

A Journal of the Gesellschaft Deutscher Chemiker A Deutscher Chemiker GDCh International Edition www.angewandte.org

Accepted Article

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To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201906394 Angew. Chem. 10.1002/ange.201906394

Link to VoR: http://dx.doi.org/10.1002/anie.201906394 http://dx.doi.org/10.1002/ange.201906394

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Unmasking of recessive, efficient ruthenium sites with interstitial silicon for Pt-like electrocatalytic activity

Hui Chen,^{[a],#} Xuan Ai,^{[a],#} Wang Liu,^[a] Zhoubing Xie,^[a] Weiqiang Feng,^[b] Wei Chen,^[c] Xiaoxin Zou^{*,[a]}

Abstract: The fundamental understanding and rational manipulation of catalytic site preference at extended solid surfaces is crucial in our efforts to search for advanced catalysts. Herein we find that the Ru top sites at metallic ruthenium surface have efficient Pt-like activity for the hydrogen evolution reaction (HER), but they are relatively recessive to their adjacent, less active Ru₃-hollow sites due to the stronger hydrogen-binding ability of the latter. We also present an interstitial incorporation strategy for the transformation of the Ru top sites from recessiveness to dominance, while maintaining Pt-like catalytic activity. Our joint theoretical and experimental studies further identify RuSi intermetallic as a highly active, non-Pt material for catalyzing the HER, because of its suitable electronic structure governed by a good balance of ligand and strain effects.

The in-depth understanding of characteristics of catalytic sites at extended solid surfaces is instructive for rational catalyst design. The Sabatier principle presents a general qualitative rule: for an optimal catalyst there is a moderate bond strength between catalytic site and key intermediate.^[1] That is, a good catalyst should bind the key intermediate to its catalytic site strongly enough to activate it, yet not too strongly to enable desorption of the product. Benefiting from the progress in density functional theory (DFT) calculations, adsorption energy of reaction intermediate can be used to quantitatively describe the bond strength and thereby to evaluate catalytic activity of each surface site.^[2] At a complex, extended solid surface, there are usually several types of possible catalytic sites with different adsorption properties (also known as catalytic site diversity). The most stable adsorption sites are the most favorable ones for catalysis, and their activities more closely reflect the real activity of catalyst (also known as catalytic site dominance).^[3] Thus, for a given catalytic site to be a desirable one, it is better to possess moderate ability to bind the key intermediate, while а simultaneously being dominant to other adjacent sites.

To demonstrate this idea, we chose HER electrocatalysis as a model reaction, which is involved in many renewable energy-related technologies. The adsorption free energy of atomic hydrogen (ΔG_{H^*}) is proven to be a reliable descriptor for quantifying the aforementioned bond strength and thereby evaluating the HER activity of a given catalytic site.^[4] For an optimum HER catalyst, its catalytic sites should have near-zero ΔG_{H^*} value. The benchmark catalyst Pt is such a material with

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suitable hydrogen adsorption properties. While a number of inexpensive materials are identified as promising alternatives to expensive Pt catalysts,^[5] most of them still exhibit catalytic activity much lower than Pt. Very recently, despite the metallic Ru catalyst with an intrinsically moderate HER activity, a few of Ru-based nanomaterials,^[6] especially those coupling with nanocarbons, are shown to give remarkable HER activity close to the Pt catalysts. However, it remains unclear what changes of Ru-based catalytic sites occur behind the activity enhancement, and a general guiding principle for engineering Ru-based catalytic sites is also not available.

Herein, we present a joint theoretical and experimental study that reveals the importance of catalytic site preference in catalytic activity for HER of Ru-based catalysts. We find that although the Ru top sites at metallic Ru surface have Pt-like catalytic activity for HER, they are recessive to the adjacent, less active Ru₃-hollow sites. By incorporating appropriate interstitial atoms to form intermetallics, we can unmask the recessive, efficient Ru top sites, generating novel non-Pt HER catalyst with Pt-like activity.



Figure 1. a) The stable H adsorption sites and b) their calculated ΔG_{H^*} on the Ru(0001) surface. c) Schematic illustration of interstitial incorporation strategy for transformation of Ru top sites from recessiveness to dominance. d) The stable H adsorption sites and e) their calculated ΔG_{H^*} on the RuSi(110) surface. f) ΔG_{H^*} at various hydrogen coverages for h1 site on the Ru(0001) surface, Ru top site on the RuSi(110) surface and Pt top site on the Pt(111) surface.

DFT calculations are conducted to evaluate the H adsorption properties and HER activities of the possible catalytic sites on the Ru(0001) surface (Figure S1 and Table S1 in Supporting Information (SI)), a representative model surface of metallic Ru.^[7] The results (Figure 1a) show that the stable H adsorption sites on the Ru(0001) surface include Ru top site and two types of Ru₃-hollow sites (*i.e.*, h1 and h2 sites). Figures 1b and S2 in SI further reveal that the Ru top site has a near-zero ΔG_{H^*} (-0.07 eV), whereas the Ru₃-hollow sites give largely negative ΔG_{H^*} values of around -0.45 eV. This indicates that despite its high Pt-like catalytic activity for HER, the Ru top site is relatively recessive because the adjacent Ru₃-hollow sites as its rival sites are energetically more favorable for hydrogen adsorption.

In order to transform the highly active Ru top site from recessiveness to dominance, we present an interstitial

incorporation strategy to eliminate the Ru₃-hollow sites (Figure 1c). Silicon is found to be an appropriate interstitial atom by constructing CsCl-type RuSi intermetallic structure. The (110) surface of RuSi is the most exposed surfaces (Figure S3 and Table S2 in SI) and accounts for the largest surface proportion of 85% within the Wulff construction (Figure S4 in SI). Hence, the RuSi(110) surface was studied for further DFT calculations (Figure S5 and Table S3 in SI). As shown in Figure 1d, the Ru atoms are isolated by the neighboring Si atoms, with the Ru₃hollow site disappearing. The stable H adsorption sites on the RuSi(110) surface include two top sites (Ru and Si top sites) and two bridge sites (b1 and b2 sites). Among these catalytic sites (Figure 1e), the Ru top site on the RuSi(110) surface is found to be the most favorable site (or dominant site) for hydrogen adsorption, whilst maintaining the near-zero ΔG_{H^*} or Pt-like catalytic activity.

Figure 1f presents the comparison of $\Delta G_{\text{H}^{*}}$ values at the preferred adsorption sites on RuSi(110), Ru(0001) as well as Pt(111) surfaces (the model surface of Pt) under different H* coverages ($\theta_{\text{H}^{*}}$). The result shows, the absolute values of $\Delta G_{\text{H}^{*}}$ for the RuSi(110) surface are close to zero over the entire $\theta_{\text{H}^{*}}$ range, and they are smaller than those for the Ru(0001) and Pt(111) surfaces. This result further suggests that RuSi should be a very competitive, non-Pt material for catalyzing the HER.



Figure 2. a) Calculated ΔG_{H^*} at the stable H adsorption sites on the RuX(110) surfaces. The inset gives stable H adsorption sites on the RuX(110) surfaces. b) Relationship between ΔG_{H^*} at Ru top site and Ru *d*-band center. The inset explains how the variation of *d*-band center affects H adsorption energy. c) The *d*-band center and corresponding *d*-band width of the RuX(110) surfaces. d) The Ru-Ru and Ru-X bond lengths of the six RuX intermetallics. e) Calculated DOS of the RuSi(110) surface and COHP of Ru-Si bond.

To further understand the role of Si interstitial atom, a family of six CsCl-type RuX intermetallics (X = Si, Ge, Sn, Al, Ga and In) are investigated (Tables S3-S8 in SI). Figure 2a presents the stable H adsorption sites on the RuX(110) surfaces and their corresponding ΔG_{H^*} values. The results show that: (i) the RuX intermetallics (X = Si, Ge and Sn) have energetically favourable adsorption at the Ru top site, with RuSi exhibiting the most optimal ΔG_{H^*} value; (ii) The ΔG_{H^*} absolute values at the Ru top site periodically increase in the order: RuSi < RuGe < RuSn and RuAl < RuGa < RuIn. These results indicate that besides the local geometric structure of Ru catalytic site, its electronic structure should also be crucial for realizing efficient catalytic activity. Figures 2b and 2c show a good linear corrolation between ΔG_{H^*} value at the Ru top site and the *d*-band center, and an inverse relationship between *d*-band center and *d*-band width, the two key characters of electronic structure (Figure S6 and Table S9 in SI). As the d-band center downs away the Fermi level (Figure 2b, inset), the antibonding states become more occupied, resulting in weaker H adsorption and smaller ΔG_{H^*} value. Among the six RuX intermetallics, RuSi exhibits the most negative *d*-band center and near-zero ΔG_{H^*} at Ru top site.

Next, we attribute the modification of electronic properties in RuX to a combination of strain and ligand effects.^[8] On one hand, the incorporation of interstitial atoms in Ru can generate chemical strains and thereby result in the expansion of crystal lattice. All the six RuX intermetallics have much larger Ru-Ru bond lengths than matallic Ru (2.73 Å) and the Ru-Ru bond lengths increase in the order: RuSi < RuGe < RuSn and RuAl < RuGa < RuIn (Figure 2d). This variation is similar with the trend in electronic structure (Figure 2c). This result implies that the tensile strain, which can decrease the metal d-orbital overlap and lead to a narrower band width and a more positive d-band center, is a significant factor responsible for the modification of electronic properties. On the other hand, orbital hybrization between Ru and X atoms (termed the ligand effect) is another significant factor can modify the electronic structure. The ligand effect always results in a broadening of the metal d-band and a more negative *d*-band center.

The much negative *d*-band center of RuSi can be explained by the fact that among the six RuX intermatellics (Figure 2d and Table S10 in SI), for RuSi the smallest expansion in Ru-Ru bond length gives rise to the weakest strain effect, and simutinously, the shortest Ru-X bond length means the strongest orbital hybrization between Ru and X atoms (or ligand effect). The orbital hybrization between Ru and Si atoms for RuSi is studied by its density of the states (DOS) and the crystal orbital Hamiltonian population (COHP) for Ru-Si bond (Figure 2e). The results reveal that there are the DOS overlap and the bonding between Ru 3d orbital and Si 2s-2p obitals. Overall, the above results imply that the good balance of strain and ligand effects render RuSi suitable electronic structure and thus a near-zero ΔG_{H^*} value at Ru top site.

Inspired by the theoretical results, we synthesized the RuSi material and then investigated its electrocatalytic activity for the HER. The phase-pure RuSi sample traditionally had to be synthesized by the direct reaction of ruthenium–silicon powders at high pressure (> 7.8 GPa).^[9] Here, we present the synthesis of phase-pure RuSi nanoparticles without high pressure by employing a magnesiothermic reduction reaction with RuCl₃, Si and Mg as the starting materials (see experimental details in SI). The formation of RuSi under relatively mild conditions is mainly because the new route significantly lowers the reaction enthalpy in comparison with the traditional element reaction route (Figure S7 in SI). This method can also be extended to obtain the other Ru-Si phase Ru₂Si₃ (Figures S8 and S9 in SI).

The X-ray diffraction (XRD) pattern of the as-synthesized sample confirms that the material contains single-phase RuSi (Figure 3a). Scanning electron microscopy (SEM) image (Figure 3b) reveals that the material is composed of RuSi nanoparticles of 100-200 nm in size. Elemental mapping images (Figure 3c) show that the Ru and Si elements are homogeneously

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distributed over the entire nanoparticles. In high-resolution transmission electron microscopy (HRTEM) image (Figures 3d), the interplanar distances of 0.29 nm and 0.21 nm can be assigned to the (001) and (110) crystallographic planes of RuSi, respectively. The angle of 90° between the two planes is consistent with the theoretical value. This result, coupled with the corresponding fast Fourier transform image (Figures 3d, inset), suggests that the exposed facet is {110}.



Figure 3. a) XRD pattern, b) SEM image, c) STEM image and the corresponding elemental mapping images, and d) HRTEM image of RuSi. Inset shows the corresponding fast Fourier transform image. The standard diffraction pattern for RuSi (red line) is also included in Figure 3a.

The RuSi is further characterized by X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS). XPS analysis presents that the surface atomic ratio of Ru and Si is close to 1:1. Figure 4a shows Ru 3d XPS spectra for RuSi and the reference samples (RuO₂ and Ru), and Figure 4b shows Si 2p XPS spectra for RuSi and the reference samples (SiO₂ and Si). The Ru 3d XPS peaks for RuSi exhibit a shift toward lower binding energy relative to those of metallic Ru, while the Si 2p XPS peak of RuSi shows a significant shift toward higher binding energy relative to that of Si. These results demonstrate that Ru atom is negatively charged and Si atom is positively charged in RuSi. The electron-richness of Ru atom in RuSi is also confirmed by X-ray absorption near-edge structure (XANES) spectra of Ru K-edge, which shows that the energy of absorption edge of RuSi is slightly lower than that of metallic Ru (Figure 4c). The charge states of Ru and Si in RuSi are also examined by Bader charge analysis, which reveals that 0.8 electrons (|e|) transfer from Si atom to Ru atom. Although the charges on Ru atom for RuSi and metallic Ru are different, the transferred charges from Ru atom to adsorbed H atom are almost the same (Figure S10 in SI).

Figure 4d shows the comparison of Fourier transform of extended X-ray absorption fine structure (EXAFS) at Ru K-edge of three Ru-containing samples. There are two prominent peaks for RuSi, which correspond to the Ru-Si bond and Ru-Ru bond, respectively. The Ru-Ru bond distance is longer than the Ru-Si bond distance in RuSi, and it is also longer than the Ru-Ru bond distance in metallic Ru. These results are consistent with their crystallographic data (Table S10, SI).



Figure 4. a) Ru 3d XPS spectra of RuSi, RuO₂ and Ru. b) Si 2p XPS spectra of RuSi, SiO₂ and Si. c) XANES spectra at the Ru K-edge of RuSi, RuO₂ and Ru. Inset is the partially enlarged detail of Figure 4c. d) Fourier transforms of the EXAFS spectra of RuSi, RuO₂ and Ru. Note that the Fourier transforms are not corrected for phase shift, so that the peak positions in Figure 4d are shorter than the actual bond lengths.

Next, the electrocatalytic activity of RuSi toward HER in acidic solution is studied (see Experimental Section and Figure S11 in SI). For comparative purpose, metallic Ru and Pt nanoparticles (Figures S12-13, SI) are also synthesized and their catalytic activities are evaluated under the same conditions. Figure 5a shows the polarization curves for the HER over RuSi, Ru, Pt and Si. While Si is inactive for HER, metallic Ru has a moderate catalytic activity. Contrary to Si and Ru, RuSi exhibits a remarkable catalytic activity toward HER, which is comparable to that of Pt and much better than that of Ru. In particular, RuSi requires an overpotential of 19 mV at 10 mA cm_{geo}⁻² current density (normalized by geometric area of the electrode). It is worth noting that RuSi also has a catalytic activity similar to the commercial 20 wt.% Pt/C catalyst (Figure S14, SI). In addition to high activity, RuSi enables good catalytic and structural stability during the HER (Figures S15 and S16, SI). Moreover, RuSi gives nearly 100 % faradaic efficiency during the HER (Figure S17 in SI), suggesting that the observed current can be exclusively attributed to the HER during electrocatalysis.

The specific activities of RuSi, Ru and Pt are further compared by normalizing the measured currents with respect to electrochemical surface areas (ECSAs). Figure 5b shows the comparison of the ECSAs of three materials and their specific activities, evaluated by overpotential required at 0.1 mA cm_{ECSA}^{-2} current density. This comparison reveals that their specific activities follow almost the same trend with their geometric area-normalized activities. The above results overall demonstrate, RuSi is a highly active, non-Pt material with Pt-like electroactivity for the HER.

Figure 5c shows the Tafel plots for RuSi, Ru and Pt. RuSi displays a small Tafel slope of 28.9 mV dec⁻¹, which is comparable to that of Pt (30.2 mV dec⁻¹) and much smaller than that of Ru (73.6 mV dec⁻¹). This suggests the rapid HER catalytic kinetics in the presence of RuSi. Additionally, the Tafel slope for RuSi suggests that the hydrogen evolution over this material should occur *via* a Volmer-Tafel mechanism, in which

the recombination of two adsorbed H atoms (H^{*} + H^{*} \rightarrow H₂) is rate-determining step.^[10] Such a Volmer-Tafel mechanism on the RuSi(110) surface is also studied theoretically. Figure 5d presents three typical steps: (i) two H atoms prefer to adsorbing on adjacent Ru top sites with H-H distance of 2.91 Å. (ii) The two H atoms form a transition state (TS) with H-H distance of 0.87 Å. (iii) A H₂ molecule forms and desorbs from the RuSi surface. The calculated activation energy (0.75 eV) for the Tafel reaction on RuSi(110) surface is a little lower than that on the Pt(111) surface (0.85 eV).^[11] The result further suggests that RuSi is an efficient catalyst for HER.



Figure 5. a) Polarization curves of RuSi, Ru, Pt and Si in 0.5 M H₂SO₄ solution with 85% *iR*-compensations. The current density is normalized by the geometric area of electrode. b) Comparison of ECSAs and overpotentials required at a current density of 0.1 mA cm⁻² (normalized by ECSAs) in 0.5 M H₂SO₄ solution. c) Tafel plots for HER over RuSi, Ru and Pt. d) Free energy diagrams of Tafel step of HER on the RuSi(110) surface. Inset shows the optimized adsorption structures for initial state, transition state (TS) and final state.

In conclusion, we have demonstrated the importance of manipulation of catalytic site preference for rational design of advanced catalysts, with Ru-based HER electrocatalyst as a model material system. We have also demonstrated that RuSi efficiently catalyzes the HER with Pt-like activity, due to the exposure of highly active Ru top sites.

Acknowledgements

X. Zou acknowledges the financial support from National Key R&D Program of China, Grant No. 2017YFA0207800, the National Natural Science Foundation of China (NSFC) Grant No. 21771079, Jilin Province Science and Technology Development Plan 20170101141JC, Program for JLU Science and Technology Innovative Research Team (JLUSTIRT) and Fok Ying Tung Education Foundation, Grant No. 161011. H. Chen acknowledges the financial support from the Postdoctoral Innovative Talent Support Program (Grant No. BX20180120) and the China Postdoctoral Science Foundation (Grant No. 2018M641771). W. Chen acknowledges the financial support from NSFC (21673093), Science and Technology Research Program of Education Department of Jilin Province (JJKH20190121KJ), Jilin Province Science and Technology Development Plan (20170101175JC). We thank NSFC (21621001) and the 111 Project (B17020) for financial support. We thank the beamline BL14W (Shanghai Synchrotron Radiation Facility) for the XAS measurements.

Keywords: site preference • hydrogen evolution reaction • electrocatalysis • electronic structure • non-Pt catalysts

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The importance of manipulation of catalytic site preference for rational design of advanced catalysts, with Rubased HER electrocatalyst as a model material system, is demonstrated. RuSi is identified as Pt-like HER electrocatalyst, due to the dominant change of efficient Ru top sites.

Efficient Ru top site: recessiveness \rightarrow dominance		
H adsorption sites		
Ru	Si atom	Si
R		000
Ru		RuSi

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Unmasking of recessive, efficient ruthenium sites with interstitial silicon for Pt-like electrocatalytic activity