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Kinetics of atom recombination at catalytic surfaces ruled by *hot atom* energy distributions

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Abstract

In the framework of the 'hot atom' reaction mechanism we report on the rate of adatom recombination at catalytic surfaces. The modeling deals with a flat surface where hot atoms are identified with the adatoms populating the excited states of the vibrational ladder of the adsorption potential well. The dynamics of the energy transfer between the adlayer and the solid, that is the exchange of vibrational quanta between the adatoms and the solid, has been explicitly taken into account in the master equations together with the adsorption and recombination processes. At steady state the analytical solution of the kinetics is found to be in good agreement with the numerical solutions for a four-levels system. It is shown that the recombination rate at steady state is strongly dependent upon the ratio between the probabilities (per unit time) of quantum dissipation to the solid and of adatom recombination. This ratio is a key quantity of the kinetic model since it rules a continuous transition towards higher rates which is ascribed to a progressive displacement of the vibrational state of the adlayer, from the equilibrium condition.

Keywords: Kinetics of adatom recombination; Adatom energy distribution; Non-equilibrium phenomena

1. Introduction

Modeling the reaction rates of exothermic processes at solid surfaces is a topic of great interest in heterogeneous catalysis also in connection to the dynamics of the energy relaxation of the adspecies at the catalyst surface. In fact, the energy released during the reaction may be either dissipated to the solid or used to excite both the desorbing molecules and the adspecies [1–3]. A fraction of the energy released during the reaction can therefore be employed to trigger reaction routes which are characterized by enhanced rates when compared to those expected under thermal equilibrium of the reacting adspecies. In the Langmuir Hinshelwood (LH) mechanism, for instance, diatom formation occurs by binary encounter of adatoms, which have thermally equilibrated with the surface, according to a second order reaction kinetics. On the other side, diatom formation can occur by direct abstraction of adatoms by gas atoms, that is according to the Eley–Rideal (ER) mechanism that implies a first order reaction kinetics [4]. A mechanism intermediate between the LH and ER calls for the *hot atom* (HA) concept, as firstly introduced in Ref. [5], concerning adatoms that are not thermally accommodated at the surface. The HA mechanism has been invoked to explain experimental data on the recombination and abstraction of hydrogen at metal surfaces [6–11] and the oxidation of carbon monoxide by atomic and molecular oxygen [12,13].

Modeling the HA mechanism requires the determination of the HA surface densities which, in the model case of flat surfaces, have been identified with the populations of the adatoms in the vibrational states of the adsorption potential well [10,13]. According to the associative model [14] the recombination rate is proportional to the product of the adatom populations provided the total energy of the couples is larger than twice the adsorption energy, that is the activation energy for desorption.

On the basis of these premises in this paper we present a multi-level HA kinetics for modeling the steady state rate of diatom formation. To this end a kinetic approach will be employed where the adsorption, the recombination and the dynamics of the vibrational relaxation of the adlayer are taken into account. One of the goals of this contribution is to investigate the role played by the dissipation of the vibrational energy of the adatoms in the recombination kinetics. The theoretical sections of the paper are mainly devoted to the

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evaluation of the steady state HA surface densities and recombination rates in case of single reaction channels, as well as to study the effect of multi-quantum energy transfer on the HA surface coverage. Besides, throughout the article the application of the main results of the theory to experimental data on adsorption stimulated desorption (ASD) will be also presented and discussed.

2. Results and discussion

2.1. Hot atom energy distribution functions

In this paper we deal with diatom recombination at a flat catalytic surface according to the process $2A_\mathrm{s} \rightarrow A_2$, where A_s stands for the adspecies. In particular, on the basis of the aforementioned hypothesis adatoms populate the vibrational ladder of the 1D adsorption potential well, $V(z)$, z being the atom-surface distance along the normal to the surface. As far as the motion on the x–y plane is concerned, adatoms are free particles and the eigenvalue of the single particle Hamiltonian is given by $E_{p_x,p_y,v} = E_\mathrm{a} + E_v + \varepsilon_{p_x,p_y}$, where ε_{p_x,p_y} is the kinetic energy for the motion on the x–y plane, E_a the adsorption energy and E_v is the vibrational energy, with v the vibrational quantum number. As anticipated in the introduction, one refers to adatoms populating the excited vibrational level as ''hot''. By means of the associative model [14] recombination and desorption of diatoms arise from adatoms in vibrational states v and v' according to $A_\mathrm{s}(v) + A_\mathrm{s}(v') \rightarrow A_2$, provided the constraint $2E_\mathrm{a} + E_v + E_{v'} = E_{A_2} > 0$ is fulfilled. In this last inequality the kinetic energy term has been neglected when compared to the vibrational one. In other words, in the adsorption the atom momentum is conserved on the plane of the flat surface, the average value of the kinetic energy, $\langle \varepsilon_{p_x,p_y} \rangle$, is expected to be of the order of $k_\mathrm{B}T \ll -E_\mathrm{a}$, k_B being the Boltzmann constant and T the surface temperature. The rate of the single reaction channel is eventually given by $Z_{vv'}\sigma_v\sigma_{v'}$, where $Z_{vv'}$ is the rate constant and σ_v the surface coverage of adatoms in the v-th vibrational level. From this expression it stems that, to evaluate the reaction rate, the knowledge of the adatom vibrational populations is mandatory. To this end a rate equation approach is employed which accounts for the relevant processes that characterize the dynamics of the vibrational relaxation of the adlayer namely, the dissipation of vibrational quanta to the solid (VL process) and the exchange of vibrational quanta among the adatoms (VV process):

$$A_\mathrm{s}(n) + L \underset{K^{(q)}_{-(n-q)}}{\overset{K^{(q)}_{n}}{\rightleftarrows}} A_\mathrm{s}(n-q) + L^* \quad \text{(VL process)} \tag{1}$$

and

$$A_\mathrm{s}(n) + A_\mathrm{s}(m) \underset{P_{n-q,m+q \rightarrow n,m}}{\overset{P_{n,m \rightarrow n-q,m+q}}{\rightleftarrows}} A_\mathrm{s}(n-q) + A_\mathrm{s}(m+q) \quad \text{(VV process)} \tag{2}$$

where K and P are the first- and the second-order rate constants and the superscript q stands for the number of vibrational quanta exchanged in the scattering event. In Eq. (1) L and L^* stand for the substrate lattice and the excited lattice, respectively. Moreover, gas atoms enter the potential well from the upper bound level, $v^*(A \rightarrow A_\mathrm{s}(v^*))$ and the vibrational energy is redistributed throughout the ladder by means of VV and VL processes.

By denoting with $I_{n,m}$ the net current of adatoms from level n to level $m < n$, due to the VV and VL scatterings, the master equations for the populations of adatoms read (see also Fig. 1):

$$\frac{\mathrm{d}\sigma_n}{\mathrm{d}t} = J(\sigma)\delta_{n,v^*} + \sum_{q=1}^{v^*-n} I_{n+q,n} - \sum_{q=1}^{n} I_{n,n-q} - \Phi_n \tag{3}$$

where Φ_n is the flux of adatoms that recombine from level n, $J(\sigma)$ the flux of atoms entering the adsorption well, $\sigma = \sum_n \sigma_n$ and $\delta_{i,j}$ is the Kronecker delta. The expression of $I_{n,n-q}$ is given by

$$I_{n,n-q} = (K_n^{(q)} + P_n^{r(q)})\sigma_n - (K_{-(n-q)}^{(q)} + P_{(n-q)}^{f(q)})\sigma_{n-q} \tag{4}$$

in which

$$P_n^{f(q)} = \sum_{s=q}^{v^*} P_{n,s \rightarrow n+q,s-q}\sigma_s \tag{5}$$

and

$$P_n^{r(q)} = \sum_{s=0}^{v^*-q} P_{n,s \rightarrow n-q,s+q}\sigma_s \tag{6}$$

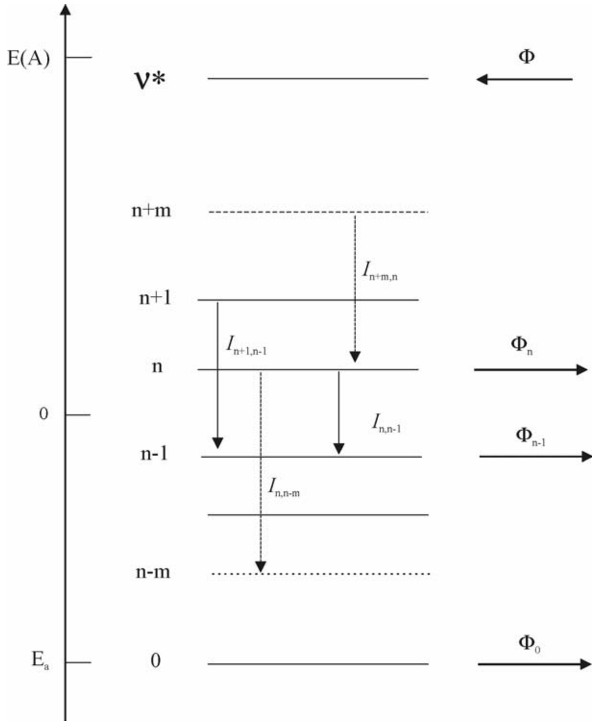

Fig. 1. Schematic representation of the vibrational ladder. Φ is the net flux of atoms incoming on the surface, Φ_n is the flux of adatoms leaving the n-th level because of the recombination process. The $I_{n,n-m}$ currents, between levels n and $n-m$, are linked to the VV and the VL quantum exchanges.