JCTC Journal of Chemical Theory and Computation

Kinetic Model of Surface Segregation in Pt-Based Alloys

Yuguang Ma and Perla B. Balbuena*

Department of Chemical Engineering, Texas A&M University, College Station, Texas 77843

Received July 11, 2008

Abstract: A new vacancy model describes the kinetic process of surface segregation on clean surfaces via atomic movement through vacancies. The detailed segregation mechanism of two impurity metals (Au and Co) in Pt(111) is examined using periodic density functional theory, carefully evaluating energy barriers for each step in the segregation process. Au shows a strong surface segregation trend to the clean Pt(111) surface, while Co segregating to the surface is neither thermodynamically nor kinetically favorable.

Introduction

Platinum has become the most popular cathode electrocatalyst in polymer electrode membrane (PEM) fuel cells. However, its relatively sluggish kinetics for the oxygen reduction reaction (ORR) significantly limits the catalytic efficiency. In recent years, Pt-based alloys, composed of Pt and other transition metals, have been extensively investigated[1–7] owing to their enhanced ORR activity. The improvement of catalytic activities can be attributed to the modification of the geometric and electronic properties in the alloys. Surface segregation has been found to play a key role in the process. For example, Stamenkovic et al. compared the kinetics of the ORR on bulk Pt_3Co alloys and on Pt-skin structures produced by Pt segregating to the outmost layer of the annealed alloy surface. They noted that the ORR is uniquely active on Pt-skin surfaces and the reaction rate is four times that of the pure Pt catalyst.[6] On the other hand, Pt-based alloys, as cathode electrocatalysts, possess enhanced stability compared to pure Pt.[8,9] Some recent studies have revealed that the surface structure of these alloys differs considerably from that in the bulk: A pure Pt-skin is formed in the outmost layer of the alloys due to surface segregation of Pt atoms.[4,6,7,10–12] Consequently, the enhanced stability of Pt-based catalysts is also closely related to surface segregation.

Owing to the importance of surface segregation for Pt-based alloys, numerous studies have been carried out using modern experimental and computational techniques.[2,6,9–11,13–27] For many Pt alloy systems, segregation trends have been unambiguously identified, and the components of surface and subsurface regions have successfully been characterized. Nevertheless, some details of segregation are not completely understood. Particularly, the kinetics of surface segregation, which is critical to elucidate the driving forces and the process of this phenomenon, has barely been addressed at a molecular level.

In this work, we study the segregation mechanism using a vacancy model, on the basis of first principles calculations. The model includes a Pt slab with impurity metal atoms which allow the metal atoms moving to the surface through vacancies. A series of steps, including vacancy formation, metal atom migration, and vacancy regeneration, are proposed to describe the kinetics of surface segregation in this model. Two impurity metals, Au and Co, are employed due to their different segregation tendencies to clean Pt(111) surfaces:[28] Au shows strong surface segregation in Pt−Au alloys,[29,30] whereas Co is usually unable to enrich Pt−Co alloy surfaces.[16,17] We remark that in this model we do not include other effects such as the presence of oxygenated adsorbates on the surface, the acid medium, and the applied electric field; all of them may influence the studied phenomena. Thus, this work focuses on a simplified analysis which in a first approximation neglects all the external effects and focuses on the kinetics and thermodynamics driven and determined only by the nature of the alloy. This is the first step before introducing other complexities in the system.

Computational Models

For Pt-based alloys, surface segregation may take place by annealing the alloys at high temperatures.[6,31] Such an annealing process generally occurs by diffusion of atoms in solid state alloys, and vacancies are needed to facilitate the movement of metal atoms. The phenomenon can also be observed in acidic solution, often with dissolution of the alloyed metal and rearrangement of Pt atoms.[4,12,32] The dissolution of metal atoms results in some defects on the alloy surface, which are critical to the rearrangement process. Based on the experimental information, we propose a vacancy model to elucidate the plausible segregation mechanism, using the basic assumption that surface segregation can be achieved by the movement of metal atoms through the vacancies. As illustrated in Figure 1, defects are initially formed on the surface by metal atoms leaving the surface and then metal atoms located at the sublayers filling out those vacant sites. The process leads to new vacancies formed in the sublayers, which allow surface metal atoms to move back to the subsurface or bulk atoms to fill out the new vacancies.

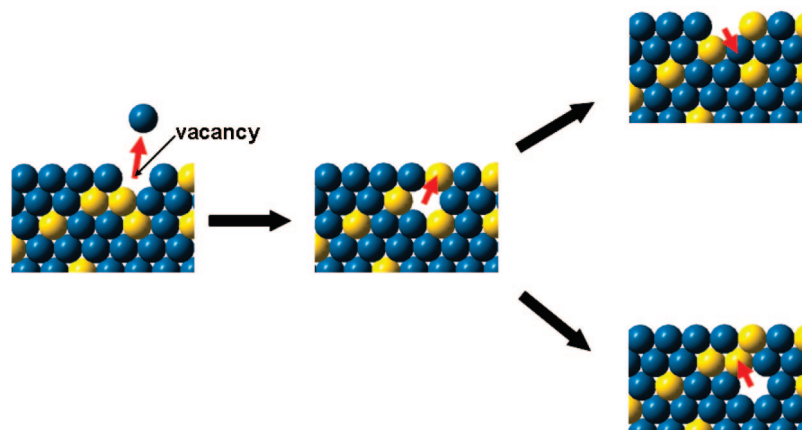* Corresponding author e-mail: balbuena@tamu.edu.

Figure 1. Plausible mechanism of surface segregation through vacancies.
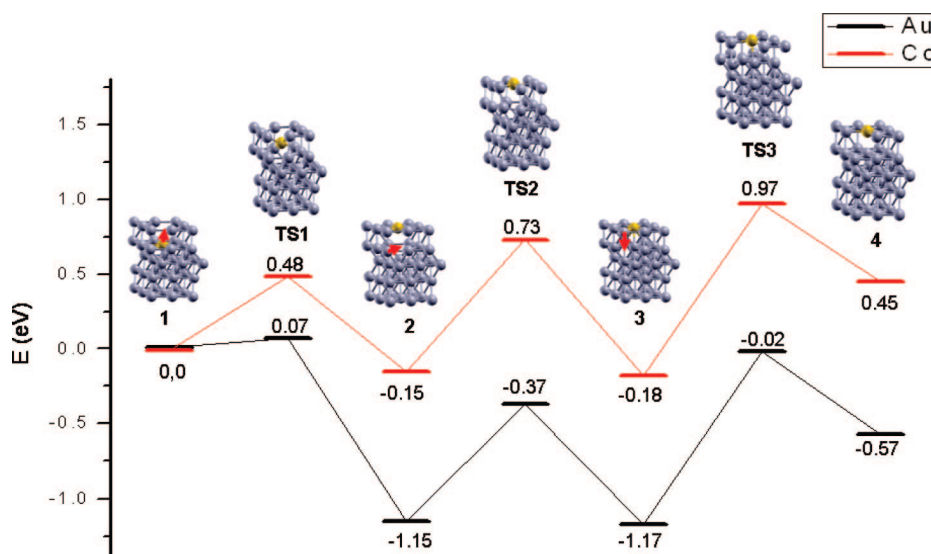

Figure 2. Calculated pathway and energetics for the impurity atoms segregating from the second layer to the Pt(111) surface. Grey and yellow spheres represent the Pt and impurity atoms, respectively.

Since Pt possesses a closed-packed fcc crystal structure and the most stable facet of the crystal is (111), our slab models were constructed using 3×3 (111) unit cells. Each slab consists of five-layers of metal atoms and six equivalent layers of vacuum. For each supercell, the initial position of the vacancy was set to the center of outmost layer, and the impurity atom was placed at the center of the second layer, as shown in Figure 2 (structure **1**). The atoms in the top three layers were allowed to relax to their lowest energy configuration, while the atoms of the bottom two layers were fixed to their bulk positions according to their optimized lattice constants.

The spin-polarized DFT calculations were performed using the Vienna *ab initio* simulation package (VASP),[33−37] in which the Kohn−Sham equations are solved by self-consistent algorithms. The valence electrons were described by plane wave basis sets with a cutoff energy of 350 eV, and the core electrons were replaced by the projector augmented wave (PAW) pseudopotentials[38,39] for improving the computation efficiency. The Brillouin zone was sampled with a $4 \times 4 \times 1$ Monkhorst-Pack k-point mesh for the periodic DFT calculations. The exchange-correlation functional was described within the generalized gradient approximation (GGA) proposed by Perdew, Burke, and Ernzerhof (PBE).[40] The Methfessel-Paxon method was employed to determine electron occupancies with a smearing width of 0.2 eV. The geometries of the slabs were relaxed until the force was convergent to 10^{-4} eV/Å. The minimum energy paths, transition states, and energy barriers were determined by the nudged elastic band method.[41,42]

Results and Discussion

We study a plausible pathway for the impurity atoms, Au and Co, moving from the second layer to the topmost layer in the Pt(111) slab. The segregation process thus includes interlayer migration of the impurity atom, vacancy movement at the second layer, and vacancy regeneration at the surface layer, as depicted in Figure 2.

The average bond lengths of Pt−Au and Pt−Co are determined as 2.81 Å and 2.74 Å in structure **1**, respectively. In the first step, the impurity atom moves to the surface layer, leaving a vacancy in the second layer. Our calculations show that Au is both thermodynamically and kinetically favorable for this migration, with a total energy change of −1.15 eV and a barrier of 0.07 eV, indicating a strong surface segregation tendency. The corresponding values for Co, −0.15 eV and 0.48 eV, are

Letter

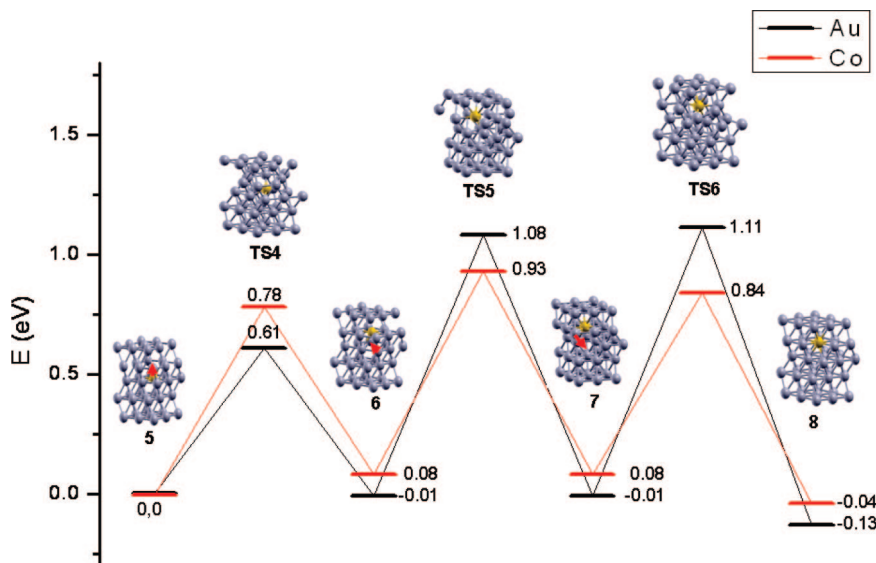*J. Chem. Theory Comput., Vol. 4, No. 12, 2008* **1993**

Figure 3. Calculated pathway and energetics for the impurity atoms segregating from the third layer to the second layer in Pt(111). Grey and yellow spheres represent the Pt and impurity atoms, respectively.

much higher than those of Au. Notably, the positions of the Au and Co atoms are considerably different in the transition state **TS1**, where the Au atom is closer to the surface layer (1.18 Å) than the Co atom (1.52 Å).

For continuing the surface segregation process, new vacancies must be formed at the surface. In acidic medium, this may be attained by dissolving surface metal atoms. The other approach, as we describe here, is via the migration of vacancies. This process is generally accomplished in two stages. The first stage (**2** to **3** in Figure 2) involves the intralayer movement of the Pt atoms neighboring the vacancies, and the second stage (**3** to **4** in Figure 2) includes the interlayer migration of the surface Pt atoms, leading to new vacancies in the surface. The detailed pathway can be found in Figure 2: From **2** to **3**, the total energy of the slab only changes very slightly, around -0.02 to -0.03 eV. The movement of a second layer Pt atom to the existent vacancy needs to surpass a barrier of 0.78 eV and 0.88 eV for the Pt−Au and Pt−Co alloys, respectively. The energy barrier arises primarily from the repulsion of neighboring Pt atoms. For the Pt−Au alloy, the Pt−Pt bond length decreases from 2.72−2.74 Å in **2** to 2.54−2.60 Å in **TS2**. A similar trend is observed for the Pt−Co alloy: the bond length varies from 2.73−2.74 Å in **2** to 2.55−2.61 Å in **TS2**. In the following step (**3** to **TS3**), the surface Pt atoms move down to occupy the vacancies in the second layer. The interlayer migration is determined as the rate-determining step (RDS) owing to its relatively high energy barrier (1.15 eV for both alloys). In the transition state (**TS3**), the migrated Pt atom is closer to the second layer than to the surface layer for both the Pt−Au and Pt−Co systems, suggesting an endothermic step in the conversion from **3** to **4**. Our calculations further verify that the step is not energetically favored, with endothermicity of 0.60 eV and 0.63 eV for Pt−Au and Pt−Co.

Previous experimental and theoretical studies have clearly revealed the segregation tendency for clean surfaces of Pt−Au and Pt−Co alloys. Au enriches strongly the surface of Pt-based alloys, whereas Co does not show segregation tendency. Our segregation model can successfully interpret these phenomena, particularly, from a kinetics viewpoint. The pathway from **1** to

4 describes a complete cycle in which an impurity atom in the second layer segregates to the Pt(111) surface. The process is exothermic (-0.57 eV) for the Pt−Au system, whereas it is endothermic (0.45 eV) for the Pt−Co system. This leads to the conclusion that Au surface segregation is thermodynamically favorable, consistent with previous studies.[26,28−30] Furthermore, our model reveals that Au segregation to the Pt(111) surface is kinetically feasible. Once vacancies are formed in the second layer, either Pt atoms or Au atoms at the surface can move down to the second layer. The steps correspond to conversions from **3** to **4** and from **2** to **1** in Figure 2. Comparing the two competitive steps, we notice that the latter one possesses a higher energy barrier (1.22 eV) than the former one (1.15 eV), indicating that Au antisegregation is unlikely to take place. For the Pt−Co alloy, the conversion from **2** to **1** has an energy barrier of 0.63 eV, much lower than that of the competitive step from **3** to **4** (1.15 eV), suggesting the surface Co atoms have a stronger tendency to migrate to the second layer compared to the Pt atoms. Accordingly, structure **4** most likely will not be formed, and thus the continuous segregation of Co cannot be reached. Therefore, Co segregating to the clean Pt(111) surface is both thermodynamically unfavorable and kinetically prohibitive according to our model.

We also examine a similar pathway involving segregation of impurity atoms from the third layer to the second layer. The complete process is shown in Figure 3. In the first step, the impurity atoms at the third layer move up to the vacancies at the second layer. The conversion from **5** to **6** only leads to a slight energy change, reported as -0.01 eV and 0.08 eV for the Pt−Au and Pt−Co systems. The energy barrier for the step (0.61 eV for Pt−Au and 0.78 eV for Pt−Co) is much higher than the similar conversion from **1** to **2**. This may be attributed to the steric effect: The half-open vacancies on the surface can provide more spacious room for the migration of metal atoms, while the vacancies at the second layer that are surrounded by atoms in all directions may result in space congestion in the process. For example, the distance of Au and the neighboring Pt atoms is 2.62−2.65 Å in **TS1** and is decreased to 2.60 Å in **TS4**. During interlayer movement of the Pt atom (**6** to **7**), energy

is approximately conserved. In this step, the barrier of the Pt−Au alloy is around 0.25 eV higher than that of the Pt−Co alloy. The step of **7** to **8** involving the downward movement of the Pt-atom, with an exothermicity of −0.12 eV for both alloys, differs considerably from the endothermic step of **3**-**4**. In addition, the energy barrier is also found to be lower than that in step of **3**-**4**, particularly, for the Pt−Co system. These results suggest that Pt diffusion from the second layer to the third layer is more energetically favorable than the similar diffusion from the surface to the second layer.

For the Pt−Co system, steps **5**-**6**, **6**-**7**, and **7**-**8** possess comparable barriers, which are 0.78 eV, 0.84 eV, and 0.75 eV, respectively. Since there is no RDS in the process, the segregation rate of Co is determined by all three steps. For the Pt−Au system, the segregation rate is mainly controlled by steps **5**-**6** and **6**-**7**, the intralayer and interlayer migration of Pt atoms. On the other hand, a small exothermicity in the conversion from **5** to **8** makes the segregation of Au/Co possibly feasible. However, as shown in Figure 3, each step in the process **5** to **8** is either mildly exothermic or mildly endothermic. Therefore, given enough energy to overcome the energy barriers, the segregation process is reversible, and the direction can be affected or determined by other related processes.

To make connection to the diffusion process of the impurity, we use the equation that gives the diffusion coefficient D due to atomic substitutional motion[43]

$$D = \frac{1}{6}\alpha^2 z \nu \chi_v \ \exp\left(\frac{-\Delta G_m}{kT}\right) \qquad (1)$$

where

$$\alpha = a/\sqrt{2}$$

is the jump distance for an fcc metal with $a = 3.97$ Å the calculated lattice constant of the Pt lattice, z is the bulk coordination number $= 12$, and ν is the vibration frequency of a metal atom, estimated as 10^{13} s^{-1}.[43] Taking ΔG_m as the calculated activation energy for migration of the Co impurity (0.48 eV), we can estimate the concentration of vacancies X_v required for a given value of the diffusion coefficient. Values of the diffusion coefficients of Co growing an ultrathin film on a Pt(111) surface have been reported[44] to follow an Arrhenius form as a function of temperature with a pre-exponential factor of 6.6×10^{-11} cm^2/s and an activation barrier of 0.90 eV; we used these experimental values to estimate the vacancy concentration needed for such diffusion using our calculated values and eq 1. For comparison, we also report the concentration of surface vacancies obtained by the Boltzmann factor using our calculated activation energy for surface vacancy formation in the case of Co impurities (−1.15 eV). The results based solely on our calculated vacancy energy formation shown in Table 1 are in closer agreement with the temperature dependence reported by a recent study of vacancy formation and atomic migration in fcc Al.[45]

Conclusions

The vacancy model presented the paper reasonably explains the well-known segregation trends of Au and Co to the Pt(111) surface. More importantly, the model provides an approach to evaluate the energy barriers in the process, which is crucial to study the kinetic properties of surface segregation. As mentioned

Table 1. Estimated Concentration of Vacancies Needed for Migration of Infinitely Diluted Co Impurities Using Eq *1* and Experimental Diffusion Coefficients from Ref 43 and Using the Activation Energies for Surface Vacancy Formation Obtained in This Work

temperature (K)	vacancy concentration according to experimental diffusion and eq 1	vacancy concentration based on calculated activation energy for vacancy formation
300	3.70691E-16	4.87946E-20
500	2.45578E-13	2.58835E-12
1000	3.2068E-11	1.60884E-06
1500	1.62692E-10	0.000137301
2000	3.66449E-10	0.001268399

in the Introduction, this is a systematic approach to evaluate the basic segregation steps of an infinitely diluted impurity determined only by the nature of the alloy. Future work using this approach may address other factors such as alloy composition, presence of adsorbates, and/or solvents, among others.

References

(1) Paulus, U. A.; Wokaun, A.; Scherer, G. G.; Schmidt, T. J.; Stamenkovic, V.; Radmilovic, V.; Markovic, N. M.; Ross, P. N. Oxygen Reduction on Carbon-Supported Pt-Ni and Pt-Co Alloy Catalysts. *J. Phys. Chem. B* **2002**, *106*, 4181–4191.

(2) Mun, B. S.; Watanabe, M.; Rossi, M.; Stamenkovic, V.; Markovic, N. M.; Ross, P. N., Jr. A study of electronic structures of Pt3M (M=Ti,V,Cr,Fe,Co,Ni) polycrystalline alloys with valence-band photoemission spectroscopy. *J. Chem. Phys.* **2005**, *123*, 204717/204711–204717/204714.

(3) Kitchin, J. R.; Norskov, J. K.; Barteau, M. A.; Chen, J. G. Modification of the surface electronic and chemical properties of Pt(111) by subsurface 3d transition metals. *J. Chem. Phys.* **2004**, *120*, 10240–10246.

(4) Toda, T.; Igarashi, H.; Uchida, H.; Watanabe, M. Enhancement of the electroreduction of oxygen on Pt alloys with Fe, Ni, and Co. *J. Electrochem. Soc.* **1999**, *146*, 3750–3756.

(5) Mukerjee, S.; Srinivasan, S.; Soriaga, M. P. Role of structural and electronic properties of Pt and Pt alloys on electrocatalysis of oxygen reduction. An in situ XANES and EXAFS investigation. *J. Electrochem. Soc.* **1995**, *142*, 1409–1422.

(6) Stamenkovic, V.; Schmidt, T. J.; Ross, P. N.; Markovic, N. M. Surface Composition Effects in Electrocatalysis: Kinetics of Oxygen Reduction on Well-Defined Pt3Ni and Pt3Co Alloy Surfaces. *J. Phys. Chem. B* **2002**, *106*, 11970–11979.

(7) Stamenkovic, V. R.; Fowler, B.; Mun, B. S.; Wang, G.; Ross, P. N.; Lucas, C. A.; Markovic, N. M. Improved Oxygen Reduction Activity on Pt3Ni(111) via Increased Surface Site Availability. *Science (Washington, DC, U. S.)* **2007**, *315*, 493–497.

(8) Yu, P.; Pemberton, M.; Plasse, P. PtCo/C cathode catalyst for improved durability in PEMFCs. *J. Power Sour.* **2005**, *144*, 11–20.

(9) Menning, C. A.; Hwu, H. H.; Chen, J. G. Experimental and Theoretical Investigation of the Stability of Pt-3d-Pt(111) Bimetallic Surfaces under Oxygen Environment. *J. Phys. Chem. B* **2006**, *110*, 15471–15477.

Letter

J. Chem. Theory Comput., Vol. 4, No. 12, 2008 **1995**

(10) Stamenkovic, V.; Schmidt, T. J.; Ross, P. N.; Markovic, N. M. Surface segregation effects in electrocatalysis: kinetics of oxygen reduction reaction on polycrystalline Pt3Ni alloy surfaces. *J. Electroanal. Chem.* **2003**, *554−555*, 191–199.

(11) Stamenkovic, V. R.; Mun, B. S.; Mayrhofer, K. J. J.; Ross, P. N.; Markovic, N. M. Effect of Surface Composition on Electronic Structure, Stability, and Electrocatalytic Properties of Pt-Transition Metal Alloys: Pt-Skin versus Pt-Skeleton Surfaces. *J. Am. Chem. Soc.* **2006**, *128*, 8813–8819.

(12) Wan, L.-J.; Moriyama, T.; Ito, M.; Uchida, H.; Watanabe, M. In situ STM imaging of surface dissolution and rearrangement of a Pt-Fe alloy electrocatalyst in electrolyte solution. *Chem. Commun. (Cambridge, U. K.)* **2002**, *n/a*, 58–59.

(13) van den Oetelaar, L. C. A.; Nooij, O. W.; Oerlemans, S.; Denier van der Gon, A. W.; Brongersma, H. H.; Lefferts, L.; van Veen, J. A. R. Surface Segregation in Supported Pd-Pt Nanoclusters and Alloys. *J. Phys. Chem. B* **1998**, *102*, 3445–3455.

(14) Deckers, S.; Habraken, F. H. P. M.; Van der Weg, W. F.; Denier van der Gon, A. W.; Pluis, B.; Van der Veen, J. F.; Baudoing, R. Segregation at the platinum-nickel (Pt0.5Ni0.5)(111) surface studied by medium-energy ion scattering. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1990**, *42*, 3253–3259.

(15) Gauthier, Y.; Senhaji, A.; Legrand, B.; Treglia, G.; Becker, C.; Wandelt, K. An unusual composition profile. A LEED-TBIM study of Pt25Cu75(1 1 1). *Surf. Sci.* **2003**, *527*, 71–79.

(16) Gauthier, Y.; Baudoing-Savois, R.; Bugnard, J. M.; Hebenstreit, W.; Schmid, M.; Varga, P. Segregation and chemical ordering in the surface layers of Pt25Co75(111). A LEED/STM study. *Surf. Sci.* **2000**, *466*, 155–166.

(17) Gauthier, Y.; Baudoing-Savois, R.; Rosink, J. J. W. M.; Sotto, M. LEED study of Pt25Co75(111). *Surf. Sci.* **1993**, *297*, 193–201.

(18) Visser, R. F.; Roux, J. P. Segregation and oxidation studies on chromium, chromium-platinum (Cr5Pt) and Cr15Pt. *Appl. Surf. Sci.* **1991**, *51*, 115–124.

(19) Creemers, C.; Deurinck, P. Platinum segregation to the (111) surface of ordered Pt80Fe20: LEIS results and model simulations. *Surf. Interface Anal.* **1997**, *25*, 177–190.

(20) Hansen, P. L.; Molenbroek, A. M.; Ruban, A. V. Alloy Formation and Surface Segregation in Zeolite-Supported Pt-Pd Bimetallic Catalysts. *J. Phys. Chem. B* **1997**, *101*, 1861–1868.

(21) Grgur, B. N.; Markovic, N. M.; Ross, P. N., Jr. Electrooxidation of H2, CO, and H2/CO Mixtures on a Well-Characterized Pt70Mo30 Bulk Alloy Electrode. *J. Phys. Chem. B* **1998**, *102*, 2494–2501.

(22) Chen, W.; Severin, L.; Goethelid, M.; Hammer, M.; Cameron, S.; Paul, J. Electronic and geometric structure of clean Pt3Ti(111). *Phys. Rev. B: Condens. Matter Mater. Phys.* **1994**, *50*, 5620–5627.

(23) Brown, D.; Quinn, P. D.; Woodruff, D. P.; Noakes, T. C. Q.; Bailey, P. Surface and sub-surface segregation at the Pt25Rh75(1 1 1) surface. A medium energy ion scattering study. *Surf. Sci.* **2002**, *497*, 1–12.

(24) Attard, G. S.; Leclerc, S. A. A.; Maniguet, S.; Russell, A. E.; Nandhakumar, I.; Bartlett, P. N. Mesoporous Pt/Ru Alloy from the Hexagonal Lyotropic Liquid Crystalline Phase of a Nonionic Surfactant. *Chem. Mater.* **2001**, *13*, 1444–1446.

(25) Gasteiger, H. A.; Ross, P. N., Jr.; Cairns, E. J. LEIS and AES on sputtered and annealed polycrystalline Pt-Ru bulk alloys. *Surf. Sci.* **1993**, *293*, 67–80.

(26) Ruban, A. V.; Skriver, H. L.; Norskov, J. K. Surface segregation energies in transition-metal alloys. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1999**, *59*, 15990–16000.

(27) Menning, C. A.; Chen, J. G. Thermodynamics and kinetics of oxygen-induced segregation of 3d metals in Pt-3d-Pt(111) and Pt-3d-Pt(100) bimetallic structures. *J. Chem. Phys.* **2008**, *128*, 164703.

(28) Ma, Y.; Balbuena, P. B. Pt surface segregation in bimetallic Pt3M alloys: A density functional theory study. *Surf. Sci.* **2008**, *602*, 107–113.

(29) Tsong, T. T.; Ng, Y. S.; McLane, S. B., Jr. Surface segregation of a platinum-gold alloy: an atom probe field ion microscope investigation. *J. Chem. Phys.* **1980**, *73*, 1464–1468.

(30) Hoernstroem, S. E.; Johansson, L. I.; Flodstroem, A. Surface segregation in platinum-gold alloys studied using Auger electron spectroscopy. *Appl. Surf. Sci.* **1986**, *26*, 27–41.

(31) Beccat, P.; Gauthier, Y.; Baudoing-Savois, R.; Bertolini, J. C. Monotonous concentration profile and reconstruction at platinum-iron (Pt80Fe20)(111): LEED study of a catalyst. *Surf. Sci.* **1990**, *238*, 105–118.

(32) Watanabe, M.; Tsurumi, K.; Mizukami, T.; Nakamura, T.; Stonehart, P. Activity and stability of ordered and disordered Co-Pt alloys for phosphoric acid fuel cells. *J. Electrochem. Soc.* **1994**, *141*, 2659–2668.

(33) Kresse, G.; Furthmueller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1996**, *54*, 11169–11186.

(34) Kresse, G.; Hafner, J. Ab initio molecular-dynamics simulation of the liquid-metal-amorphous-semiconductor transition in germanium. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1994**, *49*, 14251–14269.

(35) Kresse, G.; Hafner, J. Ab initio molecular dynamics for open-shell transition metals. *Phys. Rev. B: Condens Matter Mater. Phys.* **1993**, *48*, 13115–13118.

(36) Kresse, G.; Hafner, J. Ab initio molecular dynamics of liquid metals. *Phys. Rev. B: Condens Matter Mater. Phys.* **1993**, *47*, 558–561.

(37) Kresse, G.; Furthmuller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **1996**, *6*, 15–50.

(38) Bloechl, P. E. Projector augmented-wave method. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1994**, *50*, 17953–17979.

(39) Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1999**, *59*, 1758–1775.

(40) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

(41) Mills, G.; Jonsson, H.; Schenter, G. K. Reversible work transition state theory: application to dissociative adsorption of hydrogen. *Surf. Sci.* **1995**, *324*, 305–337.

(42) Jonsson, H.; Mills, G.; Jacobsen, K. W. *Nudged Elastic Band Method for Finding Minimum Energy Paths of Transitions*; World Scientific: Singapore, 1998.

(43) Porter, D. A.; Easterling, K. E. *Phase transformations in metals and alloys*; Stanley Thornes: Cheltenham, 2000.

(44) Tsay, J. S.; Wu, Y. E.; Shern, C. S. Growth mode and inter-diffusion of Co on Pt(111). *Chin. J. Phys* **1997**, *35*, 610–616.

(45) Mantina, M.; Wang, Y.; Arroyave, R.; Chen, L. Q.; Liu, Z. K. First- principles calculation of self-diffusion coefficients. *Phys. Rev. Lett.* **2008**, *100*, 215901.