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Catalysis Today 23 (1995) 311-316

CATALYSIS
TODAY

Quantum-chemical modelling of hydrocarbon oxidation on vanadium-based catalysts

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Abstract

Quantum-chemical modelling of the heterogeneous oxidation of hydrocarbons on an oxide catalyst can be divided in three steps: a description of the interaction of the hydrocarbon molecule with the surface of the oxide cluster, an analysis of the bonding of oxygen molecules, and a description of the reaction of oxygen and hydrocarbon molecules. Quantum-chemical calculations of the reaction of benzene and toluene at the surface of a vanadium oxide-based catalyst modelled by a V_6O_{20} cluster permit general conclusions to be formulated that pathways followed by catalytic reactions depend on the steric arrangement of the reacting molecules, which may be imposed by the properties of the active centre at the catalyst surface, its location on different crystal faces and by the type of frontier orbitals and the electronic state of the reacting molecules. Catalytic transformation is a concerted reaction in which interactions developed on the approach of reacting molecules to active centers cause the redistribution of electrons followed by the rearrangement of nuclei of both reactants and catalyst (reconstruction of the catalyst surface) and result in the desorption of the product.

1. Introduction

In oxidation reactions two reactants take part: oxygen and the hydrocarbon molecule to be oxidized. The reaction may thus start either by the activation of dioxygen to different moieties such as O_2^*, O_2^-, O^-, characterized by electrophilic properties (electrophilic oxidation), or by the activation of the hydrocarbon molecule and nucleophilic addition of O^{2-} (nucleophilic oxidation) [1]. The hydrocarbon molecule can react with oxygen along many different reaction pathways [2]. Thus, a complex reaction network appears, composed of many parallel and consecutive elementary steps, in which different electrophilic and nucleophilic oxygen species may be involved. Careful kinetic control must be exerted by the catalyst in order to accelerate only one chosen sequence of consecutive elementary steps and suppress all other possible steps which are parallel or consecutive. As an illustration of the complexity of the interactions of hydrocarbon molecules at oxide surfaces, Fig. 1 shows the reaction network of toluene at the surface of an oxide catalyst. When the surface is populated with adsorbed oxygen molecules, which have been activated by accepting to their antibonding orbital an electron from the oxide, an electrophilic attack by these molecules on the aromatic ring of toluene may take place. It may result in the formation of a peroxide-type intermediate, which then rearranges into dihydroxybenzene, or may lead to methyl-hydroquinone which transforms to methyl-quinone. The electrophilic attack of the second O_2 molecule converts it to methyl-maleic

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SSDI 0920-5861(94)00143-X

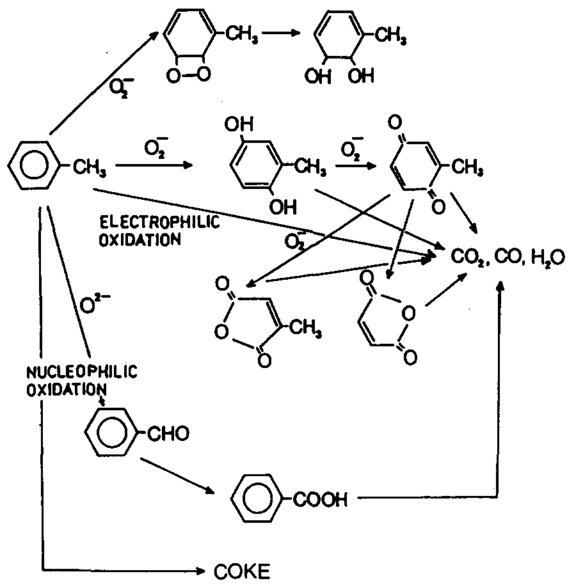

Fig. 1. Reaction network in oxidation of toluene by dioxygen in the gas phase.

anhydride or maleic anhydride. The methyl group of the toluene molecule does not react with electrophilic oxygen; its oxidation to benzaldehyde and benzoic acid proceeds through the nucleophilic addition of O^{2-} oxygen species from the surface of the oxide catalyst. Interaction of these species with carbon atoms of the ring may result in the formation of a coke deposit. However, the highly reactive oxygen moieties which have an electrophilic character may perform an electrophilic attack on any of the intermediates of the toluene reaction network resulting in a total oxidation to carbon oxides and water.

Because of the complexity of the reaction network, the high selectivity of the catalyst becomes the most important feature making possible the formation of products, which in the absence of the catalyst or at the surface of another catalyst would have never been formed because of much more rapidly proceeding competitive processes. Therefore the selection of an appropriate catalyst and reaction conditions, which direct the reaction along one selected pathway to obtain the desired product, is the principal goal of modelling the catalytic systems [3].

2. Modelling of heterogeneous reactions

One of the theoretical descriptions, by which one can try to answer this question is based on the

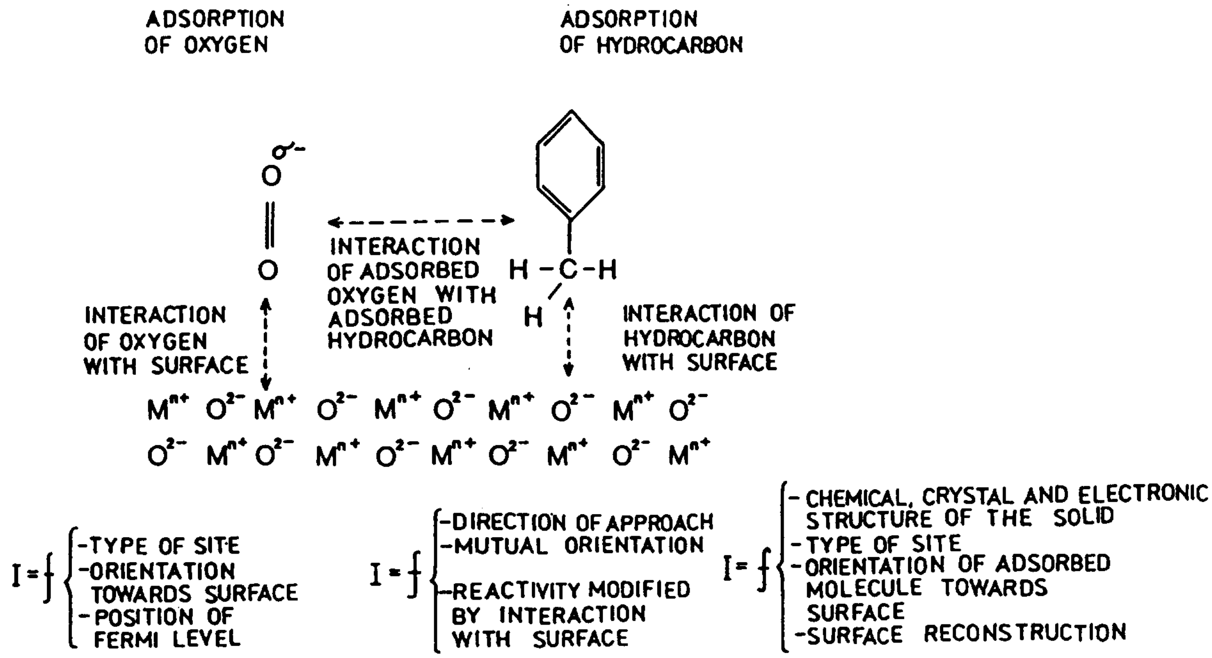

Fig. 2. The basis for modelling of heterogeneous catalytic oxidation of toluene at the surface of the oxide catalyst.

concept of the potential energy hypersurface for molecular motions. The minima on such a hypersurface correspond to stable states of the system, i.e. to reactants in the initial state and products in the final states, whereas local minima and saddle points account for metastable complexes and transition states of the investigated reaction network. This approach cannot be directly applied to the heterogenous catalytic oxidation of hydrocarbons on oxide catalysts, because oxygen and hydrocarbon molecules can approach each other from different directions and in different spatial orientations, they simultaneously interact with the surface of the catalyst, which modifies their reactivity but becomes itself reconstructed under the influence of the reactants (Fig. 2).

The problem of modelling must be thus divided into three steps:

(1) A description of the interaction of the hydrocarbon molecule with the surface of the solid oxide modelled by an appropriate oxide cluster; this should permit the unravelling of the activation mechanism of the hydrocarbon molecule and of the insertion of O^{2-} species (nucleophilic oxidation) as well as the identification of structures of adsorbed hydrocarbon species, which can be attacked by adsorbed molecular oxygen.

(2) An analysis of the bonding of the oxygen molecules at the surface of the oxide, its electronic state and surface mobility;

(3) A description of the reaction between the oxygen and the hydrocarbon molecules in the absence of the catalysts and an analysis of its modification by the presence of the catalyst.

3. Interaction of toluene with the catalyst surface

The construction of the model for step 1 is facilitated by the fact that usually the number of the crystallographically different positions of transition metal and oxygen atoms, playing the role of active sites at the surface of an oxide catalyst is limited, and the ways in which the reacting molecules approach the active sites and their orientation in respect to the surface may be reduced to a few limiting cases.

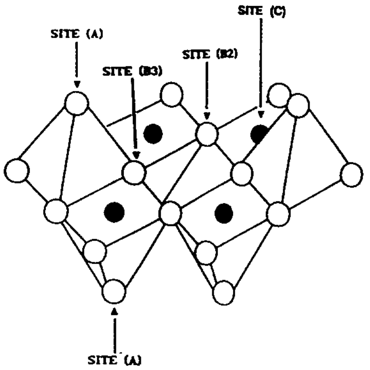

Fig. 3. A cluster model of the vanadium oxide-based catalyst.

Quantum-chemical calculations of the interactions, developing on approach of the toluene molecule to a cluster composed of six vanadium–oxygen square pyramids, assumed to be a model of supported vanadium oxide monolayer catalyst (Fig. 3), may serve as an example [4,5].

The SINDO method was used for the calculations. Toluene was approached side-on with the ring plane parallel to the plane of the cluster or end-on with the molecular axis perpendicular along a trajectory perpendicular to the plane of six

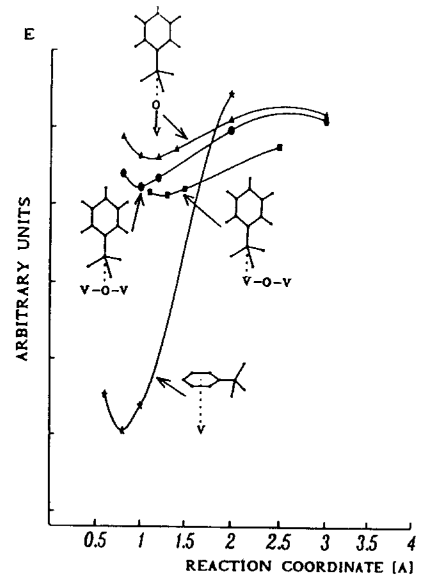

Fig. 4. Changes of the total energy on approaching toluene to different adsorption sites of the V_2O_{20} cluster as a function of the reaction coordinate.

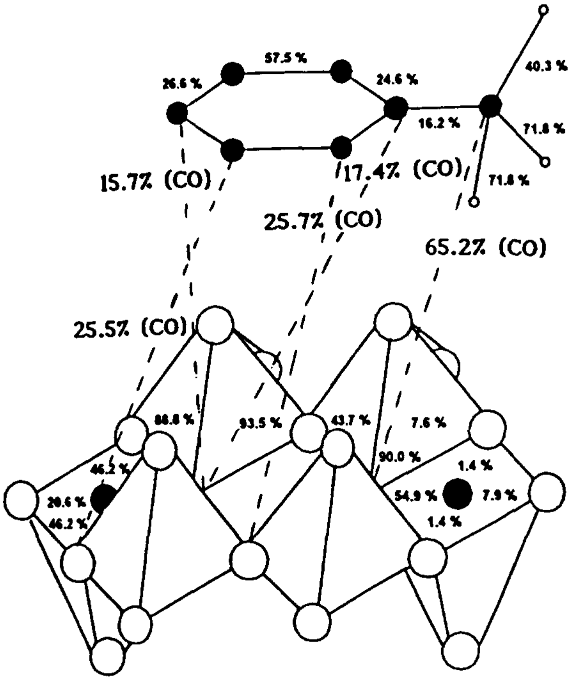

Fig. 5. Changes (in %) of the diatomic energy contributions in the site-on desorption complex in respect to the isolated cluster and toluene.

edge- and corner-linked vanadium–oxygen square pyramids, which represent an element of the (010) plane of V_2O_5. The trajectory was chosen to point either at vanadium ion or bridging oxygen ions. In all cases the plot of the total energy vs. the reaction coordinate showed a minimum, corresponding to the formation of an adsorbed complex (Fig. 4). Side-on adsorption was much stronger, with strong interactions of all carbon atoms of the ring and methyl group with oxygen atoms of the cluster, accompanied by simultaneous weakening of C–C bonds (Fig. 5). This indicates that side-on adsorption leads to complete destruction of the aromatic molecule and formation of coke or carbon oxides. End-on adsorption is most facile on bridging oxygen, and on approaching the toluene molecule two processes take place simultaneously (Fig. 6):

(1) two hydrogen atoms of the methyl group move away to finally form OH groups with oxygens of the cluster, and

(2) the bonds between the bridging oxygen atom and the vanadium atom are considerably weakened, the former moving above the surface of the cluster and forming a bond with the methine group, which finally results in the desorption of formaldehyde.

This series of consecutive elementary events, representing the nucleophilic oxidation of toluene to benzaldehyde on vanadium oxide catalysts is

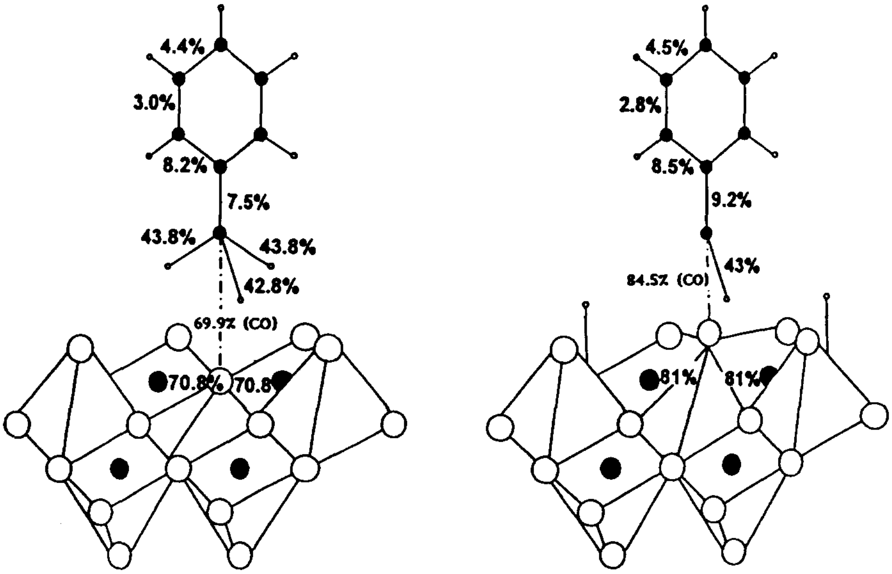

Fig. 6. Changes (in %) of the diatomic energy contributions in the adsorbate complex at a bridging oxygen site in respect to the isolated cluster and toluene.

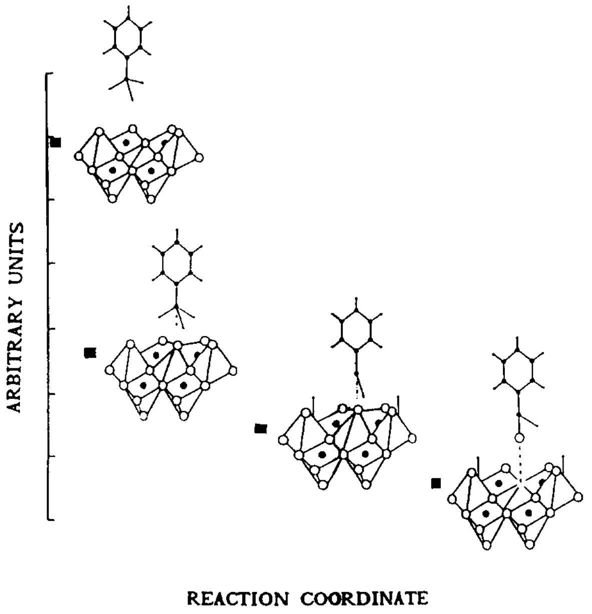

Fig. 7. The sequence of elementary steps in the oxidation of toluene.

shown in Fig. 7. In the case of benzene the interaction with the cluster results in the formation of strong bonds between carbon and hydrogen atoms of the ring and the atoms of the cluster. The molecule becomes destroyed in total oxidation. In order to selectively oxidize benzene, molecular oxygen must be used and the electrophilic oxidation route must be followed.

4. Interaction of benzene with molecular oxygen

Quantum-chemical calculations of the reaction of molecular oxygen with benzene revealed [6,7] that the type of product formed as a result of the electrophilic attack of oxygen on the hydrocarbon molecule depends on the direction of the approach and the mutual orientation of the reacting molecules and on the mode of oxygen activation. When an O_2 molecule approaches the benzene ring in-plane with the axis parallel to the side of the ring (Fig. 8 (I)), a peroxide-type intermediate may be formed which then rearranges into dihydroxybenzene. In the case of an in-plane approach but with the axis of the O_2 molecule perpendicular to the ring (Fig. 8 (II)), the C–C bond of the ring becomes cleaved and the two carbon atoms are pulled away by the approaching O_2 molecule, the benzene ring becoming split into two fragments; $C_2O_2H_2$ and C_4H_4, which are expected to be highly reactive intermediates of complete oxidation of the hydrocarbon molecule to water and carbon oxides. The approach of the O_2 molecule along the reaction pathway perpendicular to the center of the benzene ring with its axis parallel to the diagonal of the ring (Fig. 8 (III)) leads to the formation of a O–O bridge above the ring to the diagonal 1,4 carbon atoms, which rearranges through insertion of oxygen into the C–H bonds of diagonal 1,4 carbon atoms to form hydroquinone, and finally quinone. The electrophilic attack of a second O_2 molecule converts it into maleic anhydride. The mechanism of such a multistep reaction is shown in Fig. 9. Interesting conclusions may be drawn from the calculation of the total energy of the $C_6H_6+O_2$ system as a function of the angle between the axis of the oxygen molecule

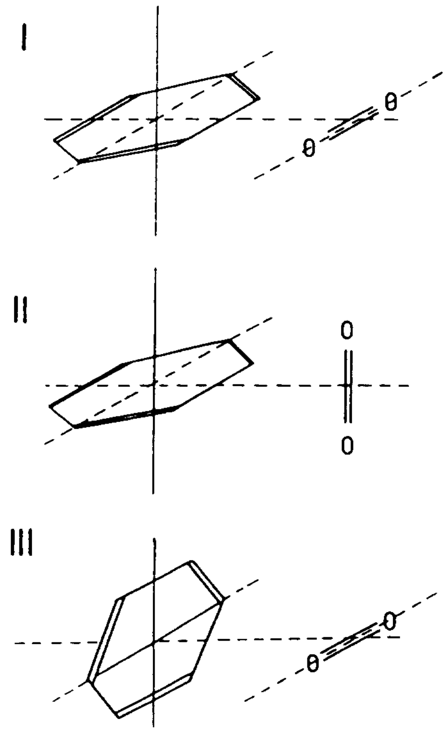

Fig. 8. Pathways of the reaction of the oxygen molecule with benzene.

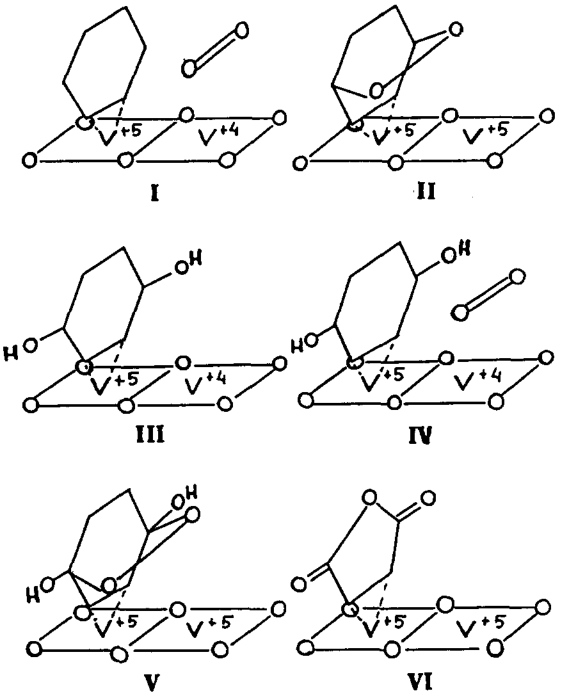

Fig. 9. Molecular mechanism of the oxidation of benzene by dioxygen at the surface of vanadium oxide-based catalysts.

and the plane of the benzene ring. When a non-activated oxygen molecule approaches the benzene ring along the reaction path in the plane of the ring, it is forced to become oriented perpendicularly to the ring plane, this being energetically the most favourable as the only orientation in which SOMOs of O_2 molecule overlap with the HOMO and LUMO of benzene. Conversely, when the oxygen molecule becomes activated and the O–O bond stretched, the position parallel to a ring plane is assumed by the approaching O_2 molecule. Thus, different reaction pathways are selected by the oxygen molecule depending on its electronic state.

5. Conclusions

Quantum-chemical calculations have already permitted three important conclusions of general significance to be formulated [8]:

(1) In electrophilic oxidation the type of product formed depends on the direction of the approach and the mutual orientation of the reacting molecules and on the mode of oxygen activation.

(2) In nucleophilic oxidation by surface lattice oxygen the site of the hydrocarbon molecule attacked and hence the reaction pathway followed is critically dependent on the structure of the active site and the orientation of the molecule approaching the surface. The desired chemo- and regioselectivity could be thus achieved by imposing a molecular field appropriately directing the incoming molecule (supramolecular catalysis).

(3) Under the influence of the approaching hydrocarbon molecule the bonds at the oxide surface are strongly influenced and surface oxygen atoms move out of the surface which undergoes reconstruction.

The elementary catalytic transformation at the surface of an oxide catalyst thus becomes seen as a dynamic interaction of reacting molecules with the group of atoms constituting the active site of the catalyst, in which redistribution of electrons takes place followed by rearrangement of nuclei in one concerted reaction. This is in line with the concept of a dynamically changing surface emerging from the development of new experimental techniques.

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