Oxide Catalysts

55

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Contents

Abstract

This chapter reviews some aspects of computational work on the catalytic chemistry of oxides. The difficulties of using density functional theory in calculations are explained. Different ways of structural or chemical modifications aimed at improving catalytic activity are reviewed. The reaction mechanism of partial oxidation reaction catalyzed by oxides is discussed. The focus is on

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qualitative design rules rather than on obtaining highly accurate computational results.

1 Introduction

The number of publications on oxide catalysts is enormous and we can only attempt to provide a summary of those properties that seem to be common to classes of oxide catalysts and/or for classes of reactions. The main subject of this section is what computations teach us about catalysis by simple oxides having the formula M_xO_y. We do not discuss compounds having two cations such as perovskites, spinels, vanadates, etc. Most zeolites are oxides of Si and Al with peculiar, porous structures. We do not examine them here since their catalytic chemistry is different from that of ordinary oxides. Within these self-imposed limitations, we will discuss pure oxides, doped oxides, submonolayers of oxides supported on oxides, and oxide submonolayers supported on metals. Among reactions, we will mention oxidative dehydrogenation and methane oxidative coupling. The topic is so vast that more is left unsaid than is presented.

Oxide catalysts are used industrially for the synthesis of sulfuric acid, the conversion of hydrogen sulfide to sulfur, of methanol to formaldehyde, of o-xylene to phthalic anhydride, of ethylbenzene to styrene, and of propane to propylene.

2 Mars–van Krevelen Mechanism

In the majority of reactions catalyzed by oxides, the gaseous feed contains a reductant and an oxidant. Hydrocarbons, alcohols, CO, H_2, etc. are reductants, and O_2 N_2O or CO_2 are oxidants. There is extensive evidence that oxidation reactions catalyzed by oxides take place through a Mars–van Krevelen mechanism. This postulates that the reductant in the feed reacts with the surface oxygen atoms, removing them and creating oxygen vacancies on the surface; the oxidant reoxidizes the surface. For example, in the reaction $CO(g) + 1/2\ O_2(g) \rightarrow CO_2(g)$, CO reduces the oxide surface to form CO_2 and oxygen vacancies; one oxygen atom in the CO_2 molecule originates from the surface of the oxide. The role of the gas-phase oxygen is to reoxidize the surface. In a slightly more complicated reaction, such as $CH_3OH + ½\ O_2(g) \rightarrow CH_2O + H_2O$ the oxygen in the water molecule is taken from the oxide surface and, after water desorbs (thus removing an oxygen atom from the surface), the gaseous oxygen reoxidizes the surface. The oxygen in the aldehyde is the oxygen atom contained in the methanol feed.

Transient kinetics experiments, experiments using $^{18}O_2$, and Density Functional Theory (DFT) calculations, all support the Mars–van Krevelen mechanism. However, it is bad practice to assume uncritically that all oxides work according to a Mars–van Krevelen mechanism, for all reactions, under all conditions. In some cases, the oxide might activate the adsorbed oxygen and this oxidizes the reductant.

According to the Mars–van Krevelen mechanism, the reductant removes oxygen from the surface of the oxide and the oxidant puts it back. Because of this, at steady state, there is a constant concentration of oxygen vacancies at the surface. The catalyst is the partially reduced oxide, not the stoichiometric oxide. For a given reductant, the surface of the catalyst is less reduced if the oxidant is O_2 and more reduced if the oxidant is CO_2. In many experiments using oxygen, it has been observed that the steady-state reaction rate is independent of the partial pressure of the oxygen. This indicates that the reoxidation of the surface by gaseous oxygen is much faster than the other reaction steps. This independence of the rate on the oxygen partial pressure does not mean that the reaction will proceed without gaseous oxygen. If the feed does not contain oxygen, the oxide will be reduced until the degree of reduction is so high that the oxide will stop providing oxygen and the oxidation reaction stops. At high temperature, this reduction may go all the way to the formation of the metal, an undesirable outcome unless one is a metallurgist.

3 Irreducible and Reducible Oxides

The Mars–van Krevelen mechanism suggests a classification of the oxide into those that provide oxygen easily (reducible oxides) and those do not (irreducible oxides). Examples of irreducible oxides are alkali oxides, alkali earth oxides, La_2O_3, Sm_2O_3, Y_2O_3, Sc_2O_3, ZrO_2, Ta_2O_5, etc. The term "irreducible" indicates that the oxide is difficult to reduce. It is reasonable to assume that an oxide that is difficult to reduce is not a good oxidant. This is why irreducible oxides are used as catalysts for partial-oxidation reactions at high temperature. An example is the oxidative methane coupling, $2\,CH_4 + 1/2\,O_2 \rightarrow C_2H_4 + H_2O$, which takes place at $\sim 800\,°C$ (Zavyalova et al. 2011). At this temperature, a reducible oxide will combust methane to CO_2 and water, or to CO and H_2, depending on the working conditions. A characteristic common to all irreducible oxides is that their cation does not make stable oxides having different cation-to-oxygen ratios. For example, in the case of La_2O_3, La does not make stable LaO or LaO_2 oxides. However, as in many cases in chemistry, the rules have exceptions. The fact that a cation forms only one oxide is not necessarily an indication that the oxide is difficult to reduce: for example, NiO and ZnO do not form an oxide containing Ni^+ or Zn^+ but they can be reduced much more easily than, for example, MgO.

Reducible oxides, such as TiO_2, CeO_2, V_2O_5, MoO_3, Mn_3O_4, WO_3, CrO_2, are grouped together because they are better oxidants than the other oxides. In other words, it is easier to partially reduce them by making oxygen vacancies on their surface. The elements in these oxides are able to make oxides having a lower oxygen content (per cation), such as Ti_2O_3, Ce_2O_3, V_2O_3, VO_2, MnO_2, Mn_2O_3, MoO_2, WO_2, Cr_2O_3. Some of them form a large number of crystalline oxides of intermediate stoichiometry. For example, vanadium forms V_nO_{2n+1} ($n = 3, 4, 5$) and V_nO_{2n-1} ($n = 4, 5, 6, 7, 8, 9$). Similar compounds are formed by Mo, Ce, and Ti. The existence of such compounds suggests that it is easy to induce these cations to release oxygen and lower their valence.

4 Oxides Whose Cations Have an Incomplete d- or f-Electronic Shell

There is another important classification of oxides, based on whether the d-shell or the f-shell of the cation is filled. The cations in rows 1, 2, and 11–16 in the periodic table have filled d- or f-shells. The rest of the cations do not, and this causes difficulties: calculations using the generalized gradient approximation of DFT (GGA-DFT) make substantial, qualitative errors. A well-studied example of an oxide having a cation with an incomplete d-shell is TiO_2; equally well studied is CeO_2, in which Ce has an incomplete f-shell. A number of things go wrong when GGA-DFT is used to calculate the properties of these oxides. (1) The d-band (or the f-band) is much too wide (i.e., the energy of the d- or f-orbitals changes substantially when the wave vector is changed) whereas experiments show them to be narrow. The narrow band detected by experiments indicates the d (or the f) electrons are localized on the cations. GGA predicts the opposite: electrons located in d orbitals are delocalized. (2) GGA does not accurately describe processes in which one or two electrons are donated to the oxide. Such donation takes place, for example, when radicals such as H or CH_3 bind to the oxide, or when an oxygen vacancy is formed. Experiments indicate that the donated electrons are localized on one cation while GGA predicts that they are delocalized. (3) In most processes in which one or two electrons are donated to the surface, GGA-DFT predicts that the energy of the orbital in which such electrons are located is at the bottom of the valence band. However, ultra-violet photoelectron spectroscopy (UPS) experiments show that their energy is in the band gap. No such difficulties are encountered when GGA is used for oxides with a complete d- or f-shell (e.g., MgO).

This tendency of GGA to delocalize electrons is attributed to a flaw in the DFT method. The DFT energy contains a term in which each electron interacts with itself. This energy is diminished if the electron distribution is diffuse rather than localized. Hence, the variational procedure will lower the energy by spreading out the electron distribution.

To correct the behavior of GGA, when one calculates the properties of such oxides, one introduces in the DFT energy a term U designed to increase the energy when more than one d or f electron is present on a cation. As a result, the d or f electrons are localized on the cations, as they should be. The theory containing this term, called GGA + U, is an improvization that does not have a firm theoretical foundation and does not provide a reliable prescription for the magnitude of U. U is determined to fit some property of interest. Chemist may pick U to give correct energy of formation of the oxide. People interested in photochemistry at the surface pick U to obtain the experimentally measured band gap. There are also recipes for calculating U from the atomic properties of the cation, but they are approximate. In some cases, people adjust the value of U, in GGA + U, to give results close to the results of hybrid functionals (e.g., B3LYP or HSE), which are deemed to be more accurate. In general, it is prudent, when using GGA + U, to perform calculations for several values of U in order to confirm that at least the qualitative conclusions of the study are independent of the magnitude of U.

The hybrid density functionals (e.g., B3LYP, HSE) give more reliable results than GGA + U. These methods add a fractional amount of Hartree–Fock exchange energy to the ordinary exchange term in the Kohn–Sham equation. This diminishes, to some extent, the self-interaction error that plagues GGA-DFT. The fraction of Hartree–Fock exchange has been determined by fitting a data set. The method works well for molecules and the consensus is that hybrid functionals are more reliable than GGA + U, when applied to oxides. Unfortunately, hybrid functional calculations require substantially more computer time than GGA + U. Since the study of a catalytic process requires many calculations, on systems having many electrons, the hybrid functionals are not used in "production runs." It is more common to use them to validate (or not) some essential step in a reaction mechanism predicted by GGA + U.

5 Oxygen Vacancy Formation

The Mars–van Krevelen mechanism assumes that the reductant in the feed reacts with surface oxygen, making oxygen vacancies. One would expect that oxides for which the energy of oxygen vacancy formation is the lowest are the best oxidation catalysts. Such oxides are likely to be the better oxidants, but they are not necessarily the best partial oxidation catalysts. For example, one would not try to use HgO as a catalyst; it reacts vigorously with reductants but it does not reoxidize easily. Nevertheless, barring a few exceptions, the energy of vacancy formation is not a bad descriptor for a preliminary screening of an oxide catalyst for partial or total oxidation.

It is very difficult to obtain reliable experimental information about the energy of oxygen vacancy formation at the surface of an oxide. Our search of the experimental literature, for the energy of oxygen-vacancy formation for CeO_2, found that numerous values between 0.5 and 4.5 eV have been proposed. There are several reasons for the discrepancies between various measurements. (1) The energy of vacancy formation seems to depend on crystallite size. Therefore, different methods of oxide preparation give different results for the energy of vacancy formation. (2) The energy of oxygen vacancy formation ought to depend strongly on vacancy concentration. As one removes a few oxygen atoms, one expects that the cations will bind more tightly the remaining oxygen. (3) The energy of vacancy formation is affected by the presence of small dopant concentrations. Even research grade oxides have 99.99% purity. In the semiconductor industry, the presence of 0.01% dopants is considered unacceptable since it could dramatically change some properties (e.g., the electrical conductivity). Calculations show that the presence of dopants whose valence is lower than that of the cations they substitute will lower substantially the energy of oxygen-vacancy formation.

Given the paucity of conclusive experimental data, the calculation of the energy of oxygen-vacancy formation plays an important role in our qualitative understanding of the properties of oxide catalysts. While the absolute values of the calculated energy are unreliable, it is likely that they can be used to compare the oxidative power of different oxides. The calculated energy of oxygen-vacancy formation, when done properly, is consistent with the oxidizing activity observed in experiments.

When an oxygen atom is removed from the oxide surface, it leaves behind (formally) two electrons that used to be tied in the bonds between the oxide and the oxygen atom being removed. The energy of vacancy formation depends on the strength of metal–oxygen chemical bond and on the fate of these "stranded electrons." If the oxide is reducible, these two electrons will reduce two cations. For example, in the case of TiO_2 the removal of an oxygen atom creates two Ti^{3+} ions. We are using here what inorganic chemists call "formal charges," a term that facilitates communication but should not be taken literally. The calculated Bader charge on a Ti atom, in TiO_2, is not 4+ nor is the charge on oxygen equal to -2. A more precise statement is that when an oxygen vacancy is formed the Bader charge on two Ti ions increases by almost one electron. The Ti^{3+} ion, together with the distortion of the oxygen atom surrounding it, is called a *polaron*. Polaron formation lowers the energy of the system (as compared to the case in which the electrons are stuck in the vacancy). It is expected that in all reducible oxides, the formation of an oxygen vacancy, at the surface or in the bulk, is accompanied by the formation of two polarons. This phenomenon has been documented for TiO_2, CeO_2, MoO_3, V_2O_5, and WO_3.

The energy of the polarons formed when an oxygen vacancy is created depends on the nature of the oxide, the position of the polarons with respect to the vacancy site, and the positions of the polaron with respect to each other. This means that to determine the lowest energy for oxygen-vacancy formation, one must study all possible locations of the two polarons.

Polarons do not form spontaneously when an oxygen atom is removed to form an oxygen vacancy. If the oxygen atom is removed and the energy is minimized, two Ti^{3+} ions are formed at the vacancy site. To form a polaron on a specific Ti ion, one must push the nearest oxygen atoms away from the cation and optimize the energy with these oxygen atoms held fixed. When a minimum energy is reached, one releases the oxygen atoms that were held in place during the first optimization, and one optimizes the geometry again. This will form a polaron at the desired location. If DFT + U is used, polarons are generally stable if U is larger than 2.5 eV (or thereabouts, depending on the oxide). The larger the value of U, the more stable is the polaron.

When DFT + U is used, the energy of the orbital involved in the polarons is in the band gap, in agreement with photoelectron experiments. Stoichiometric, pure TiO_2 has a large band gap and does not conduct electricity. However, if oxygen vacancies are created the material becomes an n-conductor. It is widely accepted that in the case of TiO_2 the electric conductivity of the oxide is due to polaron hopping from site to site. The energy barrier of site-to-site hopping has been calculated (Deskins and Dupuis 2007) to be $\sim$0.25 eV. This is consistent with conductivity experiments. The band gap of TiO_2 is $\sim$2 eV and the states in the gap are below the conduction band by $\sim$0.7 eV. Therefore, the electrical conductivity is not due to thermal promotion of an electron from a state in the gap to the conduction band.

The only possible explanation for the conductivity by n-carrier is the mobility of the polarons. This is also true if electrons are injected in the material by a cathode: the electron will form a Ti^{3+} with a polaronic distortion and the electric conductivity is due to polaron migration. The polarons caused by oxygen-vacancy formation have been detected by electron paramagnetic resonance (EPR) spectroscopy.

Experiments in Moskovits's group (Zhang et al. 2004) measured the conductivity of a SnO_2 nanowire that was reduced by CO and reoxidized by O_2. The measurements have shown that reduction increases the electrical conductivity of the wire and oxidation reduces it, as expected if polarons are formed during reduction. We are not aware of a computational study of oxygen vacancies in this oxide, which differs from TiO_2 because Sn^{3+} is unlikely to be formed.

Why is this relevant to surface chemistry? Polaron formation explains why it is much easier to form oxygen vacancies on reducible oxides. This in turn explains why such oxides are better oxidants than the irreducible ones. Furthermore, the polaron are strong Lewis bases (electron donor). Their presence facilitates the adsorption of Lewis acids, such as Au atoms, O_2, Cl_2, Br_2, and I_2.

Polarons are also invoked (in the case of reducible oxides) when H adsorption or CH_3 adsorption is studied. The binding energy of these species to reducible oxides is increased by the fact that they donate an electron and form a polaron.

The formation of oxygen vacancies on irreducible oxides does not result in polaron formation. The "stranded electrons" remain at the vacancy site where they act as strong Lewis bases, which bind Lewis acids strongly.

6 Two-Step Oxidation–Reduction

There has been quite a bit of experimental work studying the possibility of a two-step process for conversion of methane to syngas. It turns out that at high temperature many oxides react with methane to produce syngas and a reduced oxide. In a second step, the oxide can be regenerated by reacting with water, to produce H_2 and a fully oxidized oxide. An alternative second step will oxidize the reduced oxide with CO_2 to produce a stoichiometric oxide and CO. The degree of reduction must be monitored carefully to remove only a few layers of oxygen atoms from the surface of each oxide nanoparticle, so that the surface does not become purely metallic. This partial reduction will avoid coarsening and the cracking of the solid particles due to the stress created by a large change of density when cycling between a stoichiometric oxide and a strongly reduced one.

7 The Lewis Acid–Base Rule

The catalytic chemistry of oxides is very complex and it is therefore useful to have some design rules that give general guidance regarding how one might modify an oxide surface to change its catalytic chemistry. Useful in this regard is the Lewis acid–base rule that is stated below. The interaction energy between two species adsorbed on an oxide surface is increased substantially if one species can function as a Lewis acid (electron acceptor) and the other as a Lewis base (electron donor). A consequence of this rule is that two species that have several options for binding sites (e.g., could bind to the cation or to the oxygen) would prefer the binding configuration that allows one to be a Lewis acid and the other a Lewis base. For example, if they are alone on an oxide surface, H or CH_3 each prefers to bind to an oxygen atom. However, when they are coadsorbed, the energy is lower if H binds to O and donates an electron to a CH_3 bound to the cation. In this case, H is a Lewis base and CH_3 is a Lewis acid. This acid–base rule seems to be general: it has been documented by numerous calculations for the dissociative adsorption of CH_4, H_2, HX and X_2 ($X = $ Cl or Br), on the surface of a variety of oxides (e.g., MgO, La_2O_3, CaO, TiO_2, CeO_2).

8 Doped Oxides

This acid–base rule suggested a number of strategies for modifying oxide surface to make them better oxidants. One of them is doping (Metiu et al. 2012; McFarland and Metiu 2013; Nilius and Freund 2015): replacing some of the cations near or at the surface of the oxide with cations having a lower valence (e.g., MgO doped with Li). This creates a deficit of electrons in the oxide, making the surface an electron acceptor (Lewis acid), which enhances the ability of the surface to bind Lewis bases such as H and CH_3. The chemistry of the doped oxide does not involve the dopant directly. By not supplying the oxide with enough electrons, the dopant weakens the bond of one of the surface oxygen atoms to the oxide, making the atom more reactive. The use of a higher-valence dopant (e.g., MgO doped with La) has the opposite effect. Formally, the dopant is capable of donating three electrons but the oxide will only use two of them (because we replace a divalent cation in oxide with a trivalent element). The unwanted electron is stuck on to the dopant, making it a good Lewis base. According to the acid–base rule, this site will adsorb well a Lewis acid such as oxygen. In this example, the oxygen becomes negatively charged and is chemically more active than neutral O_2.

It is difficult to prove by experiments with powder catalysts that these concepts work as expected, mainly because one is not certain where the dopants are located (in the surface layer, in the second layer, in the bulk?). It is also not known whether the dopant is oxidized during reaction to form an isolated oxide cluster (the oxide of the dopant). Resolving this issue is made difficult, among other reasons, by the fact that the chemistry of a submonolayer of oxidized dopant will not behave chemically like the bulk oxide of the dopant. In a few experiments, electron microscopy has detected isolated dopants but the mechanism through which they act as catalyst cannot be verified experimentally. Most experiments find that the use of lower valence doping does make the oxide a better oxidant. Careful experiments in Freund's laboratory, working in ultra-high vacuum, with well-defined systems characterized by scanning tunneling microscopy (STM) are generally in agreement with the acid–base rules.

9 Oxides Supported on Other Oxides

Several recent articles (Wachs 2013, 2005; Stacchiola et al. 2013; Carrero et al. 2014; Freund et al. 2014) have reviewed catalysis by systems consisting of an oxide submonolayer supported on another oxide. Any oxide can be used as a submonolayer if it "wets" the support. Broadly speaking the strategy is the same as in doping: create a new bonding scheme in the system, with the goal of changing reactivity. Of course, not every new bonding is beneficial and a central goal of research is to find the ones that are. Experience indicates that the catalytic chemistry is more interesting if the submonolayer is a reducible oxide (e.g., vanadium or molybdenum oxide) but this is not an absolute rule. We examine, as an example, systems in which the submonolayer is V_xO_y. We use this symbol because we are not certain about the stoichiometry of the submonolayer. An exception is provided by experiments (Price et al. 2014) in which mass-selected V_xO_y clusters are deposited, in ultra-high vacuum, on $TiO_2(110)$ surface, and are examined in situ, by scanning tunneling microscopy (STM). Thermal desorption experiments were performed on these systems to determine the catalytic conversion of methanol to formaldehyde for different V_xO_y stoichiometry. Experiments on well-defined systems (Freund et al. 2014; Nilius and Freund 2015) are particularly important when comparison with computations is desired.

The qualitative idea in the design of these submonolayer systems is to force some oxygen atoms to have an unusual bonding. For example, in V_xO_y supported on TiO_2, some oxygen atoms form -Ti-O-V- groups (the lines indicate chemical bonds). The reactivity of these "bridging oxygen atoms" should be different from that of the oxygen atoms in TiO_2 or in V_2O_5. Experiments show that they are. By studying the oxidative dehydrogenation of propane to propylene (Carrero et al. 2014), or of methanol to formaldehyde (Wachs 2013), the following conclusions were drawn. (1) The V_xO_y submonolayer is more active than V_2O_5 powder or TiO_2 powder. The catalytic activity decreases when the amount of vanadium used in the preparation of the catalyst is sufficient to build a second vanadium oxide layer. Moreover, the selectivity changes: pure V_2O_5 is a good total combustion catalyst, while supported V_xO_y is effective for propane or methanol oxidative dehydrogenation. (2) The effect of the support is surprisingly strong. The turnover frequency on VO_x supported on CeO_2 or on TiO_2 is roughly three orders of magnitude higher than that on VO_x supported on silica or alumina. (3) One can prepare a catalyst having a very low concentration of vanadium, in which case one has isolated VO_4 clusters on the surface. Adding more vanadium leads to the formation of clusters having several V atoms connected by -V-O-V- bridges. The oxygen atoms in these bridges do not seem to have high reactivity. (4) Under working conditions, at atmospheric pressure, the catalyst is covered with reactant, intermediate, and product molecules, in addition to having an unknown and probably inhomogeneous morphology. Possible adsorbed species are C_3H_8, C_3H_7, C_3H_6, hydroxyls, oxygen vacancies, and all the intermediates of the combustion of carbon-containing species. This complexity, in surface composition and morphology, makes it difficult to obtain a detailed understanding of these catalysts (oxide submonolayer on oxide).

An important task is to develop a qualitative understanding of the V_xO_y interaction with the support.

10 Inverse Catalysts

Many catalysts used in industry or research consist of metal nanoparticles supported on an oxide. In many cases, the oxide support confers mechanical stability, inhibits coarsening, helps create a large surface for the metal catalyst, etc. In some cases, the oxide support affects the performance substantially. For example, the best support for the Ag catalyst for ethylene epoxidation is α-alumina or SiC. Other supports, such as SiO_2, MgO, TiO_2, Y_2O_3, ZrO_2, have been tried and found inadequate. Even Ag supported on γ-Al_2O_3 has poor performance because γ-alumina is more acid than α-alumina. In some cases, the oxide support covers the metal particle with a thin oxide layer. Often it seems that catalysis takes place at the border between the oxide support and the metal nanoparticle. It is natural therefore to try to create such a border differently, by using an oxide nanoparticle supported on a metal. Catalysts designed in this way are called inverse catalysts and their properties have been studied and reviewed in several publications (Hornes et al. 2010; Rodriguez and Hrbek 2010; Senanayake et al. 2010; Freund et al. 2014; Pan et al. 2014; Rodriguez et al. 2017). Inverse here means opposite to the more common catalysts that consist of metal particles on an oxide support.

11 Summary and Outlook

Several facts make computational studies of real catalysts, oxides or otherwise, difficult. In spite of great advances in in situ electron microscopy and the spectroscopy of catalysts under working conditions, we do not know in detail the morphology (steps, kink, facets) and the composition of the surface of working catalysts. At atmospheric pressure the surface is covered with reactants, products, and intermediates, which compete for surface sites and often interact strongly with each other. For example, the adsorption of O_2 is enhanced substantially by the presence of hydroxyls. While the hydroxyls might not participate in the mechanism of an oxidation reaction, they might influence it through their effect on oxygen adsorption. In many cases the support of the catalyst is important and it is possible that the border between the oxide catalyst and the support is catalytically active. Modeling such a border is difficult. The models we use to study catalysts are almost always a simplified version of reality. The divorce from reality is amplified by the fact that almost all practical catalysts contain small amounts of promoters of the desired reaction and inhibitors of unwanted reactions. Such small additives make a very substantial difference in a catalyst's performance.

A study of catalysis requires the examination of systems with many atoms, which could have a great variety of positions. Because of this, computational efficiency is an essential requirement. That requirement is the reason GGA-DFT + U is the workhorse in the field. Hybrid functionals require substantially more computer power and are mostly used to recalculate some of the critical steps in a mechanism derived by using GGA calculations. The validation of these calculations by experiment is difficult: there are few groups that can perform experiments with well-defined, single-crystal, oxide surfaces in ultra-high vacuum. Careful measurements of adsorption isotherms, for real catalysts, would be helpful but they are out of fashion. Validation of the DFT calculations by using high-accuracy quantum chemistry methods is, in principle, possible; however, modeling catalysts requires dealing with a large number of electrons and a large number of geometries, and demands too much computer time. Modeling a catalyst by a very small cluster, for which high-quality calculations are possible, is often not satisfactory. Progress in the near future is likely to come from the development of new functionals designed specifically for dealing with oxides. Another promising possibility is the development of embedded cluster methods, to accurately treat a critical group of atoms and more poorly (by DFT or classical potentials) treat the rest.

One might think that the morphology and the composition of the surface could be determined by finding the structure having the lowest energy. However, catalysis is performed at steady state and the morphology and the composition of the surface under working conditions is controlled by kinetics, not by thermodynamics. Kinetic Monte Carlo simulations could be attempted but the number of rate events is very large and the calculated rate constants are likely to have substantial errors. DFT calculations of activation energies are not accurate and unfortunately the Arrhenius formula amplifies the errors.

To summarize: if we intend to study real catalysts, we are forced to use an inaccurate computational method (DFT), in order to examine inaccurate models of systems that experiments do not describe in detail. One might have to give up, temporarily, the dream of performing a complete ab initio description of a catalytic process and accept that computation is one of the tools we have along with spectroscopy and kinetics. This frees the computational chemist to focus on those questions of the catalytic process that the experiments cannot settle. A great strength of the theory is that it has a complete control of morphology and composition. Rather than try to imitate real catalysts, theory should create, on the computer, new structures and new compositions to find the ones that have very promising properties.

References

Carrero CA, Schloegl R, Wachs IE, Schomaecker R (2014) Critical literature review of the kinetics for the oxidative dehydrogenation of propane over well-defined supported vanadium oxide catalysts. ACS Catal 4:3357–3380

Deskins NA, Dupuis M (2007) Electron transport via polaron hopping in bulk TiO_2: a density functional theory characterization. Phys Rev B 75:195212

Freund H-J, Shaikhutdinov S, Nilius N (2014) Model studies on heterogeneous catalysts at the atomic scale. Top Catal 57:822–832

Hornes A, Hungria AB, Bera P, Camara AL, Fernandez-Garcia M, Martinez-Arias A, Barrio L, Estrella M, Zhou G, Fonseca JJ, Hanson JC, Rodriguez JA (2010) Inverse CeO_2/CuO catalyst as an alternative to classical direct configurations for preferential oxidation of Co in hydrogen-rich stream. J Am Chem Soc 132:34–35

McFarland EW, Metiu H (2013) Catalysis by doped oxides. Chem Rev 113:4391–4427

Metiu H, Chrétien S, Hu Z, Li B, Sun X (2012) Chemistry of Lewis acid-base pairs on oxide surfaces. J Phys Chem C 116:10439–10450

Nilius N, Freund HJ (2015) Activating nonreducible oxides via doping. Acc Chem Res 48:1532–1539

Pan Q, Liu BH, McBriarty ME, Martynova Y, Groot IMN, Wang S, Bedzyk MJ, Shaikhutdinov S, Freund HJ (2014) Reactivity of ultra-thin ZnO films supported by Ag(111) and Cu(111): a comparison to ZnO/Pt(111). Catal Lett 144:648–655

Price SP, Tong X, Ridge C, Neilson HL, Buffon JW, Robins J, Metiu H, Bowers MT, Buratto SK (2014) Catalytic oxidation of methanol to formaldehyde by mass-selected vanadium oxide clusters supported on a TiO_2(110) surface. J Phys Chem A 118:8309–8313

Rodriguez JA, Hrbek J (2010) Inverse oxide/metal catalysts: a versatile approach for activity tests and mechanistic studies. Surf Sci 604:241–244

Rodriguez JA, Grinter DC, Liu Z, Palomino RM, Senanayake SD (2017) Ceria-based model catalysts: fundamental studies on the importance of the metal-ceria interface in co oxidation, the water-gas shift, CO_2 hydrogenation, and methane and alcohol reforming. Chem Soc Rev 46:1824–1841

Senanayake SD, Stacchiola D, Evans J, Estrella M, Barrio L, Perez M, Hrbek J, Rodriguez JA (2010) Probing the reaction intermediates for the water-gas shift over inverse CeO_x/Au(111) catalysts. J Catal 271:392–400

Stacchiola DJ, Senanayake SD, Liu P, Rodriguez JA (2013) Fundamental studies of well-defined surfaces of mixed-metal oxides: special properties of $MO_x/TiO_2(110)$ $\{M = V, Ru, Ce, \text{or } W\}$. Chem Rev 113:4373–4390

Wachs IE (2005) Recent conceptual advances in the catalysis science of mixed metal oxide catalytic materials. Catal Today 100:79–94

Wachs IE (2013) Catalysis science of supported vanadium oxide catalysts. Dalton Trans 42:11762–11769

Zavyalova U, Holena M, Schlögl R, Baerns M (2011) Statistical analysis of past catalytic data on oxidative methane coupling for new insights into the composition of high-performance catalysts. ChemCatChem 3:1935–1947

Zhang Y, Kolmakov A, Chrétien S, Metiu H, Moskovits M (2004) Control of catalytic reactions at the surface of a metal oxide nanowire by manipulating electron density inside it. Nano Lett 4:403–407