Nucleation of Pt Monolayers Deposited via Surface Limited Redox Replacement Reaction

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The ultimate configuration of ultra-thin catalyst overlayers in terms of their specific activity is two-dimensional (2D) monolayer (ML) morphology where every catalyst atom is on the surface. Most heterogeneous catalysts contain noble metals such as Pt. Due to their high surface energy and low surface diffusivity they are difficult to deposit as 2D ML at room temperature. One way to alleviate this problem has been demonstrated recently using new electrodeposition protocol. It uses an underpotentially deposited (UPD) monolayer serving as a sacrificial material for deposition of a more noble metal (catalyst). The deposition of catalyst ML occurs as an irreversible surface limited redox replacement (SLRR) reaction, i.e. galvanic displacement of the UPD ML. The deposited catalyst ML has morphology characterized by 2D nanoclusters with very tight size distribution. The coverage of catalyst nanoclusters is controlled by stoichiometry of the redox replacement reaction, structure and coverage of the UPD ML. Despite many uses of this deposition protocol for synthesis of mono- and bi-metallic catalysts ML for fuel cell applications, a few works have been done exploring conditions controlling their morphology, i.e. the size of catalyst nanoclusters.

Behavior of 2D catalyst ML differs from the bulk due to diverse structural and quantum effects dominating their properties. In the case of weak ligand (substrate electronic effects) such as gold, the energy of the d-band center of a continuous catalyst ML is mainly dependent on epitaxial relation between the catalyst and substrate. However, in the case of 2D nanoclusters, the surface stress acting on the nanocluster perimeter induces a compressive state of stress within the nanoclusters. This phenomenon, so called “2D finite size effect,” causes each nanocluster to experience a size-dependent active strain quite different from the one set by epitaxy. For Pt catalyst nanoclusters obtained by SLRR of Cu UPD ML, recent study shows that size-dependent strain has significant effect on their catalytic activity. Pt monolayer on Au(111) consisting of smaller nanoclusters were found less active for hydrogen oxidation reaction. Density functional theory (DFT) calculations concur with this observation. They suggest that size-dependent strain in Pt nanoclusters has important effect on the energy of d-band center and, therefore, on activity of Pt nanoclusters. Obviously, the size of nanoclusters in catalyst ML represents the additional knob to fine-tune its overall activity. Turning this knob in desired direction requires better understanding of the phenomena controlling the catalyst ML morphology and nanocluster size. A step toward this goal is to study nucleation of catalyst ML obtained via SLRR reaction and elucidate dominant processes involved.

The study of Pt nucleation on Au(111) deposited via surface limited redox replacement of underpotentially deposited Cu monolayer is presented. Series of Pt deposition experiments were performed where starting coverage of an underpotentially deposited Cu monolayer varied from 0 to 1. Exsitu Scanning Tunneling Microscopy and statistical image processing are used to characterize the morphology of deposited Pt monolayers. The Pt nucleation density and the average size (area) of Pt nanoclusters is used as the main descriptors of Pt monolayer morphology. Results are discussed within the framework of analytical model developed to describe qualitatively our data. The relevance of our work for design of Pt monolayer catalyst is illustrated studying the CO electrosorption on Pt monolayers with different nucleation densities and average size of Pt nanoclusters.

Experimental

The Au(111) single crystal disk, 10 mm in diameter and 2 mm in thickness (Monocrystals Company) is prepared using several steps including mechanical polishing, electropolishing and hydrogen flame annealing. Special attention is paid to avoid thermal reconstruction of Au(111) and consequent appearance of Au clusters on the surface upon immersion into electrolyte. Typical morphology of starting Au(111) surface before UPD experiments is shown in Figure 1A. All solutions used in our experiments are made from ultra high purity chemicals (99.999%, Alfa Easer, Merck) and 18.2 MΩ ultrapure water (Millipore Direct Q-UV with Barnstead A1007 pre-distillation unit). All potentials in the text related to the UPD experiments are referred as the value of underpotential (ΔE). The potentials in IR experiments are quoted with respect to saturated calomel electrode (SCE). The Pt monolayers on Au(111) (PML/Au(111) - in further text) are deposited via SLRR of Cu(ClO4)2 salt. The Cu(ClO4)2/Au(111) in further text) varied from 0 to 1 (0 ≤ θCu ≤ 1). Exsitu Scanning Tunneling Microscopy (STM) and statistical image processing are used to study morphology of obtained Pt MLs on Au(111). The main descriptors of Pt ML morphology are the Pt nucleation density and the average size (area) of Pt nanoclusters. Results are discussed within the framework of analytical model developed to describe qualitatively our data. The relevance of this work for design of Pt ML catalysts is illustrated by studying the CO electrosorption on Pt MLs with different nucleation densities and average size of Pt nanoclusters.

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form an incomplete CuUPD/Au(111) with coverage, θCu, (position 3 in Figure 1B). In following step, the potential is stepped back again to 0.4 V ΔE (position 4 in Figure 1B) and held to record the stripping charge of an incomplete CuUPD/Au(111), qCu exp. Then, the potential is stepped back to the same value of ΔE where an incomplete CuUPD/Au(111) was formed in preceding step. It was held for 30 seconds in order to form the CuUPD/Au(111) with now ‘known’ initial coverage θo,Cu. This coverage represents the fraction of the maximum one possible for CuUPD/Au(111) and it is estimated as the ratio between the stripping charge of an incomplete CuUPD/Au(111) formed at an arbitrary underpotential, qCu exp., and the charge of the full CuUPD/Au(111) formed at 0.03 V underpotential, qCu max.

$$\theta_{o,Cu} = \frac{q_{Cu exp.}}{q_{Cu max.}}$$  \[1\]

The SLRR solution was 10^{-3} M \{PtCl_6\}^{2-} + 0.1 M HClO_4, (K_{2}(PtCl_6) salt). Both, UPD and SLRR reaction solution were de-aerated with ultra-pure argon for 2 hours before deposition experiments. The Au crystal is rotated at 1000 rpm in order to prevent any transport limitations during formation of CuUPD/Au(111) and PtML/Au(111).

Previous studies of this UPD system and SLRR reaction under identical experimental conditions have determined the value of stoichiometry coefficients and parameters of the SLRR reaction kinetics.\(^4\) They are summarized in Table I, eq. 2.

$$Cu_{up}^{0} + \frac{1}{4}[PtCl_6]^{2-} + \frac{1}{2} Cl^- = [CuCl_2]^- + \frac{1}{4} Pt_1^{0}$$  \[2\]

In each experiment, the procedure for Pt deposition involves several steps. First, the CuUPD/Au(111) is formed at certain underpotential with desired coverage as described previously. Then, the crystal is removed from the solution under potential control and rinsed in 18.2 MΩ H_2O for 10 seconds at open circuit potential (OCP). The next step was the SLRR of CuUPD/Au(111) by \{PtCl_6\}^{2-} ions at OCP (10 seconds). The final step involves crystal rinse in 1:1 HNO_3 (10 sec., OCP) and rinse in 18.2 MΩ H_2O (60 sec., OCP). Upon completion of this sequence, the crystal surface has undergone characterized by STM, and/or is transferred to electrochemical cell for IR studies.

All electrochemical experiments, including the \(ex situ\) STM studies, are performed in nitrogen-purged glove box. The STM images are recorded using Nanoscope V controller with multimode scanner unit (Veeco Instruments). After each deposition experiment, up to 50 STM images are recorded at different terrace sites of the Au(111) and analyzed using our custom made digital image processing algorithm.\(^2\) This analysis provided information about Pt nucleation density (number of Pt nanoclusters per image (area), average size of Pt nanoclusters in ML (total area of Pt ML divided by the number of Pt nanoclusters), Pt coverage and the Pt clusters’ height. The image segmentation is used for differentiation and identification of each Pt nanocluster on the image/surface. For this purpose, a threshold value has been determined to segment each image into a binary image using an autonomous global thresholding method.\(^2\) The error bar for image analysis results represents the standard deviation of the data obtained from analysis of all images used for the particular experimental point (deposition experiment).

The cell for \(in situ\) IR spectro-electrochemical measurements, described previously,\(^4\) consisted of a ZnSe hemisphere serving as the ATR window and cell bottom, and a Teflon body. A Nicolet 6700 spectrometer and a BAS CV27 potentiostat are used to conduct our experiments. The collection of the spectra is computer controlled at given potential of the working electrode set prior to data acquisition. The 128 scans with 4 cm\(^{-1}\) resolution are co-added in a single step. Spectra are given as -ΔR/R using the spectrum at the highest potential as the reference one where no CO adsorption is expected. The positive-going bands therefore represent a gain of a particular species at the sample potential relative to that at the reference potential.

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Table I. The reaction kinetics parameters.

<table>
<thead>
<tr>
<th>UPD System</th>
<th>Redox Reaction</th>
<th>Reaction Solution (SLRR), ω = 1000 rpm</th>
<th>Rate Constant, K_SLRR, [s^{-1}]</th>
<th>Reaction Order, (q_{o,Cu}^{m/p})</th>
<th>Stoichiometry Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuUPD/Au(111)</td>
<td>(Cu_{up}^{0} + \frac{1}{4}[PtCl_6]^{2-} + \frac{1}{2} Cl^- = [CuCl_2]^- + \frac{1}{4} Pt_1^{0})</td>
<td>10^{-3} M {PtCl_6}^{2-} + 0.1 M H_2SO_4</td>
<td>4.08 ± 0.07</td>
<td>2^4</td>
<td>(m/p) 0.5</td>
</tr>
<tr>
<td>CuUPD/Au(111)</td>
<td>(Cu_{up}^{0} + \frac{1}{4}[PtCl_6]^{2-} + \frac{1}{2} Cl^- = [CuCl_2]^- + \frac{1}{4} Pt_1^{0})</td>
<td>10^{-3} M {PtCl_6}^{2-} + 0.1 M HClO_4</td>
<td>3.61 ± 0.03</td>
<td>2^6, 4^4</td>
<td>1 4 0.25</td>
</tr>
<tr>
<td>CuUPD/Au(111)</td>
<td>(Cu_{up}^{0} + \frac{1}{4}[PtCl_6]^{2-} + \frac{1}{2} Cl^- = [CuCl_2]^- + \frac{1}{4} Pt_1^{0})</td>
<td>10^{-3} M {PtCl_6}^{2-} + 0.1 M HClO_4</td>
<td>0.089 ± 0.0008</td>
<td>2^6, 4^4</td>
<td>1 4 0.25</td>
</tr>
</tbody>
</table>

\(^4\) Reaction order is taken based on the value of stoichiometry coefficients.

\(^6\) Reaction order determined from the fits of the reaction kinetics model to the open circuit transients obtained during SLRR reaction.
Pt nucleation density and average cluster size.—The statistical STM image analysis from nine different PtML/Au(111) obtained via SLRR of CuUPD/Au(111) with different coverage revealed that >97% of nanoclusters in PtML/Au(111) are monoatomic in height. More than 90% of nanoclusters in each PtML/Au(111) were found compact and round having shape resembling a 2D disk-like nanostructures. For each PtML/Au(111), the STM image analysis yielded the Pt nucleation density and average size of Pt nanoclusters as two representative parameters of the PtML/Au(111) morphology. They are presented in Figure 2A and 2B as a function of starting CuUPD/Au(111) coverage in SLRR reaction, \( \theta_{o,Cu} \). The Pt nucleation density measured in our experiments, \( n_{SPt}^{exp} \), shows significant dependence on \( \theta_{o,Cu} \). The relation between \( n_{SPt}^{exp} \) and \( \theta_{o,Cu} \) is a monotone function. It resembles a bell-shape dependence having the highest nucleation density of Pt for coverage of CuUPD/Au(111) equal to 0.63 (\( \theta_{o,Cu} \approx 0.63 \)). The importance to notice is that even for \( \theta_{o,Cu} \approx 0 \), there is a finite amount of Pt nanoclusters on Au(111) surface. These Pt nanoclusters are formed as result of spontaneous Pt deposition process independent on Pt deposition via SLRR of CuUPD/Au(111).\(^{4,25}\) The values of \( n_{SPt}^{exp} \) obtained in SLRR reaction with \( \theta_{o,Cu} = 1 \) and \( \theta_{o,Cu} = 0 \) have very close values. They are also the minimum ones observed among all experiments (\( \approx 1.5 \times 10^{12} \text{ cm}^{-2} \)). As one can see, the difference between minimum and maximum values of \( n_{SPt}^{exp} \) is significant, almost 35%. The analysis of STM data with \( \theta_{o,Cu} > 0.63 \) indicates that decreasing trend in nucleation density is not related to merging of Pt nanoclusters (growth stage). In all experiments, the predominant shape of Pt nanoclusters remains round and 2D disk-like and the coverage of Pt does not exceed a 2D coalescence threshold,\(^{26}\) (\( \theta_{Pt} < 0.66 \)). Therefore, we conclude that the observed \( n_{SPt}^{exp} \) vs. \( \theta_{o,Cu} \) dependence is the fundamental consequence of Pt nucleation process. Each observed/counted Pt cluster contributing to the results in Figure 2 originates from a stable Pt nucleus enlarged by attachment of Pt adatoms during growth stage.

The dependence of an average Pt nanocluster size in PtML/Au(111) is shown in Figure 2B. The average Pt nanocluster size, denoted as \( \Sigma_{Pt} \), is expressed in units of area (nm\(^2\)). It shows significant variation with increasing \( \theta_{o,Cu} \). As mentioned previously, due to spontaneous Pt deposition process there is a population of Pt nanoclusters observed for \( \theta_{o,Cu} \approx 0 \), \( \Sigma_{Pt} \approx 31 \text{ nm}^2 \). The increasing coverage of \( \theta_{o,Cu} \) results in decrease of the average Pt nanocluster size until the minimum is reached for \( \theta_{o,Cu} \approx 0.63 \) (\( \Sigma_{Pt} \approx 13 \text{ nm}^2 \)). Further increase in \( \theta_{o,Cu} \) yields almost a linear increase in \( \Sigma_{Pt} \) until the maximum value of 35 nm\(^2\) is reached for \( \theta_{o,Cu} = 1 \). The difference between the minimum and maximum point in Figure 2B is more than 250%. This indicates a very large effect of \( \theta_{o,Cu} \) on PtML/Au(111) morphology. The statistical dependence is significant, almost 35%.

Results and Discussion

Analytical model.—Following the considerations from nucleation kinetics theory,\(^{27,28}\) for room temperature growth of Pt, the steady state nucleation density is described as a function of deposition flux:

\[
\exp n_{Pt} \approx \alpha \cdot F^{1/3} + n_0
\]  

Here, \( F \) is the deposition flux [cm\(^{-2}\) s\(^{-1}\)] and \( \alpha = [1/(D_{Pt}^{S} \cdot a^3)]^{1/3} \) is a constant absorbing the Pt surface diffusivity \( (D_{Pt}^{S}) \) and the lattice parameter of the substrate, \( a \) (Table II). The term \( n_0 \) represents the areal density of Pt clusters produced by Pt spontaneous deposition process \( (n_0 = n_{SPt}^{exp} \text{ for } \theta_{o,Cu} = 0) \). We assume that it is independent on the Pt deposition via SLRR reaction. The Pt deposition flux is defined in terms of the SLRR reaction kinetics. It is equal to the SLRR reaction rate per unit area, [cm\(^{-2}\) s\(^{-1}\)] and defined it in terms of temporal coverage of CuUPD/Au(111) during SLRR reaction;\(^{29}\)

\[
F = \frac{m}{p} \Gamma_{UPD}^{Cu} \left( -\frac{d \theta_{Cu}}{dt} \right) = \frac{m}{p} \Gamma_{UPD}^{Cu} \cdot K_{SLRR}(\theta_{Cu})^N
\]

Here, \( \Gamma_{UPD}^{Cu} \) represents the surface concentration of the full CuUPD/Au(111) expressed in units of atoms per unit area [cm\(^{-2}\)]. (Figure 1B-inset and Table II).\(^{30}\) The numerical factor \( m/p \) is the ratio between stoichiometry coefficients in SLRR reaction, Table I. It accommodates the fact that more than one Cu UPD atom can be dissolved during deposition of one Pt adatom.\(^{25,29}\) The \( K_{SLRR} \) is the SLRR ratio between stoichiometry coefficients in SLRR reaction.

Table II. Parameters used in the model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Source</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a_0 ) [cm(^2)]</td>
<td>fit</td>
<td>(2.6 \pm 0.3 \times 10^{12})</td>
</tr>
<tr>
<td>( D_{Pt}^0 ) [cm(^2) s(^{-1})]</td>
<td>fit, calc.</td>
<td>(3.5 \pm 0.3 \times 10^{-8})</td>
</tr>
<tr>
<td>( \xi )</td>
<td></td>
<td>(0.991 \pm 0.006)</td>
</tr>
<tr>
<td>( \Gamma_{UPD}^{Cu} ) [cm(^{-2})]</td>
<td>fit</td>
<td>(1.15 \times 10^{-7})</td>
</tr>
<tr>
<td>( a ) [cm]</td>
<td></td>
<td>(0.408 \times 10^{-7})</td>
</tr>
<tr>
<td>( n_0 ) [cm(^2)]</td>
<td>experiment</td>
<td>(1.51 \times 10^{-12})</td>
</tr>
</tbody>
</table>
reaction rate constant \( \text{[s}^{-1}] \), and \( N \) is the order of SLRR reaction in terms of the CuUPD/Au(111) coverage, Table I.28

Combining eq. 3 and 4 we get the expression for Pt nucleation density as a function \( \theta_{\text{Cu}} \):

\[
n_{\text{Pt}} = a_0 \cdot \left( \theta_{\text{Cu}} \right)^{N/3} + n_0
\]  

[5]

The \( a_0 \) is the new numerical constant defined as

\[
a_0 = \frac{n_{\text{exp}}^{n_{\text{slrr}}}}{1 - \alpha_1 \cdot \left( \theta_{\text{Cu}} \right)^{N/3}} \]  

The eq. 5 represents the continuously increasing function of \( \theta_{\text{Cu}} \). However, the experimental data show more complex \( n_{\text{exp}}^{n_{\text{slrr}}} \) vs. \( \theta_{\text{Cu}} \) dependence. In order to proceed further with definition of the model we have to point out some specifics of the metal deposition via SLRR of UPD ML. The nucleation density description in terms of the deposition flux does not provide complete phenomenological picture of the nucleation event during metal deposition via SLRR. The probability that two or more Pt adatoms will encounter one another on the Au surface and form the stable nucleus is also a function of the conditions at the Au surface. These conditions can promote or prevent nucleation event. In a simplified picture, we describe two limiting scenarios, Figure 3. In the first one, the Pt adatom lands on the Au(111) surface free from Cu UPD layer. It can freely diffuse until it encounters another Pt adatom to form a stable nucleus. In this scenario, every Pt adatom landing on a free Au surface is likely to contribute to the nucleation process. This picture goes along with the description of the nucleation density considered by eq. 5. However, in the second scenario, the Pt adatom lands on top of the Cu UPD layer. We expect that density of defects such as kinks, vacancies or steps in dissolving Cu UPD layer is much higher than on Au surface. Because of that, it is likely that this Pt adatom will diffuse around and incorporate into a Cu UPD layer at energetically favorable defect site, Figure 3. In this case, the probability for Pt adatom to encounter others already incorporated Pt atoms within the Cu UPD layer to form a stable nucleus is low. Thus, we expect that Pt adatom in this scenario contributes mostly to the growth stage upon dissolution of its neighboring Cu adatoms. To formulate this discussion in mathematical sense, we state that probability for Pt nucleation, \( P(n_{\text{pt}}) \), is proportional to the area of Au the surface free from Cu UPD layer;

\[
P(n_{\text{pt}}) \approx (1 - \xi \cdot \theta_{\text{Cu}})
\]  

[6]

We stress the fact that the above equation represents the areal probability for Pt nucleation, which arises from the specific geometrical conditions on the Au surface during SLRR reaction. The term \( \xi \) is a numerical constant equal to 1-\( P(n_{\text{pt}}) \) at the \( \theta_{\text{Cu}} \rightarrow 1 \) limit (\( \xi = 1 - P(n_{\text{pt}}(\theta_{\text{Cu}} \rightarrow 1)) \)). At this condition, some small and finite probability of nucleation cannot be excluded and, by definition, the value of \( \xi \) is expected to be close to 1 always \( \xi < 1 \). Therefore, the nucleation density obtained as a result of Pt deposition via SLRR of CuUPD/Au(111), now denoted as \( n_{\text{Pt}}^{SLRR} \), is equal to the nucleation density term, eq. 5, multiplied by the areal probability for nucleation defined by eq. 6;

\[
n_{\text{Pt}}^{SLRR} = a_0 \cdot \left( 1 - \xi \cdot \theta_{\text{Cu}} \right) \left( \theta_{\text{Cu}} \right)^{N/3} + n_0
\]  

[7]

For room temperature growth, the nucleation time, \( t_{\text{nucl}} \) is very short.29 As compared to the half time of the SLRR reaction, \( t_{\text{slrr}} \), the relation \( t_{\text{nucl}} \ll t_{\text{slrr}} \) always holds.29 This means that the coverage of the CuUPD/Au(111) relevant for nucleation process is the one at very beginning of SLRR reaction. Hence, in the above equation, we can assume that \( \theta_{\text{Cu}} \approx \theta_{\text{Cu,nucl}} \). Using the SLRR reaction kinetics parameters from Table I, eq. 7 takes the form which is used to fit the data in Figure 2A.

\[
n_{\text{Pt}}^{SLRR} = a_0 \left( 1 - \xi \cdot \theta_{\text{Cu,nucl}} \right) \left( \theta_{\text{Cu,nucl}} \right)^{N/3} + n_0
\]  

[8]

The only adjustable parameters in our model are the surface diffusivity of Pt wrapped up in the value of \( a_0 \) and the constant \( \xi \). All other parameters are defined in Table I and Table II or they are measured experimentally (\( n_0 \)). As one can see, the model achieves a very good qualitative description of the experimental data for \( N = 4 \), Figure 2A. This value of the reaction order transpires from the stoichiometry of the SLRR.31 The proper determination of the reaction order is somewhat challenging task. In previous study of this system, the reaction order \( N = 2 \) was determined by fitting the OCP transients with reaction kinetics equation.29 The \( N = 2 \) implemented in our model does provide a good fit for the data in the range \( \theta_{\text{Cu}} \leq 1 \). For lower values of \( \theta_{\text{Cu}} \), our model diverges from experimental data, Figure 2A. At this point, we take \( N = 4 \) as the correct assumption for the reaction order and use it in our further discussions.

The obtained value of \( \xi \) from the model fit to the experimental data is very close to 1, Table II. As we discussed previously, this indicates that nucleation probability for Pt atoms landing on top of the Cu UPD layer is very low, \( P(n_{\text{pt}}(\theta_{\text{Cu}} \rightarrow 1)) = 0.009 \). The value of \( D_{\text{Pt}} \) is significantly higher than ones reported for either metal. In fundamental sense, this means that the activation energy involved in the diffusion hop of Pt on Au surface is less than for clean metal surface. The presence of Cu UPD adatoms on the surface could facilitate formation of more mobile Pt-Cu dimers as an intermediate step in formation of Pt nuclei. They could act as promoters for Pt diffusion process. In addition to that, the presence of chloride ions adsorbed on top of Cu UPD or Au surface upon liberation from Pt complex could additionally promote surface diffusion of Pt as well.4 At this point, we can state that deeper insight in the physical value and the meaning of \( D_{\text{Pt}} \) during SLRR reaction requires different approach. Perhaps, a good direction is to perform the atomistic calculations involving estimates of the bonding energies of all possible metal-metal adatom and metal atom-ion combinations from the first principles and incorporate them into the kinetic Monte-Carlo simulations of dynamic processes occurring at the Au surface during Pt deposition via SLRR reaction. This type of work is beyond the scope of this paper but our current efforts are directed toward exploring this approach.

The analytical model described here presents itself as a tool to analyze the effect of different experimental conditions on Pt nucleation density and \( P(n_{\text{pt}})/\text{Au(111)} \) morphology. In Figure 4, the plot of eq. (9) (bold line) using parameters from the Table I, and Table II, with \( N = 4 \) is presented as starting point in our discussion. In the first case, we discuss the effect of \( K_{\text{SLRR}} \). Earlier study showed that bulk concentration of Pt ions in reaction solution has significant effect on the \( K_{\text{SLRR}} \) value, Table I.29 A 100 × dilution of \( \text{[PtCl}_6^{\text{3−}} \) concentration, (from \( 10^{-3} \text{ M to } 10^{-5} \text{ M} \text{[PtCl}_6^{\text{3−}} \) results in \( 40 \times \) decrease in \( K_{\text{SLRR}} \), (\( K_{\text{SLRR}} = 0.089 \), Table I). Considering that \( a_0 \approx (K_{\text{SLRR}})^{1/3} \approx 4 \times \) lower nucleation rate is expected. The calculated functional
relation between \( n_{Pt}^{SLRR} \) and \( \theta_{Cu} \) for \( 10^{-3} \) M \{P(Cl)\} is shown in Figure 4 as dashed line. The mathematical form of the relation does not change. Yet, a lower value of \( \theta_{Cu} \) makes the difference between minimum and maximum point in nucleation density only \( \approx 9\% \). Obviously, a higher concentration of \{P(Cl)\} would produce also a large effect but in opposite direction. Based on this discussion, one should notice that the control of the average nanocluster size in PML/Au(111) is a very strong function \{P(Cl)\} concentration in electrolyte and the coverage of the \( \theta_{Cu} \) in SLRR reaction.

The choice of supporting electrolyte in SLRR reaction involving CuUPD/Au(111) has decisive effect on the oxidation state of Cu. In the case of 0.1 M HClO4, the absence of complexing ability for Cu renders the Cl\(^-\) liberated from \{P(Cl)\} as the only ligand at the interface. This situation leads to formation of \{CuCl\}\(^{2-}\) complex with Cu being +1 oxidation state and m/p = 0.25, Table 1. However, if reaction solution has an abundance of sulfate ions, (for example: 0.1 M H\(_2\)SO\(_4\)) the Cu oxidation state in SLRR reaction is \(+2\). This means that m/p ratio is 0.5. The reaction rate constant in this electrolyte is slightly higher too, \( (K_{SLRR} = 4.08 \text{ s}^{-1}) \), Table 1. Both effects make the value of \( \theta_{Cu} \approx 30\% \). The additional fact is that reaction order in terms of \( \theta_{Cu} \) changes to N = 2.29,31 This affects qualitative shape of the curve and the position of the maximum shifts to \( \theta_{Cu} \approx 0.4 \). Therefore, for the same concentration of Pt ions in solution (10\(^{-3}\) M) but with 0.1 M H\(_2\)SO\(_4\) supporting electrolyte, a roughly 30\% higher \( n_{Pt}^{SLRR} \) values are expected in 0 \( < \theta_{Cu} < 1 \) range with qualitatively different \( n_{Pt}^{SLRR} \) and \( \theta_{Cu} \) dependence, (Figure 4, dash-dot line). Following the same logic, further enhancement in nucleation density should be expected if the \{P(Cl)\}\(^{2-}\) ion is replaced with \{P(Cl)\}\(^{2-}\) making the m/p = 1. In this case, the m/p value \( \approx 60\% \) larger. In addition, one Pt ion reacts with one Cu UPD adatom and the reaction order takes N = 1.15 Both changes, in reaction stoichiometry and in reaction order, make a major impact on the Pt nucleation density, assuming that the \( K_{SLRR} \) remains the same (Figure 4, dash-dot-dot line). The maximum value in \( n_{Pt}^{SLRR} \) vs. \( \theta_{Cu} \) dependence increases almost 75\% and further shifts toward lower \( \theta_{Cu} \) (0.23). The overall conclusion is that larger m/p ratio produces higher nucleation density and PML/Au(111) with smaller nanoclusters. The opposite is true when reaction order is considered. Higher the SLRR reaction order, the lower Pt nucleation density is, i.e. PML/Au(111) morphology with larger nanoclusters is expected.

**HR results.**— An adsorbed CO molecule forms \( \sigma \) and \( \pi \) bonds with a Pt surface. The latter one represents predominant contribution to the adsorption process.13-15 The \( \pi \) bond is formed through back donation of d-electrons from Pt into the \( \pi^{*} \)-antibonding molecular orbital of CO. Changes in the d-band center energy of the Pt ML due to the 2D finite size effect influence the strength of Pt-CO and C = O bonds simultaneously.34 The shift in the energy of d-band center of Pt can be measured indirectly by observing the change in stretching frequency of the C = O bond of an adsorbed CO molecule.33 More d-\( \pi \) back donation means stronger Pt-CO bond but, at the same time, a weaker C = O bond. Shift in stretching band of CO in particular bonding configuration on Pt toward lower wave number means an increased strength of the Pt-CO bond.33 In Figure 5, the Subtractively Normalized Furrer Transform Infrared Red Spectroscopy (SNIFTIRS) data are shown for CO ML adsorbed at \( -0.1 \text{ V} \) vs. SCE on two different PML/Au(111) samples. They are deposited via SLRR of CuUPD/Au(111) with coverage of \( \theta_{Cu} \approx 0.64 \) and \( \theta_{Cu} = 1 \). According to our results in Figure 2B, they have distinct morphology in their average Pt nanocluster size (\( \xi_{P} = 13 \text{ nm}^{2} \) and \( \xi_{P} = 35 \text{ nm}^{2} \)). The SNIFTIRS data for each PML/Au(111) show stretching bands for linear and bridge Pt-CO bonding configurations. The stretching bands centered at 1884 cm\(^{-1}\) are associated with bridge-bonded CO molecule, CO\(_{L}\). The ones centered at 2048 and 2042 cm\(^{-1}\) are associated with linearly bonded CO molecule, CO\(_{B}\). The SNIFTIRS data indicate that stretching frequency for CO\(_{B}\) has no dependence on PML/Au(111) morphology. However, in the case of CO\(_{L}\), the PML/Au(111) with larger average size of Pt nanoclusters (\( \xi_{P} = 35 \text{ nm}^{2} \) has stretching band centered at \( \approx 6 \) cm\(^{-1}\) lower wave number, (2042 cm\(^{-1}\) ). Indirectly this means a stronger Pt-CO bond on PML/Au(111) with larger nanoclusters. This result can be understood following our previous discussion emphasizing the size dependent active strain in Pt nanoclusters as an important parameter describing their catalytic activity.10,13 Larger Pt nanoclusters have less size dependent compressive strain component, and thus, their active strain is closer to the epitaxial strain, \( \varepsilon_{coh} \). In the case of PML/Au(111), \( \varepsilon_{coh} \) is positive \( \approx 4\% \).10 This means that larger Pt nanoclusters have the energy of the d-band center lifted more toward the Fermi level as compared to the smaller ones.13 Therefore, PML/Au(111) with larger nanoclusters appears as more reactive and stronger Pt-CO bond is expected. The difference in stretching bands for CO\(_{L}\) for these two samples shows that morphology of the PML/Au(111) is an important parameter for understanding its electrosorption behavior. The SNIFTIRS data suggest that choice of the \( \theta_{Cu} \) in SLRR reaction affects the obtained PML/Au(111) activity. This data also emphasize the need for studying the \( n_{Pt}^{SLRR} \) vs. \( \theta_{Cu} \) relation and parameters defining reaction kinetics in order to design experimental conditions for PML/Au(111) with desired catalytic properties.

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**Figure 4.** Model predictions (eq. 8) for \( n_{Pt}^{SLRR} \) vs. \( \theta_{Cu} \) dependence on SLRR reaction kinetics parameters, and SLRR solution design.

**Figure 5.** SNIFTIRS data for CO monolayer adsorption on PML/Au(111) with \( \xi_{P} = 13 \text{ nm}^{2} \) and \( \xi_{P} = 35 \text{ nm}^{2} \). Spectra collected at 0.1 V, reference potential at 0.8 V, CO admission potential at -0.1 V. All potentials quoted with respect to SCE.
Conclusion

This is the first work studying the nucleation of Pt deposited via SLRR of Cu UPD ML. Presented results show that Pt nucleation depends directly on the coverage of Cu$_{\text{UPD/Au(111)}}$. The observed dependence has the maximum at $\theta_{\text{Cu}} = 0.63$. At the same coverage, the Pt$_{\text{ML/Au(111)}}$ with minimum average nanocluster size is observed. The analysis of deposited Pt$_{\text{ML/Au(111)}}$ and analytical model developed to interpret our data suggest that SLRR reaction stoichiometry, rate constant and reaction order are the key parameters affecting the Pt$_{\text{ML/Au(111)}}$ nucleation density and the average nanocluster size. The general conclusion derived from this work should be that SLRR reactions having faster kinetics yield higher Pt nucleation density and Pt$_{\text{ML/Au(111)}}$ with smaller clusters for a given starting coverage of Cu UPD ML. The conditions promoting larger m/p ratio and lower reaction order in terms of the $\theta_{\text{Cu}}$ do promote higher Pt nucleation density and formation of Pt$_{\text{ML/Au(111)}}$ with smaller nanoclusters. Design of the optimum experimental conditions leading to desired Pt$_{\text{ML/Au(111)}}$ morphology is a function of their intended use in particular reaction. In the case where the high activity of the Pt$_{\text{ML/Au(111)}}$ is desired, the conditions promoting low nucleation density and formation of Pt$_{\text{ML/Au(111)}}$ with larger nanocluster should be used. These include the reaction solution with no complexing ability toward Cu and low Pt$^{4+}$ ion concentration. However, if poisoning of the catalyst by intermediates hinders the particular reaction kinetics, the synthesis of Pt$_{\text{ML/Au(111)}}$ with modest activity might be beneficial to retain good reaction yield and desired reaction pathway. In this case, the conditions promoting high nucleation density and small average size of Pt nanoclusters should be chosen. This means reaction solution design with high Pt$^{2+}$ ion concentration, and supporting electrolyte containing sulfate ions. We believe that this work has a broader significance for catalysis community as an effort in bridging the gap between desired properties of catalyst ML and required conditions for its synthesis.

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References