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Use of isotope exchange for determining series of elementary steps in electrocatalysis and heterogeneous catalysis

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ABSTRACT

The use of isotope exchange was recently shown to have a potential in determining continuous series of elementary steps in surface reactions. This was demonstrated by analyzing oxidation reactions on oxides. The method is based on equilibrating the oxide in $^{16}O_2$ then exposing it to $^{18}O_2$ and determining the dependence of the rate of $^{18}O^{16}O$ molecule desorption on oxygen partial pressure and on optional acceptor doping of the oxide. The isotope $^{18}O_2$ can be applied as a step function or as a pulse. We here discuss an implicit assumption made concerning the reaction that governs the isotope desorption, discuss the integrated desorption measured after the termination of a pulse of $^{18}O_2$, extend the discussion to isotopes other than oxygen and in particular show how to cope with the mass effect when using deuterium and hydrogen and finally discuss the relevance of isotope exchange experiments, where chemical equilibrium prevails, to analyzing electrocatalysis and heterogeneous catalysis in which significant gradients in the defect concentrations may arise.

1. Introduction

The experimental determination of continuous series of elementary steps in surface reactions is a difficult task with the methods known so far. Experiments can provide partial information referring to possible steps but not all steps of a series. We have recently suggested a novel experimental method for determining continuous series of elementary steps in oxidation reactions [1]. The steps are common to the initial steps of cathodic reactions and heterogeneous catalysis of oxidation on oxides. Reference [1] also includes a review of other experimental methods used to determine the elementary steps in oxidation reactions and their limitations.

The experimental method discussed uses oxygen isotope exchange starting with an oxide equilibrated in pure $^{16}O_2$ which then is abruptly exposed to pure $^{18}O_2$ gas. The oxygen partial pressure of the oxygen $P(O_2)$ is not changed. Chemical equilibrium is established and is maintained during the isotope change. Only isotopic non equilibrium takes place. In the measurement the rate of desorption of the mixed molecule $^{16}O^{18}O$ is measured to determine its dependence on $P(O_2)$ and on optional acceptor concentration in the oxide.

In a process a few parallel reactions can take place. One of them is assumed to be the fastest and thus the dominant one. We shall refer to the series of elementary steps in the fast reaction as the fast path. We assume that this is the case and concentrate on the series of steps in one path. In the previous publication [1] we analyzed a set of ten possible oxidation reactions and have shown that the rate r_p of $^{16}O^{18}O$ generation, for the ten reactions considered, depends differently on the oxygen gas partial pressure, $P(O_2)$, and on the concentration of acceptors $[A^{z\prime}]$, if present in the oxide (We use the Kröger-Vink notation of charge). The relation for nine of those reactions is of the form $r_p \propto P(O_2)^{m_1}[A^{z\prime}]^{m_2}$. The dependence is more complex in the ten's reaction where a second dopant is introduced. The rate of $^{18}O_2$ dissociation, J_0, can also be determined in many cases and has the form $J_0 \propto P(O_2)^{m_3}[A^{z\prime}]^{m_4}$. For each of the ten reactions examined the set of four exponents m_1–m_4 is different. This allows determining, experimentally, continuous series of elementary steps in the corresponding reactions.

The purpose of the present paper is to discuss two claims made in the previous paper and widen the discussion of the method. One claim was that there is a fast path out of a few parallel ones and that the rate of the $^{16}O^{18}O$ molecules generation is determined by the backward reaction of the fast path. The second claim concerns an option of measuring the rate of dissociation by measuring the total amount of $^{16}O^{18}O$ molecules desorbed after the isotope exchange is terminated. We shall examine the possibility to extend the method to exchange of isotopes other than oxygen and the difficulty arising in H_2 to D_2 exchange due to the mass effect. Finally, we shall discuss the question, what can be learned on electrocatalysis and heterogeneous catalysis, where significant chemical gradients may exist from isotope exchange experiments in which chemical equilibrium prevails.

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2. Principles of the method

2.1. The measurement procedure

In the isotope exchange experiment, use of a constant $P(O_2)$ regardless of isotopic composition and a constant temperature allows reaching chemical equilibrium. Under equilibrium a few significant concentrations remain constant while the isotopic composition changes. This is imperative in the calculation that relates the measured rate r_p of $^{16}O^{18}O$ generation and the experimental parameters $P(O_2)$ and $[A^{z\backslash}]$. Measuring these relations allows the determination of a continuous series of the elementary steps up to a slow one. The concentrations that stay constant, having the equilibrium value, are:

$$\begin{aligned}&p, n, [V_{ad}^{x}], \left[V_{O,s}^{\cdot\cdot}\right]\left[V_{O,b}^{\cdot\cdot}\right], \left\{\left[{}^{16}O_{ad}^{c1}\right] + \left[{}^{18}O_{ad}^{c1}\right]\right\},\\ &\left\{\left[{}^{16}O_{O,s}^{c2}\right] + \left[{}^{18}O_{O,s}^{c2}\right]\right\}, \left\{\left[{}^{16}O_{O,b}^{c3}\right] + \left[{}^{18}O_{O,b}^{c3}\right]\right\}\end{aligned} \tag{1}$$

where, p is the hole concentration, n the electron concentration, V_O the concentration of oxygen vacancies. The charges c1, …, c3 are relative ones using the Kröger-Vink notation: c1, c2, c3 = x, \ or ● (i.e. neutral, negative or positive, respectively). Three layers are considered for the position of an oxygen particle on the oxide. An adsorption site on the oxide surface is denoted "ad", an absorption site in the first bulk layer, i.e. the surface layer itself, is denoted by "s" and sites deeper in the bulk below the s layer are denoted by "b". It is assumed that there is no interaction within the gas molecules and that the re-adsorption of $^{16}O^{18}O$ molecules can be neglected due to their low concentration, which is kept low by use of a high flow rate of the $^{18}O_2$ gas.

We concentrate here on the short time approximation which means that the concentration of ^{16}O particles beyond a "slow" step can be considered close to that of equilibrium. The meaning of "slow" and "fast" is clarified next.

2.2. The reactions followed are those that include O_2 dissociation

The fact that the $^{16}O^{18}O$ molecule in the gas phase is monitored while the solid is exposed first to $^{16}O_2$ and then to $^{18}O_2$ means that the method follows reactions that involve a dissociation step of O_2 species. Oxidation reactions of solids, cathodic reaction and heterogeneous catalysis involving the Eley-Riddel and the Langmuir-Hinshelwood or Bonhoeffer-Farkas reaction, also commence with the dissociation of at least one molecule. Thus the relevance of following the rate of $^{16}O^{18}O$ desorption to those measurements. An example of a dissociation reaction is,

$$O_2 + 2V_{ad}^{x} \rightarrow 2O_{ad} + 2h^{\cdot} \tag{2}$$

For this dissociation reaction one can show [1] that the $P(O_2)$, $[A^{z\backslash}]$ dependence is: $J_0 \propto P(O_2)[A^{z\backslash}]^0$ and $r_p \propto P(O_2)^{7/4}[A^{z\backslash}]^{1/2}$.

When an oxide based on ^{16}O is exposed to $^{18}O_2$ the backward reaction step of the fast path is assumed to generate of the $^{16}O^{18}O$ molecules, the rate of which is measured. We shall discuss below under what conditions that reaction is indeed the dominant source of the $^{16}O^{18}O$ molecules. The reverse of O_2 dissociation reaction recombines two single oxygen particles into a molecule which may still be charged, i.e. not necessarily neutral at that step. The molecule may also not be free yet, e.g. be chemisorbed on the surface and further steps are required to free it into the gas phase. In the following example the reaction commences with chemisorption of the molecule,

$$O_2 + V_{ad}^{x} \rightarrow O_{2,ad} + h^{\cdot} \tag{3}$$

and proceeds to dissociation by,

$$O_{2,ad} + V_{ad}^{x} \rightarrow 2O_{ad} + h^{\cdot} \tag{4}$$

Association starts with the backward reaction of Eq. (4) but for $^{16}O^{18}O$ to be desorbed, the reaction has to proceed through the backward of the reaction in Eq. (3).

2.3. The time scale of the measurement

The assumption of a fast path among the parallel ones would be plausible if the reactions would proceed in the forwards direction only. However, the reactions considered here change direction to generate the $^{16}O^{18}O$ molecule. It cannot be, a-priori, excluded that another parallel reaction interferes to allow an enhanced backward reaction, i.e. there may be cross talk between parallel paths. In particular cross talk at the dissociation step is of interest. Possible cross talk before hand or later would only redefine the fast path. Hence, the definition of the "fast path" has to be refined. It is the path among all parallel paths without cross talk, which has the highest rate of $^{16}O^{18}O$ generation.

For the fast path, three types can be identified:

Type (a): The dissociation step is the slowest in the series, i.e. is significantly slower than the preceding ones. In this case the preceding steps can be considered to be close to isotopic equilibrium. In this case the concentrations of the various ^{18}O species involved in the overall reaction up to the dissociation step are all determined by isotopic equilibrium. In the example of Eq. (3)

$$P(O_2)[V_{ad}^{x}] = K(T)\left[{}^{18}O_{2,ad}\right]p \tag{5}$$

where the same notation K(T) will be used to indicate the relevant reaction constant for any reaction. The rate of $^{16}O^{18}O$ generation is from Eq. (4),

$$r_p = \overleftarrow{k}[{}^{18}O_{ad}][{}^{16}O_{ad}]p \tag{6}$$

It is limited by the supply of ^{18}O particles to the backward reaction. In the short time approximation it is given by the, assumed slow, forward reaction in Eq. (4),

$$J_0 = \vec{k}\left[{}^{18}O_{2,ad}\right][V_{ad}^{x}] \tag{7}$$

The concentration $[{}^{18}O_{2,ad}^{\backslash}]$ is determined by the isotopic equilibrium expression of Eq. (5).

Type (b): The slowest step in the fast path takes place beyond the dissociation step and all the preceding ones are much faster. Can the rate of the dissociation step be distinguished, on a finer time scale, from those that precede it? If it can and it is significantly slower, then the situation is equivalent to type (a) on the finer time scale. This means that experimentally the time resolution should be set accordingly. If, however, the dissociation is not significantly slower than the ones preceding it then one has also to consider the further elementary steps (still within the fast path) until one reaches a step significantly slower than the dissociation one. The experiment then has to be done on a longer time scale. The analysis has to consider all fast elementary steps, including the dissociation one, to be close to isotopic equilibrium except for the last step identified as the much slower one. In this case there is ample ^{18}O particles involved in the intermediate step that generates the $^{16}O^{18}O$ particles (i.e. the reverse of the dissociation step). On the other hand the supply of ^{16}O particles is limited as they are rapidly replaced by ^{18}O particles. A limited supply of ^{16}O comes from the slow step further down in the line of steps. As an example let us take the dissociation reaction Eq. (2) as fast, followed by a slow step of incorporation, of the already dissociated molecule, into the surface layer. The

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