A More Accurate Kinetic Monte Carlo Approach to a Monodimensional Surface Reaction: The Interaction of Oxygen with the RuO$_2$(110) Surface

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ABSTRACT: The theoretical study of catalysis would substantially benefit from the use of atomistic simulations that can provide information beyond mean-field approaches. To date, the nanoscale understanding of surface reactions has been only qualitatively achieved by means of kinetic Monte Carlo coupled to density functional theory, KMC-DFT. Here, we examine a widely employed model for oxygen interaction with the RuO$_2$(110) surface, a highly anisotropic system. Our analysis reveals several covert problems that render as questionable the model’s predictions. We suggest an advanced approach that considers all the relevant elementary steps and configurations while smoothing the intrinsic errors in the DFT description of oxygen. Under these conditions, KMC provides quantitative agreement to temperature-programmed desorption experiments. These results illustrate how KMC-based simulations can be pushed forward so that they evolve toward being the standard methodology to study complex chemistry at the nanoscale.

KEYWORDS: surface reactions, computer simulations, density functional theory, kinetic Monte Carlo, RuO$_2$, oxidation

1. INTRODUCTION

Understanding microscopic processes at the nanoscale is one of the crucial developments required to achieve atomistic engineering in catalysis. Methods based on density functional theory, DFT, that determine reaction profiles have been proven useful, but as the systems become more complex, the analysis is less straightforward. Mean-field microkinetic approaches based on DFT allow the integration of time scales and can provide coverages, reaction orders, apparent activation energies, and descriptors, but that might not yet be enough. In this perspective, the successful implementation of multiscale methods based on kinetic Monte Carlo (KMC) techniques with parameters obtained through DFT represents the most robust pathway to reach fully consistent ab initio simulations. The main challenge ahead of KMC is to derive quantitative data directly comparable to experiments, an objective that seemed far-fetched just a few years ago.

Compared with other mean-field approaches, KMC properly addresses surface anisotropy and lateral interactions but implies a high computational burden because initial, final, and transition states for a wide variety of local configurations need to be located and updated for different local distributions. In addition, the accuracy problems that are intrinsic to DFT are amplified when calculating rates, and in many cases, the calculation of the prefactors through statistical mechanics is either overlooked, simplified, or reduced. As a consequence, despite the enormous potential of KMC for the study of catalytic reactions on materials, its application has been confined mostly to qualitative interpretations. In the present manuscript, we show how for a truly monodimensional system the kinetic Monte Carlo approach is accurate enough to address the most stringent tests based on simulation of temperature-programmed desorption data, provided that (i) all the relevant structures are taken into account, (ii) the intrinsic errors of DFT are alleviated, (iii) full statistical thermodynamic contributions in the transition state theory are considered, and (iv) a sufficiently complex set of lateral interactions is taken into account.

To this end, we have chosen a highly anisotropic system, with industrial interest and for which a large amount of experimental data has been collected. RuO$_2$ is a powerful catalyst in oxidation reactions that has industrial applications in the Deacon process. The most common (110) exposed surface presents a large anisotropy, thus making it a wonderful scenario to test KMC techniques. From the very beginning of active research on RuO$_2$, in-silico simulations were found essential to understand its structural and catalytic features. Naturally, the interaction of RuO$_2$(110) with oxygen is the keystone in every oxidation process on the surface and, considering the number of publications that cover various aspects of this interaction,
one may expect the subject to be well-understood and generally closed. Below, we show that such a conclusion is premature.

To the best of our knowledge, all existing models of chemical processes on RuO$_2$(110) treat oxygen adsorption and desorption from the surface as single step elementary reactions. At the same time, it is well known that oxygen may be molecularly adsorbed to the surface, and it may stay there in different possible configurations prior to its dissociation. Is it a must to be accounted for in a reliable model of RuO$_2$(110) surface chemistry and whether it may be safely omitted in some cases has not been discussed.

2. MODEL AND METHODS

To approach the above-stated question, we employ ab initio simulations of RuO$_2$(110) within density functional theory and kinetic Monte Carlo techniques. DFT was performed in a p(1 \times 2) supercell (Figure 1). The data obtained were post-treated by cluster expansion to reconstruct the energies of larger pieces of the surface and to reveal the binding energies (Figure 2; the Supporting Information contains additional details) of oxygen adsorption, we need to calculate the rates of elementary reactions. Our actual DFT values, shown at the figure by the black profile, are somewhat different from those reported in ref 20 as a result of the use of different DFT functionals (RPBE instead of PW91). RPBE is known to provide more accurate adsorption energies compared to any other GGA functional. Still, available DFT methods are not accurate in the prediction of oxygen dissociation energy because of degeneration of the O$_2$ ground state in terms of both spin and orbit. The error is estimated as high as $\zeta = 0.56$ eV in the case of the RPBE functional. The value with our setup was reduced to 0.48 eV, but it is still large enough to significantly impact outcomes of KMC simulations; thus, it must be compensated. From a comparison to previous ways to overcome the problem and by analyzing the sensitivity of the KMC simulations series to this particular parameter when compared with experimental data on temperature-programmed desorption (TPD) of oxygen from RuO$_2$(110), we learned that a shift of the DFT-calculated energy of oxygen in the gas phase by 0.39 eV (70% of $\zeta$) is necessary. Because the molecularly adsorbed oxygen still bears some leftover spin, we have correspondingly shifted the DFT-calculated energies of O$_2^*$ (mono) and O$_2^{**}$ (dihapto) configurations by the values 0.08 and 0.04 eV, proportional to the gas-phase correction and the remaining magnetic moment of the adsorbate. The resulting corrected energy profile is shown in red in Figure 2, and it is referred to in the rest of discussion.

Let us consider adsorption of an oxygen molecule to a cus surface site, surrounded by oxygen atoms, as shown at the subimages $\alpha$, $\beta$, and $\gamma$ of Figure 2. Once it has approached the site, the O$_2$ molecule binds by one of its atoms to the Ru atom corresponding to the site (configuration O$_2^*$), and it gains 0.78 (case $\alpha$) or 0.58 eV (cases $\beta$, $\gamma$), compared with the energy in the gas phase. In the absence of close neighbors in both directions along the cus row, the O$_2^*$ state is not stable, as reorientation of the molecule parallel to the surface with connection of its second atom to the neighboring Ru (configuration O$_2^{**}$) gains an extra 0.16 (case $\alpha$) or 0.36 eV (cases $\beta$, $\gamma$), without any noticeable energy barrier on the way. Further dissociation of the oxygen molecule is controlled by a 0.57 eV activation barrier; once it is crossed, the system finds itself at the energy level 1.43–1.58 eV below the initial O$_2$ state. To sum up, at moderate coverages of O*, further O$_2$ adsorption and desorption turn out to be the two-step process O$_2$ $\rightarrow$ O$_2^{**}$ $\rightarrow$ O*, rather than the one-step process, O$_2$ $\rightarrow$ 2O*, adopted in refs 9, 18, and 23 and in numerous other works of the same research groups. One has to bear in mind that crowded surfaces (or, at least, large occupation of active sites) are expected under catalytic conditions. We also note that the O$_2^*$ state permits quite an easy diffusion of a separate oxygen molecule along the cus row via “flip-flops”, O$_2^{**}$ $\rightarrow$ O$_2^*$, with only a small energy barrier of 0.12 eV. For convenience, in the rest of article, we refer to the our two-step model of oxygen desorption as M-II, and to the one-step one as M-I.

To gain a deeper insight into the mechanics of oxygen adsorption, we need to calculate the rates of elementary reactions identified above. According to transition state theory, the rate of an elementary reaction is

$$r = \frac{kT}{h} \frac{q'}{q_0} \exp\left(-\frac{\Delta E}{kT}\right)$$

where $k$ and $h$ are Boltzmann and Planck constants, $T$ is the temperature of the system, $q'$ and $q_0$ are the partition functions of the system in the transition and initial states of the reaction, and $\Delta E$ is the activation energy. In the case of the molecular adsorption step from the gas phase to the surface (O$_2$ $\rightarrow$ O$_2^*$ in our model, and O$_2$ $\rightarrow$ 2O* in the one-step adsorption models), expression 1 must be additionally multiplied by $pV/kT$, where $p$ and $V$ are the pressure and volume of the gas phase. Once it is done, and the partition functions $q'$ and $q_0$ are properly expanded, expression 1 turns into the well-known result of kinetic gas theory

$$r = \frac{pA}{\sqrt{2\pi mkT}}$$

for nonactivated adsorption, where $A$ is the area of adsorption site, and $m$ is the mass of adsorbing molecule.

Fair calculation or experimental-based fitting of partition functions for the molecules adsorbed at the surface is far more challenging than obtaining the adsorbates’ binding energies because it demands the evaluation of all relevant vibrational frequencies of the system in the initial and transitional states of
the considered elementary reaction. It is common practice, usually employed in the implementations \(^9,18,23\) of M-I, to assume that \(q'\) and \(q_0'\) are equal to unity for the molecules and atoms adsorbed to the surface, or in transition states corresponding to on-surface diffusion. In our case, to reach a better accuracy, we calculate explicitly the vibrational frequencies of the adsorbates in \(O_2^*\) and \(O^*\) states, as well as in the dissociation transition state of the elementary reaction \(O_2^* \leftrightarrow 2O^*\), and use these data to calculate all partition functions in our M-II model (check the Supporting Information for details).

3. RESULTS AND DISCUSSION

The calculated rates are presented in Figure 3. For the best interpretation, they should be examined alongside the temperature desorption profile (Figure 4) corresponding to the desorption of oxygen from cus sites. Desorption becomes possible around 400 K, when the rate of desorption from the \(O_2^*\) state (red line on Figure 3) overrides the rate of dissociation from that state (green line). However, the net rate of desorption is limited by the formation of oxygen molecules from separate atoms (thin black line on Figure 3), because \(O_2^*\) state itself is very short-lived at temperatures around 400 K. Comparison of this desorption-limiting rate to the oxygen desorption rate according to M-I, as implemented in ref 18 (thick line on Figure 3), reveals why previously reported simulations of the \(O_2\) TPD peak looked successful. The two lines (ref 18 and the present model) intersect at \(T \approx 470\) K, and they are very close to each other in the vicinity of the TPD peak. On the other hand, the difference rapidly grows with small temperature changes. It is not that important for the lower temperatures because there, both lines show that desorption of an oxygen molecule from surface is quite a rare event, but for temperatures above 500 K, the two models predict radically different lifetimes of the \(O_2\) molecule on the surface. Thus, for \(T = 600\)–800 K the average time spent by an oxygen molecule on the cus-row of the surface is two-3 orders of magnitude longer, according to M-II, than it is predicted by M-I. It should be noticed that the industrially implemented Deacon reaction (HCl oxidation) runs slightly below 600 K.\(^12\) Thus, the lifetime differences between the two models is too
the error associated with the desorption of O2 to a smaller error for the oxygen association reaction, but again, magnitude. The approximation of the partition functions leads to the most interesting range of temperatures for practical applications, T = 200–800 K, the 0.1 eV error in energies leads to subsequent errors in the rates of 1–2 orders of magnitude. The approximation of the partition functions leads to a smaller error for the oxygen association reaction, but again, the error associated with the desorption of O2 has a similar size, 1–2 orders of magnitude, for the temperatures below 400 K and above 700 K. The errors demonstrated in

large to rely on predictions of M-I when it is used in the simulations of complex reaction networks on RuO2.

At this point, we want to highlight several issues that are not obvious from the discussion so far. First of all, an additional argumentation on the inconsistency of M-I model. The way the rate of 2O* → O2 reaction is calculated within M-I, with the application of the microreversibility condition between 2O* → O2 and O2 → 2O* reactions and with the assumption of nonactivated adsorption, implies that the transition state of the molecule during adsorption and desorption is similar to the state in the gas phase and that the energy of the molecule in this state is the same as in the atmosphere. Somewhere along the way from this transition state to the surface, the molecule must split into separate atoms. With the strength of the oxygen’s double bond of D2 ≈ 5.20 eV,28 this dissociation is possible only due to the catalytic effect of the surface. However, such interaction demands a very special binding of O2 to the surface (namely, it should be in the state similar to the transition state between O2* and 2O* in M-II). Reaching such a transition state will be the bottleneck of the dissociative adsorption and associative desorption because the actual “effective” transition state is very different from the one implicitly assumed in M-I.

We also have to emphasize the errors brought into the rates by the unjustified assumption that partition functions of molecules and atoms adsorbed to the surface are approximately equal to unity. In Figure 5, we compare the rates of the O2* → O2 and 2O* → O2 reactions of M-II as we calculate them (solid lines) with their values calculated with approximations of partition functions usually applied in implementations of M-I. In addition, we compare them with the values obtained by shifting the energy barrier values by ±0.1 eV (dotted lines). In the most interesting range of temperatures for practical applications, T = 200–800 K, the 0.1 eV error in energies leads to subsequent errors in the rates of 1–2 orders of magnitude. The approximation of the partition functions leads to a smaller error for the oxygen association reaction, but again, the error associated with the desorption of O2* → O2 has a similar size, 1–2 orders of magnitude, for the temperatures below 400 K and above 700 K. The errors demonstrated in these two examples can be tolerated in many particular cases, but they obviously also may lead to crucial mistakes under other circumstances. Thus, in general, an exact consideration of partition functions is essential. Under reaction conditions, some kind of compensation29 between the rates and the coverages can be expected; however, for very complex reactions, it would be impossible to assess the correct behavior of this error cancellation.

Finally, we should notice that the previous implementation9,16,23 of the M-I model has not taken into account lateral interactions between the adsorbates. According to our approach, for example, the binding energy of O2 shifts (Figure 2) by 0.07–0.20 eV, depending on the coverage of neighboring sites by oxygen atoms. According to the evaluation provided above, such an energy shift results in a significant dependence of the rates of elementary reactions on surface coverage by adsorbates. Indeed, the explicit account of lateral interactions in M-II results in a visible alteration of the calculated O2 TPD peak (Figure 4). Instead of the symmetric peak produced18 by the M-I model, the M-II model leads to a clearly asymmetric profile, formed by several overlapping peaks of different sizes, corresponding to oxygen desorption from nearby energy levels, determined by the lateral interactions. The resulting peak shape is much closer to the experimentally measured22 one. We have further improved the match of our calculated profile with the experimental one by the application of smoothing

$$\bar{f}(t) = \int_{-\infty}^{t} f(t') \exp \left( -\frac{t - t'}{\tau} \right) dt'$$

on the simulated oxygen desorption signal f(t’), where t’ is the system’s time, and \(\tau\) is a smoothing constant. Underlying this formula is the fact that in an experimental setup, desorption spectra are recorded as the amount of desorbed molecules seen.
by a spectrometer’s detector at each moment of time. It is
to assume a finite delay between the actual desorption of
a molecule out from the sample’s surface and its registration
by the detector. Avoiding a complicated account for exact
geometry of an experiment, it is natural to assume that the
mentioned delays between desorption and registration of
molecules are distributed exponentially, effectively leading to
smoothing 3 of the spectra. The resulting TPD profile (Figure
4, red line), calculated for \( \tau = 4.0 \) s, matches the experimentally
measured one almost perfectly (dependence of the result on
the choice of \( \tau \) is further explored in Figure S1 in the
Supporting Information). We consider that such smoothing
efﬁciently imitates the response curve of a spectrometer used in
TPD experiments.

4. CONCLUSIONS

In conclusion, we have investigated some features of a widely
applied model (M-I) of oxygen interaction with so-called
cus sites of RuO\(_2\)(110) surface. Although a number of works report
successful application of the M-I model (single step O\(_2\)
adsorption/desorption) for calculations of O\(_2\) temperature
desorption proﬁles and for investigation of various chemical
processes on the RuO\(_2\)(110) surface without visible problems,
we have found signiﬁcant hidden differences in the oxygen
desorption rates predicted by M-I and our alternative, more
complex, model, M-II. These differences emerge from (i)
oversimpliﬁcation of the oxygen adsorption process in M-I; (ii)
the lack of lateral interactions of the adsorbates on the surface;
(iii) the assumptions on equality of partition functions of
adsorbed atoms and molecules to unity; and ﬁnally, (iv) intrinsic
errors associated with the accuracy of DFT. Our results for the
very stringent test of O\(_2\) TPD, obtained with the use of the M-
II model, show a visible improvement in the shape of the
simulated desorption peak. We also expect that improvements
of M-II compared with M-I are crucial for simulations of
complex chemical processes on RuO\(_2\)(110) surfaces, especially
at temperatures above 500 K, where most of the interesting
oxidation chemistry appears.\(^{12}\)

We ﬁrmly believe that the analysis presented paves the way
for a quantitative use of kinetic Monte Carlo tools for systems
showing high anisotropy at the nanoscale.

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**ASSOCIATED CONTENT**

2 Supporting Information
A summary with the detailed models. This material is available
free of charge via the Internet at http://pubs.acs.org/.

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Notes
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