained by HF method for (a) $V_2O_9H_8$, and (b) V_2O_9 clusters.

Table 1
Results of Mulliken population analyses for the vanadium–oxygen, V_2O_9, $V_2O_9H_8$ $V_{10}O_{31}H_{12}$, $V_{16}O_{49}H_{18}$ clusters obtained by HF, DFT and ZINDO methods

Cluster	Method	Number of electrons			Bond order	
		V	O(a)	O(b/c)	V–O (a)	V–O (b/c)
V_2O_9	HF	21.32	8.43	9.33	2.02	0.33
$V_2O_9H_8$	HF	20.96	8.39	8.99	1.97	0.63
$V_2O_9H_8$	DFT	22.02	8.29	8.51	2.17	0.97
$V_{10}O_{31}H_{12}$	DFT	21.47	8.25	8.55	2.17	0.91
$V_{16}O_{49}H_{18}$	DFT	21.73	8.25	8.55	2.16	0.90
$V_2O_9H_8$	ZINDO	21.78	8.42	8.44	2.53	1.17
$V_{10}O_{31}H_{12}$	ZINDO	21.92	8.37	8.45	2.53	1.09
$V_{16}O_{49}H_{18}$	ZINDO	21.92	8.38	8.45	2.52	1.09

4. Adsorption of hydrogen

Adsorption of hydrogen on structurally different oxygen sites of the vanadium pentoxide (010) surface is studied as a model reaction to simulate the first step of selective hydrocarbon oxidation. This reaction proceeds according to the nucleophilic mechanism, i.e., it starts with the activation of the hydrocarbon molecule via abstraction of the hydrogen from the organic molecule near an oxygen center present at the surface. Here the question may be raised as to which of the structurally different oxygen sites of the V_2O_5 (010) surface is involved in hydrogen abstraction from the hydrocarbon.

The interaction of H with the vanadium pentoxide surface is modeled by $V_2O_9H_9^+$ ($V_2O_9H_8$ + H^+) and $V_{10}O_{31}H_{13}^+$ ($V_{10}O_{31}H_{12} + H^+$) clusters. For the smaller cluster calculations by means of HF, DFT, and ZINDO methods are carried out while the larger cluster is examined with the ZINDO methods only. The geometry of the substrate cluster is kept fixed at the bulk geometry. The position of hydrogen is varied perpendicular to the surface for each of the three oxygen sites to give the respective interaction potentials and equilibrium positions. Fig. 4 shows the potential energy curves for hydrogen

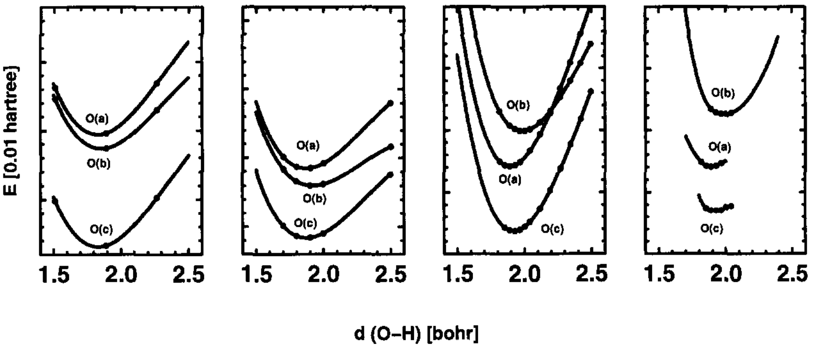

Fig. 4. Potential energy curves for hydrogen adsorption on vanadium–oxygen clusters: (a) H adsorption on $V_2O_9H_8$ cluster-HF calculations, (b) H adsorption on $V_2O_9H_8$ cluster-DFT calculations, (c) H adsorption on $V_2O_9H_8$ cluster-ZINDO calculations, (d) H adsorption on $V_{10}O_{31}H_{12}$ cluster-ZINDO calculations.

adsorption on $V_2O_9H_8$ cluster calculated with the HF, DFT, and ZINDO methods (Fig. 4a–4c) and on $V_{10}O_{31}H_{12}$ cluster calculated using ZINDO method (Fig. 4d). The results of the calculations suggest that hydrogen can stabilize at all adsorption sites forming a hydroxyl group. The strongest binding occurs with the oxygens bridging two vanadium atoms. These conclusions depend neither on the geometrical model nor on the quantum chemical method. It suggests that in the first step of the nucleophilic hydrocarbon oxidation bridging oxygens rather than vanadyl ones will be involved. More detailed studies on hydrogen adsorption are summarized in [16–18].

5. Adsorption of propene on V_2O_5 (010) surface

As an example of a more complicated catalytic system where hydrogen abstraction forms as important step the reaction of propene at the V_2O_5 (010) surface modelled by a $V_{10}O_{30}H_{12}$ cluster is considered in the following. The propene approach to the surface is studied for two different geometries. First, the carbon plane is assumed parallel to the surface (parallel approach). Second, the carbon plane is perpendicular to the surface with the CH_3 group pointing towards the surface (perpendicular approach). The geometry of the substrate cluster unit is kept frozen whereas a full optimization on the propene is performed. Such a constrained geometry optimization gives only the local minima and one has to check several different lateral approaches in order to find the final reaction product.

The reorganization of the adsorbed propene molecule and the formation of bonds with the V_2O_5 (010) surface atoms is shown on Fig. 5 where for both approaches the starting and the final geometries are plotted. The detailed analysis of the geometry optimization indicates that already at the long distances from the surface the hydrogen from the methyl group feels the bridging oxygen. At equilibrium geometry (for both approaches) the hydrogen is abstracted from the propylene molecule and forms a surface hydroxyl group with the bridging oxygen. In the perpendicular approach the abstracted hydrogen is bound to the oxygen O(c) bridging two bare vanadium atoms and the remaining allyl species forms a bond with a different bridging oxygen. So the structure of this surface complex suggests the possible addition of a surface oxygen into the allyl species. In the parallel approach both the abstracted hydrogen and one of the allyl carbon atoms form bonds with the same surface oxygen O(c). Thus, the structure of this surface complex indicates insertion of the oxygen into the activated C–H bond. For a full account of the adsorbed reaction the two reaction paths considered above have to be

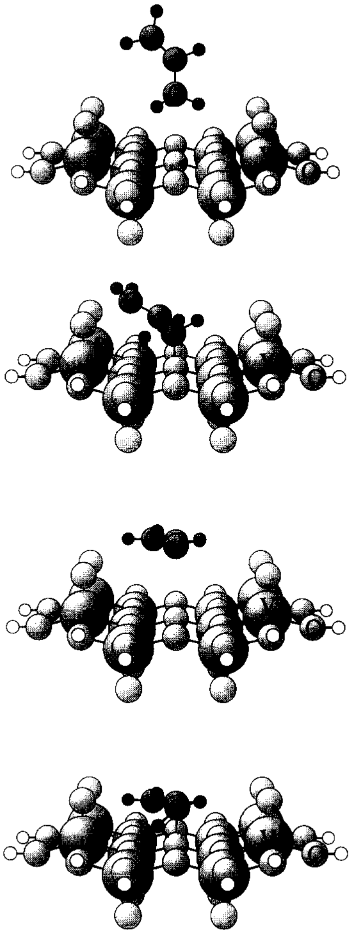

Fig. 5. Interaction of C_3H_6 molecule with $V_{10}O_{31}H_{12}$ cluster: (a) the starting geometry for the perpendicular approach, (b) the final geometry for the perpendicular approach, (c) the starting geometry for the parallel approach, (d) the final geometry for the parallel approach. The biggest balls denote for V, the smaller light for O, and the smallest ones for H atoms (light for H saturating the cluster and black for H from propylene molecule).

extended to a complete study of the potential hypersurface yielding all transition states and reaction paths.

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