A microscopic perspective on heterogeneous catalysis

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Abstract: A general formalism is presented to describe the turnover frequency (TOF) during heterogeneous catalysis beyond a mean field treatment. The turnover frequency (TOF) measures the number of molecules of the product of interest generated per second and is traditionally expressed in terms of the partial pressures of the reactants. However, this expression must be modified when adsorbate-adsorbate interactions are considered. For every elementary reaction, we define its multiplicity as the number of times the reaction can be performed within some temperature range. Thus, the overall catalytic reaction occurs as if a single reaction would be the dominant reaction (say λ) is sufficiently low so that it acts as a bottleneck or rate-determining step (RDS)1–4. Based on this, traditional descriptions of surface reactions using standard models, such as the Langmuir-Hinshelwood mechanism—for reactions between two adsorbed molecules—lead to expressions for the TOF in terms of the adsorbate coverages (See Section S1 of the Supporting Information for some examples). For instance, if the recombination of the adsorbates, A and B, is the RDS, with rate constant λ, one writes: TOF = rλ = kλθAθB, where the coverage product θAθB assumes A and B are high mobilefreely intermix (random homogeneous mixing or mean field approximation).

I. INTRODUCTION

Enabling life through enzymatic acceleration of biochemical processes, catalytic reactions are also a key element of modern society, speeding up the production of a wide variety of chemical, pharmaceutical, petrochemical and fertilizing compounds. In a typical heterogeneous reaction, many elementary reactions continuously compete with each other at the catalytic surface. This includes elementary adsorption, desorption, diffusion and reaction steps, with temperature dependent rate constants, kα = e⁻Eα/kBT, where kB is Boltzmann’s constant, T is the temperature and Eα is the activation energy for reaction α. On the other hand, the turnover frequency (TOF) measures the overall number of molecules of the product of interest generated per active site per unit time. Interestingly, the TOF typically increases with temperature according to an Arrhenius behavior, TOF ∝ e⁻Eapp/kBT, where Eapp is referred to as the apparent activation energy—usually constant within some temperature range. Thus, the overall catalytic reaction occurs as if a single reaction would be in control.

Traditionally, this is accounted for by considering every elementary reaction as an elementary step and the overall reaction as a sequence of such elementary steps, assuming that the rate of one particular elementary reaction (say λ) is sufficiently low so that it acts as a bottleneck or rate-determining step (RDS)1–4. Based on this, traditional descriptions of surface reactions using standard models, such as the Langmuir-Hinshelwood mechanism—for reactions between two adsorbed molecules—lead to expressions for the TOF in terms of the adsorbate coverages (See Section S1 of the Supporting Information for some examples). For instance, if the recombination of the adsorbates, A and B, is the RDS, with rate constant λ, one writes: TOF = rλ = kλθAθB, where the coverage product θAθB assumes A and B are high mobilefreely intermix (random homogeneous mixing or mean field approximation).

By assuming Langmuir adsorption-desorption equilibria for all adspecies (A, B and AB) and their gaseous counterparts (A(g), B(g) and AB(g)), the coverages are traditionally expressed in terms of the partial pressures (pA, pB and pAB): θA = KpA/D, θB = √KpBpAB/D and θAB = KpAB/D, with D = 1 + KpA + √KpBpAB + KpAB. Here, KX = kX/kY ∝ e⁻ΔHx/kBT is the equilibrium constant for the adsorption of X, with ΔHx = EαX - EαY the formation enthalpy (or heat of adsorption) of X (α = A, B, AB) is the activation barrier for adsorption (desorption) of X, with kα ∝ e⁻Eα/kBT (kα ∝ e⁻Eα/kBT) the rate constant for adsorption (desorption). This leads to: TOF = kλθAθB = kλ(KpA)(KpB)(D)⁻², which is re-written as: TOF = kλ(KpA)²(KpB)²y(KpAB)⁻², where x = dlogTOF, y = dlogTOF, and z = dlogTOF are the partial reaction orders, effectively transferring the original coverage dependence into them. Since the temperature dependence is TOF ∝ e⁻Eapp/kBT, where kα ∝ e⁻Eα/kBT and KX ∝ e⁻ΔHx/kBT, for X = A, B, AB, this gives rise to the...
familiar Temkin formula\textsuperscript{3–6}:
\[ \text{ETOF}^{\text{app}} = E_k^\alpha - x\Delta H_A - y\Delta H_B - z\Delta H_{AB}. \]  
(1)

Eq. 1 provides a traditional explanation to the convoluted nature of $E_{\text{app}}^{\text{TOF}}$, departing from the activation barrier of the RDS, $E_k^\alpha$, due to a weighted sum of formation enthalpies with coverage-dependent reaction orders as weights. Beyond the mean field treatment ($\text{TOF} = r_\lambda = k_\lambda\theta_A^\alpha\theta_B^\gamma$), Eq. 1 remains valid in the presence of correlated configurations on the catalyst surface, since in this case one may still write $r_\lambda = k_\lambda\theta_A^\alpha\theta_B^\gamma$, which preserves the general form of Eq. 1. Once more, this transfers the details about the dependence on the spatial configuration (including any possible correlations) to the pressure-dependent reaction orders, thus diverting the focus from the actual surface configuration. Nevertheless, this has proved very useful in practice, since the reaction orders can be determined experimentally with relative ease.

In this study, however, we stress the importance of considering the spatial structure of the surface, explicitly describing the presence of correlated configurations via an alternative formulation: $\text{TOF} = k_\lambda M_\lambda$. Here, the general phenomenological term $\theta_A^\alpha\theta_B^\gamma$ is replaced by the multiplicity, $M_\lambda$, which directly accounts for the actual number of locations where reaction $\lambda$ can be performed per active site. To our best knowledge, the presence of a quantity like $M_\lambda$ has been traditionally obviated, directly replacing it by simple/sophisticated functions of the averages and, correspondingly, of the pressures through Langmuir-type adsorption equilibria. However, here we assign $M_\lambda$ a central role, directly relating it to configurational entropy in Section II. Amongst other benefits, the use of the multiplicity enables an alternative description of the complex behavior of $E_{\text{app}}^{\text{TOF}}$.

Turning away from Eq. 1, $E_{\text{app}}^{\text{TOF}}$ is sometimes attributed to (i) the elementary reaction with the largest activation energy (slowest rate constant), $E_{\text{app}}^{\text{TOF}} = \{ E_k^\alpha \}_{\text{max}}$, or (ii) the activation energy of the bottleneck itself (slow enough rate constant), $E_{\text{app}}^{\text{TOF}} = E_k^\alpha$ without any modifying contribution in either case. The idea that $E_{\text{app}}^{\text{TOF}}$ corresponds to the largest $E_k^\alpha$ contradicts careful computational studies outside the mean field formulation, where $E_{\text{app}}^{\text{TOF}}$ deviates (usually by large) from any of the $E_k^\alpha$’s present in the system\textsuperscript{7,8}. To describe the surface anisotropy and lateral interactions outside the mean field treatment, those studies use the Kinetic Monte Carlo (KMC) method\textsuperscript{9–17}. By accounting for fluctuations, correlations and the spatial distribution of the reaction intermediates—even including adsorbate clustering/islanding intrinsically—KMC provides a thorough picture of the ongoing competition between the various elementary reactions, whose modeling within a rate-equation approach would be rather complex. Within this framework, detailed consideration of the \textit{degree of rate sensitivity} ($\xi_\alpha$, originally referred to as the \textit{rate sensitivity} in\textsuperscript{18}), concludes that $E_{\text{app}}^{\text{TOF}}$ can be formally described as an \textit{average} over all forward and backward elementary activation energies\textsuperscript{1}:
\[ E_{\text{app}}^{\text{TOF}} = \sum_\alpha \xi_\alpha E_k^\alpha, \]  
(2)

where $\xi_\alpha = \frac{k_{\text{app}}}{k_{\text{TOF}}} \frac{\partial \text{TOF}}{\partial k_\alpha} |_{k_\alpha \rightarrow 0}$ and the partial derivative with respect to rate constant $k_\alpha$ is taken by keeping fixed all other rate constants $k_\alpha'.\alpha$. In fact, a closely related quantity, the \textit{degree of rate control} ($\chi_\alpha = \xi_\alpha + \xi_\alpha'$, where $\alpha'$ designates the combined forward-and-backward reaction) has been successfully and repeatedly used in many systems to identify (i) the RDS, which is defined as the elementary reaction for which $\chi_\alpha = 1$, if it exists, and (ii) the Rate Controlling Steps (RCSs), which are defined as those elementary reactions for which $\chi_\alpha$ significantly deviates from $0\textsuperscript{4,7,8,19}$. Furthermore, a combined analysis of both $\chi_\alpha$ and $\xi_\alpha$ provides crucial knowledge on the relative importance of the various elementary reactions\textsuperscript{7,8}, giving valuable guidance as to which reactions need to be determined with higher accuracy\textsuperscript{20,21}.

In practice, however, the determination of $\chi_\alpha$ and $\xi_\alpha$ outside a mean field formulation requires a formidable effort\textsuperscript{7,8}. Not only these quantities form a high-dimensional space, but every value needs to be determined by carefully analyzing the numerical derivative of the TOF for various values of $k_\alpha$, while every TOF value must be obtained by averaging over several stochastic KMC simulations after reaching the steady state, which in turn is achieved at the long time limit on computationally inefficient stiff systems (where some reactions are executed many orders of magnitude less frequently than others). Thus, in practice the description of $E_{\text{app}}^{\text{TOF}}$ by Eq. 2 is time-consuming and relatively inaccurate (see the Discussion for details). Indeed, the computational effort required to determine $\chi_\alpha$ and $\xi_\alpha$ is so large that alternative ‘practical approaches’ are being sought\textsuperscript{22}.

In addition, Eq. 2 does not formally fit the requirements of a \textit{weighted average}. Although the sensitivities sum one ($\sum_\alpha \xi_\alpha = \sum_\alpha \chi_\alpha = 1$, see Ref.\textsuperscript{7}), they are unbounded (taking any possible value: positive, negative or zero)\textsuperscript{7}. While this is a valuable feature for sensitivity analysis, with positive (negative) values denoting promotion (hindering) of the TOF, a problem appears when $\xi_\alpha$ and $\chi_\alpha$ are used effectively as weights to describe the most dominant contributions to the apparent activation energy, as in Eq. 2 for the case of $\xi_\alpha$ (or Eq. 34 below, for $\chi_\alpha$). Mathematically, the weights in a weighted average are probabilities and, thus, they should be non-negative, between 0 and 1. This enables a simple interpretation of the dominant/vanishing contributions. From the perspective that an average is a middle value, negative weights may lead to a result outside the range of the data, in which case one will be confronted with a linear combination, not a weighted average. Unfortunately, linear combinations in general, and Eqs. 2 and 34 in particular, are not the most suitable approach to describe dominance. If one truly wishes to find out which elementary reactions have a dominant role, then the weights
need to be positive and, thus, $\xi_\alpha$ and $\chi_\alpha$, need to be reconsidered.

Given such limitations in the use of Eqs. 1 and 2, we propose a different approach to analyze heterogeneous catalytic reactions in general. Simply stated, we present the idea that, at any given instant, every elementary reaction occurring on a catalyst can be performed at different locations and, thus, every elementary reaction has an associated multiplicity. In this manner, while tradition considers the adsorbate coverages as the natural (irreducible) variables required to describe the evolution of the system, we put forward the idea that it is the collection of these multiplicities—for each and every elementary reaction—that provides the natural description of the configurational structure of the surface and, thus, the evolution of the system.

Compared to Eq. 2, explicit use of the multiplicities provides access to an alternative, more accurate weighted average for $E_{app}^{\alpha}$ (Eq. 26 below). The new expression is both simpler to use in practice and theoretically robust, incorporating always-positive-and-properly-normalized probabilities as weights. Compared to Eq. 1, when a RDS exists, the corresponding new expression (Eq. 31 below) describes how the elementary activation energy of the RDS, $E_A^k$, contributes to $E_{app}^{\alpha}$ with a modified value due to changes in configurational entropy, remaining valid even when adsorbate-adsorbate interactions are taken into account. Furthermore, we show below that the proposed multiplicities also provide an alternative route in order to determine the RDS as well as the sensitivity of the TOF to the different elementary reactions. In this manner, the proposed multiplicities enable an alternative perspective for the analysis of heterogeneous catalysis in general.

We finally stress that, for other surface processes, such as two-dimensional epitaxial growth and three-dimensional anisotropic etching, the origin of the apparent activation energy has been previously explained via similar multiplicity-based formulations.

### II. THEORY

#### A. Multiplicity of an elementary reaction

Let us consider a general heterogeneous catalytic system evolving in time. The system consists of a surface with a number of active sites as well as various adsorbates and their respective gases, all of them acting as reactants/products in a complex network of elementary reactions. Starting from a given initial configuration, the system evolves in time and currently, at time $t$, it displays some specific configuration. Note that $t$ denotes any instant along the initial transient or during the final steady state.

In this context, elementary reaction $\alpha$ (with rate constant $k_\alpha$) is associated an instantaneous multiplicity, $M_\alpha = \tilde{m}_\alpha / \dot{s}$, which denotes the number of times the reaction can be performed in the current configuration, $\tilde{m}_\alpha$, divided by the number of active sites, $\dot{s}$ (see Fig. 1). In other words, the instantaneous multiplicity describes the number of locations where the elementary reaction can occur (at the current instant and per active site), i.e. the actual abundance of the reaction per active site. Beyond the simplistic, periodic array of active sites depicted in Fig. 1, the proposed multiplicity remains valid for more general scenarios, e.g. for randomly distributed active sites on a complex, three dimensional support.

Although the number of active sites $\dot{s}$ typically remains constant, the value of $\tilde{m}_\alpha$ (and, thus, that of $M_\alpha$) changes dynamically as new configurations of the surface are visited during the transient, eventually settling down to some value and fluctuating around it at the steady state. In this context, the average value of any instantaneous variable $\dot{A}$ is defined as $\dot{A} = \langle \dot{A} \rangle$, where $\langle \dot{X} \rangle = \int \dot{X} \, dt = \frac{\sum_{\alpha} X \Delta t_\alpha}{\sum_\alpha \Delta t_\alpha}$ is the time average of $X$, and $\langle \dot{X} \rangle$ is the mean value of $X$ for a total of $K$ evolutions from the initial state, in the limit of large $K$. Below, we focus on performing the time average $\langle \dot{X} \rangle$ within the steady state,

| $\alpha$ | reaction | times present, $\tilde{m}_\alpha$ | multiplicity, $M_\alpha = \tilde{m}_\alpha / \dot{s}$ |
|---|---|---|---|
| 1 | adsorption A | 41 | 41/49 |
| 2 | adsorption B | 41 | 41/49 |
| 3 | desorption A | 4 | 4/49 |
| 4 | desorption B | 3 | 3/49 |
| 5 | desorption AB | 1 | 1/49 |
| 6 | diffusion A | 12 | 12/49 |
| 7 | diffusion B | 10 | 10/49 |
| 8 | diffusion AB | 4 | 4/49 |
| 9 | recombination A+B | 2 | 2/49 |

**FIG. 1.** Simplistic example of an instantaneous configuration on a catalyst, showing the instantaneous multiplicity values for a reaction mechanism with nine elementary reactions. Diffusion and recombination are limited to nearest neighbor active sites. The system has $\dot{s} = 7 \times 7 = 49$ sites.
since most catalytic systems are of interest in that condition. In addition, it is implied below that any variable not preceded by the word 'instantaneous' and/or not displayed with the 'hat' symbol (\( \hat{} \)) is either a constant or it designates the steady-state average value, even if the word 'average' is not mentioned. While the instantaneous values (such as \( M_a, \hat{m}_a \) or \( \hat{s} \)) apply to a particular configuration of the system, the steady-state averages (such as \( M_a, m_a \) or \( s \)) describe features of the macroscopic state (or 'average' configuration).

### B. Rate equations and master equation

Typical rate equations in heterogeneous catalysis describe the time evolution of the coverage for every adsorbate \((\theta_X)\) in terms of (i) the coverage of the other adsorbates \((\theta_Y)\) and (ii) the rate constants of the elementary reactions where \( \theta_X \) is modified. For instance, for a standard Langmuir-Hinshelwood mechanism,

\[
\begin{align*}
A(s) & \xrightarrow{k^A_{[R1]}} B(s) \xrightarrow{k^B_{[R2]}} C(s) \\
& \quad \xrightarrow{k^C_{[R3]}} k^C_{[R4]} \xrightarrow{k^C_{[R5]}} \xrightarrow{k^C_{[R6]}} C,
\end{align*}
\]

where the irreversible reaction between adsorbates \( A \) and \( B \) is considered as the Rate Determining Step (RDS), the rate equations are:

\[
\begin{align*}
\dot{\theta}_A &= 1 - \theta_A - \theta_B - \theta_C \\
\dot{\theta}_B &= p_A k^A_{[R1]} \theta_s - k^A_{[R2]} \theta_A - k^a_{[R2]} \theta_B \\
\dot{\theta}_C &= p_B k^B_{[R2]} \theta_s - k^B_{[R3]} \theta_B - k^a_{[R3]} \theta_A \\
\dot{\theta}_x &= p_C k^C_{[R3]} \theta_s - k^C_{[R4]} \theta_C + k^a_{[R4]} \theta_B.
\end{align*}
\]

Here, \( \theta_s \) is the coverage by all the empty sites while \( \theta_x \) is the coverage by all empty site pairs (in the mean field approximation) and \( \theta_A \theta_B \) is the coverage by all site pairs occupied by \( A \) and \( B \) (also under random mixing).

In this study, however, we stress the view that the rate equations can be written in terms of the multiplicities. For systems with a spatial representation (an important feature for the study of correlations beyond mean field), this seems more natural. Not only one has direct access to the multiplicities themselves, as shown below, but also the resulting equations remain valid beyond the mean field picture.

For this purpose, let us consider a spatial representation of a catalytic system evolving according to the reactions in Eq. 3:

\[
\begin{align*}
\{s_i\} & \rightarrow \{s_j\} \\
\star \star \star \star \star & \rightarrow \star \star \star \star \star \\
A & \rightarrow A \\
B & \rightarrow B \\
C & \rightarrow C
\end{align*}
\]

Here, configuration \( \{s_i\} \) has changed into configuration \( \{s_j\} \) due to the elementary reaction \( A + B \rightarrow C + \star \) (under the assumption that \( C \) always replaces \( A \) and \( \star \) replaces \( B \); the reverse leads to simple modifications). Traditionally, the time evolution of the system is described by the master equation:

\[
\frac{dp_{\{s_i\}}}{dt} = \sum_{\{s_j\}} k_{\{s_j\} \rightarrow \{s_i\}} p_{\{s_j\}} - \sum_{\{s_j\}} k_{\{s_i\} \rightarrow \{s_j\}} p_{\{s_i\}},
\]

where \( p_{\{s_i\}} \) is the probability to observe configuration \( \{s_i\} \) at time \( t \) and \( k_{\{s_i\} \rightarrow \{s_j\}} \) is the transition rate (\( = \) rate constant) for the elementary reaction that transforms \( \{s_i\} \) into \( \{s_j\} \).

Because an elementary reaction can be performed only if the correct local configuration of the adsorbates and/or empty sites is present on one or more locations in the current configuration, the multiplicity of an elementary reaction corresponds to the multiplicity of that particular local configuration of the adsorbates and empty sites. Thus, for any given configuration \( \{s_i\} \), we consider the instantaneous multiplicity of local configuration \( \{l\} \), \( \hat{M}_{\{l\}} = m_{\{l\}} / \hat{s} \), where \( \hat{s} \) is the number of active sites (as before) and \( m_{\{l\}} \) is the number of times the local configuration \( \{l\} \) appears on \( \{s_i\} \). Here, \( \{l\} = \{A, B, C, \ldots, Z\} \) refers to any collection of sites, such that one site is occupied by adsorbate \( A \), which has a neighbor site occupied by adsorbate \( B \), which in turn has a neighbor site occupied by adsorbate \( C \) and so on. Thus, local configurations \( \{A, B, C, \ldots, Z\} \) and \( \{Z, \ldots, C, B, A\} \) are the same, and empty sites are included by using the symbol \( \star \). This way, \( \hat{M}_{\{X\}} \) refers to the instantaneous coverage by adsorbate \( X \) while \( \hat{M}_{\{X,Y\}} \) and \( \hat{M}_{\{X,Y,Z\}} \) indicate the instantaneous concentration of adsorbate pairs and adsorbate trios (per active site, respectively). Note that \( \sum_{\{X\}} \hat{M}_{\{X\}} = 1 \) and, similarly, \( \sum_{\{X,Y\}} \hat{M}_{\{X,Y\}} = b, \sum_{\{X,Y,Z\}} \hat{M}_{\{X,Y,Z\}} = c, \sum_{\{S,T,U,V\}} \hat{M}_{\{S,T,U,V\}} = d, \ldots \), where \( b, c, d, \ldots \) depend on the actual spatial representation (see some specific values below). Eventually, the focus is on monitoring the multiplicities of the elementary reactions, \( \hat{M}_a \), each corresponding to a particular \( \hat{M}_{\{l\}} \).

Any change in the spatial configuration \( \{s_i\} \) of the system due to an elementary reaction leads to modifications in the multiplicities. For instance, considering the system of Eq. 8 and restricting the formation of neighbor pairs to the (periodic) horizontal and vertical directions, the multiplicities of the seven elementary reactions in Eq. 3, \( \{a = R1, R2, \ldots, R7\} \) have changed as follows: \( \hat{M}_{R1} = \hat{M}_{\{A\}} = 5 \rightarrow 4, \hat{M}_{R2} = \hat{M}_{\{\star\}} = 11 \rightarrow 12, \hat{M}_{R3} = \hat{M}_{\{B,B\}} = 1 \rightarrow 1, \hat{M}_{R4} = \hat{M}_{\{\star,\star\}} = 15 \rightarrow 17, \hat{M}_{R5} = \hat{M}_{\{C\}} = 0 \rightarrow 1, \hat{M}_{R6} = \hat{M}_{\{\star\}} = 11 \rightarrow 12, \hat{M}_{R7} = \hat{M}_{\{A,B\}} = 6 \rightarrow 4 \). Although we may monitor many other local configurations (e.g. \( \hat{M}_{\{\star,\star\}} = 6 \rightarrow 5, \hat{M}_{\{\star,\star\}} = 8 \rightarrow 6, \hat{M}_{\{A,B,\star\}} = 3 \rightarrow 1, \hat{M}_{\{B,B,A\}} = 1 \rightarrow 1, \ldots \)), it is important to realize that none of these is strictly required to determine the \( \hat{M}_a \)'s, since these can be directly obtained from the spatial configuration itself.
The previous definitions allow rewriting Eqs. 5-7 as:

\[
\frac{d\hat{M}_\alpha}{dt} = p_{A^\alpha} \hat{M}_\alpha - k_d^A \hat{M}_\alpha - k_r \hat{M}_{A,B} 
\]  

(10)

\[
\frac{d\hat{M}_{A,B}}{dt} = p_{B^A} \hat{M}_{A,B} - k_d^B \hat{M}_{A,B} - k_r \hat{M}_{A,B} 
\]  

(11)

\[
\frac{d\hat{M}_{A,C}}{dt} = p_{C^A} \hat{M}_{A,C} - k_d^C \hat{M}_{A,C} + k_r \hat{M}_{A,B} 
\]  

(12)

The corresponding equation for \( \frac{d\hat{M}_{(x)}{dt}} \) is redundant, since \( \sum_{(X)} \hat{M}_X = 1 \). Note that, in general, \( \frac{d\hat{M}_{(x)}{dt}} \) depends on \( \hat{M}_{U,V} \). Thus, these equations need to be completed by rate equations for \( \frac{d\hat{M}_{(x,y)}{dt}} \):

\[
\frac{d\hat{M}_{A,B}}{dt} = p_{A^\alpha} k_d^A \hat{M}_{A,B} + p_B k_d^B \hat{M}_{A,B} - k_d^B \hat{M}_{A,B} - k_r \hat{M}_{A,B} 
\]  

(13)

\[
\frac{d\hat{M}_{A,B}}{dt} = -p_{A^\alpha} k_d^A \hat{M}_{A,B} - p_B k_d^B \hat{M}_{A,B} + k_r \hat{M}_{A,B} 
\]  

(14)

\[
\frac{d\hat{M}_{(x,y)}}{dt} = p_{(x,y)} \hat{M}_{(x,y)} - k_d \hat{M}_{(x,y)} - k_r \hat{M}_{(x,y)} 
\]  

(15)

and similar equations for the derivatives of \( \hat{M}_{A,C}, \hat{M}_{B,C}, \hat{M}_{C,C} \), \( \hat{M}_{A,A} \), \( \hat{M}_{A,A} \) and \( \hat{M}_{(x,y)} \), with one of them redundant, since \( \sum_{(X,Y)} \hat{M}_{(X,Y)} = 2 \) in this example. As before, \( \frac{d\hat{M}_{(x,y)}{dt}} \) depends on \( \hat{M}_{U,V,W} \).

Thus, additional equations are written for \( \frac{d\hat{M}_{(x,y)}{dt}} \) (with \( \sum_{(X,Y,Z)} \hat{M}_{(X,Y,Z)} = 6 \), and for \( \frac{d\hat{M}_{(x,y,z)}{dt}} \) (with \( \sum_{(S,T,U)} \hat{M}_{(S,T,U)} = 36 \) and so on.

Accordingly, for a general reaction mechanism, containing elementary reactions of different types, including adsorption (a), desorption (d), diffusion (h) and recombination (r), the generic rate equation for \( \hat{M}_{(l)} \) is:

\[
\frac{d\hat{M}_{(l)}}{dt} = \sum_{g=a,d,h,r} \sum_{(l)} k_{(l)}^{g} \hat{M}_{(l)}^{l} - \sum_{g=a,d,h,r} \sum_{(l)} k_{(l)}^{g} \hat{M}_{(l)}^{l},
\]  

(16)

where \( k_{(l)}^{g} \) is the rate constant for an elementary reaction of type \( g \) that transforms local configuration \( (l) \) into local configuration \( (l) \), and local configuration \( (l) \) contains \( (l) \) in such a way that the reaction \( (l) \rightarrow (l) \) destroys \( (l) \). For instance, \( (l) \rightarrow \{B, B, A\} \) contains \( \{B, B, A\} \) and the recombination of \( B \) and \( A \) and \( B \) will lead to \( \{B, B, A\} \), thus destroying \( \{B, B, A\} \) and decreasing \( \hat{M}_{(B, B)} \) (see Eq. 16).

Eq. 16 is the master equation considered in this study, written in terms of the time evolution of occupation variables, i.e. the instantaneous multiplicities of local configurations. Together with the expressions linking the multiplicities (\( \sum_{X} \hat{M}_{(X)} = 1, \sum_{X,Y} \hat{M}_{(X,Y)} = b \)), the initial values of the \( \hat{M}_{(l)} \)’s will enable obtaining their future values and, thus, the values for the multiplicities of the elementary reactions. For extended catalytic systems, however, it is easier to monitor the multiplicities of the elementary reactions directly from the visited spatial configurations. Thus, in practice, the use of a spatial representation enables solving the master equation for the instantaneous multiplicities (Eq. 16). After this, the average values are easily determined (Section II A).

The KMC simulations presented in this study demonstrate that monitoring a small number of relevant multiplicities works well in practice. Note that such monitoring is applicable to other methods (e.g. Molecular Dynamics) and, more generally, to a generic description of the evolution of the system, where all atoms and molecules interact with each others—as in reality—and the elementary reactions take place. Provided that any changes in the spatial configuration of the system are monitored, then (i) the actual transition rates (= rate constants) can be determined, under the widely-accepted assumption in Transition State Theory and Chemical Kinetics that the rate constant from one configuration to another is independent of any previously visited configurations (Markov chain), and (ii) the actual changes in the multiplicities of the elementary reactions can be tracked, thus directly solving the variables of interest in Eq. 16.

Note that Eq. 16 is valid beyond the mean field approximation, since the multiplicities themselves have been defined for this purpose, directly carrying information about the presence of correlations. Within mean field, Eq. 16 decays naturally into typical rate equations for the coverages of the adsorbates, such as Eqs. 5-7. In this manner, the proposed formalism provides a generalization of the traditional coverage-based approach, directly enabling the study of heterogeneous catalytic systems outside the mean field approach.

While traditionally one considers the adsorbate coverages as the natural variables required to describe the evolution of the system, here we have presented the idea that it is the collection of the multiplicities of a few local configurations that provides a natural description of the configurational structure of the surface and, thus, its evolution.

Finally, we stress that it is possible to identify the instantaneous multiplicity of a reaction with the instantaneous coverage for the corresponding local configuration. For this purpose, the instantaneous coverage of a local configuration is defined as \( \hat{M}_{(l)} / Z \), where \( Z \) is the number of sites participating in the local configuration, and \( \hat{M}_{(l)} \) is the total number of sites participating in reaction \( \alpha \), with \( \hat{M}_{(l)} \) and \( Z \) as already defined. As an example, for dissociative adsorption of a triatomic molecule, the local configuration requires three neighbor empty sites and, thus, \( \hat{M}_{(l)} = 3 \). Similarly, \( \hat{M}_{(l)} = 2 \) for bi-
molecular recombination reactions (since two neighbor sites participate in every elementary reaction) and also zα = 2 for typical diffusion reactions (since the adsorbate hops between two sites). Considering Fig. 1 as a specific example, the instantaneous multiplicity for the desorption of A is equal to the instantaneous coverage for all sites occupied by molecules of type A, namely, \( \frac{1}{4}/49 = 4/49 \). Similarly, the multiplicity for the recombination of A and B is equal to the coverage by all pairs of nearest neighbor sites such that one site is occupied by A and the other by B (\( \frac{1}{4}/49 = 2/49 \)). Since the relation between coverage and multiplicity is valid at any instant, it remains valid also between their averages.

### C. Rate constant for an elementary reaction

For a typical rate law, \( r_\alpha = k_\alpha \theta_x \theta_y \), the specific reaction rate, \( k_\alpha \), also known as the specific rate or rate constant, refers to the part of the rate, \( r_\alpha \), that does not depend on concentration/coverage, i.e. the part that does not depend on the number of locations where the reaction can be performed. The statistical formulation of transition state theory (TST)\(^{3,24,25} \) describes the specific rate for an elementary reaction as \( k_\alpha = k_0^\alpha e^{-\Delta S_\alpha^k/k_BT} \), where \( k_0^\alpha = \frac{k_BT}{h} q^\alpha \) is the attempt frequency, with \( q^\alpha \) and \( \eta \) the partition functions of the system in the transition and initial states of the reaction, respectively, and \( h \) is Planck's constant. Determination of the partition functions leads to \( k_0^\alpha = \frac{P_A}{\sqrt{2\pi m\rho g}} \) for nonactivated adsorption, where \( m \) and \( P \) are the mass and pressure of the adsorbed gas, respectively, and \( A \) is the adsorption site area\(^3 \). Similarly, \( q^\alpha \approx 1 \) and \( k_0^\alpha = \frac{k_BT}{h} \) for diffusion, recombination and desorption\(^{10,17,26,27} \).

See Eqs. S6-S7 in the Supporting information for a more complex treatment of the desorption case.

Complementarily, the thermodynamic formulation of TST\(^{3,25,28,29} \) states that \( k_\alpha = \frac{k_BT}{h} e^{\Delta S_\alpha^k/k_BT} e^{-\Delta H_\alpha^k/k_BT} \), where \( \Delta S_\alpha^k \) and \( \Delta H_\alpha^k \) are the entropy change and enthalpy change, respectively, from the initial to the transition state. Note the superindex \( k \), which stresses the fact that both changes are contained in the value for the specific rate \( k_\alpha \). The entropy barrier, \( \Delta S_\alpha^k \), is usually assigned to the variation in the number of energy states that can be occupied at a given temperature, i.e. the difference in the partition functions of vibration, rotation and/or translation at the ground state of the reactants and at the transition state\(^3 \). In fact, for elementary reactions at constant pressure for which the volume change is negligible (\( \Delta V_\alpha^k \approx 0 \) and, thus, \( \Delta H_\alpha^k = E_\alpha^k + p\Delta V_\alpha^k \approx E_\alpha^k \)), equating the statistical and thermodynamic formulations of \( k_\alpha \) leads to \( e^{\Delta S_\alpha^k/k_BT} = \frac{q^\alpha}{q} \).

This results in negligible entropy barriers (\( \Delta S_\alpha^k \approx 0 \)) for those reactions where \( \frac{q^\alpha}{q} \approx 1 \), while noticeable barriers are expected for other descriptions of the partition function ratio.

Section II F shows that the ‘rate’ \( r_\alpha \) (which contains both the specific rate, \( k_\alpha \), and the number of locations where the elementary reaction can be performed per active site, \( M_\alpha \)) can be formulated similarly as \( k_\alpha \) itself, simply by replacing \( \Delta S_\alpha^k \) with \( \Delta S_\alpha^k + S_M^\alpha \), where the configurational entropy \( S_M^\alpha \) is directly related to the multiplicity \( M_\alpha \).

### D. Total rate and the probability of an elementary reaction

Let us define the instantaneous total rate as the sum of the specific rates (= rate constants) for all elementary reactions that can be performed at the current configuration: \( \tilde{r} = \sum_{\alpha \in \{ P \}} m_\alpha k_\alpha \). Here, the symbol \( \{ P \} \) denotes ‘in’ so that \( \alpha \notin \{ P \} \) means that the sum is over any elementary reaction \( \alpha \) contained in the entire collection of elementary reactions \( \{ \} \). The corresponding average, referred to as the total rate, is:

\[
\bar{r} = \langle \tilde{r} \rangle = \sum_{\alpha \in \{ \} } m_\alpha k_\alpha. \tag{17}
\]

The abundance of each reaction \( (m_\alpha) \) is useful to stress the dependence of the total rate on the configuration of the system, a feature that remains hidden if one uses the form \( \tilde{r} = \sum_i k_i \) (no grouping of identical reactions).

Similarly, we consider another average quantity, the total rate per active site:

\[
R = \frac{\tilde{r}}{s} = \sum_{\alpha \in \{ \} } M_\alpha k_\alpha \tag{18}
\]

\[
R = \sum_{\alpha \in \{ a \} } M_\alpha k_\alpha + \sum_{\alpha \in \{ d \} } M_\alpha k_\alpha + \sum_{\alpha \in \{ b \} } M_\alpha k_\alpha + \sum_{\alpha \in \{ r \} } M_\alpha k_\alpha \tag{19}
\]

\[
R = R_a + R_d + R_h + R_r \tag{20}
\]

Here, we have explicitly separated all the elementary reactions \( (\alpha \in \{ \} ) \) into adsorption reactions \( (\alpha \in \{ a \}) \), desorption reactions \( (\alpha \in \{ d \}) \), diffusion reactions \( (\alpha \in \{ b \}) \) and recombination reactions \( (\alpha \in \{ r \}) \). Additionally, we have defined \( R_g = \sum_{\alpha \in \{ g \} } M_\alpha k_\alpha \) with \( g = a, d, h, r \) to denote (per active site): the total adsorption rate \( R_a \), total desorption rate \( R_d \), total hop rate \( R_h \) (diffusion) and total recombination rate \( R_r \).

Based on these definitions, we also define the probability to observe reaction \( \alpha \):

\[
\omega_\alpha^R = \frac{M_\alpha k_\alpha}{R} = \frac{M_\alpha k_\alpha}{\sum_{\alpha \in \{ \} } M_\alpha k_\alpha} = \frac{M_\alpha k_\alpha}{\sum_{\alpha \in \{ \} } M_\alpha k_\alpha}. \tag{22}
\]

As shown in this study, the reaction probabilities of Eq. 22 provide a complete and accurate picture of the underlying competition between the different elementary reactions, for a fraction of the cost required to obtain similar insights based on the degrees of rate control and sensitivity (\( \chi_\alpha \) and \( \xi_\alpha \)).
All averaged quantities defined above have corresponding instantaneous counterparts, which are well defined at any instant (during the transient or within the steady state). For instance, the instantaneous total rate per active site is \( \tilde{R} = \Sigma_{\alpha \in \{x\}} \tilde{M}_\alpha k_\alpha \), and the instantaneous probability to observe an elementary reaction is \( \tilde{\omega}_\alpha = M_\alpha k_\alpha / \Sigma_{\alpha \in \{x\}} M_\alpha k_\alpha \). The traditional ‘rate’ \( r_\alpha = k_\alpha \theta_\alpha^A \theta_\alpha^B = k_\alpha M_\alpha \), which is an average quantity, is described as the total rate per active site for reaction \( \alpha \) in our formalism. The corresponding instantaneous value is: \( \tilde{r}_\alpha = M_\alpha k_\alpha \).

E. Turnover frequency

The turnover frequency (TOF) refers to the number of molecules of the product of interest in the gas phase, generated per active site per unit time\(^7\). It is the rate in ‘degree of rate control’ and ‘rate sensitivity’. Traditional mathematical formulations, such as \( \text{TOF} = k_\alpha \theta_\alpha^A \theta_\alpha^B \), are based on the assumption that the rate of one particular reaction (\( \Lambda \), in this case) is sufficiently low so that it acts as the RDS. Here, we follow previous theoretical studies, where it was recognized that the gaseous product of interest will typically be generated in different elementary reactions\(^7\) and/or different products of interest will be generated\(^1\).

As an example, let \( AB \) refer to the product of interest and let us consider two different elementary reactions where \( AB(\delta) \) is generated: (1) a recombination reaction with direct desorption: \( A_X + B_X \rightarrow 2V + AB(\delta) \), and (2) a desorption reaction: \( AB_Y \rightarrow V + AB(\delta) \). Here, \( V \) refers to a vacant site, while \( X \) and \( Y \) denote different site types populated by species \( A, B \) and \( AB \). Note that, in this example, the way \( A_X, B_X \) and \( AB_Y \) are formed in previous elementary reactions is irrelevant in order to determine the TOF, since the production of \( AB(\delta) \) occurs through reactions (1) and (2) only. If \( k_1 \) and \( k_2 \) are the specific rates (or rate constants) for both reactions, respectively, and the two reactions are present \( m_1 \) and \( m_2 \) times on the surface with a total of \( s \) active sites, then the TOF is simply formulated as: \( \text{TOF} = (m_1 k_1 + m_2 k_2) / s \). This can be re-written as: \( \text{TOF} = \Sigma_{\alpha \in \{1,2\}} M_\alpha k_\alpha \), where \( M_\alpha = \Sigma_{\alpha \in \{1,2\}} M_\alpha k_\alpha \) is the multiplicity for reaction \( \alpha \). Note that \( M_\alpha k_\alpha = \Sigma_{\alpha \in \{1,2\}} M_\alpha k_\alpha \) describes how many molecules of \( AB(\delta) \) are generated per unit time per active site due to reaction \( \alpha \).

If more than two reactions explicitly contribute to the generation of the gaseous product of interest, the TOF is generalized as:

\[
\text{TOF} = \sum_{\alpha \in \{x\}} M_\alpha k_\alpha ,
\]

where \( \{x\} \) denotes the collection of elementary reactions where the target product exists the catalyst surface (i.e. those reactions whose final state contains the target product in the gas phase). The use of the multiplicities in Eq. 23 (instead of traditional products/powers of the adsorbate coverages) is justified by the master equation (Eq. 16), which shows that the multiplicities are the natural variables describing the evolution of the system.

If the target gaseous product is generated in reversible elementary reactions (e.g. \( A_X + B_X \leftrightarrow 2V + AB(\delta) \) and/or \( AB_Y \leftrightarrow V + AB(\delta) \)) with \( k_\alpha^{+} (k_\alpha^{-}) \) denoting the corresponding forward (backward) rate constant, the TOF is defined as:

\[
\text{TOF} = \sum_{\alpha \in \{x\}} (M_\alpha^{+} k_\alpha^{+} - M_\alpha^{-} k_\alpha^{-}) .
\]

If we are interested in more than one product, the TOF is simply the sum of several expressions, one for each product \( P \):

\[
\text{TOF} = \sum_{P \alpha \in \{x\}} (M_\alpha^{P,+} k_\alpha^{P,+} - M_\alpha^{P,-} k_\alpha^{P,-}) .
\]

In Section III we consider a system with one product of interest (CO\(_2\)) and another system with two products of interest (NO and N\(_2\)). Note that Eq. 25 transforms into Eq. 24 by simply summing over \( \alpha \in \{x_1\}, \{x_2\}, \ldots \) in Eq. 24. In turn, Eq. 24 can be formulated as Eq. 23 by simply using negative multiplicities for the reverse reactions. Thus, without loss of generality, we focus on using Eq. 23 as a general description for the TOF.

As with other variables in previous sections, we have defined the TOF as an average quantity, determined in the steady state: \( \text{TOF} = \Sigma_{\alpha \in \{x\}} M_\alpha k_\alpha \). However, our formalism allows considering also the instantaneous value, \( \text{TOF} = \sum_{\alpha \in \{x\}} M_\alpha k_\alpha \), which is well defined at any instant, during the transient and within the steady state.

F. Apparent activation energy of the TOF

As shown in Section II B, the values of the multiplicities, \( M_\alpha \), are functions of the actual values of the rate constants, \( k_\alpha \). In this manner, the \( M_\alpha \)’s are functions of temperature. Thus, for an Arrhenius plot of log(TOF) vs inverse temperature, \( \beta = 1/k_B T \), the apparent activation energy, \( E_{\text{app}}^{\text{TOF}} = -\partial \log(\text{TOF}) / \partial \beta \), is given by:

\[
E_{\text{app}}^{\text{TOF}} = -\frac{1}{\Sigma_{\alpha \in \{x\}} M_\alpha k_\alpha} \partial \Sigma_{\alpha \in \{x\}} M_\alpha k_\alpha / \partial \beta .
\]

Using \( k_\alpha = k_\alpha^0 e^{-E_\alpha^0 / \beta} \) and \( E_\alpha^M = -\partial \log(M_\alpha) / \partial \beta \), and applying the chain rule to \( \Sigma_{\alpha \in \{x\}} M_\alpha k_\alpha \) easily lead to:

\[
E_{\text{app}}^{\text{TOF}} = \sum_{\alpha \in \{x\}} \omega_\alpha \text{TOF}(E_\alpha^0 + E_\alpha^M) ,
\]

where \( E_\alpha^0 = -\partial \log(k_\alpha^0) / \partial \beta \) and the weight \( \omega_\alpha \text{TOF} \) for \( \alpha \in \{x\} \) is the probability of observing reaction \( \alpha \) amongst all reactions explicitly contributing to the TOF. Since these weights are normalized between 0 and 1, Eq. 26 describes the apparent activation energy as a proper weighted average.
If \( k_0^\alpha \) depends on temperature, its energy contribution \( (E_k^0) \) needs to be added, as indicated in Eq. 26. Assuming momentarily that \( k_0^\alpha \) is temperature-independent, then Eq. 26 is a weighted-average over the elementary activation energies \( (E_k^\alpha) \), each one modified by an effective energy \( (E_M) \), which originates from the temperature dependence of the corresponding multiplicity. From a traditional perspective, this can be understood as an underlying change in configurational entropy, since modifying the temperature alters the morphology (and the configuration) of the system.

Recalling Boltzmann’s exact formulation of entropy (\( S \)) as the natural logarithm of the number of possible microscopic configurations (\( \Omega \)) multiplied by the Boltzmann constant (\( k_B \)), \( S = k_B \log \Omega \), in our case \( \Omega \) can be directly identified as \( M_\alpha \), i.e. the number of local microscopic configurations where reaction \( \alpha \) can be performed on the surface per active site. Thus, we simply define the configurational entropy \( S_M^\alpha \) for reaction \( \alpha \) as:

\[
S_M^\alpha = k_B \log M_\alpha \quad \Rightarrow \quad M_\alpha = e^{S_M^\alpha/k_B}.
\]

(27)

Then, the total rate per active site for reaction \( \alpha \) becomes \( r_\alpha = M_\alpha k_\alpha = k_B T e^{(S_M^\alpha + \Delta S_M^\alpha)/k_B} e^{-\Delta H_M^\alpha/k_BT} \). Thus, the ‘rate’ (\( r_\alpha \)) can be formulated in a similar manner as the ‘rate constant’ (\( k_\alpha \)) by simply considering the entropy sum \( S_M^\alpha + \Delta S_M^\alpha \), where the configurational entropy, \( S_M^\alpha \), is directly related to the multiplicity of reaction \( \alpha \), and the entropy barrier for the reaction itself, \( \Delta S_M^\alpha \), is related to the change in the number of molecular energy levels due to vibration, rotation and/or translation from the initial to the transition state. While traditionally the latter is contained in the value of the rate constant \( k_\alpha \), in this study we explicitly consider the presence of the configurational part \( M_\alpha = e^{S_M^\alpha/k_B} \) in \( r_\alpha \). This enables a direct analysis of the role of the relative abundance of each elementary reaction in describing the apparent activation energy.

The equation \( S = k_B \log \Omega \) (and, correspondingly, Eq. 27) is valid under the fundamental assumption of equiprobable microscopic configurations in Statistical Mechanics (all microscopic configurations are equally probable). The number of possible microscopic configurations (\( \Omega \)) should not be confused with the partition function (\( Q \)), typically used to derive expressions for all thermodynamic variables (including the entropy) in the canonical ensemble (see e.g. Section 3.3.3 in Ref. 3): \( S = \left[ \frac{\partial (k_B T \log Q)}{\partial T} \right]_{N,V} = k_B \log Q + k_B T \left[ \frac{\partial \log Q}{\partial T} \right]_{N,V} \), where the derivatives are taken at constant particle number (\( N \)) and volume (\( V \)).

Based on Eq. 27, the change in configurational entropy with inverse temperature is:

\[
\frac{\partial S_M^\alpha}{\partial T} = k_B \frac{\partial \log M_\alpha}{\partial T} = -k_B E_M^\alpha.
\]

(28)

Thus, \( E_M^\alpha \) is essentially the negative of the change in configurational entropy with inverse temperature and we refer to it as the configurational contribution to the apparent activation energy.

This perspective agrees well with recent reports, where the configuration and energy dependence of the TOF has been discussed\(^8,27,30 \). As an example, modifications in the coverage of the empty sites give rise to configurational entropy contributions to the apparent activation energy\(^27 \). In our case, however, a more general scenario is considered. Some elementary reactions may involve several sites/species and, thus, cannot be simply described in terms of the coverage of the intermediates under all possible circumstances. Instead, the multiplicities, which characterize the coverage for rather complex collections of sites, appear as the natural variables to describe the relative presence of the various reactions on the surface. Note that our formalism places the emphasis on the determination of the multiplicities and their variation with temperature in order to describe the apparent activation energy. The configurational entropy is not really needed and has been provided here as a link to traditional thinking.

### G. Apparent activation energy of \( R \)

From the resemblance of Eq. 19 to Eq. 23, also the apparent activation energy of the total rate per site \( R \) is easily obtained:

\[
E_{app}^R = \sum_{\alpha \in \{\epsilon\}} \frac{k_B}{R} \frac{k_\alpha}{M_\alpha} \left( \frac{\omega_\alpha^R (E_\alpha^k + E_\alpha^M)}{M_\alpha k_\alpha} \right),
\]

(29)

where \( \omega_\alpha^R \) for \( \alpha \in \{\epsilon\} \) is the probability of observing elementary reaction \( \alpha \) amongst all elementary reactions. Thus, the probabilities of Eq. 22 appear naturally within our formalism (Eq. 29), regulating the contribution of every reaction to the apparent activation energy of \( R \). Since \( M_\alpha \) may increase, decrease or remain constant with temperature, \( E_M^\alpha \) can be positive, negative or zero. Thus, Eqs. 26 and 29 may lead to positive, negative or zero apparent activation energy, just as Eqs. 1 and 2.

### H. Rate Determining Step and Rate Controlling Steps

If a particular reaction (say \( \lambda \)) can be assigned as the RDS, then, by definition, the TOF can be written solely in terms of that reaction:

\[
TOF = M_\lambda k_\lambda \text{ (for } \lambda = \text{ RDS),}
\]

(30)

This means that the apparent activation energy is:

\[
E_{app}^{TOF} = E_\lambda^k + E_\lambda^k + E_\lambda^M \text{ (for } \lambda = \text{ RDS).}
\]

(31)

This is a very simple, yet meaningful result. Even if \( E_{app}^{TOF} \) is dominated by a single reaction (\( \lambda \)), in general,
$E_{\text{TOF}}^{\text{app}}$ should not be identified with the corresponding elementary activation energy alone, $E_k^\lambda$, as still accepted by some researchers (see the Discussion below). This will neglect the configurational contribution, $E_\chi^M$, as well as the temperature dependence of the rate prefactor, $E_k^\nu$, should it be relevant.

In general, the RDS may change as the temperature and/or partial pressures are modified. To assign the RDS to a particular reaction, we consider Eq. 30 and define the relative error in representing the TOF using reaction $\alpha$:

$$\delta_{\text{TOF}}^\alpha = \left| 1 - \frac{M_\alpha k_\alpha}{\text{TOF}} \right| \quad (\alpha \in \{ e \}),$$

(32)

which is 0 if $\alpha = \text{RDS}$, while it may take unbound, positive values if $M_\alpha k_\alpha$ deviates largely from the TOF. Then, we define the proximity to the TOF as:

$$\sigma_{\text{TOF}}^\alpha = 1 - \min(1, \delta_{\text{TOF}}^\alpha) \quad (\alpha \in \{ e \}),$$

(33)

so that $0 \leq \sigma_{\text{TOF}}^\alpha \leq 1$, taking 1 if $\alpha = \text{RDS}$ and 0 if $M_\alpha k_\alpha$ deviates significantly from the TOF. By definition, the proximity $\sigma_{\text{TOF}}^\alpha$ is comparable to $\chi_\alpha$ (the degree of rate control), both taking the value 1 when reaction $\alpha$ is the RDS. In addition, similarly to $\xi_\alpha$ (the rate sensitivity), also the proximity $\sigma_{\alpha, \text{TOF}}$ provides crucial information about the sensitivity of the TOF to the different reactions.

Considering Eq. 29, we note that the probability of observing any reaction explicitly contributing to the TOF is given by $\omega_{\text{TOF}}^R = \text{TOF}/R$. Thus, those reactions with probability $\omega_\alpha^R >> \omega_{\text{TOF}}^R$ (i.e. $M_\alpha k_\alpha >> \text{TOF}$) will occur much more frequently than any reaction explicitly contributing to the TOF and, thus, a small variation in their rate constants, $k_\alpha$, will essentially leave the TOF unchanged (see below one exception, due to time scaling). The same applies to the reactions with $\omega_\alpha^R << \omega_{\text{TOF}}^R$ (i.e. $M_\alpha k_\alpha << \text{TOF}$). Only those reactions with $M_\alpha k_\alpha/R$ around $\text{TOF}/R$ may noticeably affect the TOF. In this manner, in probability space, proximity to the TOF means sensitivity by the TOF. This provides a procedure to identify any RCS, in addition to the RDS (if it exists).

An advantage of our formulation is the direct use of the values of the TOF and $M_\alpha k_\alpha$ in the definition of $\sigma_{\alpha, \text{TOF}}$, instead of the derivatives of the TOF with respect to the rate constants $k_\alpha$, as required in the determination of $\chi_\alpha$ and $\xi_\alpha$ (see text after Eq. 2). Thus, our approach avoids (i) the need of performing a large amount of simulations (as required by previous methods, in order to characterize the dependence of the TOF on every rate constant) as well as (ii) the emergence of potential inaccuracies from the additional processing (as required by previous methods, in order to determine the derivatives of the TOF and, thus, $\chi_\alpha$ and $\xi_\alpha$).

Finally, we note that any reaction with $\omega_\alpha^R \sim 1$ is exceptional, affecting the TOF by scaling the time increment, even if its proximity to the TOF is very low. This results from the fact that the inverse of the total rate $r = Rs$ has dimensions of time and, in fact, it provides a natural variable to determine the time increment. For instance, in a KMC simulation the instantaneous time increment is calculated as $\Delta t = - \log(u)/\hat{r}$, where $u \in (0, 1)$ is a uniform random number. Thus, considering the average values in the steady state, those reactions with large $\omega_\alpha^R$ essentially control the value of $R$ and, accordingly, the value of $\Delta t$. In this manner, variations in their rates end up affecting the value of TOF by scaling $\Delta t$. It is not the same generating $n$ molecules per site per minute than generating the same $n$ molecules per site every five minutes. In this manner, we distinguish between two sources for variations in the TOF in general, proximity and scaling. Proximity is signaled by $\sigma_{\alpha, \text{TOF}} \sim 1$ or, equivalently, $\omega_\alpha^R \sim \omega_{\text{TOF}}^R$. Scaling is indicated by $\omega_\alpha^R \sim 1$.

### III. APPLICATION

To illustrate the validity of the proposed multiplicity analysis we consider a reaction mechanism containing a total of 21 elementary reactions for the oxidation of CO on RuO$_2$(110)$^7,10,13,15,22,26,30,31$ We also consider a distinctively different reaction mechanism containing a total of 18 elementary reactions for the selective oxidation of NH$_3$ on RuO$_2$(110) as well$^22$. The two reaction mechanisms are schematically shown on Figures 2(a) and 2(b). Note that in general the surface dictates the actual symmetry of the neighborhood around each surface site as well as the particular collection of elementary reactions that may take place. Since the collection of elementary reactions (and elementary activation energies) is very different for the two selected applications and symmetry is incorporated through the actual values of the multiplicities, we believe the two cases are sufficient to illustrate the general applicability of our formalism to different catalytic reactions. In fact, we emphasize that similar multiplicity formulations have already been successfully applied to other surface processes, such as two-dimensional epitaxial growth (with triangular and rectangular lattices) and anisotropic etching (in 3 dimensions)$^{16,23}$.

The oxidation of NH$_3$ provides an example of a highly sequential catalytic reaction, taking place as a cascade of elementary abstraction reactions (between adsorbed NH$_3$/NH$_2$/NH and adsorbed O/OH), progressively stripping the H atoms until bare N is present at the surface, where it recombines with either adsorbed O (to form NO, which is desorbed later) or with itself (to form N$_2$, which is desorbed immediately). On the contrary, the oxidation of CO is an example of a highly parallel reaction mechanism, where basically all elementary reactions are enabled on all active sites. Below, we concentrate on the presentation of the case for the oxidation of CO, leaving the corresponding information for NH$_3$ to the Supporting Information.

Until occurrence of desorption, diffusion or recombination, the adsorbed CO and O adspecies remain chemisorbed on the RuO$_2$(110) surface on both bridge
(a) Reaction mechanism and corresponding graphical representation for the oxidation of CO on RuO₂{110} according to Ref.¹⁰ (elementary barriers, in eV, are for model I, see main text). (b) Same as (a), now for the selective oxidation of NH₃ on RuO₂{110} according to Ref.²². In this case, all elementary reactions occur only at C sites (see main text).

(B) and cus (C) sites, which form alternating morphological rows (B-C-B-C…), with every row parallel to the [110] crystallographic direction¹⁵. Such an array of adsorption sites can be described using a rectangular unit cell, with lattice parameters $a_x = 6.43$ Å and $a_y = 3.12$ Å along the [110] and [110] directions, respectively, with two sites per unit cell¹⁵: one B site located at (0,0) and one C site located at ($\frac{1}{2}$,0). Thus, the area per site $A_s$ is half the unit cell area $A_{u.c.}$: $A_s = \frac{1}{2}A_{u.c.} = \frac{1}{2}a_xa_y = 10.03$ Å². For the purposes of this report, the system can be treated as a two-dimensional array of $L \times L$ total sites with periodic boundary conditions.

As shown in Figure 2(a) and extensively described in Section S2 A of the Supporting Information, the currently accepted reaction mechanism for the oxidation of CO on RuO₂{110} contains a total of 21 elementary reactions, including dissociative adsorption of O₂ on two neighbor vacant sites (Vₓ + Vᵧ → Oₓ + Oᵧ, where X and Y stand for either B or C sites), non-dissociative adsorption of CO on vacant sites (Vₓ → COₓ), associative desorption of O₂ from two neighbor O atoms (Oₓ + Oᵧ → Vₓ + Vᵧ), direct desorption of CO (COₓ → Vₓ), surface diffusion of CO and O from B or C sites to B or C sites (COₓ → COᵧ and Oₓ → Oᵧ), and recombination of CO on B or C sites with neighboring O on B or C sites (COₓ + Oᵧ → CO₂). The reaction mechanism assumes
that CO$_2$ is immediately desorbed after recombination. Thus, potential diffusion and/or decomposition of CO$_2$ adatoms on the surface is disregarded. As a result, the TOF in this system corresponds to the total recombination rate: $\text{TOF} = R_e = \sum_{\alpha(x)} M_{\alpha} R_{\alpha}$.

A more complete description of the adsorption of oxygen can be obtained by considering both adsorbed O$_2$(mono) and O$_2$$^{**}$ (dihapto) adsorbes on the C sites, leading to a two-step adsorption-desorption reaction $O_2 \rightleftharpoons O_2$$^{**} \rightleftharpoons 2O^*$ at moderate coverages$^9$, rather than the one-step reaction $O_2 \rightleftharpoons 2O^*$ assumed in the traditional reaction mechanism$^7,10,13,15,22,26,30$. To directly compare our results to the traditional mechanism, the one-step route is considered. The proposed multiplicity analysis can also be applied to the two-step route.

Table S1 in Section S2A of the Supporting Information provides the values for the attempt frequencies ($k_0$) and activation energies ($E_k$) used in four different models for the same reaction mechanism, here referred to as: I. Reuter, II. Seitsonen, III. Kiejna, and IV. Farkas. The four models differ in the actual values for the atomistic activation energies $E_k$, which where obtained using different implementations of Density Functional Theory (models I-III) and experiment (model IV). Moreover, model IV considers explicitly the presence of repulsion between nearest neighbor COs located at C sites, thus allowing to test the validity of the proposed formalism when adsorbate-adsorbate interactions are included beyond the adsorbate correlations already occurring at high coverages in the other models.

Since the adsorption rate of CO on both B and C sites is the same in models I through IV, both reactions $V_x \rightarrow COO$ (with $X = B$ and C) have the same rate and, thus, are jointly referred to as $V \rightarrow CO$ in the rest of the report. Similarly, provided there is at least one vacant nearest neighbor (NN) to accommodate another O atom, the adsorption rate of an O atom is the same for B and C sites and, thus, simply referred to as $V \rightarrow O$ below.

Further details about the reaction mechanism for the oxidation of NH$_3$ on RuO$_2$(110) are provided in Section S2B of the Supporting Information. In either case, oxidation of CO or NH$_3$, the catalytic process is simulated using a typical lattice-gas model and the rejection-free, time-dependent implementation of the KMC method$^{10-14,16}$. See Section S3 of the Supporting Information for details.

**IV. RESULTS**

Here we concentrate on the presentation of the results for the oxidation of CO, leaving the case of the oxidation of NH$_3$ to the Supporting Information (see Section S7B). Fig. 3(a) shows the temperature dependence of the total rate per site ($R$) for model I at $p_{CO} = 1$ atm and $p_{O_2} = 2$ atm. The plot also displays $R_a$, $R_d$, $R_b$, and $R_e$ (i.e. TOF), as well as the corresponding TOF data from Meskine et al.$^7$. This demonstrates that our implementation is similar to that by Reuter and Scheffler$^{7,10,15}$. This is further confirmed in Fig. 3(b), where basically the same pressure dependence is observed for our TOF and that in Ref.$^7$. The small, horizontal shift in the data for both temperature (Fig. 3(a)) and pressure (Fig. 3(b)) is assigned to (i) minor differences in some parameters used in the attempt frequencies (we carefully tried following every detail of their implementation) and, perhaps, (ii) differences in the detection of the onset of the steady state, which in our case is carried out automatically (see Section S3 of the Supporting Information). The validity of our implementation is further confirmed in Fig. S1 for models II, III and IV, as shown in Section S4A of the Supporting Information.

Without crossing each other, the curves in Fig. 3(a) display three regions, labelled A, B and C for the total rate per site $R$, and I, II and III for the TOF. Accordingly, this model is dominated by adsorption and desorption reactions in the complete range of temperature, with both recombination and diffusion occurring much less frequently. The derivative of the TOF of Fig. 3(a), i.e. the apparent activation energy $E_{\text{app}}^{\text{TOF}} = -\frac{\partial \ln(TOF)}{\partial \sigma}$, is displayed in Fig. 4(a). Beyond the constant value in region I, an excursion through negative values is observed in region II and a positive, roughly linear increase occurs in region III. The temperature dependence of $E_{\text{app}}^{\text{TOF}}$ in all three regions is accurately described by Eq. 26 (absolute error $|E_{\text{app}}^{\text{TOF}} - \sum_{\alpha(x)} \epsilon_\alpha^{\text{TOF}}| < 0.07$ eV). In region I, where $E_{\text{app}}^{\text{TOF}}$ remains constant at ~2.87 eV (2.85 eV was reported in Ref.$^7$), three recombination reactions participate. The dominating reaction changes from $CO_B + OC \rightarrow CO_2$ (at the lowest temperatures) to $CO_C + OC \rightarrow CO_2$ (near the onset of region II), with the third reaction, $CO_C + O_B \rightarrow CO_2$, losing importance with increasing temperature. Since $E_k$, is constant for each reaction and $E_{\text{app}}^{\text{b}}$ is weakly dependent on temperature (see Eqs. S13-S15 in Section S2A of the Supporting Information), the overall temperature dependence of each contribution $\epsilon_\alpha^{\text{TOF}}$ in Eq. 26 is mainly due to (i) the slope $E_{\text{app}}^{\text{M}}$ of the multiplicity $M_\alpha$, as shown in Figs. 4(b) and 5(e-f), and (ii) the actual recombination probability, $\omega_\alpha^{\text{TOF}}$, as shown in Fig. 4(c).

Alternatively, considering the presence of a Rate Determining Step (RDS), Fig. 4(d) shows that the temperature dependence of $E_{\text{app}}^{\text{TOF}}$ in all three regions is accurately described also by Eq. 31 (absolute error $|E_{\text{app}}^{\text{TOF}} - (E_k + E_\alpha^{\text{b}} + E_\alpha^{\text{M}})| < 0.05$ eV). While at higher temperatures ($\beta < 21$) the RDS is one recombination reaction ($\lambda = CO_C + OC \rightarrow CO_2$) at lower temperatures ($\beta > 21$) it corresponds to O adsorption ($\lambda = V \rightarrow O$). Based on the similarity of $M_{\alpha}k_{\alpha}$ with respect to the TOF, as shown in Fig. 4(e), the actual proximity to the TOF ($\sigma_\alpha^{\text{TOF}}$) is presented in Fig. 4(f). This allows assigning the RDS, since $\sigma_\alpha^{\text{TOF}} = 1$ for $\alpha = COC + OC \rightarrow CO_B$ and $\alpha = V \rightarrow O$ at high and low temperatures, respectively.

Fig. 4(d) shows that merely observing a linear Arrhenius behavior within some range of temperatures (region...
I) does not guarantee that \( E_{\text{app}}^{\text{TOF}} \) (\( \approx 2.87 \text{ eV} \)) corresponds to the highest elementary activation energy in the system \( E_{\text{R}}^{\alpha,\text{max}} \) (\( \approx 4.6 \text{ eV} \), for the desorption \( O_B + O_B \rightarrow V_B + V_B \)). The RDS depends on the whole reaction mechanism and does not necessarily correspond to the reaction with the highest elementary activation energy. In addition, even if \( E_{\text{app}}^{\text{TOF}} \) can be assigned to one reaction (\( \lambda \)), \( E_{\text{app}}^{\text{TOF}} \) should not be identified with the elementary activation energy alone, \( E_{\lambda}^b \) (\( \lambda = V \rightarrow O \)), since this disregards the configurational contribution, \( E_{\lambda}^c \) (\( \approx 2.87 \text{ eV} \), for \( \lambda = V \rightarrow O \)) and the term \( E_{\lambda}^o \) (negligible here). We conclude that Eqs. 26 and 31 are more accurate than Eq. 2, previously applied to region I only, resulting in an error of 0.25 eV\(^7\). Similarly, Eqs. 26 and 31 are more accurate than the traditional Temkin formula (Eq. 1), as shown in Section S5 of the Supporting Information.

In addition to enabling the determination of the RDS, Fig. 4(f) provides crucial information by showing which reactions affect the TOF significantly, i.e., the Rate Controlling Steps (RCSs). For \( \beta \gg 21 \), in addition to the RDS (\( \lambda = V \rightarrow O \)), the TOF is sensitive to the three recombination reactions discussed in Figs. 4(a)-(c), as well as one diffusion type (\( CO_B \rightarrow CO_B \), especially for \( \beta \approx 26-28 \)) and one desorption reaction (\( CO_B \rightarrow V \), for \( \beta \approx 23-24 \)). For \( \beta \ll 21 \), the TOF is sensitive only to the RDS (\( CO_C + OC \rightarrow CO_2 \)), with a sensitivity spike for one desorption reaction (\( OC + OC \rightarrow V_C + V_C \), at \( \beta \sim 19 \), approaching 1 sharply from both left and right).

Although these proximity curves might look whimsical—especially the spikes—they can be easily understood from the actual reaction probabilities shown in Fig. 5(a). The figure also displays the probability to observe any reaction explicitly contributing to the TOF, \( \omega_{\text{TOF}} \), \( \omega_{\text{TOF}}^a \), as well as two additional curves, namely, \( 2 \omega_{\text{TOF}}^a \) and \( 0.05 \omega_{\text{TOF}}^a \). Any elementary reaction with probability \( \omega_{\text{TOF}}^a \) between \( \omega_{\text{TOF}}^a \) and \( 2 \omega_{\text{TOF}}^a \) will lead to proximity values \( \sigma_{\text{TOF}}^a \) between 1 and 0. Likewise, if \( \omega_{\text{TOF}}^a \) falls between \( \omega_{\text{TOF}}^a \) and \( 0.05 \omega_{\text{TOF}}^a \), the probability will lie between 1 and 0.05. [See Section S6 of the Supporting Information for further details about the cut-offs \( 2 \omega_{\text{TOF}}^a \) and \( 0.05 \omega_{\text{TOF}}^a \).] Thus, a spike in \( \sigma_{\text{TOF}}^a \) (approaching value 1 from left and right) will appear when \( \omega_{\text{TOF}}^a \) crosses \( \omega_{\text{TOF}}^a \) within a small range of temperature.

Similarly, any curve for \( \sigma_{\text{TOF}}^a \) in Fig. 4(f) can be easily interpreted from the actual behavior of the corresponding reaction probability within the band displayed in Fig. 5(a). Most importantly, Fig. 5(a) stresses that, in probability space, proximity to the TOF means sensitivity by the TOF. As explained in the last paragraph of Section II H, the TOF is also sensitive to variations in the rates of those reactions with \( \omega_{\text{TOF}}^a \sim 1 \) through their scaling of time. Such reactions essentially control the total rate \( r = (RS) \) and, thus, the time increment \( \Delta t \sim 1/r \). In this manner, according to Fig. 5(a), the TOF will also be sensitive to the adsorption and desorption of CO (\( V \rightarrow CO \) and \( CO_C \rightarrow V \), respectively), in agreement with Fig. 5 of Ref.7.

Furthermore, the reaction probabilities of Fig. 5(a) are useful to directly extract meaningful information about the catalytic process. For this purpose, Fig. 5(a) is best analyzed jointly with Fig. 5(b), which shows the temperature dependence of the coverage by all adspecies (\( \theta_{CO_B}, \theta_{CO_C}, \theta_{O_B}, \theta_{O_C}, \theta_{V_B} \), and \( \theta_{V_C} \)). For completeness, Fig. 5(c) additionally shows typical surface morphologies (configurations) for the system at four characteristic temperatures \( T_1 < T_2 < T_3 < T_4 \) (410, 510, 560 and 700 K). At any temperature, the adsorption of CO and the desorption of CO from C sites (\( V \rightarrow CO \) and \( CO_C \rightarrow V \), respectively) are so overwhelmingly probable (\( \omega_{\text{TOF}}^a \sim 0.5 \)) with respect to the TOF (\( \omega_{\text{TOF}}^a \sim 10^{-2} - 10^{-7} \)) that the two reactions can be regarded as completely equilibrated (one to one), thus minimally interfering with any TOF event. At \( T_1 \), the next most probable reaction is the desorption of CO from B sites (\( CO_B \rightarrow V \), with \( \omega_{\text{TOF}}^a \sim 10^{-4} \)), which is also equilibrated with the corresponding adsorption of CO at B sites (included in the \( V \rightarrow CO \) curve). With probabilities between \( 3 \times 10^{-7} \) and \( 2 \times 10^{-8} \), we then find a diffusion reaction (\( CO_B \rightarrow CO_B \)), an adsorption...
reaction (V → O) and the three recombination reactions already discussed in relation to Figs. 4(a)-(c). Since the surface is essentially CO-terminated (Fig. 5(b)), for these recombinations to occur the adsorption of O must take place. In other words, V → O is the RDS, in agreement with Fig. 4(f). The corresponding Rate Controlling Steps (RCSs) at T1 are summarized in Fig. 6(a).

At T2, recombination now occurs mostly due to the COC + O2 → CO2 route, rather than COB + O2 → CO2 (which dominated at T1), while the COC + O2 → CO2 channel becomes gradually less relevant with increasing temperature. Another difference with respect to T1 is that there is plenty of O on the B sites at T2 (Fig. 5(b)), but the previous sentence concluded that COC and COB typically react with OC. Thus, the system is ready to generate CO2 as soon as O is adsorbed on the C sites. In this manner, V → O remains as the RDS, as shown in Fig. 4(f). The corresponding RCSs at T2 are summarized in Fig. 6(b). At T3, there is plenty of O on both B and C sites (see Fig. 5(b)) while the small coverage of the C sites by CO is large enough to enable recombination through the COC + O2 → CO2 route, with probability $\omega_2^R \sim 9 \times 10^{-3}$ comparable to that for O adsorption ($V \rightarrow O$, with $\omega_2^R \sim 1 \times 10^{-2}$). Although COC and OC units are constantly in contact, their recombination takes some time. Thus, the recombination itself is the RDS, in agreement with Fig. 4(f). Finally, at T4, not only the adsorption and desorption of CO are equilibrated ($\omega_2^R \sim 0.4$) but also the adsorption and desorption of molecular O2 ($\omega_2^R \sim 0.2/2 = 0.1$ and $\sim 0.1$, respectively). Thus, on a mostly O-covered surface (see Fig. 5(b)), adsorption and desorption of CO at C sites occurs frequently, but hardly ever this leads to a recombination (COC + O2 → CO2, with $\omega_2^R \sim 2 \times 10^{-3}$). Thus, the recombination itself is the RDS, in agreement with Fig. 4(f). The RCSs at T3 and T4 are summarized in Figs. 6(c)-(d).

Finally, Figs. 5(d)-(f) show the corresponding contributions to the apparent activation energy for the total rate per site R according to Eq. 29 (absolute error $[E_{app} - \sum_{\alpha \epsilon (e)} \epsilon_{\alpha R}] < 0.03$ eV). This demonstrates that
monitoring the multiplicities enables describing both easily and accurately any of the total rates per site \( \langle R_a, R_d, R_b, R_c, R_r \rangle \) and \( R \). As in Fig. 3(a), Fig. 5(d) confirms that the total rate is dominated by adsorption and desorption reactions, in particular, the adsorption and desorption of \( CO \) \( (V \rightarrow CO) \) and \( CO_C \rightarrow V \), while the adsorption of \( O \) \( (V \rightarrow O) \) becomes relevant in region C. As indicated above, the TOF is sensitive to variations in the rates of these reactions through their ability to scale the time increment \( \Delta t \propto 1/r \) with \( r = R_s \).

We stress that the temperature dependencies of \( E_{R}^{TOF} \) and \( E_{R}^{app} \) are well expressed by Eqs. 26 and 31 also for models II-IV (for the oxidation of \( CO \)) as well as for a distinctively different model that describes the selective oxidation of \( NH_3 \) on \( RuO_2(110) \) (see Sections S7A and S7B of the Supporting Information, respectively). This is valid even in the case of model IV, which explicitly considers adsorbate-adsorbate interactions. Similarly, based on directly inspecting the corresponding reaction probabilities, essential understanding is obtained about the overall catalytic reaction for each model, including the assignment of the RDS to one or more elementary reactions. These results strongly indicate that the proposed multiplicity analysis can be used to obtain a deep understanding for any reaction mechanism / catalytic model.

V. DISCUSSION

A. Novelty

This study presents the use of the multiplicities to formulate novel expressions for the TOF (Eq. 23) and its apparent activation energy (Eqs. 26 and 31), as well as to describe the relative importance of every elementary reaction via the reaction probabilities (Eq. 22). The application to two model catalytic reactions (the oxidation of \( CO \) on \( RuO_2(110) \) and the selective oxidation of \( NH_3 \) on the same surface) and the computational aspects (the Kinetic Monte Carlo simulations) are secondary features, used to confirm the validity of the proposed equations.

The primary result is Eq. 23. This formulation of the
FIG. 6. Temperature dependence for model I (cf Figs. 4 and 5): Elementary reactions having a leading role (Rate Controlling Steps, RCSs) according to the multiplicity analysis proposed in this study ($\omega_R^s \sim \omega_{TOF}^s$ and $\omega_R^s \sim 1$ in Fig. 5(a)): (a) 410 K, (b) 510 K, (c) 560 K, (d) 700 K.

TOF follows from the observation that every elementary reaction occurring on a catalyst surface is available at different locations. Thus, in addition to a characteristic rate constant, $k_\alpha$, each elementary reaction has an associated multiplicity, $M_\alpha$, which is directly linked to configurational entropy (Eq. 27). While traditionally one considers the adsorbate coverages as the natural variables to describe the system (and, thus, the TOF), the proposed master equation (Eq. 16) shows that, instead, one may consider the multiplicities of the local configurations as the irreducible variables. For spatially extended systems whose morphology (spatial configuration) can be monitored, the multiplicities of the elementary reactions can then be tracked and the proposed expression for the TOF is fully justified.

Considering all elementary reactions, $\{e\}$, the proposed expression, $\text{TOF} = \sum_{\alpha \in \{e\}} M_\alpha k_\alpha$, focuses on the particular subset of reactions, $\{x\}$, whose reaction products explicitly contain the desired target molecule (or molecules) in the gas phase. If there happens to be an elementary reaction, $\lambda \in \{e\}$, so that $M_\lambda k_\lambda = \sum_{\alpha \in \{x\}} M_\alpha k_\alpha$, then that reaction is the RDS. In this particular case, our expression ($\text{TOF} = k_\lambda M_\lambda$) can be directly compared with traditional formulations (e.g. $\text{TOF} = k_\lambda \theta_A \theta_B$), if the RDS is the recombination of two adsorbates, $A$ and $B$, in the mean field approximation, or $\text{TOF} = k_\lambda \theta_A^x \theta_B^y$, considering the two adsorbates have partial reaction orders $x'$ and $y'$, which describe phenomenologically the presence of correlated configurations beyond the mean field approach). Thus, the traditional coverage dependence is replaced with the multiplicity, $M_\lambda$, which is an exact measure of the ‘concentration of the reaction’, i.e. the reaction abundance per active site, valid within and beyond mean field.

In spite of the simplicity of Eq. 23, we are not aware of any previous, similar approach. Direct formulation of the TOF in terms of the multiplicities (or their traditional counterparts, the coverages by the reaction intermediates) was explicitly disregarded in Ref. 7 (see the text after Eq. (9) in that study). However, formulations of the TOF in terms of the coverage of one or several intermediates are a standard procedure in chemical kinetics2–6,27 (see several examples in Section S1 of the Supporting Information). Furthermore, the present study strongly supports the idea that the TOF is described naturally by using the multiplicities.

Regarding Eq. 26 (Eq. 31), every configurational contribution $E_M^\alpha$ ($E_M^s$) to the apparent activation energy $E_{TOF}^\alpha$ reflects the temperature dependence of the coverage for a particular collection of sites. As shown in Section S1 of the Supporting Information for the Langmuir-Hinshelwood model with recombination as the RDS ($\lambda = COC + OC \rightarrow CO_2$), the configurational contribution $E_M^\alpha$ contains the temperature dependence of $M_\lambda$ in the same manner as the Temkin contribution $-x\Delta H_{CO} - y\Delta H_O$ carries the temperature dependence for the approximation $M_A \approx \theta_{CO} \theta_O$. Since here $M_\lambda$ characterizes the coverage of all neighbor site pairs occupied
by CO and O, replacing $M_\lambda$ by $\theta CO \theta O$ becomes a poor approximation when the interplay of all reactions leads to structured morphologies (i.e. non-random configurations).

Regarding Eq. 22, the probability of observing any particular elementary reaction, $\omega_\alpha^R$, provides a precise measure of the relative importance of every reaction. In addition to enabling a deep understanding of the way the overall reaction is conducted, $\omega_\alpha^R$ allows easy identification of the Rate Determining Step (RDS), if it exists, as well as the Rate Controlling Steps (RCSs). Overall, this provides a straightforward alternative to computationally-expensive approaches based on the degree of rate control ($\xi_\alpha$) and/or the rate sensitivity ($\xi_\alpha$).

**B. Sensitivity analysis**

Regarding the analysis of the promotion or hindering of the TOF, traditionally $\xi_\alpha$ and $\chi_\alpha$, provide this information by construction, directly measuring the changes in the TOF by varying one rate constant ($\xi_\alpha$) or two rate constants ($\chi_\alpha$) while keeping all other rate constants fixed. In this context, the proposed multiplicity approach should become very useful, substantially reducing the overall cost of the traditional sensitivity analysis. By designating which elementary reactions significantly modify the TOF, the sensitivity analysis for all other elementary reactions can be directly discarded, with the corresponding enormous saving in computational effort.

This is summarized in various plots, such as Fig. 5(a), where the probability of any elementary reaction—or any desired combination of reactions, such as the TOF—is shown as a function of inverse temperature. Similar plots are possible as a function of the partial pressure for any desired gas species. By considering such plots, the sensitivity analysis can be reliably restricted to only those elementary reactions whose probability is either (i) larger than about 0.01 (thus affecting the TOF by scaling the time increment), or (ii) lies within the indicated band around the TOF (thus affecting the TOF by proximity). In other words, the proposed multiplicity analysis performed at fixed conditions directly indicates which elementary rate constants will affect the TOF and which ones will not. The actual promotion or hindering of the TOF can then be determined by performing the sensitivity analysis only on the affecting rate constants.

Regarding the RDS for model I (Fig. 4(f)), our results agree with (and clarify) the data presented in Fig. 5 of Ref. 7 (see Section S8 of the Supporting Information for a deeper comparison). In fact, some of the values shown for the rate sensitivity $\xi_\alpha$ in Fig. 5 of Ref. 7 have the same qualitative shape as $E_{\text{app}}^{\text{TOF}}$ in Fig. 4(d) and various $E_{\alpha}^{M}$ curves in Fig. 5(f) of this study. This shows that their sensitivity analysis and our multiplicity approach contain similar information. However, according to Fig. 4(f) at low temperature, we expect the TOF to be rather sensitive to the same three recombination reactions that describe $E_{\text{app}}^{\text{TOF}}$ accurately in Fig. 4(a). We find it puzzling that no sizable values for $\chi_\alpha$ and/or $\xi_\alpha$ were found in region I in Ref. 7 for any of the three recombination reactions.

This suggests that, in addition to the large computational effort, the actual numerical determination of some $\xi_\alpha$ might be quite difficult in practice, presumably due to the inherent noise in the KMC simulations. As evidenced by the ongoing search for ‘practical approaches’ and there is a need to reduce the computational cost of the $\xi_\alpha$ analysis. Our method provides an alternative, only requiring the monitoring of the multiplicities of the different reactions, thus reducing the computational burden to a minimum. In particular, our approach avoids the determination of noisy derivatives, thus resulting in clearer trends, and it includes detailed information about the relative competition between the different reactions, simply by plotting the reaction probabilities, as in Fig. 5(a). Furthermore, our approach distinguishes between two different sources for variations in the TOF (proximity: $\omega_\alpha^R \sim \omega_\text{TOF}^R$, and scaling: $\omega_\alpha^R \sim 1$).

**C. Comparison to traditional descriptions of $E_{\text{app}}^{\text{TOF}}$**

According to one line of traditional thinking, when there is only one dominating reaction, the apparent activation energy $E_{\text{app}}^{\text{TOF}}$ coincides with the elementary activation energy $E_{\lambda}^{\text{act}}$ of that particular reaction (the RDS or bottleneck). An example is Eq. 2, which exactly gives $E_{\text{app}}^{\text{TOF}} = E_{\lambda}^{\text{act}}$ when a single RDS exists. This was seen as a positive feature in Ref. 7 (see text after Eq. (12) in that study). However, according to Eq. 31 of this report, a better description when a RDS exists is $E_{\text{app}}^{\text{TOF}} = E_{\lambda}^{\text{act}} + E_{\text{app}}^{\text{v}} + E_{\text{app}}^{\text{M}}$. Since $E_{\lambda}^{\text{act}}$ is typically small, the important difference with respect to such traditional view is that $E_{\text{app}}^{\text{TOF}}$ differs from $E_{\lambda}^{\text{act}}$ due to the presence of an important configurational entropy contribution, $E_{\lambda}^{M}$, which contains the actual changes experienced by the coverage of the collection of sites where the RDS takes place.

Another line of traditional thinking, represented by Eq. 1, correctly considers the presence of an additional contribution to $E_{\text{app}}^{\text{TOF}}$, but describes it as a weighted sum of formation enthalpies (or adsorption heats) with phenomenological reaction orders as weights. Although this formulation remains valid beyond the mean field approximation, the reasoning behind is based on general arguments about the mathematical dependence on real-valued powers of the adsorbate coverages in the presence of correlated configurations. Effectively, this transfers the dependence on the spatial configuration (including any possible correlations) into a dependence on gas properties (the partial pressures), thus shifting the focus from the surface to the gas phase and masking the actual microscopic origin, which ultimately lies on the multiplicities themselves, as stressed in the present study. The
introduction of the multiplicities in the present work di-
rectly enables placing the focus back on the actual structure of the surface.

A recent attempt to explain the apparent activation energy uses a generalized version of Eq. 2 based on \( \chi_\alpha \) (instead of \( \xi_\alpha \))\(^3\):

\[
E_{app}^{\text{TOF}} = \sum_{\alpha \in \{d, a, r, s\}} \chi_\alpha \left( E_{\alpha}^F + k_BT + T^2 \frac{\partial (\Delta S_{\alpha}^F)}{\partial T} \right) \\
+ \sum_{\alpha \in \{a, s\}} \chi_\alpha \left( E_{\alpha}^F - k_BT/2 + k_BT^2 \frac{\partial \log s_\alpha}{\partial T} \right) \\
- k_BT^2 \sum_X \frac{\partial \alpha X}{\partial T} \log p_X,
\]

where \( s_\alpha \) is the sticking probability for adsorption reaction \( \alpha \), \( p_X \) is the partial pressure for species \( X \) and \( n_X \) is the corresponding reaction order, which stems from the assumption of a power-law dependence on pressure\(^3\):

\[
\text{TOF} = A e^{-E_{app}^{\text{TOF}}/k_BT} \prod_X p_X^m.
\]

Since each \( \chi_\alpha \) considers simultaneously the forward and backward rates, the summations in \( \alpha \) run over the forward reactions only \( (\alpha \in \{d, a, r, s\} \) for desorption, diffusion and recombination, and \( \alpha \in \{a, s\} \) for adsorption). For diffusion, recombination and desorption, Ref.\(^3\) assumes the rate constants to be: \( k_\alpha = k_\alpha^0 e^{-E_{\alpha}^F/k_BT} \), where \( k_\alpha^0 = k_BT \Delta S_{\alpha}^F/k_BT \). Considering the thermody-
namic formulation of the reaction rate in TST (see Section II C), Ref.\(^3\) effectively approximates the enthalpy change by using the energy barrier \( (\Delta H_{\alpha}^F = E_{\alpha}^F) \). In turn, the rate constants for adsorption in Ref.\(^3\) are: \( k_\alpha = s_\alpha A_\alpha \sqrt{2\pi m_X k_BT} \), where \( A_\alpha \) is the adsorption site area, \( s_\alpha \) is the sticking probability, \( m_X \) is the mass of the adsorbed molecule and the typical dependence on pressure \( p_X \) (as in \( \sqrt{2\pi m_X k_BT} )) is modeled outside \( k_\alpha \) (see Eq. 35).

Using \( k_BT^2 \frac{\partial \text{TOF}}{\partial T} = -\frac{\partial \text{TOF}}{\partial T} \), we re-write Eq. 34 simply as:

\[
E_{app}^{\text{TOF}} = \sum_{\alpha \in \{a, s\}} \chi_\alpha \left( E_{\alpha}^F + k_\alpha^0 \right) \sum_X \frac{\partial \alpha X}{\partial T} \log p_X,
\]

where we have used the definition in Eq. 26 for \( E_{\alpha}^F \) = \( -\frac{\log k_\alpha^0}{\partial T} = k_BT \frac{2\partial \log k_\alpha^0}{\partial T} = k_BT \frac{2\partial k_\alpha^0}{\partial T} \), resulting in \( E_{\alpha}^F \) = \( k_BT + T^2 \frac{\partial (\Delta S_{\alpha}^F)}{\partial T} \) for diffusion/recombination/desorption, and \( E_{\alpha}^F \) = \( -\frac{k_BT}{2} + k_BT^2 \frac{\partial \log s_\alpha}{\partial T} \) for adsorption.

In this study, we consider various expressions for \( E_{\alpha}^F \) (see Eqs. S13-S15 in Section S2A of the Supporting Information). For desorption, as an example, equating the value of \( E_{\alpha}^F \) in Ref.\(^3\) (\( E_{\alpha}^F = k_BT + T^2 \frac{\partial (\Delta S_{\alpha}^F)}{\partial T} \) and that in Eq. S14 of the Supporting Information gives:

\[
T^2 \frac{\partial (\Delta S_{\alpha}^F)}{\partial T} = 2k_BT k_BT \frac{\partial \log s_\alpha}{\partial T} = s_\alpha \sqrt{2\pi m_X k_BT}.
\]

Thus, the present study considers the temperature dependence of the entropy barrier \( (\Delta S_{\alpha}^F) \) for some reactions.

The use of the standard expression for non-activated adsorption \( (k_\alpha = s_\alpha \sqrt{2\pi m_X k_BT} \), see Section S2A of the Supporting Information) does not limit the conclusions of the present report. Although we may complicate the study by including more complex adsorption rate constants involving entropy barriers and/or energy barriers, this will only affect the actual value of \( k_\alpha \) for the modified reactions and, accordingly, the value of \( E_{\alpha}^F + E_{\alpha}^{\theta} \). However, the important configurational term emphasized in this report, \( E_{\alpha}^{\theta} \), will still be needed in order to describe \( E_{app}^{\text{TOF}} \) properly according to Eq. 26.

Although Eq. 36 shares two energy contributions with Eq. 26, namely, \( E_{\alpha}^F + E_{\alpha}^{\theta} \), there are marked differences between the two formulations. In Eq. 36, the first summation is over all forward reactions \( (\alpha \in \{e_+\}) \) while the corresponding summation in Eq. 26 is over those reactions explicitly contributing to the TOF. Similarly, the first summation in Eq. 36 uses \( \chi_\alpha \) as the weight, thus making it difficult to apply this formula to systems outside a mean field formulation (due to the huge computational effort as well as the impact on accuracy due to the numerical derivatives for noisy variables). On the other hand, the weights appearing in Eq. 26 are reaction probabilities, which can be effortlessly determined and easily interpreted within the range \([0,1]\).

In addition, Eq. 36 contains a second summation over the partial pressures of the gas species, directly resulting from the power-law approximation for the overall prefactor of the TOF (Eq. 35). In comparison, our formulation avoids any such approximation, not even including an overall prefactor (see Eq. 23), simply recognizing that every elementary reaction is present on the surface with a relative abundance \( (M_\alpha) \). The use of the multiplicities and the lack of an overall prefactor makes a key difference, leading to a single summation with probabilities as weights (Eq. 26) instead of splitting the dependence into two complex summations (Eq. 36).

D. Eley-Rideal mechanism

For reactions between an adsorbed molecule and a gas molecule, the Eley-Rideal mechanism can be formulated as:

\[
A \quad + \quad B_{(g)} \quad \xrightarrow{RDS} \quad C,
\]

where typically the irreversible reaction between \( A \) and \( B_{(g)} \) is considered as the Rate Determining Step (RDS). Thus, traditionally one writes: \( \text{TOF} = r_7 = k_7 \theta_{AB} \) (mean-field approximation). Further assuming Langmuir adsorption equilibria one obtains: \( \theta_A = K_A p_A / D \), with \( D = 1 + K_A p_A + K_B p_B + K_C p_C \) and \( K_X = \exp \left( -\Delta H_X / k_BT \right) \), with \( \Delta H_X \) the heat of adsorption of \( X \), as described in the Introduction, before
Eq. 1. This directly leads to the traditional expression: \( \text{TOF} \approx k_r \theta_A p_B = \frac{k_r}{K_B} (K_A p_A)(K_B p_B)/D = k_r K_B^{-1} (K_A p_A)^x (K_B p_B)^y (K_C p_C)^z \), where \( x, y \) and \( z \) are the partial reaction orders. Thus, the general expression in Eq. 1 for \( E_{\text{app}}^{\text{TOF}} \) remains valid for the Eley-Rideal mechanism. Even if the adsorbates are not well-mixed on the catalyst surface (e.g. forming islands, so that \( B_{(g)} \) may react with \( A \) only if \( A \) is located at specific sites, e.g. along the island perimeters), one can still write: \( \text{TOF} \approx k_r \theta_A^x p_B^y \), which leads to the same general dependence for \( E_{\text{app}}^{\text{TOF}} \) (Eq. 1).

In comparison, our formulation leads to: \( \text{TOF} = M_r k_r \), where \( M_r \) is the multiplicity of the local configuration where the recombination reaction \( A + B_{(g)} \rightarrow C \) can be performed. Thus, disregarding the small contribution \( E_A^0 \), the apparent activation energy is given by: \( E_{\text{app}}^{\text{TOF}} \approx E_r^a + E_r^M \). This way, \( E_{\text{app}}^{\text{TOF}} \) differs from \( E_r^a \) due to the configurational entropy contribution, \( E_r^M \), which contains the actual change with temperature in the multiplicity of the local configuration where the recombination reaction can be performed. More generally, even if the RDS cannot be clearly assigned to any particular elementary reaction, the proposed multiplicity approach allows describing any regime of Eq. 37, especially for the study of configurational correlations appearing beyond the mean field approximation in systems with a spatial representation.

VI. CONCLUSIONS

Focusing on the description of heterogeneous catalysis beyond the mean field approximation, the traditional formulation of the turnover frequency (TOF) in terms of the coverage by certain reaction intermediates is generalized by considering the multiplicity of each elementary reaction. Directly characterizing the number of precisely those surface sites involved in each elementary reaction, the multiplicities enable determining the changes experienced in configurational entropy with temperature. This allows formulating the probability of observing any particular elementary reaction, thus providing a complete understanding of the relative importance of every reaction in the overall network. In addition, it allows identifying the Rate Determining Step (RDS), if it exists, as well as the Rate Controlling Steps (RCSs). In this manner, monitoring the multiplicities provides a straightforward alternative to computationally-expensive approaches based on the Degree of Rate Control \( (\chi_o) \) and/or the Degree of Rate Sensitivity \( (\xi_o) \).

The use of the multiplicities also allows formulating a simple expression to describe the temperature dependence of the apparent activation energy of the TOF \( (E_{\text{app}}^{\text{TOF}}) \). Even in the simplest case, when \( E_{\text{app}}^{\text{TOF}} \) remains constant within some temperature range, we show that \( E_{\text{app}}^{\text{TOF}} \) does not correspond to the largest elementary activation energy available in the system, as still believed by some researchers. In fact, \( E_{\text{app}}^{\text{TOF}} \) does not even correspond to the elementary activation energy of the RDS, when it exists, as also amply believed. In addition to the elementary activation energy of the RDS, \( E_{\text{app}}^{\text{TOF}} \) contains an important, unbound configurational entropy contribution from the temperature dependence of the multiplicity of the dominating reaction (i.e. the coverage for those surface sites participating in the RDS). Due to this contribution, \( E_{\text{app}}^{\text{TOF}} \) may depart from a constant value even when a single RDS is controlling the overall reaction.

In comparison, the traditional Temkin formulation of \( E_{\text{app}}^{\text{TOF}} \) in terms of the formation enthalpies (or adsorption heats) of one or several intermediates in typical Langmuir-Hinshelwood and/or Eley-Rideal mechanisms is limited in practice by difficulties in determining the required reaction orders. Similarly, alternative formulations of \( E_{\text{app}}^{\text{TOF}} \) in terms of sensitivities (Eqs. 2 and 34) also suffer in practice from difficulties in determining the actual sensitivities as well as from underlying assumptions about the existence and mathematical form of an overall prefactor. Altogether, our results strongly indicate that monitoring the surface morphology should allow a deeper understanding of heterogeneous catalysis as an alternative to focusing on the determination of reaction orders and/or sensitivities.

SUPPORTING INFORMATION AVAILABLE

A PDF file is provided with the following content: (S1) Apparent activation energy in the Langmuir-Hinshelwood model, (S2) Description of the elementary reactions: S2A Oxidation of CO [with Tables S1 and S2], and S2B Selective oxidation of \( \text{NH}_3 \) [with Table S3], (S3) Computational method, (S4) Comparison to previous TOF results for additional models: S4A Oxidation of CO using models II, III and IV [with Figure S1], and S4B Selective oxidation of \( \text{NH}_3 \) [with Figure S2], (S5) Wrong apparent activation energies based on the Temkin formulation [with Examples S1 and S2], (S6) Cut-offs in the proximity \( \sigma_{\alpha}^{\text{TOF}} \), (S7) Multiplicity analysis for additional models: S7A Oxidation of CO using models II, III and IV [with Figures S3 and S4], and S7B Selective oxidation of \( \text{NH}_3 \) [with Figure S5], (S8) Rate Determining Step for model I.

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Supporting information:
A microscopic perspective on heterogeneous catalysis

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S1. APPARENT ACTIVATION ENERGY IN THE LANGMUIR-HINSHELWOOD MODEL

In a typical Langmuir-Hinshelwood mechanism,

\[
\begin{align*}
A_{(g)} & \iff k^A_{pA} k^A_{dA} & AB_{(g)} & \iff k^A_{dAB} k^A_{pAB} \\
A & + & B & \xrightarrow{k_3 \text{ RDS}} & AB
\end{align*}
\]

molecules A, B2 and AB with partial pressures pA, pB and pAB compete for adsorption on the same surface sites and the reaction between A and B adsorbrates generates the adspecies AB at a rate \( k_3 \propto e^{-E_3^A} \), which is the Rate Determining Step (RDS). [Here, \( \beta = 1/k_B T \).] This means that \( k_3 \) is much smaller than the adsorption and desorption rate constants of the reactants and products (\( k^A_{dA} \) \( k^A_{dAB} \)), with \( X = A, B, AB \). Assuming the adsorbrates A, B and AB are highly mobile and freely intermix (random homogeneous mixing or mean field approximation), the rate of production of AB per unit area is traditionally described as: \( \text{TOF} = k_3 \theta_A \theta_B \), where the coverages are written out assuming Langmuir-like adsorption-desorption equilibrium for A, B and AB: \( \theta_A = K_{APA}/(1 + K_{APA} + K_{ABPAB} + K_{BAPB}) \), \( \theta_B = \sqrt{K_{BAPB}}/(1 + K_{APA} + K_{ABPAB} + K_{BAPB}) \) and \( \theta_{AB} = K_{ABPAB}/(1 + K_{APA} + K_{ABPAB} + K_{BAPB}) \), where \( K_X = k^A_X / k^A_d \propto e^{\Delta H_X} \) is the equilibrium constant for adsorption-desorption of molecule X, with \( \Delta H_X = E^a_X - E^A_X \) the formation enthalpy (or heat of adsorption) of \( X \). Here, \( E^a_X \) \( (E^A_X) \) is the atomistic activation energy for adsorption (desorption) of X and the temperature dependence of \( K_X \) can be easily obtained by considering that \( k^X_d \propto e^{-E^A_d} \) and \( k^X_d \propto e^{-E^A_d} \).

If A is strongly adsorbed and both B and AB are weakly adsorbed, traditionally one obtains: \( \text{TOF} = k_3 (K_{APA})^{-1} (K_{BAPB})^{-1/2} \propto e^{-E_3^A} e^{-\Delta H_A} e^{-1/2 \Delta H_B} \). Since by definition we also have that \( \text{TOF} \propto e^{-E_{app}^{TOF}} \), the apparent activation energy is identified as: \( E_{app}^{TOF} = E^a_3 - \Delta H_A - 1/2 \Delta H_B \). In turn, if B2 is strongly adsorbed and both A and AB are weakly adsorbed, one obtains: \( \text{TOF} = k_3 (K_{APA})(K_{BAPB})^{-1/2} \propto e^{-E_3^A} e^{\Delta H_A} \Delta H_B \Delta H_B/2 \) and \( E_{app}^{TOF} = E^a_3 - \Delta H_A + 1/2 \Delta H_B \). Similarly, if both A and B are weakly adsorbed and AB is strongly adsorbed, one obtains: \( \text{TOF} = k_3 (K_{APA})(K_{BAPB})^{1/2} (K_{ABPAB})^{-2} \) and \( E_{app}^{TOF} = E^a_3 - \Delta H_A + 1/2 \Delta H_B + 2 \Delta H_B \). Thus, in general, for some suitable range of pressure and temperature, one may use the phenomenological Power Rate Law, \( \text{TOF} = k_3 (K_{APA})^{x} (K_{BAPB})^{y} (K_{ABPAB})^{z} \), where \( x, y \) and \( z \) are the reaction orders for A, B and AB, respectively, which leads to the Temkin formula \( E_{app}^{TOF} = E^2_3 - x \Delta H_A - y \Delta H_B - z \Delta H_{AB} \).

Our formalism (as proposed in Section II of the main report) agrees completely with these descriptions, although we substitute \( \theta_A \theta_B \) by \( M_3 \) in the expression for the TOF (i.e., \( \text{TOF} = k_3 M_3 \), where \( M_3 \propto e^{-M_3^B} \) is the multiplicity for the recombination process) and focus on determining \( M_3 \) instead of making assumptions on its dependence on pressure and temperature. This is useful when the homogeneous mixing approximation fails and/or the adsorption-desorption equilibria for A and/or B and/or AB do not hold. We obtain \( E_{app}^{TOF} = E^2_3 + E^M_3 + E^0_3 + E^M_3 \) (see Eq. 31 of the main report), where \( E^M_3 \) and \( E^0_3 \) are usually small while \( E^3_3 \) contains the temperature dependence of \( M_3 \) in the same way as \( -x \Delta H_A - y \Delta H_B \) carries that dependence for \( \theta_A \theta_B \sim (K_{APA})^{x} (K_{BAPB})^{y} \) in the Temkin formulation.

If instead the adsorption of B2 is the RDS,

\[
\begin{align*}
A_{(g)} & \iff k^A_{pA} k^A_{dA} & 1/2 B_{(g)} & \iff k^B_{dAB} k^B_{pAB} & AB_{(g)} & \iff k^B_{dAB} k^B_{pAB} \\
A & + & B & \xrightarrow{k_3} & AB
\end{align*}
\]
Similarly, if the adsorption of A is the RDS,\[ A \rightarrow \begin{array}{c} \frac{1}{2} B \rightarrow AB \end{array} \]
\[ A_{(g)} \rightarrow \frac{1}{2} B_{(g)} \rightarrow AB_{(g)}, \quad (S3) \]
and, as previously, we can write the phenomenological rate expression:
\[ TOF = k_{\alpha}^{d} p_{A} \theta_{B}. \]

Traditionally one will write: \[ TOF = k_{d}^{\alpha} A_{(g)} \rightarrow \frac{1}{2} B_{(g)} \rightarrow AB_{(g)}, \quad (S3) \]
and \[ A_{(g)} \rightarrow \frac{1}{2} B_{(g)} \rightarrow AB_{(g)}, \quad (S3) \]
with \[ \theta_{B} = \sqrt{\frac{k_{B} T}{2 \pi m_{B}}}. \]

Finally, if the desorption of AB is the RDS,
\[ A_{(g)} \rightarrow \frac{1}{2} B_{(g)} \rightarrow AB_{(g)}, \quad (S4) \]
and, as previously, we can write the phenomenological rate expression:
\[ TOF = k_{d}^{\alpha} A_{(g)} \rightarrow \frac{1}{2} B_{(g)} \rightarrow AB_{(g)}, \quad (S4) \]
with \[ \theta_{B} = \sqrt{\frac{k_{B} T}{2 \pi m_{B}}}. \]


S2. DESCRIPTION OF THE ELEMENTARY REACTIONS

A. Oxidation of CO

Table S1 provides the 21 elementary reactions considered in models I, I-bis, II, III and IV for the oxidation of CO on RuO₂(110). The data for models I-bis, II and III were collected in one publication by Hess et al.

and Over, and Kiejna et al., respectively. Model I corresponds to the original report by Reuter and Scheffler, where (i) the final values (used in their KMC simulations) regarding the activation energies for the four recombination processes differ from those collected by Hess et al., in model I-bis (which is thus discarded in this study), and (ii) some attempt frequencies \( k_{\alpha}^{0} \) were determined differently from models II, III and IV (and the discarded I-bis), as described in those reports and summarized below. In turn, model IV corresponds to our implementation of the parameter set reported by Farkas et al. Based on experiment, this model additionally contains repulsion between nearest neighbor (NN) COs located at C sites, which leads to several differentiated processes (rows 22 through 29). Depending on temperature and pressure, some of these models are dominated by adsorption-desorption processes while others are dominated by diffusion events.

In all four models the adsorption barrier is zero \( (E_{k_{\alpha}}^{a} = 0 \text{ eV}, \alpha = 1, 2, 3, 4) \). Considering \( k_{\alpha}^{0} \) is the attempt frequency from kinetic gas theory (the number of collisions per site per unit time), the adsorption rate constant is:
\[ k_{\alpha}^{0} = \frac{s \cdot p_{X}}{\sqrt{2 \pi m_{X} k_{B} T}}, \quad X = \text{CO or O}_2 \]

Since the adsorption of O₂ requires two nearest neighbor empty sites, every empty site having at least one empty neighbor is assigned an adsorption rate for atomic O \( (k_{V_{\rightarrow O}}) \) that is half the adsorption rate for molecular O \( (k_{V_{\rightarrow O}}) \): \[ k_{V_{\rightarrow O}} = \frac{1}{2} k_{v_{\rightarrow O}}. \]

In this context, \( M_{V_{\rightarrow O}} k_{V_{\rightarrow O}} = 2 M_{V_{\rightarrow O}} k_{V_{\rightarrow O}} = M_{V_{\rightarrow O}} k_{V_{\rightarrow O}} \) is the total adsorption rate of O₂ molecules per active site, where we have used the fact that the multiplicity of empty site pairs \( (M_{V_{\rightarrow O}}) \) is half the multiplicity of empty sites having at least one empty neighbor \( (M_{V_{\rightarrow O}}) \): \[ M_{V_{\rightarrow O}} k_{V_{\rightarrow O}} = \frac{1}{2} M_{V_{\rightarrow O}} k_{V_{\rightarrow O}}. \]

Thus, the probability of adsorbing an O atom is twice that of adsorbing an O₂ molecule.

In all plots of the report, the label \( V \rightarrow O \) refers to the adsorption of atomic O. Thus, for the plots showing the temperature dependence of the total rate per ac-
tive site for each elementary reaction (Mαkα vs β) [i.e. Fig. 4(e) of the main text and Figs. S3(e)-S4(e) of this Supporting Information] we display 2Mν→Oν/kBν [i.e. the total rate of adsorption of O atoms per active site]. Similarly, for the plots showing the reaction probabilities (ωαβ vs β) [i.e. Fig. 5(a) of the main text and Figs. S3(g)-S4(g) of this Supporting Information], we display 2Mν→Oν/kBν/R [i.e. the probability of adsorption of O atoms].

The desorption rate constant is computed to satisfy detailed balance (or microreversibility) with respect to the reverse reaction (adsorption). The used expression is (see Eqs. (9) and (13) in in^3, with ΔE^ad_{st,i} = 0 and q_{st,i}^{vib} = 1 or, equivalently, see Eq. A2 in^9, where we believe that the argument in the exp() function should be preceded by a negative sign):

$$k_{\alpha} = \frac{k^0_{\alpha} e^{-(E^\alpha_{\nu} + \mu_X)/k_B T}}{P_X^\alpha q_t^\alpha q_r^\alpha q_v^\alpha}$$ (S6)

where $k^0_{\alpha} = s \cdot \frac{P_X^\alpha}{\sqrt{2 \pi m_X k_B T}}$ is the attempt frequency for the reverse adsorption reaction (Eq. S5), $E^\alpha_{\nu}$ is the activation barrier for desorption and $\mu_X$ is the chemical potential for species X (= CO or O2):

$$\mu_X = -k_B T \log \left( \frac{k_B T q_t^\alpha q_r^\alpha q_v^\alpha}{P_X^\alpha} \right).$$ (S7)

Here, $q_t^X$, $q_r^X$ and $q_v^X$ are the translational, rotational and vibrational partition functions, assuming an ideal mixture of diatomic molecules (see Eq. (8) in^3 and the text after Eq. A2 in^9):

$$q_t^X = \left( \frac{2\pi m_X k_B T}{\hbar^2} \right)^{3/2},$$ (S8)

$$q_r^X = \frac{8\pi^2 I_X k_B T}{\sigma_X \hbar^2},$$ (S9)

$$q_v^X = \frac{1}{1 - e^{-h\nu_X/k_B T}},$$ (S10)

where $I_X = m_1^X m_2^X R_X^2$, with $m_1^X$ and $m_2^X$ the masses of the two atoms in the molecule, and $R_X$ the distance between them (1.13 Å for CO and 1.21 Å for O2), $\sigma_X$ is the symmetry number (we use 0.98 for CO and 1.32 for O2), and $\nu_X$ is the vibrational frequency (we use 6.5 x 10^13 Hz for CO and 4.7 x 10^13 Hz for O2).

The recombination rate constants are computed according to:

$$k_{\alpha} = k^0_{\alpha} e^{-E^\alpha_{\nu}/k_B T}, \alpha = 10, 13, 14, 17, 21, 26$$ (S11)

where $k^0_{\alpha} = g \cdot \frac{k_B T}{h}$, with $g = 1$ for models II - IV and $g = \frac{1}{2}$ for model I (see Ref.5). Similarly, using $k^0_{\alpha} = \frac{k_B T}{h}$ the diffusion rate constants are computed according to:

$$k_{\alpha} = k^0_{\alpha} e^{-\nu_\alpha/k_B T}, \alpha = 14, 21, 27, 29.$$ (S12)

Because the reaction mechanism assumes that CO2 is immediately desorbed after recombination, the decomposition of CO2 admolecules on the surface is disregarded in all four models and, thus, there is no need to consider microreversibility for recombination. On the other hand, the collection of activation energies used for diffusion are such that the diffusion rates comply with detailed balance.

In summary, while desorption and diffusion are formulated identically in all four models, adsorption and recombination differ in model I, due to using a different sticking coefficient (1/2 instead of 1) for adsorption and a different prefactor ($\frac{1}{2} \frac{k_B T}{\hbar}$ instead of $\frac{k_B T}{\hbar}$) for recombination. For completeness, particular values of the rate constants are shown in Table S2 for models I and II at representative temperatures and pressures.

Since the attempt frequencies (or prefactors) for adsorption, desorption, diffusion and recombination depend on temperature, we can directly determine their effective energies, $E^\alpha_{\nu} = -\frac{d\ln(k^0_{\alpha})}{dT}$, required in Eq. 26 of the report. Here, $\beta = 1/k_B T$. For adsorption (Eq. S5) we have:

$$E^\alpha_{\nu} = -\frac{1}{k^0_{\alpha}} \frac{dk^0_{\alpha}}{d\beta} = \frac{k_B T}{2}, \alpha = 1, 2, 3, 4.$$ (S13)

Similarly, for desorption (Eq. S6) the overall prefactor is $k^0_{\alpha} = s \cdot \frac{P_X^\alpha}{\sqrt{2 \pi m_X k_B T}} e^{-\mu_X/k_B T}$, where $\mu_X$ depends on $\beta = 1/k_B T$ according to Eqs. S7 - S10. Thus:

$$E^\alpha_{\nu} = 3k_B T + \frac{h\nu_X e^{-h\nu_X/k_B T}}{1 - e^{-h\nu_X/k_B T}}, \alpha = 5, ..., 9, 22, 23.$$ (S14)

Similarly, inspection of Eqs. S11 - S12 for recombination and diffusion gives the prefactor as $k^0_{\alpha} \propto \beta^{-1}$. Thus, the effective energies are:

$$E^\alpha_{\nu} = k_B T, \alpha = 10, 13, 14, 17, 21, 24, 29.$$ (S15)

This study considers the coverages of certain collections of sites as the multiplicities for the various processes. For the reaction mechanism introduced above, we have the following. For diffusion ($A_X \rightarrow A_Y$, where $A = CO, O$ and $X, Y = B, C$), the multiplicity is equal to the coverage of all empty sites of type Y surrounding all the X sites populated by A. Similarly, for recombination (COX + OY $\rightarrow$ CO2, where X, Y = B, C), $M_a$ is equal to the coverage by all NN pairs of COX and OY adparticles. In turn, for the five desorption types, $M_a$ equals, respectively, the coverage by COB, COC and three NN pairs of adsorbed O (OB-OB, OB-OC and OC-OC). Finally, for the adsorption of CO (O2) the multiplicity is equal to the coverage by all empty sites (all NN pairs of empty sites).

### B. Selective oxidation of NH3

Table S3 shows the reaction mechanism consisting of 18 elementary reactions proposed by Hong et al. in order to
TABLE S1. Elementary reactions, indicating the attempt frequency ($k_0 \theta \alpha$, 1/s) and activation energy ($E_k \theta \alpha$, eV or KJ/mol) used in four different models for the same reaction mechanism (oxidation of CO on RuO$_2$(110)): I. Reuter$^a$ / I-bis. (discarded)$^b$, II. Seitsonen$^b$, III. Kieja$^b$, and IV. Farkas$^b$. Model IV contains repulsion between nearest neighbor (NN) COs located at C sites, which leads to several differentiated reactions (rows 22 through 29).

| Reactions | Attempt freq. ($k_0 \theta \alpha$) | Activation energy ($E_k \theta \alpha$) |
|-----------|----------------------------------|-----------------------------------|
| 1 Adsorption V$_2$ + CO$_B$     | Eq. S5 $k_0 \theta \alpha$ | 5.1 + 0.9 | 95.6 + 0.6 |
| 2 Adsorption V$_C$ + CO$_C$     | Eq. S5 $k_0 \theta \alpha$ | 5.1 + 0.9 | 95.6 + 0.6 |
| 3 Adsorption V$_2$ + OB (at least one vacant NN) | Eq. S5 $k_0 \theta \alpha$ | 2.4 + 0.9 | 95.6 + 0.6 |
| 4 Adsorption V$_C$ + OC$_C$ (at least one vacant NN) | Eq. S5 $k_0 \theta \alpha$ | 2.4 + 0.9 | 95.6 + 0.6 |
| 5 Desorption CO$_B$ + V$_2$     | Eq. S6 $k_0 \theta \alpha$ | 6.9 + 0.9 | 95.6 + 0.6 |
| 6 Description CO$_B$ + V$_C$     | Eq. S6 $k_0 \theta \alpha$ | 6.9 + 0.9 | 95.6 + 0.6 |
| 7 Description CO$_B$ + OB + V$_B$ | Eq. S6 $k_0 \theta \alpha$ | 2.7 + 0.9 | 95.6 + 0.6 |
| 8 Description O$_B$ + CO$_B$ + V$_B$ | Eq. S6 $k_0 \theta \alpha$ | 2.7 + 0.9 | 95.6 + 0.6 |
| 9 Description O$_B$ + OC$_B$ + V$_B$ | Eq. S6 $k_0 \theta \alpha$ | 2.7 + 0.9 | 95.6 + 0.6 |
| 10 Recombination CO$_B$ + OC$_B$ + CO$_B$ | Eq. S6 $k_0 \theta \alpha$ | 2.7 + 0.9 | 95.6 + 0.6 |
| 11 Recombination CO$_B$ + OC$_B$ + CO$_B$ | Eq. S6 $k_0 \theta \alpha$ | 2.7 + 0.9 | 95.6 + 0.6 |
| 12 Recombination CO$_B$ + OC$_B$ + CO$_B$ | Eq. S6 $k_0 \theta \alpha$ | 2.7 + 0.9 | 95.6 + 0.6 |
| 13 Recombination CO$_B$ + OC$_B$ + CO$_B$ | Eq. S6 $k_0 \theta \alpha$ | 2.7 + 0.9 | 95.6 + 0.6 |
| 14 Diffusion CO$_B$ + CO$_B$     | Eq. S6 $k_0 \theta \alpha$ | 2.7 + 0.9 | 95.6 + 0.6 |
| 15 Diffusion CO$_B$ + CO$_B$     | Eq. S6 $k_0 \theta \alpha$ | 2.7 + 0.9 | 95.6 + 0.6 |
| 16 Diffusion CO$_B$ + CO$_B$     | Eq. S6 $k_0 \theta \alpha$ | 2.7 + 0.9 | 95.6 + 0.6 |
| 17 Diffusion CO$_B$ + CO$_B$     | Eq. S6 $k_0 \theta \alpha$ | 2.7 + 0.9 | 95.6 + 0.6 |
| 18 Diffusion CO$_B$ + CO$_B$     | Eq. S6 $k_0 \theta \alpha$ | 2.7 + 0.9 | 95.6 + 0.6 |
| 19 Diffusion CO$_B$ + CO$_B$     | Eq. S6 $k_0 \theta \alpha$ | 2.7 + 0.9 | 95.6 + 0.6 |
| 20 Diffusion CO$_B$ + CO$_B$     | Eq. S6 $k_0 \theta \alpha$ | 2.7 + 0.9 | 95.6 + 0.6 |
| 21 Diffusion CO$_B$ + CO$_B$     | Eq. S6 $k_0 \theta \alpha$ | 2.7 + 0.9 | 95.6 + 0.6 |

$^a$ In model I, the attempt frequency for recombination is $\frac{k_BT}{h}$, instead of $k_BT$, as used in the other models. See Ref.5 for details.

TABLE S2. Rate constants at three representative temperatures (in K) for model I (pCO = 1 atm, pO$_2$ = 2 atm) and model II (pCO = 1 x 10$^{-10}$ bar, pO$_2$ = 2 x 10$^{-10}$ bar).

| Reaction | I. Reuter | II. Seitsonen |
|----------|-----------|---------------|
| 450 K    | 550 K     | 650 K         |
| 400 K    | 340 K     | 275 K         |

All elementary reactions occur only at C sites and the attempt frequencies are taken to be 10$^{13}$ Hz, except for the adsorption reactions ($\alpha = 1$, 3), where Eq. S5 is used (with the sticking coefficient equal to 1$^3$). In the implementation by Hong et al. the desorption of NH$_3$ and NO ($\alpha = 2$ and 11, respectively) considers lateral interactions (repulsion) in such a manner that the desorption rate is given by $k_\alpha = k_0 \alpha e^{-E_\alpha/k_BT}e^{-\epsilon_\alpha/k_BT}$, where $\theta_\alpha$ represents the coverage by NH$_3$ and NO, respectively, $\epsilon_\alpha = 0.34$ and 0.16 eV for NH$_3$ and NO, respectively, and $k_\alpha = 10^{13}$ Hz for both. After implementing this feature, we observed that: (i) The lateral interactions effectively introduce a large number of elementary activation energies as a function of the local coverage around the desorbing NH$_3$/NO molecules. Correspondingly, the multiplicities for the desorption reactions of NH$_3$ and NO should be split into additional sub-multiplicities (one for each identified elementary activation energy). However, this requires a rather sophisticated programming effort while it is believed to add little value from a physical/chemical perspective, simply splitting the number of contributions that explain the actual value of the apparent activation energy. This is specially notable considering that (ii) the lateral interactions modify the behavior of the system only marginally, as shown in section S4.2 (see Fig. S2(a)), while repulsive lateral interactions are already ex-
TABLE S3. Elementary reactions, indicating the attempt frequency ($k^0_{\alpha}$, 1/s) and activation energy ($E^k_{\alpha}$, eV) used in the reaction mechanism for the selective oxidation of NH$_3$ on RuO$_2$(110)$^{18}$. All reactions occur only at/between C sites.

| a | Type | Process | Attempt freq. (1/s) | Act. energy (eV) |
|---|------|---------|---------------------|------------------|
| 1 | Adsorption | $V_C \rightarrow NH_3$ | 10$^{-13}$ | 0.0 |
| 2 | Desorption | $NH_2 + V_C \rightarrow O + O$ | 10$^{-13}$ | 1.46 |
| 3 | Adsorption | $O + O \rightarrow V_C + V_C$ | 10$^{-13}$ | 0.0 |
| 4 | Desorption | $OHH + V_C \rightarrow NH + V_C + H_2O(y)$ | 10$^{-13}$ | 0.27 |
| 5 | Recombination (abstraction) | $NH_2 + O + NH_2 + OH$ | 10$^{-13}$ | 0.55 |
| 6 | Recombination (abstraction) | $NH_H + OH \rightarrow NH + V_C + H_2O(y)$ | 10$^{-13}$ | 0.27 |
| 7 | Recombination (abstraction) | $NH + O \rightarrow NH + V_C + H_2O(y)$ | 10$^{-13}$ | 0.0 |
| 8 | Recombination (abstraction) | $NH + O \rightarrow NH + V_C + H_2O(y)$ | 10$^{-13}$ | 0.0 |
| 9 | Recombination (abstraction) | $N + O \rightarrow NO + V_C$ | 10$^{-13}$ | 0.14 |
| 10 | Desorption | $NO + V_C + O + V_C$ | 10$^{-13}$ | 0.27 |
| 11 | Desorption | $N + N + V_C + V_C$ | 10$^{-13}$ | 1.49 |
| 12 | Diffusion | $O \rightarrow OH$ | 10$^{-13}$ | 0.96 |
| 13 | Diffusion | $NH \rightarrow NH + OH$ | 10$^{-13}$ | 0.93 |
| 14 | Diffusion | $NH + V_C \rightarrow OH + V_C$ | 10$^{-13}$ | 1.12 |
| 15 | Recombination (abstraction) | $NH_2 + O + NH + OH$ | 10$^{-13}$ | 1.0 |
| 16 | Recombination | $NH + OH \rightarrow NH_2 + O$ | 10$^{-13}$ | 0.0 |
| 17 | Recombination | $NH_2 + OH \rightarrow NH + OH$ | 10$^{-13}$ | 0.26 |
| 18 | Recombination | $NH + O \rightarrow NH + OH$ | 10$^{-13}$ | 0.9 |

S3. COMPUTATIONAL METHOD

KMC. The KMC simulations are performed using a typical lattice-gas model with the rejection-free, time-dependent implementation$^{9,11–15}$. Every time step ($k$) starts by updating time as $t^{k+1} = t^k + \Delta t$, where $\Delta t = -\log(u)/\bar{r}$ is the inverse of the instantaneous total rate, $\bar{r} = \bar{r}_a + \bar{r}_d + \bar{r}_h + \bar{r}_r$, with $\bar{r}_a, \bar{r}_d, \bar{r}_h$ and $\bar{r}_r$ the instantaneous total adsorption rate, total desorption rate, total hop rate and total recombination rate, respectively. The factor $-\log(u)$, where $u$ is a uniform random number in (0,1], enforces the correct Poisson distribution for the time steps, with a mean value of 1. All instantaneous total rates ($\bar{r}$ and $\bar{r}_g$) with $g = a, d, h, r$) are simply related to the instantaneous total rates per active site ($\bar{R}$ and $\bar{R}_g$): $\bar{R} = \bar{r}/\bar{s}$ and $\bar{R}_g = \bar{r}_g/\bar{s}$, where $\bar{s}$ the number of active sites. After updating $t$, the next reaction type (adsorption, desorption, diffusion or recombination) is selected by performing a linear search (LS) amongst $\bar{r}_a$, $\bar{r}_d$, $\bar{r}_h$ and $\bar{r}_r^{12,16}$. Once one of the four main reaction types has been chosen, say $\bar{r}_x$, one particular elementary reaction is selected by performing either a LS or a binary search (BS) amongst the rate constants contained in $\bar{r}_x^{12,16}$. Note that $\bar{r}_x$ typically contains the rate constants of many elementary reactions for various reaction types. The use of LS or BS is automatically selected by the program, depending on the number of rate constants $n$ contained in $\bar{r}_x$. In particular, LS is performed if $n \leq 100$ and BS is used otherwise. Once an elementary reaction has been selected, it is executed, thus modifying the neighborhoods of the origin and/or end sites. As a result, the corresponding rate constants and total rates ($\bar{r}_a, \bar{r}_d, \bar{r}_h, \bar{r}_r$ and $\bar{r}$) are updated. In this manner, the simulation is continued by incrementing time, selecting a new elementary reaction, executing it, and updating the neighborhoods until the simulation is finished (see Termination below).

Steady state. The steady state is reached after a transient from the chosen initial state (see Initial State below). The steady state is characterized by the fact that the instantaneous coverage of any adspecies fluctuates with time about a constant value. This includes four adspecies ($\theta_{CO}, \theta_{C}, \theta_{NO}, \theta_{C}$ and $\theta_{O}$) for the case of the oxidation of CO, and seven adspecies ($\theta_{NH_3}, \theta_{NH_3}, \theta_{NH}, \theta_{NO}, \theta_{N}, \theta_{O}$ and $\theta_{OH}$, all at C sites only) for the oxidation of NH$_3$. Thus, in the steady state the tendency for any of these coverages is to become independent of time and the correlation coefficient $R^2$ of any computed linear regression between coverage and time should become 0.

On the other hand, before reaching the steady state, even if the dependence between coverage and time is not linear, the correlation coefficient $R^2$ will necessarily deviate from 0. Based on this, we sample the various coverages every $E = 10^5$ executed elementary reactions and mark the onset of the steady state as follows: (i) For the case of the oxidation of CO, the steady state starts when the four $R^2$ coefficients of the linear regressions become less than 0.1 simultaneously for the last P sampled- coverages, where $P = 20\sqrt{L_xL_y}$, with $L_xL_y$ the total number of catalyst sites. For the typical size of the simulations (30 × 30, see Size below) this gives $P = 600$. (ii) For the oxidation of NH$_3$, the system is considered to enter the steady state when the seven coverages satisfy simultaneously the condition $|\theta_{MAX} - \theta_{MIN}| \leq 0.05$, where $\theta_{MAX}$ and $\theta_{MIN}$ are the maximum and minimum values of the coverage for adspecies X for the last P sampled- coverages, where $P = 10\sqrt{L_xL_y}$. For the typical size of the simulations (30 × 40, see Size below) this gives $P = 346$. These criteria are rather useful, since the total number of events (including adsorption, desorption, diffusion and recombination) required to reach the steady state varies.
by orders of magnitude, depending on the physical model, the temperature and the partial pressures (of CO and O₂, for the oxidation of CO, and of NH₃ and O₂, for the oxidation of NH₃). Some models are overwhelmingly dominated by adsorption and desorption reactions while others are dominated by diffusion reactions. And this depends on temperature and pressure. Thus, it is difficult to estimate beforehand the total number of executed elementary reactions required to enter the steady state. The use of the previous criterion provides a robust procedure to simplify data collection, especially regarding the accuracy of the apparent activation energy.

Purpose to eliminate any chance of affecting the analysis of the KMC simulations. We use the expression: 

\[
\text{TOF} = \frac{Z}{k_3 L_x L_y (t)},
\]

where \(Z\) is the total number of catalyst sites and \(k_3\) is the average time.

Initial state. Simulations were performed with different initial states (e.g. O-terminated, CO-terminated, random with 50% O-terminated + 50% CO-terminated, all empty, etc...) and the obtained steady states were confirmed to be essentially identical.

Acceleration. Although we are aware of various acceleration algorithms to increase the computational efficiency of the KMC simulations, we have avoided them on purpose to eliminate any chance of affecting the analysis of the apparent activation energy.

Size. Oxidation of CO: The simulations were performed on systems with \(L_x L_y = 30 \times 30, 60 \times 60,\) and \(100 \times 100\) active sites and repeated \(K\) times to obtain ensemble averages of all quantities, with \(K = 10.\) Any error bars indicated in the main text correspond to the standard deviations of the corresponding variable amongst the \(K\) runs. As expected, on going from \(L_x = 30\) to 100 we observe the same overall behavior with a reduction in the fluctuations in all variables and a huge increase in computational time. In other words, \(L_x = 30\) provides similar results to 60 and 100, for a fraction of the computational effort. The reported results correspond to \(L_x L_y = 30 \times 30\) (900 active sites). This is larger than in previous studies (20 \(\times\) 20). Oxidation of NH₃: We use \(K = 10\) and \(L_x L_y = 30 \times 40.\) Since in this system the elementary reactions take place only on C sites, this makes a total of 15 \(\times\) 40 = 600 active sites. This is the same size used by Hong, et al. (confirmed by private communication).

Temperature and pressure. We use a wide range of temperatures and pressures. Oxidation of CO: \(T = 250-750\ \text{K}\) and \(p = 1 \times 10^{-10} - 2 \times 10^9\ \text{bar.}\) Oxidation of NH₃: \(T = 455-590\ \text{K}\) and \(p = (0.5 - 20) \times 10^{-7}\ \text{mbar.}\)

### S4. Comparison to Previous Results for Additional Models

#### A. Oxidation of CO using models II, III and IV

Fig. S1(a) shows the temperature dependence of \(R, R_a, R_d, R_h,\) and \(R_r (= TOF)\) as well as the corresponding \(TOF\) data obtained by Hess et al. for model II at \(p_{\text{CO}} = 2 \times 10^{-7}\ \text{mbar}\) and \(p_{\text{O}_2} = 10^{-7}\ \text{mbar.}\) The corresponding pressure dependence of the \(TOF\) for \(T = 350\ \text{K}\) and \(p_{\text{O}_2} = 10^{-7}\ \text{mbar}\) is shown in Fig. S1(b). In turn, Figs. S1(c)-(d) show the temperature dependence of \(R, R_a, R_d, R_h,\) and \(R_r (= TOF)\) as well as the corresponding \(TOF\) data obtained by Hess et al. and Farkas et al. for models III and IV, respectively. The pressure dependence of the \(TOF\) for model II in Fig. S1(b) is practically identical, while a small, horizontal shift is observed in the temperature dependence for both models II and III in Figs. S1(a) and S1(c), presumably due to our improved steady state detection. Regarding model IV in Fig. S1(d), our \(TOF\) depart from the reference results at low temperature \((\beta > 35).\) This is probably due to differences in the details of the implementation of repulsion, which we may have carried out differently from Ref. Overall, comparison of six \(TOF\) curves (considering Fig. 2of the main text and Fig. S1 of this Supporting Information) strongly indicates that our implementation of the KMC method and the reaction mechanism is correct.

#### B. Selective oxidation of NH₃

Fig. S2(a) compares our results for the coverage of various adspecies as a function of the O pressure, as obtained with and without lateral interactions at 530 K. The figure also includes the corresponding results from Hong, et al. (with lateral interactions). The results strongly indicate that our implementation of the KMC method and the reaction mechanism is correct. Fig. S2(b) shows the temperature dependence of \(R, R_a, R_d, R_h, R_r\) and the total desorption rates per active site \((M_a k_a)\) for NO and \(N_2\), as well as the sum of the last two \((TOF)\) at \(p_{\text{N}_2} = 0.1 \times 10^{-7}\ \text{mbar}\) and \(p_{\text{O}_2} = 1.5 \times 10^{-7}\ \text{mbar, as obtained without lateral interactions for the desorption of NH₃ and NO. No reference data is available for the temperature dependence.}

### S5. Wrong Apparent Activation Energies Based on the Temkin Formulation

Although the Temkin formulas derived in Section S1 \((E_{\text{app}}^\text{TOF} = E_h^k - x \Delta H_A - y \Delta H_B\) when the recombination of \(A\) and \(B\) is the RDS, \(E_{\text{app}}^\text{TOF} = E_d^A - y \Delta H_B\) when the adsorption of \(A\) is the RDS, etc...) have a strong mathematical basis, the following examples show that, in practice,
FIG. S1. Typical results for models II, III and IV for the oxidation of CO on RuO$_2$(110): (a) Arrhenius plot for the total rates per active site $R_a$, $R_d$, $R_b$, $R_f$ ($=$ TOF), and $R = R_a + R_d + R_b + R_f$ vs inverse temperature $\beta = 1/k_BT$ for model II. (b) CO pressure dependence of $R_e$ ($=$ TOF) for model II. (c)-(d) Same as frame (a), now for models III and IV, respectively. Reference TOF data: (a)-(c) Ref.$^4$, (d) Ref.$^8$. Experimental data in frame (b): Ref.$^{26}$. Experimental data in frame (b): Ref.$^{16}$.

these expressions may result in wrong apparent activation energies due to difficulties in determining the reaction orders ($x$, $y$, etc...), that multiply the adsorption heats / formation enthalpies. The present study stresses the perspective that the apparent activation energy includes configurational entropy contributions (see Eq. 31 of the main report), rather than the traditional adsorption heats / formation enthalpies.

**Example S1.** Let us focus on model I at $T_1$, where recombination type $COCO + OCO \rightarrow CO_2$ is the RDS (see Fig. 4(f) of the main report) and $A = CO$ ($B_2=O_2$) is weakly (strongly) adsorbed (see Fig. 5(b) of the main report). Traditionally, in the mean-field approximation one will write (see Section S1): $TOF = k_{COCO+OC+CO_2} = k_{COCO+OC+CO_2}(K_{COPO})(K_{PO})^{-1/2}$, and $E_{TOF} = E_{COCO+OC+CO_2} - \Delta H_{CO} + \frac{1}{2}\Delta H_{O}$. Thus, using the values in Table S1, we obtain: $E_{TOF} = 0.9 - 1.3 + \frac{1}{2}2.0 = 0.6$ eV. Here, we have considered that desorption of CO occurs dominantly from C sites ($\omega_a^R \sim 0.5$ in Fig. 5(a) of the main report), with $E_{RCOO+OC}^k = 1.3$ eV in Table S1), which gives $\Delta H_{CO} = E_{COCO+OC}^k - E_{V+CO} = 1.3 - 0 = 1.3$ eV. In comparison, CO desorption from B sites is negligible ($\omega_a^R \sim 10^{-5}$ in Fig. 5(a) of the main report, with $E_{RCOO+OC}^k = 1.6$ eV in Table S1). Similarly, desorption of O occurs dominantly from C sites ($\omega_a^R \sim 0.1$ in Fig. 5(a) of the main report, with $E_{OCO+OC}^k = 2.0$ eV in Table S1), which gives $\Delta H_{O} = E_{OCO+OC}^k - E_{V-O}^k = 2.0 - 0 = 2.0$ eV. Since $E_{TOF} = 1.3$ eV at $T_1$ according to Fig. 5(a) of the main report, the Temkin value of 0.6 eV fails by about 0.7 eV. This cannot be explained only by the fact that the Temkin expression for $E_{TOF}$ neglects the term $E_{RCOO+OC+CO_2}^k = k_B T$ (Eq. S15), since this term is small ($\approx 0.06$ eV at $T_1$). The error can be assigned to the failure of random mixing, due to the presence of strong adsorbate correlations at high coverage (of $O$). In this case, the adsorption of $CO$ is not random, occurring preferentially at $C$ sites, as a result of preferential desorption of $CO$ and $O_2$ from $C$ sites. Thus, substituting $M_{COOC+OC+CO_2} \theta_{CO} \theta_{O_2} = (K_{COPO})(K_{PO})^{-1/2}$ is a poor approximation in this system, due to the failure of random mixing. The present study shows that $E_{TOF}$ is described accurately when $M_{COOC+OC+CO_2}$ is determined correctly.
FIG. S2. Typical results for selective oxidation of NH$_3$ on RuO$_2$(110): (a) Coverage vs pressure for various surface intermediates at 530 K, as implemented in this study, with and without lateral interactions (repulsion) in the desorption reactions of NH$_3$ and NO. Reference data obtained with lateral interactions are shown from Hong et al.$^{10}$. (b) Arrhenius plot for the total rates per active site $R_a$, $R_d$, $R_r$, $R_n$, and $R = R_a + R_d + R_r + R_n$ vs inverse temperature $\beta = 1/k_BT$ at $p_{NO} = 0.1 \times 10^{-7}$ mbar and $p_{O_2} = 1.5 \times 10^{-7}$ mbar, as obtained in this study (no lateral interactions). The total desorption rates per active site ($M_ak_\alpha$) for NO and N$_2$, as well as their sum (TOF), are also shown.

**Example S2.** When the RDS in the Langmuir-Hinshelwood model is the adsorption of $B_2$, traditionally one will write (see Section S1): $TOF = k_B^R p_B \theta^2_\alpha$, where $\theta_\alpha$ is the coverage by all empty sites and $\theta^2_\alpha$ describes the coverage by all empty pairs of sites in the homogeneous mixing approximation. Since the adsorption of $B_2$ is the RDS, traditionally one assumes adsorption-desorption equilibrium for $A$, thus leading to the Langmuir isotherm: $\theta_A = K_{AP_A}/(1 + K_{AP_A})$ and $\theta_\alpha = 1/(1 + K_{AP_A})$. If $A$ is strongly adsorbed, then $\theta_\alpha = 1$ (large) and $\theta_\alpha = (K_{AP_A})^{-1}$ (small), which is the situation at low temperatures for models I-IV, with $A = CO$ and $B_2 = O_2$.

Then, traditionally one obtains: $TOF = k_B^R p_B (K_{AP_A})^{-2}$ and, thus, $E_{app}^{TOF} = E^R + 2 \Delta H_A$. Focusing on the temperature range between $T_1$ and $T_2$ for model I (see Figs. 4(d)-f) and 5(a,b) of the main report), we obtain: $E_{app}^{TOF} = E^{k_{CO}\rightarrow CO} + 2 \Delta H_{CO} = 0 + 2 \times 1.3 = 2.6$ eV. Here, we have used the fact that the activation energy for adsorption of $O_2$ is zero ($E^{k_{V\rightarrow O}} = 0$ eV in Table S1, as for any other adsorption process in models I-IV) and desorption of CO occurs dominantly from C sites ($\omega^R_\alpha = 0.5$ in 5(a) of the main report, with $E^{k_{CO\rightarrow V_C}} = 1.3$ eV in Table S1), which gives $\Delta H_{CO} = E^{k_{CO\rightarrow V_C}} - E^{k_{V\rightarrow CO}} = 1.3 - 0 = 1.3$ eV. In comparison, CO desorption from $B$ sites is negligible ($\omega^R_\alpha = 10^{-4}$ in Fig. 5(a) of the main report, with $E^{k_{CO\rightarrow V_C}} = 1.6$ eV in Table S1). Since $E_{app}^{TOF} = 2.87$ eV between $T_1$ and $T_2$ according to Fig. 4(d) of the main report, the Temkin value of 2.6 eV fails by about 0.27 eV. This is due to the inadequacy of the approximation to describe the coverage by all empty pairs of sites using $\theta_\alpha^2$, which ultimately is due to the failure of the random mixing approximation. The present study shows that $E_{app}^{TOF}$ is described accurately when the coverage for this collection of sites is determined correctly as the multiplicity for the adsorption of $O_2$.

**S6. CUT-OFFS IN THE PROXIMITY $\sigma_{\alpha}^{TOF}$**

Fig. 5(a) of the main report and Figs. S3(g), S4(g) and S5(g) of this Supporting Information display the probability to observe any elementary reaction ($\omega^R_\alpha = M_\alpha k_\alpha/R$) together with the probability to observe any reaction explicitly contributing to the TOF, $\omega^{R}_{\alpha}^{TOF} = TOF/R$. In addition, these figures display two more curves, namely, $2\omega^{R}_{TOF}$ and $0.05\omega^{R}_{TOF}$. Considering the definition of the proximity $\sigma_{\alpha}^{TOF}$ in Eq. 33 of the main text, any elementary reaction with probability $\omega^R_\alpha$ between $\omega^{R}_{\alpha}^{TOF}$ and $2\omega^{R}_{TOF}$ will lead to proximity values between 1 and 0. Likewise, if $\omega^R_\alpha$ falls between $\omega^{R}_{\alpha}^{TOF}$ and $0.05\omega^{R}_{TOF}$ the proximity will lie between 1 and 0.05.

Although the definition of the proximity implies the use of an upper cutoff ($2\omega^{R}_{TOF}$, beyond which the sensitivity is 0), no actual lower cutoff is used. In practice, any reaction with probability $< 0.05\omega^{R}_{TOF}$ will occur so rarely (with respect to the TOF) that the reaction itself becomes irrelevant, thus justifying the use of $0.05\omega^{R}_{TOF}$ as a visual lower cut-off in Fig. 5(a) of the main report and Figs. S3(g), S4(g) and S5(g) of this Supporting Information. Regarding the upper cut-off, a general value $c\omega^{TOF}_{\alpha}$ with $c > 1$ can be used by modifying the definition of the proximity to: $\sigma_{\alpha}^{TOF} = 1 - min(c - 1, \delta_{\alpha}^{TOF})/(c - 1)$. 

While we use $c = 2$, $c = 4 - 10$ will leave Fig. 5(a) of the main report and Figs. S3(f), S4(f) and S5(f) of this Supporting Information essentially unchanged, only modifying the left or right half of the sensitivity spikes, i.e. that half corresponding to the reaction probabilities falling between $\omega_{\text{TOF}}^R$ and $c \cdot \omega_{\text{TOF}}^R$.

S7. Multiplicity Analysis for Additional Models

A. Oxidation of CO using models II, III and IV

Fig. S1(a) shows that model II is dominated by adsorption and desorption at low temperatures (region $A_1$ for $R$), while diffusion becomes the leading reaction above $\sim 305 \text{ K}$ (regions $A_2$, $B$ and $C$ for $R$). Although $R$ displays four regions, the curves for $R_a$, $R_d$, $R_b$ and $R_c$ exhibit three regions, labelled as I, II and III for the TOF ($\sim R_a$). Here, region II displays a larger slope than region I, as evidenced in the corresponding derivative, shown in Fig. S3(a). As in the main report, the analysis of the apparent activation energy of the TOF performed here for model II, as displayed in Figs. S3(a)-(c), concludes that $E_{\text{TOF}}^R$ is accurately explained by Eq. 26 of the report, with the absolute error remaining $\lesssim 0.062 \text{ eV}$ across all regions. Similarly, the analysis of $E_{\text{TOF}}^R$ based on determining the RDS, as shown in Figs. S3(d)-(f), concludes that also Eq. 31 of the report explains accurately the atomistic origin of $E_{\text{TOF}}^R$, with the absolute error remaining $\lesssim 0.036 \text{ eV}$ across all regions. In this model, the RDS is assigned to the adsorption of O atoms ($V \to O$) in all three regions.

As already found in the main report, the mere observation of a linear Arrhenius behavior (in region I, see Fig. S1(a)) does not imply that $E_{\text{TOF}}^R$ ($\approx 2.82 \text{ eV}$) can be assigned to the elementary reaction with largest activation energy (4.82 eV, for $O_B + O_B \to V_B + V_B$) nor to only the elementary activation energy of the RDS, $E_N^R (\approx 0 \text{ eV}, \text{for} \lambda = V \to O)$, since this will neglect the configurational contribution, $E_R^N \approx 2.82 \text{ eV}$, which in this case fully explains the value of $E_{\text{TOF}}^R$.

Figs. S3(g)-(i) provide detailed information about the relative competition between the different elementary reactions. The situation at $T_1$ is similar to that for model I, involving equilibrated adsorption and desorption of CO ($V \to CO$ and $CO_C \to V$, with probability $\omega^R_a \sim 0.5$), diffusion ($CO_B \to CO_{OB}$, with $\omega^R_a \sim 10^{-6}$), adsorption of O ($V \to O$, with $\omega^R_a \sim 2.5 \times 10^{-7}$), and recombination ($CO_B + O_C \to CO_2$, with $\omega^R_a \sim 2 \times 10^{-7}$). The next probable reaction, $CO_C + O_B \to CO_2$, has roughly four times lower probability ($\omega^R_a \sim 5 \times 10^{-8}$) than $CO_B + O_C \to CO_2$ and, thus, can be neglected. As in the similar context for model I at $T_1$, the adsorption of O ($V \to O$) is the RDS. This agrees with Fig. S3(f).

At $T_2$, the description from $T_1$ remains essentially valid, although now diffusion ($CO_B \to CO_{OB}$, with $\omega^R_a \sim 0.2$) is almost as probable as the adsorption and desorption of CO ($V \to CO$ and $CO_C \to V$, with $\omega^R_a \sim 0.4$). As for $T_1$, recombination occurs essentially through the $CO_B + O_C \to CO_2$ route (now with $\omega^R_a \sim 4 \times 10^{-7}$) and the adsorption of O ($V \to O$, with $\omega^R_a \sim 4 \times 10^{-4}$) remains the RDS, in agreement with Fig. S3(f).

At $T_3$, the picture has changed significantly. Now, the diffusion of CO along the B rows dominates the activity of the system ($CO_B \to CO_{OB}$, with probability $\sim 1.0$). The next most probable reaction is the adsorption of CO ($V \to CO$, with $\omega^R_a \sim 2.5 \times 10^{-3}$), followed by the adsorption of O ($V \to O$, with $\omega^R_a \sim 2 \times 10^{-3}$), two recombinations ($CO_B + O_C \to CO_2$ and $CO_C + O_B \to CO_2$, with $\omega^R_a \sim 10^{-4}$ and $\sim 8 \times 10^{-5}$, respectively), the desorption of CO ($CO_C \to V$, with $\omega^R_a \sim 5 \times 10^{-5}$), and diffusion of O ($O_B \to O_B$, with $\omega^R_a \sim 3 \times 10^{-5}$). Any other elementary reaction is significantly less probable. Thus, the situation is as follows. If CO is adsorbed on a B site, recombination has to wait until an O is adsorbed on a C site. On the other hand, if CO is adsorbed on a C site, there is a small chance that adsorption occurs next to an existing $O_B$, thus leading to recombination, but in most cases recombination has to wait until an O is adsorbed on a B site. In other words, the system is ready for recombination as soon as O is adsorbed on either B or C sites. Thus, the adsorption of O ($V \to O$) is the RDS, as shown in Fig. S3(f).

Finally, at $T_4$, we have a rather different situation. Compared to the super-frequent random diffusion of CO along the B rows ($CO_B \to CO_{OB}$, with $\omega^R_a \sim 1$), the next most probable elementary reaction is the diffusion of O, also along the B rows ($O_B \to O_B$, with $\omega^R_a \sim 3 \times 10^{-3}$), while the rest of the reactions are executed with much lower probabilities, in the range $10^{-4}$ to $10^{-5}$. Since the C rows are essentially empty (see Fig. S3(h)), in relative terms, the adsorptions of CO and O (both predominantly at C sites) occur rather frequently ($V \to CO$ and $V \to O$, respectively, with $\omega^R_a \sim 10^{-4}$ for both). In turn, inter-row diffusion of O ($O_C \to O_B$, with $\omega^R_a \sim 5 \times 10^{-5}$) has become comparable to the two recombination reactions ($CO_C + O_B \to CO_2$ and $CO_B + O_C \to CO_2$, with probabilities $\sim 8 \times 10^{-5}$ and $\sim 4 \times 10^{-5}$, respectively) while the desorption of CO has become relatively infrequent ($CO_C \to V$, with $\omega^R_a \sim 10^{-5}$). Thus, the situation is as follows. Minor adsorption of both CO and O at B sites essentially restores their overall coverage, compensating their desorption as CO$_2$. On the other hand, after the adsorption of CO at a C site, recombination is attempted many times (and eventually occurs) as many O atoms pass by, diffusing along the left and right neighbor B rows. Similarly, after the adsorption of O at a C site, recombination is also attempted many times, eventually occurring with one of the many CO molecules passing by as they diffuse along either neighboring B row. In this manner, the system is rather sensitive to the actual values of the recombination rates for $CO_C + O_B \to CO_2$ and $CO_B + O_C \to CO_2$, as shown in Fig. S3(f). However, quantitatively, Fig. S3(f) shows that it is the adsorption of CO ($V \to CO$) and, especially, the adsorption of O ($V \to O$) that must be considered as the RDS. The
FIG. S3. Temperature dependence for model II (oxidation of CO on RuO$_2$(110)): (a) Apparent activation energy ($E_{\text{app}}^{\text{TOF}}$) for the TOF in Fig. S1(a). $E_{\text{app}}^{\text{TOF}}$ is described well by $\Sigma_{\alpha(x)} e_{\alpha(x)}^{\text{TOF}}$, where $e_{\alpha(x)}^{\text{TOF}} = \omega_{\alpha(x)}^{\text{TOF}}(E_{\alpha} + E_{\alpha}^{0} + E_{\alpha}^{M})$. The absolute error $|E_{\text{app}}^{\text{TOF}} - \Sigma_{\alpha(x)} e_{\alpha(x)}^{\text{TOF}}|$ is also plotted. (b), (c) Multiplicities ($M_{\alpha}^{R}$) and probabilities ($\omega_{\alpha}^{R}$) for those elementary reactions explicitly contributing to the TOF, respectively. (d) Same as (a), now describing $E_{\text{app}}^{\text{TOF}}$ as $E_{\alpha}^{\lambda} + E_{\alpha}^{0} + E_{\alpha}^{M}$ for the RDS. The absolute error $|E_{\text{app}}^{\text{TOF}} - (E_{\alpha}^{\lambda} + E_{\alpha}^{0} + E_{\alpha}^{M})|$ is also plotted. (e) $M_{\alpha}k_{\alpha}$ for any elementary reaction with probability $\omega_{\alpha}^{R} \geq 10^{-8}$ at any temperature. The TOF is matched by $M_{\lambda}k_{\lambda}$ for some $\lambda$ within some range of temperature. (f) Proximity to the TOF ($\sigma_{\alpha(x)}^{\text{TOF}}$), enabling the assignment of the RDS at every temperature. (g) Reaction probabilities $\omega_{\alpha}^{R}$ for the A1 coverage for all adspecies ($\theta_{\text{CO}}$, $\theta_{\text{OC}}$, $\theta_{\text{OB}}$, $\theta_{\text{COC}}$, $\theta_{\text{COB}}$, $\theta_{\text{OCB}}$, and $\theta_{\text{COC}} \geq 10^{-5}$). (h) Morphology snapshots at various temperatures. (i) Apparent activation energy ($E_{\text{app}}^{R}$) for the total rate per active site $R$ in Fig. S1(a). $E_{\text{app}}^{R}$ is described well by $\Sigma_{\alpha(x)} e_{\alpha(x)}^{R}$, where $e_{\alpha(x)}^{R} = \omega_{\alpha(x)}^{R}(E_{\alpha} + E_{\alpha}^{0} + E_{\alpha}^{M})$. The absolute error $|E_{\text{app}}^{R} - \Sigma_{\alpha(x)} e_{\alpha(x)}^{R}|$ is also plotted. (j), (l) Multiplicities ($M_{\alpha}$) and effective configurational energies ($E_{\alpha}^{M}$) for any elementary reaction with probability $\omega_{\alpha}^{R} \geq 10^{-8}$ at any temperature, respectively. $E_{\alpha}^{M}$ valid for both frames (b) and (k).

special role of $V \rightarrow O$ (as the true RDS) can be understood from the fact that, once adsorbed, an $O_C$ has
a sizable chance to change row and become $O_B$ due to diffusion ($OC \rightarrow OB$). Thus, the adsorption of $O$ on $C$ sites contributes indirectly to the recombination of type $CO_C + O_B \rightarrow CO_2$, in addition to contributing directly to $CO_B + O_C \rightarrow CO_2$. This shows how the proposed formalism allows understanding the assignment of the RDS based on $c^\text{TOF}_a \approx 1$.

Lastly, Figs. S3(j)-(l) confirm that the overall reaction for model II is dominated by adsorption and desorption at the lower temperatures of region $A_1$, while diffusion already dominates at the higher temperatures of region $A_2$, fully prevailing in both regions $B$ and $C$. As indicated in the last paragraph of Section "Theory" of the main text, the $TOF$ will be sensitive to variations in the rates of these processes due to their ability to scale the time increment $\Delta t \propto 1/\tilde{R}$. The analysis of the apparent activation energy of the total rate per active site $R$, displayed in Fig. S3(j), concludes that $E^R_{\text{app}}$ is accurately explained by Eq. 29 of the report, with the absolute error remaining $\leq 0.068$ eV across all regions.

Regarding model III, comparison of Figs. S1(a) and S1(c) shows that models II and III behave essentially the same, except for the fact that: (i) the cross-over between regions $A_1$ and $A_2$ is located at lower temperature in model III, and (ii) region $C$ displays small fluctuations around a constant value in model III, instead of the small—but steady—increase observed in model II. Due to these similarities, model III does not provide any novelty with respect to model II and its detailed analysis is skipped.

Model IV considers the presence of repulsion between nearest neighbor $CO$s located at $C$ sites, which leads to several differentiated elementary reactions (rows 22 through 29 in Table S1). Thus, compared to models I through III, model IV involves a larger number of atomistic activation energies $E^k_a$. In spite of this, Fig. S1(d) shows that, qualitatively, model IV shares some similarities with models II and III, with adsorption and desorption dominating at low temperature and diffusion leading the activity at high temperature. In fact, the total rates per active site for adsorption ($R_\alpha$), desorption ($R_\delta$), diffusion ($R_\delta$) and recombination ($R_e = TOF$) can also be broken into three regions (labelled I, II and III for the $TOF$) while the total rate per active site $R$ displays four regions ($A$, $B$, $C_1$ and $C_2$), in this case due to diffusion overtaking adsorption and desorption at high temperature, while the corresponding cross-over takes place at low temperature for models II and III.

Despite the larger number of elementary reactions, the analysis of the apparent activation energy of the $TOF$, as shown in Figs. S4(a)-(c), concludes that $E^{TOF}_{\text{app}}$ is accurately explained by Eq. 26 of the report, with a small absolute error $\leq 0.033$ eV across all regions. Similarly, the analysis of $E^{TOF}_{\text{app}}$ based on finding the RDS, as shown in Figs. S4(d)-(f), concludes that also Eq. 31 of the report explains accurately the temperature dependence of $E^{TOF}_{\text{app}}$, with the absolute error also remaining $\leq 0.032$ eV across all regions. In spite of the complexity of the model, the RDS is clearly assigned to the adsorption of $O$ atoms ($V \rightarrow O$) in the complete range of explored temperatures.

As before, the observation of a linear Arrhenius behavior (in region I) does not imply that $E^{TOF}_{\text{app}} (\approx 2.65 eV)$ can be assigned to the elementary reaction with largest activation energy (4.29 eV, for $O_B + O_B \rightarrow V_B + V_B$) nor to only the elementary activation energy of the RDS, $E^k (0 = 0 eV, for \lambda = V \rightarrow O)$, since this will neglect the important configurational contribution, $E^M = 2.65 eV$, which fully explains the value of $E_{\text{app}}$ also in model IV.

In turn, Figs. S4(g)-(i) provide detailed information about the relative competition between the different elementary reactions. The situation at $T_1$ through $T_4$ is very similar to that for models II and III, and thus we refrain from giving all the details. Overall, the reaction at $T_1$ and $T_2$ occurs with equilibrated adsorption and desorption of $CO$, and a dominating recombination ($CO_C + O_C \rightarrow CO_2(1NN)$), which is triggered as soon as the adsorption of $O$ takes place. Thus, $V \rightarrow O$ is the RDS. At $T_3$ the same picture is valid, with also $V \rightarrow O$ as the RDS, but now the dominating combination is $CO_B + O_C \rightarrow CO_2$ and, the adsorption and desorption of $CO$ are not (one-to-one) equilibrated anymore (equilibration is through the overall network of reactions). Finally, at $T_4$, the predominant recombination ($CO_B + O_C \rightarrow CO_2$) occurs soon after the adsorption of $O$ at a $C$ site ($V \rightarrow O$), which reacts with one of the many $CO$ molecules passing by as they diffuse along either neighboring $B$ row ($CO_B \rightarrow CO_B$). In probability space, the other possible recombination ($CO_C + O_B \rightarrow CO_2$) lies about 4 times below $V \rightarrow CO$, thus making the adsorption of $CO$ less critical than the adsorption of $O$. In this manner, $V \rightarrow O$ is the RDS, in agreement with Fig. S4(f). Thus, at $T_4$ the picture is very similar to that for models II and III, with $V \rightarrow CO$ having a less significant role.

Lastly, Figs. S4(j)-(l) confirm that the overall reaction for model IV is dominated by adsorption and desorption events at low temperature (regions $A$ and $B$, dominated by the adsorption and desorption of $CO$) while the diffusion reactions dominate at high temperature (regions $C_1$ and $C_2$, with diffusion of both $CO$ and $O$ along the $B$ rows). In region $C_1$, there is a complex mixture of elementary reactions with relative relevance for the overall catalytic reaction. Nevertheless, in terms of the $TOF$, the important reactions in that region are displayed in Fig. S4(f). Fig. S4(j) shows that the apparent activation energy of the total rate per active site $R$, $E^{R}_{\text{app}}$, is accurately explained by Eq. 29 of the report, with the absolute error remaining $\leq 0.051$ eV across all regions.

### B. Selective oxidation of NH$_3$

Regarding our results for Hong et al.’s reaction mechanism for the oxidation of NH$_3$ on RuO$_2$\{110\}$^{10}$, Fig. S2(b) shows how the overall reaction is dominated by recombinations at low temperature (region A) and diffu-
sion hops at high temperature (region C), with a clear crossover at around 530 K (region B). According to this figure, the adsorption and desorption reactions occur much less frequently (roughly about one adsorption/desorption every 10⁴ recombinations/hops). In particular, the desorption of the target products (NO and N₂) occurs even less frequently (approximately about one desorption of NO every 10⁵ recombinations/hops and roughly one desorption of N₂ every 10⁶ recombinations/hops). Thus, the two reactions explicitly contributing to the TOF in this system (the desorption of NO and the formation-and-direct-desorption of N₂) occur rather infrequently. This is clearly reflected by the fact that, in probability space, the TOF appears roughly in the range between 10⁻⁵ and 10⁻⁶ for the considered temperature span (see Fig. S5(g)).

As with previous models, assuming negligible temperature dependence of the multiplicity prefactors (E₀ = 0), the analysis of the apparent activation energy of the TOF performed in Figs. S5(a)-(c) concludes that E_app is ac-

FIG. S4. Same as Fig. S3, now for model IV in relation to the TOF and total rate R shown in Fig. S1(d).
curately explained by Eq. 26 of the main report, the absolute error remaining $\leq 0.052$ eV across all regions. Note that, in Hong et al.'s model the rate prefactors are constant and, thus, $E^0_{\alpha} = 0$ for most processes (except for the adsorption of NH$_3$ and O$_2$, which have no contribution to Eq. 26). Similarly, the analysis of $E_{\text{app}}^{\text{TOF}}$ based on determining the RDS, as shown in Figs. S5(d)-(f), concludes that also Eq. 31 of the main report explains accurately the atomistic origin of $E_{\text{app}}^{\text{TOF}}$, the absolute error remaining $\leq 0.071$ eV across all regions in this case. Again, in Hong et al.'s model $E^0_{\alpha} = 0$ for the RDS.

According to Fig. S5(f), we conclude that (i) the desorption of NO (reaction P11) is the Rate Determining Step (RDS) in all three regions, and (ii) there is a wide variety of Rate Controlling Steps (RCSs), i.e. the TOF is strongly sensitive to the rate constants of many elementary reactions. These include H abstraction reactions and their reverse processes (P5 and P17; P15 and P16; and P6, which has no reverse reaction in Hong et al.'s mechanism) and the formation of NO (P9). Note that the corresponding formation (and direct desorption) of N$_2$ is not a RCS, since this reaction represents a tiny contribution to the TOF. Finally, we note that also the reactions for which $w^0_{\alpha} \approx 1$ need to be considered as RCSs, since they affect the TOF by scaling the total rate and, thus, time (see the last paragraph of Section II of the main report). Accordingly, considering Fig. S5(g) we conclude that also the abstraction reaction P8 and its reverse P18 are RCSs, especially below 530 K, as well as the diffusion reaction P13, especially above 530 K. In fact, the strong dependence of the total rate per active site on the elementary reactions P8, P18 and P13 is clearly reflected in Fig. S5(j).

Considering Fig. S5(g), the previous information about the RDS and RCSs can be used to draw a simple picture about the overall catalytic reaction at any particular temperature (such as $T_1$, $T_2$ and $T_3$ in Figs. S5(g)-(i)). Namely, the reaction takes place as a cascade of abstraction reactions (between adsorbed NH$_4$/NH$_2$/NH and adsorbed O/OH), sequentially stripping the H atoms until bare N is present at the surface, where it recombines with either adsorbed O (to form NO, which is desorbed later) or with itself (to form N$_2$, which is desorbed immediately). Although having a relatively low energy barrier (0.27 eV), the formation of N$_2$ occurs rarely (see Fig. S5(g)) due to the low chance for two N atoms to meet each other as nearest neighbors (very low $M_2$ for this reaction combination, as shown in Fig. S5(b),(k)). On the contrary, having the largest energy barrier (1.49 eV), the desorption of NO occurs relatively frequently (see Fig. S5(g)) due to the large chance for the N atoms to meet O atoms as nearest neighbors (very high $M_5$ for this reaction, as shown in Fig. S5(b),(k)). Nevertheless, the desorption of NO is relatively infrequent with respect to the other rate controlling reactions (H abstractions, formation of NO and the diffusion of O), thus justifying its role as RDS. All of the aspects described here are in excellent agreement with the analysis of the overall reaction presented by Hong et al., as summarized in Fig. 2(b) of Ref.\textsuperscript{10}.

### S8. RATE DETERMINING STEP FOR MODEL I

Following the main report, let us use $\xi_\alpha$ to refer to the degree of rate sensitivity, as defined in Refs.\textsuperscript{19,20}. Similarly, as previously considered in Refs.\textsuperscript{20–22}, let us refer to the degree of rate control as $\lambda_\alpha = \xi_\alpha - \xi_{\alpha^*-} \approx 0$ for the adsorption/desorption of CO in the whole range of temperature. This means that the RDS cannot be assigned to the adsorption/desorption of CO in this system.

On the other hand, by summing the $\xi_\alpha$ curves for the adsorption and desorption of O$_2$ shown in Fig. 5 of Ref.\textsuperscript{20} the resulting $\lambda_\alpha$ becomes 0 below $\sim 1.7 \times 10^{-3}$ K$^{-1}$ and stands as the only non-zero curve above $1.8 \times 10^{-3}$ K$^{-1}$, with value $\sim 0.5$ at low temperatures. Similarly, the recombination O$_2$ + CO$_2$ → CO remains as the only process with non-zero $\lambda_\alpha$ value below $\sim 1.7 \times 10^{-3}$ K$^{-1}$, also with value 0.5. Assuming the value $\lambda_\alpha \approx 0.5$ may be treated as $\lambda_\alpha \approx 1$ (perhaps due to a factor of 2 somewhere in the equations/analysis of Ref.\textsuperscript{20}), the RDS will correspond to (i) the adsorption/desorption of O$_2$ above $1.8 \times 10^{-3}$ K$^{-1}$ and (ii) the recombination of CO$_2$ and O$_2$ below $\sim 1.7 \times 10^{-3}$ K$^{-1}$, which would be in excellent agreement with our result, as shown in Fig. 4(d) of the main report. Note that our data are clearer, presumably due to the lack of any additional processing in our case.

This designation of the RDS in region I to the adsorption of O in both studies is in conflict with the assignment of the apparent activation energy (2.85 eV) to the desorption of CO from C sites in Ref.\textsuperscript{20} ($E_{\text{app}}^{\text{TOF}} \approx \xi_\Delta \Delta E_\lambda \approx 2 \times 1.3 = 2.6$ eV, resulting in an error of 0.25 eV). In fact, such assignment contradicts the first paragraph of this section, which concludes that the RDS ($\lambda$) cannot be assigned to the desorption of CO (nor to its adsorption). According to Example S2 in Section S5, the value $2 \times 1.3$ eV corresponds to the contribution $x \Delta H_{\text{CO}}$ with $x = 2$, due to the approximate dependence $TOF \propto \theta_\alpha^2$, where $\theta_\alpha^2$ describes the coverage by all empty pairs of sites in the homogeneous mixing approximation. Thus, the sensitivity value $\xi_\alpha \approx 2$ for the desorption of CO in Fig. 5 of Ref.\textsuperscript{20} might be related to the reaction order $x = 2$ for CO. Although the adsorption-desorption equilibrium for CO is a good approximation in this system, the accurate determination of the reaction order and/or the sensitivity seems a
difficult task.

From our perspective, the desorption of CO from C sites (CO\textsubscript{C} → V\textsubscript{C}) plays an important role in this system, essentially controlling the total rate per active site \(R = \frac{r}{s}\) in combination with the adsorption of CO at C sites (V \to CO) \((\omega_{\text{C}}^R = 0.5\) for both processes in Fig. 5(a) of the main report; see also Fig. 5(d)). Thus, the two processes affect the TOF by scaling the time increment \(\Delta t \propto \frac{1}{r}\) (see last paragraph of Section II of the main report). However, neither the adsorption of CO nor its desorption are the RDS.

When the actual multiplicity for the adsorption of O is carefully monitored, Fig. 4(d) of the main report shows that \(E_{\text{app}}^{\text{TOF}}\) is explained with great accuracy in all regions. This strongly indicates that monitoring the surface morphology should allow a deeper understanding of heterogeneous catalysis as an alternative to focusing on the determination of reaction orders and/or sensitivities.
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