Effect of nanoscale flows on the surface structure of nanoporous catalysts

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The surface structure and composition of a multi-component catalyst are critical factors in determining its catalytic performance. The surface composition can depend on the local pressure of the reacting species, leading to the possibility that the flow through a nanoporous catalyst can affect its structure and reactivity. Here, we explore this possibility for oxidation reactions on nanoporous gold, an AgAu bimetallic catalyst. We use microscopy and digital reconstruction to obtain the morphology of a two-dimensional slice of a nanoporous gold sample. Using lattice Boltzmann fluid dynamics simulations along with thermodynamic models based on first-principles total-energy calculations, we show that some sections of this sample have low local O₂ partial pressures when exposed to reaction conditions, which leads to a pure Au surface in these regions, instead of the active bimetallic AgAu phase. We also explore the effect of temperature on the surface structure and find that moderate temperatures (≈ 300 – 450 K) should result in the highest intrinsic catalytic performance, in apparent agreement with experimental results. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4984614>]

I. INTRODUCTION

Developing improved catalytic systems with high selectivity and activity is highly desirable for oxidation reactions, which are critical processes in the production of industrial chemicals. Nanoporous Au, an unsupported, nanostructured catalyst with a composition of roughly Au_{0.97}Ag_{0.3}, is a highly selective catalyst for certain oxidation reactions, including the oxidative coupling of methanol to methyl formate.^{1–3} AgAu alloys in other forms have also proven to be effective catalysts, often exhibiting improved performance over both pure Ag and pure Au, spurring interest in understanding their structure and reactivity.^{4–17} A limiting factor in this quest is the fact that the effects of the nanoporous structure on the flow of the reactants and products and the effects of variability in local pressures on the surface structure are not well understood. Here, we combine fluid dynamics calculations employing the lattice Boltzmann method (LBM) with thermodynamic models based on density functional theory (DFT) to predict the surface structure of an experimentally measured section of nanoporous Au.

Mass transport to and from a catalyst surface can play an important role in the overall catalytic performance of the system. Therefore, there is significant interest in combining models for surface reactions or surface structures, ideally from first-principles calculations, with simulations of the flow.^{18–27} Previous studies have focused on reactor-scale or device-scale computational fluid dynamics, with the domain for the fluid dynamics calculations on the order of millimeters to centimeters. These studies show that there can be significant heterogeneity in reactivity throughout a catalytic substrate due to variations in the flow field.^{18,24}

In the present work, we study the flow on the nanoscale to realistically account for the features of nanoporous Au catalysts. The flow through nanoscale materials can be complex and has not been well-studied in the context of catalysis. For nanoscale flow, the continuum approximation can break down, and the LBM, being rooted in kinetic theory, may offer additional information in the non-equilibrium, finite-Knudsen regime at a more affordable cost than the direct solution of the Boltzmann equation.²⁸ So far, LBM simulations have been reported on a fictitious porous medium generated to reproduce the main features of nanoporous Au.²⁹

A crucial piece of information for understanding a catalyst is the understanding of its surface structure; this can

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be particularly challenging in oxidizing conditions. The local pressure can affect the surface structure and composition of a catalyst, which can significantly affect its reactivity.^{30–33} In previous work, we predicted that dilute AgAu alloys, such as nanoporous Au, have pure Au surfaces at low O₂ partial pressures and high temperatures, while the active AgAu phase only appears at higher O₂ partial pressures and lower temperatures.³⁴ It is unclear whether this is at variance with experiment. Comparison with the experimental work on surface segregation in AgAu alloys is complicated by the influence of conditions, synthesis procedures, nanoscale effects, the local surface facet or curvature, and qualitative changes in surface segregation trends as the bulk composition changes.^{35–39} Experimental techniques have difficulty in distinguishing between the first and second surface layers, and DFT calculations predict that Ag is most stable in the second layer of a dilute AgAu alloy under high vacuum conditions. Even in well-controlled experiments on the bulk AgAu alloys, there is a disagreement as to whether Ag preferentially segregates to the surface, although at higher Ag concentrations it is likely that the surface segregation of Ag occurs.^{9,10,40–44} We note that DFT calculations correctly predict that Au inserted into an Ag(110) surface prefers the second and not the top layer, in agreement with the experiment.^{6,16} When Ag enrichment is observed under vacuum or reducing conditions, the Ag surface concentration is ≈ 1.1 –2 times higher than the bulk concentration, depending on the amount of Ag in the bulk. Since nanoporous Au usually contains $\leq 3\%$ Ag, the surface coverage of Ag is not more than a few percent, unless there is a strong driving force for the Ag segregation, for instance, due to adsorbed O. Therefore, we believe our DFT results are reliable, despite the lack of clear confirmation from the experiment.

Overall, previous results suggest that a high local O₂ pressure is necessary to produce a significant Ag surface coverage in nanoporous Au and other dilute AgAu alloys. This raises the question: Does the shape of nanoporous Au prevent incoming O₂ from accessing parts of the surface, causing them to remain inactive? In this work, we show that parts of nanoporous Au can indeed remain inactive due to the flow properties and local pressures, depending on the temperature. We also show that if the temperature is too high or too low, the surface becomes highly enriched in Ag or Au, instead of forming the AgAu structures that give the highest activity and selectivity.

II. METHODS

A. Focused ion beam-scanning electron microscopy

Focused ion beam-scanning electron microscopy (FIB-SEM) analyses were performed using an FEI Helios Nanolab 660 Dualbeam FIB-SEM. The preparation is as follows: (1) deposition of a W protective layer (3 kV, 13 nA in SEM mode, then 30 kV, 0.45 nA in FIB mode with W(CO)₆ as the gas precursor); (2) milling the sample in the vicinity of the protective layer (Ga beam at 30 kV, 2.5 nA in the FIB mode); (3) cleaning the cross section at low kV to avoid any damage (5 kV, 80 pA in the FIB mode). The first step consists of SEM image acquisition at 2–3 kV and 50–100 pA. Due to the configuration of the system, the SEM images of the cross sections were

acquired at an angle of 52°. Consequently, a tilt correction was applied to acquire the SEM image. The second step consists of the removal of a thin layer (5 nm) by ion milling, exposing a deeper layer of the sample that can then be imaged by SEM.

B. SEM image analysis

The sample has been digitally reconstructed from the SEM images by employing the image processing software ImageJ.⁴⁵ The SEM images have been stacked together and aligned, by means of the StackReg⁴⁶ plugin, so as to obtain a set of aligned (untilted) slices of the nanoporous ingot. The untilted SEM slices were then post-processed with Matlab in order to obtain the digital, three-dimensional, binarized nanoporous sample employed in the simulations. The digital 3D porous sample was cut with an $x-z$ midplane so as to obtain the two-dimensional porous domain employed in the simulations. The main steps for the reconstruction of the nanoporous sample are shown in Fig. 1.

The surface structure of an AgAu alloy depends on the identity of the surface facet as well as the conditions. Therefore, we must make a reasonable assignment of the facet to which each point on the surface belongs. Given a two-dimensional slice through a three-dimensional object at an unknown angle relative to the crystal structure, there is little hope of determining the true surface facet in the original material. However, this level of accuracy is unnecessary when considering a reasonably sized sample; simply having a representative sample of the surface facets throughout the material will suffice.

We first broke the surface of each grain, defined as each section of the material not attached to any other section, into surface planes. Since each plane is forced onto a grid, planes that are oriented on a diagonal will become “stairsteps.” We tested several options for identifying these planes and settled on the following simple algorithm. First, we order the surface points in each grain using the FindShortestTour function in

FIG. 1. Process for the digital reconstruction of the nanoporous catalyst from the SEM images. The images are binarized into fluid and solid regions, stacked and aligned, and then post-processed in order to obtain a three-dimensional reconstruction. The LB simulations are then performed on a two-dimensional slice of the reconstructed nanoporous medium.

Mathematica. We then choose a point on the surface and construct lines from that point to each of the subsequent points. For each line, we find the maximum distance between the line and all of the surface points between the endpoints. If the maximum distance is small, then the endpoint of that line is part of the same plane as the original point, as all of the points lie nearly along the same line. If the maximum distance is large (>0.6 lattice units), then the endpoint of the line may correspond to the start of a new plane, or this may be due to the stairstep nature of a diagonal plane being forced onto a grid. Therefore, we check if the maximum distance between the *next* line and its corresponding points is larger or smaller than this previous maximum distance. If the maximum distance decreases, then the next point is roughly in the same direction as the current plane, and we therefore assume that all of the points are part of the same plane. If the maximum distance between the next line and the corresponding points *increases*, then we assume that the surface continues in a significantly different direction and assign the line's endpoint to a new plane. The algorithm then repeats from this new endpoint until all of the points have been assigned to planes. This procedure appears to give reasonable planes, as shown in Fig. 2.

To assign a set of Miller indices to each plane identified by this algorithm, we must determine the angle of the viewing plane of the original SEM and the rotation angle of the image, both relative to the underlying crystal structure. Again, the true angle and orientation are not necessary; reasonable values will give reasonable results when applied to the entire image. We calculate the angles between low-index Miller planes (the $\{100\}$, $\{110\}$, and $\{111\}$ families) as a function of the viewing angle by varying the angle of a 2D slice through 3D space and find the viewing angle that best corresponds to the set of angles between the adjacent planes we identified in the material. We then choose a rotation angle where the orientations of the low-index Miller planes best correspond to the set of planes that we found in the material. Using the viewing plane's angle and the rotation angle, we then assign Miller indices to each plane

FIG. 2. A representative grain and the surface planes identified by our algorithm. The algorithm essentially identifies breaks between the planes as locations where two successive points increasingly deviate from a straight line. The points in each plane are colored separately and lines are drawn from the first point to the last point in each plane. A few examples are labeled with their plane family.

based on its angle. We assume that all the facets are part of the $\{100\}$, $\{110\}$, or $\{111\}$ families, and therefore each angle is assigned to the specific plane among these families that most closely matches that angle. For example, taking 0° as being along the long axis of the material (the horizontal direction in Fig. 2), there are $\{111\}$ -family planes at angles of 2.5° and 96.6° (among others), and there is a $\{110\}$ -family plane at an angle of 49.5° . Hence, a plane with an angle of 0° or 90° is assigned as a $\{111\}$ surface, while a plane with an angle of 45° would be assigned as a $\{110\}$ surface. We assume that the $\{111\}$ facets have $\{211\}$ steps with a density of 15%, which is well within the range of estimates from a previous electron microscopic study.⁴⁷

C. Lattice Boltzmann simulations

In this section, the main features of the multi-component LBM for reactive flows are briefly recalled. In the last two decades, the LBM has gained a prominent role in the simulation of complex hydrodynamic problems across a broad range of scales.^{48,49} A recent overview has been given by Aidun and Clausen⁵⁰ and a more comprehensive account has been provided by Succi.⁵¹ Applications of the LBM to the reactive flows and heterogeneous catalysis in complex media can be found in Refs. 52–55. The lattice Boltzmann (LB) equation for reactive species reads as follows:

$$f_i^{(k)}(\vec{x} + \vec{c}_i, t + 1) - f_i^{(k)}(\vec{x}, t) = \omega(\bar{f}_i^{(k)} - f_i^{(k)}), \quad (1)$$

where $f_i^{(k)}$ is the probability density function of finding a particle of the species k at site $\vec{x}$ at time t , moving along the i th lattice direction defined by the discrete speeds $\vec{c}_i$, with $i = 0, \dots, b$, where $b = 8$ for the two-dimensional nine speed lattice (D2Q9) used in this work, and $\bar{f}_i^{(k)}$ is the equilibrium value. The left-hand side of Eq. (1) represents the free-streaming of molecules, whereas the right-hand side accounts for the collisional relaxation toward a local Maxwellian equilibrium, on a time scale $\tau = 1/\omega$. The macroscopic density $\rho^{(k)}$ and momentum $\rho^{(k)}\vec{u}$ of the k th-species are given by $\rho^{(k)}(\vec{x}, t) = \sum_{i=0}^b f_i^{(k)}(\vec{x}, t)$ and $\rho^{(k)}(\vec{x}, t)\vec{u}(\vec{x}, t) = \sum_{i=0}^b f_i^{(k)}(\vec{x}, t)\vec{c}_i$, respectively. The equilibrium distribution function is given by a low-Mach, second-order expansion of a local Maxwellian, namely,

$$f_i^{(k)} = w_i \rho^{(k)} \left[1 + \frac{\vec{c}_i \cdot \vec{u}}{c_s^2} + \frac{(\vec{c}_i \cdot \vec{u})^2}{2c_s^4} - \frac{\vec{u} \cdot \vec{u}}{2c_s^2} \right], \quad (2)$$

where $\vec{u}$ is the flow velocity of the carrier species and $c_s = \frac{1}{3}$ is the lattice sound speed. In order to span a wide range of Knudsen number values beyond the usual hydrodynamic limits, it is beneficial to filter out non-hydrodynamic modes from the pre-collisional distribution, a procedure known as “regularization.”²⁸

We employ the standard version of the LBM for a three-component system, consisting of an inert carrier (C), reactants (R), and products (P). Chemical reactions are patterned after the following methanol oxidation reaction:

We take into account the interconversion of species due to catalytic reactions at the pore surface by considering a local

exchange of populations as they meet and react on the solid walls of the pore. For the case of heterogeneous catalysis, such reactions take place whenever gas populations hit the surface of the porous catalyst. Here, we consider a first-order chemical reaction of the generic form $R \rightarrow P$. The reactive boundary condition is designed such that, upon colliding with a solid site, the reactant R converts into the product P with a given probability p . Thus, each molecule of R colliding with a catalytic site is re-emitted along a random direction, either as species R with probability $1 - p$ (no-reaction) or as species P with probability p .⁵⁶

First-order surface chemical reactions have been modeled by implementing a “sputtering” boundary condition,

$$\begin{aligned} f_i^{(R,in)}(\vec{x}) &= (1-p) \sum_{j=1}^{b(\vec{x})} S_{ij} f_i^{(R,out)}(\vec{x} - \vec{c}_j), \\ f_i^{(P,in)}(\vec{x}) &= p \sum_{j=1}^{b(\vec{x})} S_{ij} f_i^{(R,out)}(\vec{x} - \vec{c}_j), \end{aligned} \quad (4)$$

where $S_{i,j}$ is a random sputtering matrix obeying the mass conservation constraint, $\sum_{j=1}^{b(\vec{x})} S_{ij} = 1$, and $0 \leq b(\vec{x}) \leq 8$ is the number of active links at any given lattice site $\vec{x}$. The superscript “in” denotes the incoming distributions (from solid to fluid), while “out” stands for the outgoing ones (from fluid to solid). According to this model, each node of the porous medium in direct contact with the gas nodes acts as a catalytic site. The boundary condition is built in such a way as to locally preserve the $R + P$ mass, while the C mass is conserved anyway since the carrier does not take part in the reaction.

The flow inside the medium is obtained by applying a constant mass force to the carrier distribution and imposing unit concentration along the inlet. Zero-gradient and periodic boundary conditions are applied, respectively, at the outlet section and across all crossflow directions. The simulations are advanced in time until negligible variations of both the flow and the concentration are obtained.

D. Density functional theory and *ab initio* thermodynamics

The DFT and thermodynamic methods have been described in detail previously.³⁴ Briefly, we use the VASP code^{57,58} with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional⁵⁹ and the Tkatchenko-Scheffler correction⁶⁰ to calculate total energies, which were used to obtain the surface free energies using *ab initio* atomistic thermodynamics.⁶¹ The O chemical potential as a function of the temperature and pressure is obtained from the experimental data for the free energy of O_2 in the gas phase, and the chemical potentials of Ag and Au are approximated as the DFT energy of the bulk phases. For Au, we use a pure Au bulk, and for Ag, we use an isolated Ag atom in bulk Au.

The phase diagram of the dilute AgAu system is somewhat unusual, in that all four facets studied only have two stable phases in the range of conditions we considered, one at low O_2 chemical potential $\mu(O_2)$ and one at high $\mu(O_2)$.³⁴ The values of $\mu(O_2)$ at which the surface structure changes as well as the Ag and O coverages $\theta(Ag)$ and $\theta(O)$ of each structure are given in Table I. The values given for $\mu(O_2)$ are relative to the isolated

TABLE I. Critical chemical potential $\mu(O_2)$ at which the most stable surface structure changes for each surface facet (in eV), and the surface coverage of Ag and O $\theta(Ag)$ and $\theta(O)$ in each structure, in monolayers (ML).

Surface facet	Critical $\mu(O_2)$	Low $\mu(O_2)$		High $\mu(O_2)$	
		$\theta(Ag)$	$\theta(O)$	$\theta(Ag)$	$\theta(O)$
(111)	−1.31	0	0	0	0.31
(110)	−1.45	0	0	0.50	0.50
(100)	−0.79	0	0	1.00	0.33
(211)	−1.23	0	0	0.66	0.66

O_2 molecule chemical potential, which is what is calculated directly by DFT. For the (110) facet, which undergoes the missing-row reconstruction, we include all first and second layer metal atoms, as well as half of the third layer atoms, as surface atoms for the purpose of computing the coverage.

We estimate the configurational entropy as $\Delta S = k_B \ln(N_b/N_s)$, where N_b and N_s are the number of bulk and surface atoms, respectively, following previous work.⁶² As noted in this previous work, slow bulk diffusion rates in metals prevent a complete equilibrium throughout the material, resulting in a quasiequilibrium in the surface region. For the purposes of estimating the entropy, we assume that this region is 10^3 metal layers ($N_b/N_s = 10^3$); varying this value by one or two orders of magnitude has only a small effect on our results. Entropy will drive the surface to have the same Ag concentration as the bulk, which is low in nanoporous Au ($\approx 2\% - 3\%$), and we therefore only include this term as the destabilization of structures that have a high Ag surface concentration. We use ΔS to estimate the region of phase space over which entropy will have an effect and linearly interpolate the Ag and O coverages throughout this region. For example, after this framework is applied to the (100) facet, the Ag coverage will still be 0 when $\mu(O_2)$ is low and will increase gradually after $\mu(O_2)$ reaches its critical value (see Table I) at which the Ag-terminated structure

FIG. 3. The pressure fields of the reactants (O_2 and the species to be oxidized, such as methanol or CO) and products (water and the oxidation product, such as methyl formate or CO_2) from the LBM simulations, on a logarithmic scale. A portion of the reactants (shown in the box) is expanded. The flow is from left to right. As expected, the concentration of reactants (products) generally decreases (increases) from left to right, as the gas passes over the catalyst. The reactant pressure in the catalyst varies significantly (see the inset).

becomes more favorable. When the Ag-terminated structure becomes more favorable by $T\Delta S$, the Ag coverage becomes 1 ML.

III. RESULTS

The results from the LBM simulation show that there is a significant variation in the local partial pressure, from roughly 10^{-2} to 10^4 Pa, as shown in Fig. 3. As expected, the reactants generally decrease in partial pressure in the direction of the flow (from left to right), while the products generally increase. As noted previously,²⁹ much of the reaction occurs in the region of the material near the incoming flow. Figure 3 also indicates that the top and bottom regions of the material show lower levels of conversion, while the middle has lower

reactant levels and higher product levels. Finally, it is apparent that some inner surfaces of the catalyst experience low local reactant pressures, much lower than the surfaces that are more accessible to the incoming flow.

By examining the pressure at the surface, we can appreciate the range of conditions to which the catalytic surface is exposed. We focus on the reactant pressure, as O_2 is expected to have the largest effect on the surface structure and composition due to its high reactivity. As shown in Figs. 4(a) and 4(b), the surface is indeed exposed to a wide range of reactant pressures. Since Au cannot dissociate O_2 , the surface will only be catalytically active in places where there is Ag on the surface, as demonstrated by the inactivity of nanoporous Au with no Ag.⁴ In particular, bimetallic (211) steps have been previously suggested to be good models for the active site on nanoporous Au,³⁴ and these structures only form if the local O_2 pressure is high enough. To understand how pressure affects the formation of these sites, we first assume that all of the surface is the (211) facet and plot which regions of nanoporous Au are predicted to have a pure Au surface layer and which regions are predicted to have a bimetallic surface layer at a typical reaction temperature of 425 K; see Fig. 4(c). This shows, deconvoluted from variations in the surface facet, that low pressures in regions that are not easily accessible to the flow can prevent significant portions of the material from being active. In

FIG. 4. The local pressure at the surface varies significantly, which can affect the surface reactivity. (a) The local pressure of the reactants at the surface of nanoporous Au, with the colors on a logarithmic scale as shown in part b. (b) A histogram of the pressures at the surface. (c) Assuming all of the surface of the material consists of the (211) facets and that the steps are the active sites, at 425 K only some of the material (in red) has a high enough local O_2 pressure for Ag to be stabilized on the surface, while the rest of the material (in black) contains only Au on the surface (see Table I for the Ag and O coverages of both states).

FIG. 5. Maps of the predicted local Ag coverage at various temperatures, calculated by applying our method for identifying the surface facet at each point and then applying the thermodynamic model based on DFT. The flow direction is from bottom to top in each case (indicated by the arrows). As the temperature increases, the surface coverage of Ag generally decreases, depending also on the surface facet and local O_2 pressure.

particular, regions that are far from the edge of the material and are not near an inlet from the edge of the material tend to be inactive.

To generate a realistic picture of the surface coverage of Ag, we assign a surface facet to each point on the surface as described in Sec. II. This allows us to plot maps of the local Ag coverage based on the pressure and the facet at each surface point as a function of the temperature (see Fig. 5). Overall, increasing the temperature drives O to the gas phase, which results in lower Ag surface coverages. The (111) surfaces are always mostly Au, but since we assumed a 15% step density they are partly Ag at high O₂ chemical potentials, which corresponds to low temperatures and high local reactant pressures. The (100) surfaces are pure Ag at high O₂ chemical potentials and become pure Au at lower chemical potentials. The (110) surfaces are bimetallic at high O₂ chemical potentials, with both Ag and Au on the surface, and become pure Au at lower

chemical potentials. Regions that are not easily accessible to the flow tend to become Au terminated at lower temperatures than regions that are accessible, due to the lower local O₂ reactant pressures.

This analysis also allows us to calculate the average Ag coverage across the entire material, as shown in Fig. 6(a). Below ≈ 200 K, the surface is Ag-rich and unaffected by changes in the temperature or pressure. The Ag coverage then decreases until it approaches 0 around 550 K. Most reactor studies are performed between 325 and 450 K^{1-3,63} in which the average Ag coverage is predicted to be 0.1 to 0.2 ML. This generally agrees with the 0.11 Ag/Au ratio found in an X-ray photoelectron spectroscopy study of nanoporous Au that was exposed to methanol oxidation conditions.⁶⁴

An important limitation of our analysis is that it predicts the thermodynamically most stable states, but does not account for kinetics. For example, at low temperatures, O₂ dissociation may be too slow for a significant amount of O to build up on the surface, or the metal diffusion rates may be too slow for the surface to restructure. Similarly, if the surfaces of the material are initially pure Au, O₂ will be unable to dissociate and the material will be unable to reach its thermodynamic ground state. This may be related to the utility of exposing nanoporous Au to ozone in order to reproducibly activate it for catalytic oxidation.⁶³

IV. DISCUSSION AND CONCLUSIONS

To gain insight into the catalytic activity and selectivity of the material, we can examine the range of local Ag coverages at different temperatures, as shown in Fig. 6(b). If the local Ag coverage is too low (the exact threshold is unclear), then the material will be inactive. Based on previous catalytic results,^{4,5} we expect the activity for most oxidation reactions to be highest for moderate Ag coverages and to decrease as the Ag coverage becomes too high. Further, the catalyst will become less selective as the Ag coverage increases.¹ At 225 K, some of the surface is pure Ag, which we expect to be non-selective and less reactive than a bimetallic surface. At 325 and 425 K, a large fraction of the surface is bimetallic, which we expect to be both active and selective, whereas at 525 K, most of the surface is pure Au, which we expect to have a low activity. Therefore, we expect moderate temperatures, in the range of those used in most reactor studies, to lead to surface structures with the best catalytic performance.

Our results are consistent with previous experimental work on the activity of Au, Ag, and AgAu catalysts as a function of the temperature. For a fixed surface composition, the activity is expected to increase and the selectivity is expected to decrease as the temperature increases. Indeed, for the supported nanoparticle catalysts, the activity of pure Au and pure Ag increases monotonically as the temperature increases.⁵ However, the AgAu catalysts show a peak in activity at a moderate temperature, around 300 K for the 8:1 Au:Ag sample, which is the most dilute in Ag of those tested. The activity of this sample then decreases between 300 and 430 K. Based on our results, we suggest that this decrease in activity is due to a change in the surface composition from AgAu to Au. After the surface is primarily Au, the observed activity should

FIG. 6. (a) The average Ag surface coverage across the entire material as a function of the temperature. [(b)-(e)] Histograms of Ag coverages at various temperatures.

increase again as the temperature increases, which is what is observed experimentally. Further, in the case of nanoporous Au, where the pure Au surface is inactive, the activity of the AgAu material increases to a peak around 310 K and then decreases monotonically.⁴ Thus, our results provide a possible explanation for why the activity of AgAu catalysts varies with the temperature and can have a peak at a moderate temperature.

The properties and behavior of nanoporous Au catalysts can depend on the preparation method and the reaction, which may affect our general conclusions. For example, we assume a dilute alloy with an Ag concentration of approximately 2%, which is typical for nanoporous Au, but the Ag concentrations can range from <1% to $\approx 10\%$.⁶⁵ The surface structure can be expected to vary depending on the bulk concentration, and indeed reactor studies show that the Ag concentration affects both the activity and selectivity.^{1,4} Further, Ag may not be uniformly distributed throughout the material.⁶⁶ Similarly, the ligament size can vary with the preparation method and time.⁶⁵ We assume that Ag is necessary for O₂ dissociation, based on the inactivity of nanoporous Au without its presence⁴ and on the results from previous experimental and computational studies,^{15,34,67,68} however, other mechanisms for O₂ dissociation have also been suggested.⁶⁹ Finally, reactions with more complex chemical pathways may require further care. Therefore, while these results give insight into an important, well-defined system, they might not be directly applicable to all experiments on nanoporous Au. Some of these assumptions can potentially be relaxed in future work.

In conclusion, we have studied the surface structure of a section of nanoporous Au taken from an experimental sample by combining LBM simulations of hydrodynamic flows and thermodynamic modeling based on DFT calculations. The reactant and product pressures at the surface vary by several orders of magnitude, resulting in different surface structures throughout the material. At typical reaction temperatures, significant portions of the material are inactive due to the low local O₂ pressure. Our results rationalize the temperature dependence of the AgAu alloys for oxidation reactions, as at high temperatures the surface becomes pure Au, which has a lower intrinsic activity than the AgAu alloy surface. Our work sets the stage for future studies on three-dimensional fluid dynamic effects or the explicit coupling of kinetic models to the nanoscale flow.

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