Effects of pressure, temperature and atomic exchanges on phase separation dynamics in Au/Ni(111) surface alloy: Kinetic Monte Carlo study

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**A B S T R A C T**

Instability of the Au/Ni(111) surface alloy is studied in different CO gas pressure, \(p\), and temperature limits using kinetic Monte Carlo simulations. We analyze the reaction front dynamics and formation of Au clusters using the model which takes into account surface adatom pair and three-body interactions, CO adsorption and desorption, catalytic carbonyl formation reaction, Au and Ni adatom diffusion and their concerted exchange. Variation of interaction parameters allows us to identify three possible reaction front propagation limits with different pressure dependencies: (i) slow channel-like flow in agreement with experimental data \([1]\) (step flow rate, \(R\), increases with \(p\)), (ii) intermediate regime (weak \(p\)-dependence), and (iii) fast homogeneous flow \((R\) decreases with \(p\)). We find that only Au–Ni exchange, contrary to both Ni–CO and Au–CO exchanges, significantly reduces the number of screened Ni atoms inside the Au clusters and stimulates the occurrence of Ni-free Au clusters. The size of Au islands depends on both pressure and temperature. At a fixed temperature it decreases with pressure due to an increased step flow rate. In the high temperature limit, despite the step flow rate exponential increase with temperature, the cluster size increases due to an enhanced Au mobility.

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1. Introduction

Incorporation of different adatoms into catalysts surface creates alloys with improved catalytic properties \([1–3]\). Modification of surface composition and structural evolution occurs in many candidate alloys under reactive or oxidizing conditions. The CO adsorption is a driving force for Pd preferential surface segregation on Au/Pd(111) \([4,5]\) and induces migration of Cu on top of Cu/ Pt(111) generating a stable CO/CuPt surface alloy \([6]\). The CO-induced surface segregation energies for gold-based alloys with transition metals (Ag, Cu, Pt, Pd, Ni, Ir, Rh, Co) are calculated by the density functional theory (DFT) \([7]\). An efficient segregation of Cu is demonstrated in Ag/Cu(100) alloy due to adsorption of O\(_2\) \([8]\). Experimental and DFT \([9–11]\) studies reveal surface segregation in Pt-transition metal (e.g. Co, Ni, Fe, Cr, Mn) surface alloys on Pt(111) under oxidizing conditions. In relation to segregation of bimetallic alloys, the concerted surface adatom exchange mechanism is

studied both experimentally and theoretically \([4,12–15]\). Thus, DFT calculations of Pd/Au(111) surface alloy \([4]\) show that the rate of Pd–Au concerted exchange over a surface (and subsurface) vacancy can be as high as 0.5 s\(^{-1}\), while in the absence of an associated vacancy it is many orders of magnitude lower.

Nickel-based alloys have been used in industry for catalytic steam reforming of hydrocarbon fuels. Ni surface alloying at sub-monolayer coverage with adatoms of a second metal, such as Au, Ag or Pt \([1,16,17]\), improves resistivity against carbon surface poisoning and prolongs lifetime of the catalyst \([18,19]\). However, stability of such catalysts has to be examined. Thus at high CO gas pressures bimetallic Au/Ni(111) catalyst becomes unstable \([10]\) due to surface Ni atom reaction with carbon monoxide resulting in de-alloying and deactivation of the catalyst. Segregation of Au–Ni alloy and formation of Au islands at high CO pressures is demonstrated in STM experiment \([1]\).

The rate-limiting step for carbonyl (Ni + 4CO → Ni(CO)\(_4\)) production is the Ni(CO)\(_2\) formation at step edges (kink sites) at high CO pressures with the rate \(10^{-2} \text{s}^{-1}\) \([20]\). DFT calculations \([1]\) demonstrate that activation energy of carbonyl formation is much lower for Au/Ni(111) surface alloy, and therefore the reaction rates...
in the direct vicinity of Au atoms are greatly enhanced in comparison with pure Ni sites.

Thermal annealing promotes Au redistribution on the catalyst surface [21]. Annealing at 200–225 °C initiates slight Au enrichment of Au–Ni surface alloy, but a complete precipitation of a pure Au phase does not occur until about 400 °C over sufficiently long annealing time (~1 h). Studying the instability of Au/Ni(111) alloy in Ref. [1], the alloy is annealed in a preparation stage for 10 min at 527 °C. Therefore, Au atom redistribution is expected which in turn can lead to the experimentally observed delay of the carbonyl formation reaction [22].

A detailed insight into energetics and kinetics of CO-induced Au and Ni phase separation in Au/Ni(111) surface alloy is provided by combined experimental and DFT [1] as well as kinetic Monte Carlo (KMC) [22,23] studies. The experimental study [1] shows nearly linear dependence of the step flow rate on CO pressure in the range from 7 to 53 mbar. However, in both KMC studies [22,23] the effect of CO pressure is investigated to a limited extent. The CO coverage is treated implicitly in Ref. [22] by assuming that the coverage is high and it forms a medium for adatom reaction and diffusion. While simulations in Ref. [23] are performed at a fixed CO pressure (1 Torr).

The KMC method is a standard tool for verifying the underlying microscopic models of complicated kinetic processes on solid surfaces [22–26]. In this work we extend our model [23] to study the CO pressure effect (in the range 0–5 Torr) on dynamics of Au–Ni phase separation in Au/Ni(111) surface alloy using KMC simulations [23–25]. We also analyze the hypothetical concerted particle exchange mechanism, as well as explore the temperature effect on phase separation dynamics. Moreover, the alloy annealing effect is discussed in detail.

The paper is organized as follows: we describe the mathematical model and simulation algorithm in Section 2. The KMC simulation results are presented in Section 3. In Section 3.1, we explore different pressure and interaction constant limits. The effect of alloy annealing on reaction delay in different pressure limits is studied in Section 3.2. In Section 3.3 the influence of concerted adatom exchange on step flow rate and Au island contamination by Ni adatoms is examined. The effect of temperature is studied in Section 3.4.

2. Mathematical model and simulation details

Three different types of particles are distinguished in the model: Au and Ni surface adatoms and adsorbed CO molecules are each assumed to occupy a single discrete site on a hexagonal lattice of size $L_a \times L_i$ (where lattice width, $L_a$, is given in the lattice constant units, $a_0 = 2.49 \text{Å}$ and length, $L_i$, is given in $(\sqrt{3}/2)a_0$ units) that mimics the Ni(111) surface. Periodic boundary conditions are implemented for both side boundaries of the lattice, while both top and bottom boundaries are left free. The initial Au–Ni alloy is prepared by randomly filling whole lattice with Au (30%) and Ni (70%) atoms except the top six rows of the lattice that resemble the alloy step. The as-prepared, random for each run, Au/Ni initial distribution is used in Section 3.1 simulations, while alloy annealing in Sections 3.2–3.4 is performed as a separate simulation.

In accordance with the experimental conditions [1], we consider the following steps.

(i) We allow for adsorption on an empty site and desorption of CO molecules, while we neglect their diffusion. We consider no CO adsorption on Au/Ni alloy. One can assume that CO effectively diffuses via desorption-adsorption step. Then adsorption rate of CO, see Table 1, is defined according to kinetic gas theory

$$k_a = p_s / \sqrt{2 \pi m k_B T / \rho_{ads}}$$

where $p$ is the pressure, $s_o = 1$ is the initial sticking coefficient, $m$ is the mass of CO molecule, $k_B$ is the Boltzmann constant, $T$ is the temperature, and $\rho_{ads}$ is the density of adsorption sites on the surface.

(ii) Desorption rate of CO, see Table 1, is defined by Arrhenius equation, $k_d = k_d^0 \exp(-E_d/k_b T)$, with a typical prefactor $k_d^0 = 10^{13} \text{s}^{-1}$ and activation energy $E_d = 1.2 \text{eV}$ [27].

(iii) Both Au and Ni adatoms are mobile. Their surface diffusion is implemented as adatom jumps to unoccupied nearest neighbor (NN) sites with equal rates, $k_{diff} = k_{diff}^0 \exp(-E_{diff}/k_b T)$, using activation energy $E_{diff} = 0.4 \text{eV}$ and frequency prefactor $k_{diff}^0 = 5.8 \times 10^{11} \text{s}^{-1}$ [23] giving $k_{diff}^0 = 10^5 \text{s}^{-1}$ at room temperature (RT), $T = 298 \text{K}$.

(iv) We consider either (a) Au–Ni (with rate $k_{Au-Ni}$), (b) Au–CO ($k_{Au-CO}$), or (c) Ni–CO ($k_{Ni-CO}$) exchange, or combination of exchanges (a) and (b), or (a) and (c), see Table 1. The activation energy for exchange is set identical to Au and Ni jump activation energy $E_{diff}$, leading to $k_x = k_{x}^0 \exp(-E_{diff}/k_b T)$, where $x$ is Au–Ni, Au–CO and Ni–CO, respectively, while the prefactor, $k_x^0$, is a variation parameter. In order to save the computational time, the exchange is allowed only in a part of the lattice. So, the exchange is not considered for those Au and Ni atom rows that form bulk alloy and the distance from the alloy row to the closest row that is empty or occupied by CO exceeds the effective length, $L_{eff}$, value. By the advance of the reaction front, the region with allowed exchange reaction is correspondingly updated.

(v) The nickel carbonyl, Ni(CO)$_4$, formation reaction is a multi-step process where the rate limiting step is either Ni(CO)$_2$ [20,28] or Ni(CO)$_3$ formation according to DFT calculations [1]. Moreover, it is shown in Refs. [1,27] that in the direct vicinity of Au adatoms the carbonyl formation is greatly enhanced. We mimic the reaction by assuming that Ni adatom can react with a single CO molecule in NN position with rate $k_i = k_i^0 \exp(-E_i/k_k T)$, if Ni adatom has at least one CO atom in NN position, see Table 1. Activation energy for the reaction, $E_i = 0.645 \text{eV}$, is selected on the basis of ab initio calculations in Ref. [1], while a prefactor, $k_i^0$, is a free parameter in the model. We considered the following values of prefactors, $k_i^0 = 2.4 \times 10^{10} \text{s}^{-1}$, $k_i^0 = 8.1 \times 10^{10} \text{s}^{-1}$, $k_i^0 = 4 \times 10^{12} \text{s}^{-1}$, and $k_i^0 = 6.4 \times 10^{14} \text{s}^{-1}$ corresponding to reaction rates $k_i = 0.3, k_i = 1$, and $k_i = 50 \text{s}^{-1}$ at RT, and $k_i = 50 \text{s}^{-1}$ at $T = 248 \text{K}$, respectively. In this way an empty site (where CO can adsorb) is required for reaction condition to occur. Further, if reaction takes place, we remove both the corresponding CO molecule and Ni adatom, implying that the

<table>
<thead>
<tr>
<th>Step</th>
<th>Reaction</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) Adsorption</td>
<td>CO(gas) + □ → CO</td>
<td>$k_a$</td>
</tr>
<tr>
<td>(ii) Desorption</td>
<td>CO → □ + CO(gas)</td>
<td>$k_d$</td>
</tr>
<tr>
<td>(iii) Hopping</td>
<td>Ni + □ → □ + Ni</td>
<td>$k_{diff}$</td>
</tr>
<tr>
<td>(iv) Adatom exchange</td>
<td>Au + Ni → Ni + Au</td>
<td>$k_{Au-Ni}$</td>
</tr>
<tr>
<td>(v) Reaction</td>
<td>Ni$_{ads}$ + CO → □ + □</td>
<td>$k_x$</td>
</tr>
</tbody>
</table>

Table 1 List of steps in the KMC model. Here □ denotes an empty surface site. Note that rates of adsorption, desorption, exchange, and hopping are further modified by local interactions [23].
KMC simulations are performed using standard model kinetics and pair algorithm approach [23–25]. The standard model kinetics alters the rates of the Au and Ni hopping and exchange, as well as CO adsorption and desorption, due to adatom interactions. The attractive pair \( V_{\text{Au-Au}} = -0.15 \text{ eV} \), \( V_{\text{Ni-Ni}} = -0.4 \text{ eV} \), and \( V_{\text{Au-Ni}} = -0.30 \text{ eV} \) and three-body (trio) interaction energies are taken from the DFT calculations [23,29]. The trio interactions are attractive for the linear adatom configurations and repulsive for the triangular ones, denoted as \( V_{\text{b-L}} \) and \( V_{\text{b-T}} \), respectively, see Table 2.

We further group triangular, \( V_{\text{b-T}} \); repulsive interactions leading to two unique values: \( V_{\text{h}} \) (‘homogeneous’) for both \( \delta = \text{Au–Au–Au} \) and \( \text{Ni–Ni–Ni} \) and \( V_{\text{i}} \) (‘inhomogeneous’) for \( \delta = \text{Au–Au–Ni}, \text{Au–Ni–Au}, \text{Ni–Au–Ni} \). Triplet interaction energies \( V_{\text{g}}, V_{\text{h}}, V_{\text{i}} \) are varied within the DFT accuracy limits [23,29] given in Table 2. Firstly, this assesses the sensitivity of the step flow dynamics on interaction energy values. And, secondly, it identifies particular trio interactions that lead the simulated system to resemble such key properties of experiment [1] as SFR increase with pressure, reaction delay, and Ni-free islands.

Estimates for the NN CO–CO and Au–CO interactions, \( V_{\text{CO-CO}} = 0.3 \text{ eV} \) are obtained self-consistently in a separate KMC simulation [23] which reproduces experimental CO saturation coverage on Au/Ni(111) surface alloy at different Au concentrations [27].

3. Simulation results

In order to analyze the simulation results, let us introduce the flow distance, \( d \), that the flow covers between time, \( t \), and initial simulation time, \( t_0 = 0 \). Then, the position of the Ni step edge at time, \( t \), can be expressed as

\[
d(t) = L'_t (c_{\text{Ni}}(t_0) - c_{\text{Ni}}(t)) / c_{\text{Ni}}(t_0),
\]

where \( c_{\text{Ni}}(t_0) = 0.7 \) is the initial Ni concentration, \( c_{\text{Ni}}(t) \) is the Ni concentration at time \( t \), and \( L'_t \) is the lattice length (in the units of \( a_0 \sqrt{3}/2 \)) occupied by the alloy at \( t_0 \). Note that \( L'_t \) is smaller than the total length of the modeled lattice, \( L_t \), due to empty rows at the top of the lattice. The step flow rate (SFR) is obtained as

\[
R(t) = \Delta d(t)/\Delta t.
\]

by averaging over up to 10 identically repeated simulations. The mean SFR, \( \langle R \rangle \), is defined as \( \langle R \rangle = \lim_{t \to \infty} R(t) \).

We allow the CO adsorption on the Ni surface and neglect the CO adsorption on top of Au/Ni alloy. Therefore, the area of alloy-free surface increases in the course of simulation and we define the rescaled concentration of CO on Ni surface by excluding all sites occupied by Au and Ni atoms as follows:

\[
c_r(t) = c_{\text{CO}}(t)/(1 - c_{\text{Au}}(t) - c_{\text{Ni}}(t)).
\]

3.1. CO pressure dependence

Variation of trio interactions \( V_{\text{g}} \) and \( V_{\text{i}} \) within the accuracy limits of DFT calculations [23] have a significant impact on Au–Ni phase separation and Au cluster growth process. Thus, at a fixed pressure, \( p = 1 \text{ Torr} \), we have identified [23] three regimes of the SFR dynamics: (i) fast mode accompanied by formation of Ni-free Au clusters (homogeneous regime); (ii) intermediate regime; and (iii) slow mode (channel-like regime).

Here we study the SFR dependence on CO pressure in all three regimes at RT. In order to avoid periodic boundary effect we ensure that clusters of adatoms are much smaller than the lattice width, \( L_w = 90 \). The length of the lattice, \( L_t = 600 \), is selected by condition that the reaction front does not reach the bottom line of the lattice during simulation time. In this section we use the model with all steps of Table 1 except for adatom exchange, and random Au–Ni distribution in alloy.

We fix the linear trio interactions \( V_{\text{b-L}} = -0.12 \text{ eV} \) \( \delta = \text{Au–Au–Au} \), \( V_{\text{b-T}} = -0.10 \text{ eV} \) \( \delta = \text{Au–Au–Ni}, \text{Ni–Au–Ni} \), reaction rate prefactors \( k_{\text{Ni}}^{g} \) for the homogeneous and \( k_{\text{Ni}}^{i} \) for the intermediate and channel-like regimes and explore the SFR dependence on CO pressure in a phase space of triangular interaction energies \( V_{\text{h}}-V_{\text{i}} \), see Fig. 1. The results show three qualitatively different \( p \)-dependencies that are in agreement with different SFR propagation regimes: (i) SFR is inversely proportional to pressure in homogeneous regime, (ii) SFR is independent of...
pressure in intermediate regime, and (iii) SFR increases with pressure in channel-like regime. The SFR pressure dependence is thus a unique quantitative characteristics of each flow regime.

In the homogeneous regime-(i), Au–Ni cohesion is reduced due to stronger repulsive trio interactions $V_h$ and $V_i$ which enables creation of vacancies in a wide continuous zone of Au–Ni alloy along the step edge. The Au–Ni phase segregation is driven by enhanced diffusion of adatoms and adsorption of CO molecules in this vacancy-rich zone. The step edge moves nearly uniformly across entire width of the sample, leaving behind Au islands with a few Ni inclusions, Fig. 2(a). In this regime, contrary to experiment [1], the SFR decreases with CO pressure (see Fig. 2(d)), since the number of the NN Au–Ni pairs is reduced due to faster segregation.

The characteristic feature of the channel-like SFR regime-(iii) is accumulation of Au adatoms on the step edge that strongly inhibits the Ni–CO reaction. The reaction proceeds only in narrow channels between growing Au adatom clusters, and the step edge gains a sinuous, channel-like appearance (Fig. 2(c)), in agreement with experimental results [1]. The carbonyl reaction occurs predominantly at the step edge, since weak triangular repulsion energy (strong adatom cohesion) prevents penetration of vacancies inside the alloy, which in turn are required for CO adsorption and further reaction. Just formed Au clusters are highly contaminated by Ni, particularly at low pressures ($p < 1$ Torr). Later, part of these Ni atoms move to cluster boundary, where they react with CO, while a considerable amount of Ni atoms still remain screened. Although absolute values of the SFR are low, they increase with CO pressure, Fig. 2(f).

The intermediate SFR regime-(ii), Fig. 1, is characterized by the channel-like step flow with Au clusters formed on the step edge, Fig. 2(b), similarly to the regime-(iii). However, SFR values are approximately twice higher for identical reaction rate values than in the regime-(iii). The SFR pressure dependence, Fig. 2(e), is undetectable within the calculation accuracy. This implies that the weakening of SFR pressure dependence occurs in the intermediate regime-(ii) due to fast Au–Ni segregation, similarly to the homogeneous flow regime-(i).

The channel-like regime-(iii) most closely resembles the experimental results [1] regarding the SFR pressure dependence, as well as shape of the propagating step. Moreover, the trio interaction energies of regime-(iii) agree well with the average trio values given by DFT calculations [23]. The amount of screened Ni atoms left within Au clusters in this regime contradicts the experimental findings [1].

3.2. Alloy annealing

For further studies we prepare the Au–Ni alloy differently. Following the experiment [1], instead of a random distribution of Au and Ni adatoms, we perform thermal annealing of the alloy as a separate KMC simulation. Starting from a random Au adatom distribution in a Ni matrix, we allow for an Au–Ni adatom simultaneous (concerted) exchange with jump rate prefactor $k_{Au-Ni} = 3.3 \times 10^8$ s$^{-1}$ at $T = 800$ K for approximately $10^{-2}$ s, i.e. sufficient to reach an equilibrium Au–Ni spatial distribution. Since the exchange probability depends on all pair and trio interaction energies

**Fig. 2.** Lattice fragments (90 × 140) at different pressures for (a) homogeneous regime at $t = 220$ s, $V_h = 0.22$ eV, $V_i = 0.25$ eV, $k_{0}$, (b) intermediate regime at $t = 250$ s, $V_h = 0.14$ eV, $V_i = 0.20$ eV, $k_{0}$, and (c) channel-like regime at $t = 600$ s, $V_h = 0.14$ eV, $V_i = 0.18$ eV, $k_{0}$, Au atoms are yellow, Ni – red and CO molecules – green. The corresponding $R(t)$ dependencies at pressures $p = 0.5$ (blue filled diamonds), $1$ (red open squares) and $5$ Torr (black filled circles) are shown in (d), (e) and (f), respectively, and <R> values are indicated by horizontal dashed lines. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
between Au and Ni adatoms, the annealing can be viewed as a method to verify that the Au–Ni interaction values (especially the trio interactions \(V_V\) and \(V_{i}\)) are chosen appropriately: they should promote strong mixing tendency of Au and Ni adatoms without creation of Au clusters within the alloy, while still ensure the Au adatom segregation on alloy steps \([22]\). KMC simulation of alloy annealing (using \(V_V = 0.14\ eV, V_i = 0.17\ eV\) and \(V_{i+} = -0.08\ eV\) for both mixed linear trio interactions \(\delta = \text{Au–Au–Ni, Ni–Au–Ni} \) (see Table 2) demonstrates that the aggregation of large Au clusters is suppressed inside the alloy, and Au concentration on the step edge (first row of the alloy) increases to 0.83 for \(V_{\text{Au–Au–Au–L}} = -0.10\ eV\) and even to 0.88 for \(V_{\text{Au–Au–Au–L}} = -0.12\ eV\) contrary to 0.3 for random Au distribution.

Further we study the alloy annealing effect on the experimentally observed reaction delay \([1]\) caused by increased Au coverage at the step edge. We use \(V_{\text{Au–Au–Au–L}} = -0.10\ eV\), reaction rate prefactor \(k_{R}^{\text{eff}}\) and perform the simulations at RT by neglecting the adatom exchange. To quantify the reaction delay, we define the delay time, \(\tau_{\text{del}}\), as the time which is needed for the reaction front to travel a distance \(d_{R} (= 20, 40\) or \(60\) Å\) from the initial position at the start of the CO exposure. Since delay time is strongly fluctuating, a mean value is calculated as an average over 10 independent simulations at each pressure, Fig. 3. To distinguish the alloy annealing effect on the delay time, we prepare annealed, as well as random, initial alloy configurations. In a high pressure limit, \(p > 0.5\) Torr, the delay times of random and annealed configurations coincide and are of the order of a few seconds. However, in a low pressure limit, e.g., at \(p = 0.01\) Torr, the delay of an annealed alloy is a few times longer than that of a random Au/Ni(111) alloy. The main reason leading to this effect is a gold rim at the reaction front, caused by a phase separation, which makes the SFR close to zero at initial stages. Qualitatively, the pressure dependence of a delay time is independent of the particular threshold value \(d_{R}\), see Fig. 3.

### 3.3. Concerted adatom exchange

The channel-like flow regime is characterized by Au clusters rather strongly contaminated by Ni atoms. In order to explain the absence of Ni contamination in experiment \([1]\), we propose to complement the model by the concerted adatom exchange step (iv), see Table 1, that might occur in a real systems via, e.g., vacancy mechanism. We distinguish direct concerted exchange within a pair of NN surface particles (Au–Ni, Au–CO and Ni–CO).

In further KMC simulation we use thermally annealed alloy with \(L_w = 100\), since we verified that an increase of the width to \(L_w = 200\) has a minor effect on the SFR results. The lattice length is increased to \(L_l = 7000\) in order to follow the SFR kinetics for a longer time. We also find that the SFR depends on the exchange length parameter, \(L_{\text{eff}}\). SFR decreases with an increase of \(L_{\text{eff}}\) due to formation of Au islands, which occurs as a result of Au–Ni exchange inside the alloy. However, in order to take the exchange effect into account and perform the simulations in a reasonable time, we set \(L_{\text{eff}} = 50\).

We perform the KMC simulations in the channel-like regime (iii) at RT using trio interactions identical to Section 3.2 \((V_V = 0.14\ eV, \ V_{i} = 0.17\ eV, V_{i+} = -0.08\ eV\) for \(\delta = \text{Au–Au–Ni, Ni–Au–Ni, and V}_{\text{Au–Au–Au–L}} = -0.10\ eV\) (see Table 2). Since the SFR in this regime is rather low, we use the reaction rate prefactor \(k_{R}^{\text{eff}}\) that allows us to increase the speed of computer simulations.

The particular values of the exchange rate prefactors are set phenomenologically. With require, on one hand, that the exchange has no effect on SFR pressure dependence, as well as the channel-like regime that resembles experimental findings \([1]\). On the other hand, the adatom exchange should effectively lead to Ni-free Au clusters.

We find that Au–CO concerted exchange rate prefactor could be set as high as Au hopping rate prefactor \(k_{R}^{\text{CO}} = 5.8 \cdot 10^{14} \text{ s}^{-1}\). The exchange facilitates the penetration of the CO molecules into the alloy, stimulates the reaction and increases the average SFR, see Fig. 4(a). The amount of screened Ni adatoms in the absence of exchange, see Fig. 4(b), is reduced by Au–CO exchange, however, clusters still contain a considerable amount of Ni adatoms, Fig. 4(c).

The Ni–CO exchange rate prefactor has to be decreased to \(k_{\text{Ni–CO}} = 5.8 \cdot 10^{8} \text{ s}^{-1}\), to prevent the creation of CO islands inside the alloy, since Ni concentration (70%) is larger than that of Au. Similarly to effect of Au–CO exchange, the average SFR increases, Fig. 4(a), but the clusters are still contaminated by Ni adatoms, Fig. 4(d).

The Au–Ni exchange rate prefactor should be limited to \(k_{\text{Au–Ni}} = 5.8 \cdot 10^{6} \text{ s}^{-1}\), to prevent the segregation of Au atoms into clusters inside the alloy far from the reaction front. The Au–Ni exchange step has a minor effect on the average SFR both when considered independently and in combination with Au–CO or Ni–CO exchange steps, Fig. 4(a). Despite the smallest prefactor value, the Au–Ni exchange step leads to the Ni-free Au clusters, Fig. 4(e–g), similarly to experiment \([1]\) and demonstrates the decrease of Au island size with CO pressure.

KMC simulations demonstrate that the SFR is proportional to the reaction rate prefactor at a given pressure, see curves 5 and 7 (with Au–Ni exchange), and 6 and 8 (no exchanges) of Fig. 4(a), respectively, that differ by reaction rate prefactor ratio \(k_{R}^{\text{CO}}/k_{R}^{\text{Ni–CO}} = 50\). In turn this implies that the experimental SFR values \([1]\) could be reached by decreasing the reaction rate prefactor,\( k_{R}^{\text{Ni–CO}}\), further by one order. In a low \(p\) limit when the surface CO molecules interact weakly, the CO surface concentration increases linearly with pressure. For higher CO pressures, the increase of CO concentration is hindered due to an increasing NN CO–CO repulsion. As a result, the increase of SFR with pressure becomes slower but it still demonstrates the linear pressure dependence. These estimates agree well with the experimentally found linear SFR pressure dependence \([1]\).

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**Fig. 3.** Dependence of step flow delay time, \(\tau_{\text{del}}\), on CO pressure for annealed alloy (filled symbols) and random Au distribution (open symbols) for arbitrary threshold distance \(d_{R} = 20\) Å (blue diamonds), 40 Å (yellow squares) and 60 Å (black circles). Here \(L_w = 100\) and lines are guides for the eye. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
3.4. Temperature dependence

The developed model allows us to study the SFR and characteristic Au cluster size dependence on temperature. We consider a constant pressure \( p = 0.5 \text{ Torr} \) limit and perform simulations in channel-like regime-(iii) for annealed system using trio interactions identic to Section 3.2 (\( V_h = 0.14 \text{ eV}, V_i = 0.17 \text{ eV}, V_d = 0.08 \text{ eV} \) for \( d = \text{Au} - \text{Ni} \), \( \text{Ni} - \text{Au} \) and \( \text{Au} - \text{Au} - \text{Au} - \text{L} = 0.10 \text{ eV} \) (see Table 2). We include the Au–Ni exchange step (\( k_{\text{Au-Ni}} = 5.8 \times 10^6 \text{ Å/s} \)) to obtain the Ni-free Au clusters and use the reaction rate prefactor \( k_{\text{r3}} \) unless stated otherwise.

In the simulated temperature interval \( T = 248 – 328 \text{ K} \) the average SFR increases with temperature almost exponentially, Fig. 5(d), and can be fitted by an exponent \( \langle R \rangle \sim R_0 \exp(-E_R/k_BT) \), where \( R_0 = 8 \times 10^6 \text{ Å/s} \) and \( E_R = 0.33 \text{ eV} \). It follows that the dominant contribution in an increase of the SFR arises from the exponential temperature dependence of both hopping and reaction rates. In turn, the reduction of rescaled CO concentration, \( c_r \), (Eq. (3)) with temperature, see Fig. 5(d), plays a minor role, though the number of CO molecules that are available for reaction on the Ni surface decreases.

The Au cluster size and distance between clusters increase with temperature, Fig. 5(a,b). It can be estimated using a well-known formula, \( l = (k_{\text{diff}}/\zeta)^{1/4} \), relating distance, \( l \), between clusters and the ratio of diffusion and deposition, \( \zeta \), rates in case of adsorption and diffusion of a single sort of particles. Here exponent \( z = 1/4 \) might come from scaling considerations for two-dimensional case. Assuming that diffusion of Au is described by hopping rate, \( k_{\text{diff}} \), we estimate the “release rate” of Au atoms that is interpreted as a

![Figure 4](image1.png)

**Fig. 4.** (a) Average SFR dependence on CO pressure for concerted adatom exchanges at reaction rate prefactor \( k_{\text{r3}} \): (1) \( \text{Ni} - \text{CO} \) and \( \text{Au} - \text{Ni} \), (2) \( \text{Ni} - \text{CO} \), (3) \( \text{Au} - \text{CO} \) and \( \text{Au} - \text{Ni} \), (4) \( \text{Au} - \text{CO} \), (5) \( \text{Au} - \text{Ni} \), (6) no exchanges; and reaction rate prefactor \( k_{\text{r2}} \): (7) \( \text{Au} - \text{Ni} \) and (8) no exchanges. Lattice fragments (100 × 100) at \( t = 80 \text{ s} \) for the following exchange models and pressures: (b) in the absence of exchange (curve 6), \( p = 1 \text{ Torr} \), (c) \( \text{Au} - \text{CO} \) (curve 4), 1 Torr, (d) \( \text{Ni} - \text{CO} \) (curve 2), 1 Torr, (e) \( \text{Au} - \text{Ni} \) (curve 5), 0.08 Torr, (f) \( \text{Au} - \text{Ni} \) (curve 5), 1 Torr, and (g) \( \text{Au} - \text{Ni} \) (curve 5), 2 Torr.

![Figure 5](image2.png)

**Fig. 5.** Lattice fragments (100 × 100) of Au islands formed behind the reaction front at:
(a) \( T = 248 \text{ K}, k_{\text{r3}}, t = 1690 \text{ s} \), (b) \( T = 328 \text{ K}, k_{\text{r3}}, t = 40 \text{ s} \), (c) \( T = 248 \text{ K}, k_{\text{r4}}, t = 55 \text{ s} \). (d) Average SFR (solid line with filled circles) and rescaled CO concentration (dashed line with open squares) dependence on temperature. The snapshots (a) and (b) correspond to limiting temperatures \( T = 248 \text{ K} \) and 328 K, respectively.
deposition rate. The process of Au release from bulk alloy involves CO adsorption, Ni hopping, Ni + CO reaction/desorption and subsequent release of Au atoms for aggregation, i.e., it has a strong temperature dependence. To demonstrate this effect, let us first compare the cluster sizes at two temperatures, \( T_2 = 328 \text{ K} \) (Fig. 5(b)) and \( T_1 = 248 \text{ K} \) (Fig. 5(a)). We obtain the ratio \( l_2/l_1 = 1.5 \) which indicates that the Au release rate at 328 K is approximately 15 times higher than at 248 K.

Next we eliminate the temperature effect by estimating the Au release rate at a fixed temperature \( T = 248 \text{ K} \) and increasing the reaction rate prefactor to \( k_{fi}^2 = 160k_{fi}^1 \), Fig. 5(c). We find that the average distance between Au clusters is reduced twice, \( l_2/l_1 = 0.5 \), indicating that Au release becomes 16 times faster. Faster Au release allows for nucleation of Au clusters at shorter distances at a fixed temperature. Finally, since in both cases Au release increases approximately 15 times, but the distance between clusters increased 1.5 times with temperature effects included and decreased twice at a fixed temperature, we conclude that the temperature effects (hopping rate, adsorption/desorption, and reaction rate) in the considered example are responsible for a threefold increase of average distance between clusters.

4. Conclusions

We perform a KMC study of phase separation dynamics in Au/Ni(111) surface alloy and analyze its response to variation of CO pressure. We find three regimes of reaction front propagation denoted as the channel-like (slow), homogeneous (fast) and intermediate. The simulation results demonstrate that only the channel-like reaction front propagation exhibits a reaction delay and the step flow rate increase with CO pressure, in accordance with experiment [1].

The KMC model is extended to include three types of concerted particle exchange (Au–Ni, Au–CO, and Ni–CO). A weak Au–Ni exchange is found to be sufficient to effectively reduce the amount of screened Ni atoms within the Au clusters left behind the reaction front leading to an agreement with experimental results [1]. The average distance between clusters decreases with increase of pressure and/or reaction rate prefactor at a fixed temperature, while it increases due to strong temperature effects. The delay time until the onset of Ni–CO reaction was found to increase at low CO pressures while becoming negligible at high pressures.

We further employ the model with Au–Ni exchange as the closest to experiment to estimate the temperature dependence of the step flow rate. We find that the step flow rate increases exponentially with temperature with the activation energy of 0.33 eV. The main factors governing the step flow rate behavior are temperature-dependent diffusion and reaction rates.

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References