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Theory of surface chemistry and reactivity of reducible oxides[☆]

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ABSTRACT

The increasing availability of computational data from quantum-chemical calculations on the reactivity and electronic structure of catalytically active oxidic systems make a revisitation of the classical questions on chemical bonding aspects of catalytically reactive systems useful.

This Perspective paper starts with a short review of the different available systems. The elementary reactions that are part of the selective oxidation catalysis, such as substrate bond activation or oxygen insertion, are introduced.

This is followed by a discussion of basic electronic features of the valence electron structure of oxide materials. We will initially compare the chemical bonding and reactivity of compounds with dominantly ionic versus covalent bonding. Surface reactivity descriptors for the two types of chemical bonds are indicated. It will appear that, except for longer range ionic interactions, binding to the metal cations is dominated by local covalent interactions and that ligand field theory type atomic orbital splitting as well as rehybridisation are important. Trends in bonding as a function of position of reducible metal in the periodic system are emphasized throughout the paper.

At the surface, in addition to the changes in electronic structure, atom position relaxation and surface reconstruction effects may also have a large influence on the differences in reactivity.

The reactivity of the oxygen atoms varies. They can be proton acceptors and generate Brønsted acidity, can assist heterolytic or radical type C–H bond activation or when electrophilic will insert into hydrocarbon double bonds.

At the end of the paper trends in catalytic reactivity are analyzed. The double volcano type curve found for the dependence of catalytic reactivity on the position of cation in the third row of the periodic system is shown to relate to the distribution of electrons with high spin over the ligand field split atomic orbitals of the respective cations. This will be discussed in the context of classical catalytic results that are based on Balandin type volcano plots of reactivity versus the catalyst material reactivity parameters.

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1. Introduction

Energy production by combustion has been essential to the early rise of human civilization. Currently the need to selectively produce energy without detrimental NO_x production has become important. It is one of the driving forces to develop new catalytic systems for total combustion [1]. Because of the temperatures involved, such catalysts will have to be heterogeneous. Catalytic partial oxidation is an important route to convert natural gas into synthesis gas, olefins and hydrogen [2]. Also, to produce chemicals, selective oxidation catalysis has become essential for the production of

chemical intermediates [3–6]. Catalysis for renewable energy processes as, for instance, the production of solar fuels is attracting increased attention nowadays [7–9].

The class of materials on which such catalytic processes are based are the reducible oxides. Their surface chemical reactivity and its relation to chemical bonding features will be the subject of this paper. The purpose is to identify the relevant reactivity parameters of a material that determine its activity and selectivity.

As a start, this requires basic knowledge of the types of reactions that occur between reagent and catalyst. We will initiate this paper with a short introduction of the different bond activation and oxygen insertion mechanistic steps that are currently known. Whereas experimental information is essential, this is currently rapidly complemented by detailed computational chemical studies [10–18].

[☆] Dedicated to: W.M.H. Sachtler, founder of Heterogeneous Catalysis Leiden.

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It is specifically our goal here to review the new insights obtained from such calculations to highlight the relation between chemical reactivity and surface chemical bonding features.

We will emphasize chemical concepts and insights, mainly based on results of recent quantum-chemical computational data obtained from state of the art DFT calculations. We will not review details of such calculations here, but refer to the existing literature [19–25]. It is worthwhile to mention that electronic correlation effects in reducible oxides are generally different from those in metals and molecules. Computational quantum chemical methods are available that account for this. They have been devised mainly by empirically adapting one center repulsion energy integrals of the localized *d*-electrons [26].

The chemical bond in a reducible oxide can be considered a balance of covalent and ionic bonding interactions. We will introduce the ionic bonding view from computed electronic and reactivity properties of essentially ionic compounds. We selected TiO₂ and CeO₂ as prototypical reducible oxides dominated by ionic bonding. Reducibility and water activation are reactivity aspects that we will discuss for these systems.

This will be followed by a subsection on materials in which covalent bonding dominates. We will discuss in detail the chemical bonding and reactivity of PdO, which is a prototype of a compound with dominantly covalent bonding. We will also discuss essential differences in the bonding between oxygen adsorbed to a metal surfaces and that in the oxide. We will see that the covalent bond in the oxide has similarities with ligand field type bonding as in coordination complexes. Catalytic reactivity aspects of methane activation will be used to illustrate the reactivity of PdO.

A section follows that uses now known concepts to the reader to analyze trends in chemical bonding and reactivity of the reducible oxide surface as a function of reactive cation position in the periodic system. We will see that generally an increase in valence electron count as well as of charge on the reactive cation will decrease the strength of M–O bonds.

The paper will conclude with a discussion of trends in catalytic activity. The question is addressed of the observation of double volcano plots in the catalytic [27] as well as electrocatalytic reactivity of the first row oxides [28] when this is plotted as a function of the position of the metal along a row of the periodic system.

2. The different types of elementary activation reactions in heterogeneous oxidation catalysis

In this section as an introduction to the later analysis of the reactivity of oxide surfaces we will discuss some examples of catalytic oxidation reactions. One can distinguish two different types of elementary reaction steps. In one type of reaction a C–H or C–C bond is activated by a surface oxygen atom, but the M–O bond is initially maintained. In the other type of reaction an O atom is inserted into a C–C or C–H bond, and the M–O bond is fully broken. As will be explained in detail in the following subsections, the first elementary reaction, of substrate bond activation type, can occur with or without a change of the valency of the metal atoms. In the second case the oxygen anion that inserts into a reacting molecule donates electrons to the surface cations and the formal valence of the surface cation(s) that release the oxygen atom reduces with 2 charge equivalents. The different activation modes are summarized in Fig. 1 and will be discussed in the following subsections.

A generally important question with respect to oxidation catalysis is whether reactions occur with a surface oxygen species of dissociatively adsorbed gas phase O₂, or whether reacting surface oxygen atoms can be considered bulk oxygen atoms. In the latter case the only function of O₂ dissociation is to reoxidize the surface. There is no need to be a correlation between the site where O₂ dissociates

and the site where (selective) oxidation of the reagent occurs. This combination of reaction events is called the Mars-van Krevelen mechanism [29]. Experimentally this can be investigated by using isotope-labeled gas phase O₂ molecules and to observe whether gas phase oxygen or oxide oxygen appears first in the product.

An important over all observation is that the products of the oxidation reaction are generally coordinately saturated molecules that have the singlet as spin state. However, the reacting oxygen molecule has initially a triplet spin state. In such a case the catalyst has also to take care of the required spin-flip and to relax the non-singlet spin state left on the catalyst after the reaction by fast consecutive electron spin-flip dissipation processes.

2.1. Substrate bond activation

As a reference to the later discussion on activation of the C–H bond by the metal oxide surface we will discuss first the activation of a C–H bond by a transition metal surface. This is the prototype reaction of the activation of a σ -type bond. Bond dissociation on a transition metal results in an adsorbed alkyl intermediate and an H atom. This reaction can be considered as homolytic. The dissociated fragments form qualitatively similar bonds with the surface metal atoms. It is the equivalent of oxidative addition as defined in organometallic chemistry and the valence state of the metal atom involved changes by 2+. The corresponding transition state of C–H activation of methane on a transition metal surface is shown in Fig. 1a.

On an oxide surface, in addition to homolytic C–H bond activation on a single cation, also heterolytic bond cleavage can occur. This is illustrated in Fig. 1b. In this case the H atom will attach to the oxygen atom and the alkyl group to the cation. The H atom and alkyl species now form chemically different bonds, one with the oxygen atom, and the other one with the metal atom. There is then no change in the formal valence of the cation. A computationally well studied example is the activation of a C–H bond by small Ga_xO_y or Zn_xO_z clusters located within the micropores of zeolites [30]. In the left part of Fig. 1b the transition state of the C–H bond cleavage in ethane is shown for heterolytic activation on a Ga₂O₂²⁺ cluster embedded in the zeolite micropore. Another example of a heterolytic reaction is the dissociative H₂O adsorption on non-reducing oxide surfaces. In this case the OH group attaches to the cation and the proton to a surface oxygen atom.

In summary, in a homolytic dissociation reaction two equivalent bonds are formed between the adsorbate fragments and the reactive surface cation, while in a heterolytic dissociation reaction one of the fragments attaches to the cation, the other to the anion. If in the first case the redox state of the cation will change, this does not have to happen in the second case.

Although this does not concern an oxidation reaction, it is useful to compare the heterolytic dissociation reaction with proton activation of a C–H bond of methane, shown in the right part of Fig. 1b. This also leads to qualitatively different bonds of reaction fragments with the metal-oxide surface. In this example the activation of the organic molecule by the zeolite proton generates a H₂ molecule and a positively charged carbenium ion that will re-adsorb to the negatively charged surface oxygen atom. The H atom that is generated by C–H bond cleavage forms a σ H–H bond whereas the CH₃ cation reacts with the zeolite framework anion to give a methoxy species [31–33]. C–H bond cleavage by solid acids also proceeds without change of the redox state of the proton charge compensating cation in the zeolite framework.

Case 1c illustrates radical-type bond activation. The surface oxygen atom reacts with the H atom of the C–H bond and generates a radical intermediate. This reaction of the O atom with the C–H bond can be considered electrophilic. This is in contrast to the previous heterolytic elementary reactions when a nucleophilic O anion

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