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Interfacial and Alloying Effects on Activation of Ethanol from First-Principles Calculations

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ABSTRACT

We present first-principles density-functional theory study of ethanol activation at oxide/Rh(111) interface and the alloying effect on mitigating carbon deposition, which are essential to direct ethanol fuel cell (DEFC) anode reaction and steam reforming of ethanol (SRE) reaction. Our calculated results show that charge can transfer from Rh(111) substrate to MO_x chain (e.g., MoO₃ and MnO₂), or from MO_x chain (e.g., MgO, SnO₂, ZrO₂, and TiO₂) to Rh(111) substrate. The OH-binding strength is increased exponentially with M^{δ+} charge ranging from 1.4 to 2.2, which renders MnO₂/Rh(111) and MgO/Rh(111) interfaces weaker OH-binding, and thereby enhanced oxidizing functionality of OH* for promoting ethanol oxidation reaction (EOR) at DEFC anode. For efficient C-C bond breaking, a large number of Rh ensemble sizes are critically needed at the interface of MO_x/Rh(111). We found that Rh₁Au₃ near surface alloy has the weakest C* and CO* binding, followed by Rh₁Cu₃ and Rh₁Pd₃ near surface alloys, while Rh₁Ir₃ and Rh₁Ru₃ surface alloys have the C* and CO* binding strength similar to pure Rh metal. The general implication of this study is that by engineering alloyed structure of weakened C* and CO* binding augmented with metal oxides of weakened OH-binding, high-performance DEFC anode or SRE catalysts can be identified.

1. Introduction

The increasing demand for clean energy has put bio-ethanol in the limelight as a sustainable fuel resource owing to its increased availability, ease of transportation/storage, higher energy density, less-toxic and environmental-benign nature. At current stage, ethanol has been used as raw material for many fuel-cell related processes including direct ethanol fuel cell (DEFC) (eq. 1-3) which generates electricity without constrained by Carnot cycle limitation¹, steam reforming of ethanol (SRE) (eq. 4), partial oxidation of ethanol (POE) (eq. 5), and autothermal reforming of ethanol (ARE) (eq. 6), all of which produce hydrogen feedstock for proton exchange membrane fuel cell (PEMFC).²⁻⁶ These processes provide promising routes of utilizing bio-ethanol as raw material for clean energy conversion and for realizing green chemistry:

However, ethanol oxidation reaction (EOR) (eq. 1) at DEFC anode is a complex twelve-electron transfer reaction involving various C₂ and C₁ reaction intermediates (e.g., acetaldehyde, acetic acid, CO, CH_x, and C).⁷⁻¹¹ Complete electro-oxidation of ethanol into CO₂ via direct C-C bond cleavage is mechanistically difficult except at extreme positive potentials.⁸⁻¹¹ Similarly, SRE is also a complex reaction network in which multiple reaction pathways are interconnected as a result of various C₂ and C₁ reaction intermediates produced at high reaction temperature.^{2, 6} Unlike EOR at low temperature of <100°C, SRE requires high reaction temperature of >400°C which can significantly affect both catalyst activity and product distributions. Both EOR and SRE face the similar challenges that (1) The C-C bond cleavage is the key elementary step for the subsequent reactions but kinetically difficult; (2) The formed CO*, CH_x*, and C* species are strongly adsorbed on the surface of metal catalysts (e.g., either base metals for SRE or noble metals for EOR) resulting in blocking active sites, slowing reaction kinetics, deterioration of catalyst's performance and stability. Thus, it's imperative to effectively remove these residues *in situ* by hydroxyl group OH* generated from H₂O dissociation on adjacent sites, most likely, of metal oxide.

For enhanced performance in reaction kinetics, it is vital to design a catalyst that can effectively break the C-C bond of ethanol in EOR and SRE while mitigating the accumulation of these over-bound carbon-containing deposits on metal catalyst. Much advancement has been achieved along this line. For example, bottom-up approach of catalyst design has been established for anode catalyst of DFEC by forming bimetallic alloy, introducing oxophilic metal, and synthesizing novel nanostructure of catalyst.^{7, 12-17} In optimizing alloy compositions, the binary or ternary systems including PtRh/SnO₂,⁷ PtIr/SnO₂/C,¹⁴ Ir₇₇Ru₂₃/C,¹³ Pd₈₆Sn₁₄/C,¹² Ir₇₁Sn₂₉/C,¹⁵ Pt₅₂Sn_(36-x)Rh₁₂/Sn_xO_{2x},¹⁷ and core-shell Pt₄₆@(SnO₂)₅₄¹⁶ have all demonstrated significantly higher electrochemical activity toward EOR compared to the commercial Pt/C catalyst.

At molecular scale, either EOR or SRE requires activation of C-H, O-H, C-C and C-O bonds of ethanol,¹⁸⁻¹⁹ leading to a series of reactions including dehydrogenation, decomposition, dehydration, hydrogenolysis and carbon deposition, which can occur competitively to generate various end-products. Among several noble metals, rhodium (Rh) is known to be not only an active component for the anode catalyst of DEFC,^{1, 7, 17} but also arguably the best and the most commonly used catalyst for SRE.^{2, 6, 20-24} The breaking of C-C bond catalyzed by metal surface is crucial,²⁵ but Rh alone is not sufficient to fully accomplish the catalytic activity for EOR or SRE. Several metal oxides (MO_x)^{3, 17, 21-24} such as MgO, ZnO, CeO₂, La₂O₃ and the most well-known SnO₂^{7, 14, 16-17} have exhibited indispensable catalytic functionality for promoting EOR or SRE due to their intrinsic basic and/or redox properties, which render them the natural active sites for H₂O dissociation and for promoting ethanol dehydrogenation while inhibiting dehydration. More importantly, the abundant hydroxyl OH* of high surface mobility²⁶ can effectively promote EOR or SRE via the removal of CO*, CH_x*, and C* residues deposited on metal surface while alleviating their poison effect. Accordingly, the choice of suitable metal oxide can significantly affect activity and selectivity of MO_x-supported Rh nanoparticle (NP) catalysts towards target products, i.e., CO₂ and H₂O in EOR, and CO₂ and H₂ in SRE.

The active sites of realistic supported NP catalyst can be found either on metal surface, or on support surface, or at the interface.²⁷ The fundamental understanding of reaction mechanism and active sites is still limited for ethanol activation on metal/oxide catalysts. In this regard, theoretical studies have been carried out mainly concerning ethanol decomposition in both EOR^{7, 13, 28-29} and SRE^{2, 6, 22, 30-34} on metal surface including Rh. Few studies were focused on interfacial effect,^{7, 33} which can be challenging due to its ill-defined and complex nature for theoretical modeling.³⁵⁻³⁶ Nonetheless, catalytic behavior at the interface has been known to be intriguing that can often yield improved catalytic activity and

selectivity.³⁷⁻³⁸ For metal-catalyzed EOR or SRE, little is known about the behavior of ethanol activation at the metal/support interface. Herein, we systematically investigated ethanol activation at $\text{MO}_x/\text{Rh}(111)$ interface, where $\text{M}=\text{Mo}, \text{Zr}, \text{Ti}, \text{Sn}, \text{Mg}, \text{Mn}$, by means of the spin-polarized periodic density functional theory (DFT) method. Furthermore, the alloying effects on mitigating C deposition were examined using alloyed Rh_1M_3 ($\text{M}=\text{Ir}, \text{Ru}, \text{Cu}, \text{Pd}, \text{Au}$) model aiming at exploring the alternative catalyst system.

2. Models and Methods

2.1. Models The interfacial interactions between MO_x ($\text{M}=\text{Mo}, \text{Zr}, \text{Ti}, \text{Sn}, \text{Mg}, \text{Mn}$) and Rh NPs were simulated using inverse-catalyst model,³⁹ in which MO_x chains were anchored on a four-layer Rh (111) surface of varied sizes with a vacuum of 15 Å between the slabs, ensuring the periodicity of MO_x chains best match that of Rh (111) and the introduced strain is minimal. Depending on the lattice of MO_x bulk, a slab of $p(4\times4)$, $p(6\times6)$, $p(5\times5)$, $p(6\times6)$, $p(4\times3)$, and $p(4\times4)$ Rh (111) supercell was assigned to MoO_3 , ZrO_2 , TiO_2 , SnO_2 , MgO , and MnO_2 chains, respectively, which introduces the lattice strain of 2.0%/MoO₃ unit, 1.5%/ZrO₂ unit, 0.6%/TiO₂ unit, 2.7%/SnO₂ unit, 3.3%/MgO unit, and 0.5%/MnO₂ unit into their initial structures of supported MO_x chain, respectively. The introduced strain is intended to be as small as possible without drastically increasing the supercell size and the computational cost therein. The initial structure of MO_x chain was adopted from the motif of MO_x bulk with which the most stable facet of NP catalyst is grown.

Alloys of Rh/M(111) ($\text{M} = \text{Cu}, \text{Pd}, \text{Ir}, \text{Au}$) and Rh/M(0001) ($\text{M} = \text{Ru}$) were used to explore their alloying effects on mitigating carbon deposition on metal surface and on catalyst stability. It's known that the equilibrium alloy surface is the outcome of minimizing Gibbs free energy after reordering of the atoms near the surface at a given temperature and pressure. Following the energetics that dictates segregation or antisegregation preference of Rh in M host,⁴⁰ we built four-layer $p(2\times2)$ Rh_1M_3 surface alloy (SA) by replacing the topmost layer of M with Rh, where $\text{M} = \text{Ir}, \text{Ru}$, and built four-layer $p(2\times2)$ Rh_1M_3 near surface alloy (NSA) by replacing the second topmost layer of M with Rh, where $\text{M} = \text{Cu}, \text{Pd}, \text{Au}$.

2.2. Computational Methods. The calculations were performed by using periodic DFT as implemented in the Vienna ab-initio simulation package (VASP)⁴¹⁻⁴². Ion-core electron interactions were described using the projected augmented wave method (PAW)⁴³⁻⁴⁴, and Perdew-Wang functional (GGA-PW91) with the generalized gradient approximation (GGA) was used to describe exchange-correlation effects.

The spin-polarized GGA-PW91 exchange-correlation functional⁴⁵ was used with [Rh]-5s¹4d⁸, [Mo]-4p⁶5s¹4d⁵, [Zr]-4s²4p⁶5s²4d², [Ti]-3s²3p⁶4s²3d², [Sn]-4d¹⁰5s²5p², [Mg]-2p⁶3s², [Mn]-3p⁶4s²3d⁵, [O]-2s²2p⁴, [C]-2s²2p², and [H]-1s treated as valence electrons. The Kohn–Sham orbitals are expanded in a plane-wave basis set with a kinetic energy cutoff of 400 eV. The conjugate gradient algorithm was used in optimization allowing the convergence of 10⁻⁴ eV in total energy and 10⁻² eV/Å in Hellmann-Feynman force on each atom. All atoms were allowed to fully relax except those of the bottom two layers that were fixed at their optimized bulk positions. The Brillouin-zone was sampled by a grid of k-points using the Monkhorst–Pack scheme⁴⁶ that should satisfy the convergence criteria for each supercell mentioned above. First-order Methfessel–Paxton smearing⁴⁷ of 0.1 eV was employed in the integration to speed up the convergence.

Binding energy (BE) is defined as $BE = E(\text{ads/slab}) - E(\text{ads}) - E(\text{slab})$, where E represents the total energy of ads/slab, adsorbate, and bare slab, respectively, ads=OH, or H, or ethanol in gas phase, and $E(\text{OH}) = E(\text{H}_2\text{O}) - E(\text{H}_2)/2$, $E(\text{H}) = E(\text{H}_2)/2$. The climbing-image nudged elastic band (CI-NEB) method⁴⁸⁻⁴⁹ was used to locate the transition state (TS) structure for C-C bond scission in elementary-step reaction: $\text{CHCO}^* \rightarrow \text{CH}^* + \text{CO}^*$.

3. Results and Discussion

3.1. $\text{MO}_x/\text{Rh}(111)$ surface structures and surface mobility of hydroxyl OH on MO_x

Fig.1. Optimized structures for MO_x ($\text{M}=\text{Mo}, \text{Zr}, \text{Ti}, \text{Sn}, \text{Mg}, \text{and Mn}$) chain deposited on $\text{Rh}(111)$ surface (upper panel) and OH pre-adsorbed at $\text{M}^{\delta+}$ sites of $\text{MO}_x/\text{Rh}(111)$ (lower panel). (a) $\text{MoO}_3/\text{Rh}(111)$, (b) $\text{ZrO}_2/\text{Rh}(111)$, (c) $\text{TiO}_2/\text{Rh}(111)$, (d) $\text{SnO}_2/\text{Rh}(111)$, (e) $\text{MgO}/\text{Rh}(111)$, (f) $\text{MnO}_2/\text{Rh}(111)$.

It's well established that an inverse model is important for a catalyst where the active participation of oxide support in elementary reactions plays an essential role in boosting the catalytic activity.^{37, 50} Herein, MO_x chain/ $\text{Rh}(111)$ (Figure 1) is only a simplified inverse model to simulate the interfacial effect of oxide-supported Rh NPs of optimal size (2–5 nm). Due to its high reactivity, on one hand, stand-alone MO_x chain would interact with $\text{Rh}(111)$ much stronger than realistic MO_x NP, on the other hand, additional under-coordinated sites under lattice strain are still available for representing interfacial sites albeit in a somewhat extreme form.³⁹ Note that the lattice strain of MO_x cannot be measured accurately in experiment but is likely to be introduced at the interface and may affect the activity of the NP catalysts. In Figure 1, various $\text{M}^{\delta+}$ and $\text{O}^{\delta-}$ sites can be seen to have the distinct bonding situations depending on the nature of MO_x , and the OH pre-adsorbed $\text{MO}_x/\text{Rh}(111)$ models were employed to mimic the realistic environment in which certain hydroxylation of MO_x surface is inevitable, i.e., the OH^* adsorbed at $\text{M}^{\delta+}$ sites and the H^* adsorbed at $\text{O}^{\delta-}$ sites via H_2O dissociation. Given that, OH^* essentially serves as an oxidizing agent in elementary steps of EOR (eq. 1) or SRE (eq. 4).

One can see that except for $\text{MoO}_3/\text{Rh}(111)$, adsorbed OH^* can only slightly affect the local structure of MO_x chain of $\text{MnO}_2/\text{Rh}(111)$, $\text{MgO}/\text{Rh}(111)$, $\text{SnO}_2/\text{Rh}(111)$, $\text{TiO}_2/\text{Rh}(111)$ and $\text{ZrO}_2/\text{Rh}(111)$, where OH -binding energy (BE-OH) is 0.20 eV, -0.15eV, -0.32eV, -0.33eV, and -0.42eV, respectively, stronger than those on metal surface (e.g., 0.12eV on $\text{Rh}(111)$, 0.89eV on $\text{Pt}(111)$ based on our calculations). Hydroxyl group OH^* from dissociated H_2O acts as Lewis base with its lone-pair electrons while $\text{M}^{\delta+}$ acts as Lewis acid, and OH -binding strength is primarily controlled by relative strength of Lewis acidity of $\text{M}^{\delta+}$ sites. Our Bader charge calculations verify that charge transfer is a two-way process: charge can transfer from $\text{Rh}(111)$ substrate to MO_x chain, or *vice versa*. We found that $\text{MoO}_3/\text{Rh}(111)$ and $\text{MnO}_2/\text{Rh}(111)$ have charge transfer from $\text{Rh}(111)$ to MO_x chain by $0.34e^-$ and $0.25e^-$ per MO_x unit, whereas $\text{MgO}/\text{Rh}(111)$, $\text{SnO}_2/\text{Rh}(111)$, $\text{ZrO}_2/\text{Rh}(111)$, and $\text{TiO}_2/\text{Rh}(111)$ have charge transfer from MO_x chain to $\text{Rh}(111)$ substrate by $0.69e^-$, $0.39e^-$, $0.34e^-$, and $0.01e^-$ per MO_x unit, respectively. This is not uncommon for MO_x/metal interfacial system,⁵¹⁻⁵² for example, the similar behavior was also found from Nb_xO_y clusters supported on $\text{Cu}(111)$ substrate⁵², where the reduced clusters donate electrons to the substrate. In general, the further away from its highest oxidation state,

the weaker Lewis acidity MO_x is. Relative Lewis acidity of MO_x chain is mainly determined by the differentiation of charge that $\text{M}^{\delta+}$ can possess with respect to its fully oxidized stoichiometric form. It's therefore expected that OH-binding strength is weaker at $\text{M}^{\delta+}$ sites of $\text{MoO}_3/\text{Rh}(111)$ and $\text{MnO}_2/\text{Rh}(111)$, but stronger at $\text{M}^{\delta+}$ sites of $\text{MgO}/\text{Rh}(111)$, $\text{SnO}_2/\text{Rh}(111)$, $\text{ZrO}_2/\text{Rh}(111)$ and $\text{TiO}_2/\text{Rh}(111)$ with respect to pure MO_x surfaces.

Fig.2. Binding energy of OH (BE-OH) on MO_x chain ($\text{M} = \text{Mo}, \text{Zr}, \text{Ti}, \text{Sn}, \text{Mg}$, and Mn) deposited on $\text{Rh}(111)$ surface as a function of Bader charge ($\text{M}^{\delta+}$). Empty square: deviation due to O-H...O hydrogen bonding being formed.

Indeed, our results show that OH-binding strength is increased exponentially with $\text{M}^{\delta+}$ charge ranging from 1.4 to 2.2, but is gradually leveled off as charge is further increased (Figure 2). Here, BE-OH on $\text{MoO}_3/\text{Rh}(111)$ is an anomaly (-1.64eV) falling off the fitted line of the exponential correlation. In Figure 1a, one can see that the OH^* adsorbed at $\text{Mo}^{\delta+}$ site forms strong H-bond with the adjacent $\text{O}^{\delta-}$ of MoO_3 leading to the substantial change of the local structure, even breaking the integrity of MoO_3 chain. The shorter O-H...O bond length of $2.49\text{\AA}$ indicates such an H-bond is indeed very strong that contributes to the extra binding ability. We should note that such a scenario of breaking O-Mo-O bonds by the dissociative adsorption of H_2O may not be the case for realistic interfaces considering the coordination of NP surface is much higher than stand-alone MO_x chain. Nonetheless, our calculated results provide a clear indication of such a tendency if OH-binding enhanced by H-bonding is too strong.

As is known, the weaker the OH binding is, the higher surface mobility of OH* it has. In this sense, MnO₂/Rh(111) and MgO/Rh(111) may work as good model catalysts to facilitate EOR or SRE by effectively removing CO*, CH_x*, and C* deposits on Rh surface.

3.2 Interfacial effect of MO_x (M= Mg, Mn)/Rh(111)

Fig.3. Optimized structures for ethanol adsorption at Rh site and at M^{δ+} sites. (a) Rh(111), (b) MnO₂/Rh(111), (c) OH-preadsorbed MnO₂/Rh(111), (d) MgO/Rh(111), (e) OH-preadsorbed MgO/Rh(111). Numeric values denote adsorption energy (in eV) and bond distance (in Å).

It's known that complete electro-oxidation of ethanol into CO₂ via direct C–C bond cleavage is mechanistically difficult.⁸⁻¹¹ Dehydrogenation of ethanol to acetaldehyde (CH₃CHO*) intermediate involving the activation of both the C–H and O–H bonds was suggested to be the important steps for subsequently producing a mixture of CO* and CH_x* intermediates and eventually the complete oxidation product (i.e., CO₂ and H₂O).⁸⁻¹¹ Previous studies^{7, 22, 28-34} have shown that in EOR or SRE, Rh preferentially catalyze ethanol dehydrogenation to acetaldehyde at initial stage followed by the sequential reactions involving the breaking of C–C and C–O bonds. It's also suggested that early dehydrogenation steps are likely more kinetically relevant than the cracking reactions as the early dehydrogenation possess activation barriers comparable to or greater than the C–C and C–O scissions of surface species which can be dehydrogenated further.¹⁸ Herein, we used early ethanol dehydrogenation to form acetaldehyde as a probe reaction to explore the interfacial effect introduced by MnO₂ and MgO chain on Rh(111). Two reaction pathways are most likely to occur on Rh(111):^{18, 30} (1) alkoxy route:

$\text{CH}_3\text{CH}_2\text{OH}^* \rightarrow \text{CH}_3\text{CH}_2\text{O}^* + \text{H}^* \rightarrow \text{CH}_3\text{CHO}^* + 2\text{H}^*$, via O-H bond scission forming ethoxy ($\text{CH}_3\text{CH}_2\text{O}^*$) intermediate; (2) hydroxyl route: $\text{CH}_3\text{CH}_2\text{OH}^* \rightarrow \text{CH}_3\text{CHOH}^* + \text{H}^* \rightarrow \text{CH}_3\text{CHO}^* + 2\text{H}^*$, via $\text{C}_\alpha\text{-H}$ bond scission forming 1-hydroxyethyl (CH_3CHOH^*) intermediate, where an effective dehydrogenation catalyst can be equally as an effective hydrogenation catalyst.⁵³

We first examined ethanol adsorption at both Rh and $\text{M}^{\delta+}$ ($\text{M}=\text{Mn}$ and Mg) site. As shown in Figure 3a, ethanol is adsorbed on Rh(111) surface via $\eta^1(\text{O})$ -configuration through hydroxyl O with C-C bond tilted away from the surface normal. The calculated BE is -0.41eV. Our results are consistent with previous findings that the same configuration was obtained up to 1/3 ML of ethanol coverage (BE:-0.36eV).³¹ In comparison, ethanol is only weakly adsorbed at $\text{Mn}^{\delta+}$ site via $\eta^1(\text{O})$ -configuration (BE:-0.08eV, Figure 4b), but is much stabilized at the interface of OH-preadsorbed $\text{MnO}_2/\text{Rh}(111)$ (BE:-0.79eV) due to H-bonding of hydroxyl H and $\text{O}^{\delta-}$ of MnO_2 ($\text{O}\cdots\text{H}$: 1.62 Å, Figure 4c). The bonding mechanism is different in that in the former case, 4d electron of Rh is donated to anti-bonding orbital of ethanol and in the latter case, lone-pair electrons of hydroxyl O is donated to empty states of $\text{M}^{\delta+}$ site. At $\text{Mg}^{\delta+}$ site, ethanol adsorption via $\eta^1(\text{O})$ -configuration is moderately strong (BE:-0.51eV, Figure 4d). This can be explained by that charge is transferred from MgO chain to Rh(111) substrate leaving $\text{Mg}^{\delta+}$ site more Lewis acidic, against weaker Lewis acidic site of $\text{Mn}^{\delta+}$ which accepts charge transfer from Rh(111) substrate. Note also that binding strength is only slightly changed for ethanol adsorbed at Rh site (BE:-0.30eV) if without H-bonding of hydroxyl H and $\text{O}^{\delta-}$ of MgO ($\text{O}\cdots\text{H}$: 2.24 Å, Figure 4d), suggesting MO_x chain can affect initial ethanol adsorption at Rh sites via H-bonding due to $\text{O}^{\delta-}$ of MO_x , rather than by altering the donation capability of Rh 4d electron from large-size Rh substrate.

Fig.4. Dehydrogenation of ethanol (a) resulting in the formation of ethoxy (b), 1-hydroxyethyl (c), and acetaldehyde (d) on Rh(111) surface.

As shown in Figure 4, the initial ethanol dehydrogenation on Rh(111) surface is feasible via either hydroxyl or alkoxy route. Formation of CH_3CHOH^* via $\text{C}_\alpha\text{-H}$ bond scission is slightly exothermic (ΔE : -0.03eV), while formation of $\text{CH}_3\text{CH}_2\text{O}^*$ via O-H bond scission has 0.11eV of endothermicity, agreeing well with the previous results (ΔE : -0.04eV and 0.16eV, respectively) on Rh(111).³⁰ This energetic ordering can also be found from dehydrogenation of ethanol on Pd(111) (ΔE : 0.32eV and 0.91eV, respectively).¹² Further dehydrogenation of CH_3CHOH^* to form CH_3CHO^* via O-H bond scission is also slightly exothermic (-0.04eV), and the adsorption mode for both species is $\eta^2(\text{C},\text{O})\mu^2$ -di- σ -configuration.

We noticed there existed discrepancies regarding the calculated energetics of reaction energy and activation barrier for ethanol dehydrogenation on Rh(111) surface.^{18, 30, 34, 54} For instance, Choi and Liu^{18, 30} reported -0.20eV of exothermicity for dehydrogenation of $\text{CH}_3\text{CH}_2\text{O}^*$ forming CH_3CHO^* with a barrier of 1.76eV, indicating forming acetaldehyde is less likely. By contrast, Sutton and Vlachos^{18, 30} reported -0.50eV of exothermicity and 0.69eV of activation barrier via ethoxy route, against those (-0.35eV and 0.61eV) via 1-hydroxyethyl route, suggesting both pathways are comparable and likely to occur. Consequently, the proposed reaction mechanism for ethanol decomposition can be varied, particularly, in the main route towards C-C and C-O bonds breaking. For example, the formation of the oxametallacycle ($\text{CH}_2\text{CH}_2\text{O}^*$) species was proposed to be the rate-determining step (RDS), subsequently leading to the formation of CHCO^* species, which is the precursor for C-C bond breaking.³⁰ In contrast, decomposition of ethanol on Rh was proposed to occur via sequential $\text{C}_\beta\text{-H}$ abstractions of CH_3COH^* to form CHCOH^* species, which undergoes C-C cleavage producing CH^* and COH^* species, or via a parallel pathway starting from CH_3CO^* to CHCO^* .¹⁸ Our main focus is on the interfacial effect of $\text{MO}_x/\text{Rh}(111)$ on C-H and O-H bond activation in elementary steps of ethanol dehydrogenation using Rh(111) as a reference, rather than on exploring which reaction route is most likely.

Fig.5. Key elementary steps in dehydrogenation of ethanol at the interface of OH-preadsorbed MnO₂/Rh(111). Formation of acetaldehyde (a) by C_α-H bond scission from ethoxy (b) and by O-H bond scission from 1-hydroxyethyl (c), formation of ethylene oxide (d) by C_β-H bond scission from ethoxy via transition state (e).

Our calculated results show that MnO₂ chain promotes neither hydroxyl nor alkoxy route in initial ethanol dehydrogenation (ΔE : 0.54eV vs 0.55eV), and forming acetaldehyde (Figure 5a) is equally accessible from either ethoxy or 1-hydroxyethyl intermediate in a thermoneutral process. Notably, O^{δ-} of MnO₂ chain can also serve as an active site for β -H abstraction forming ethylene oxide (CH₂CH₂O*, Figure 5d) in a endothermic process (ΔE :0.39eV) with a barrier of 0.96eV, nearly identical to those (ΔE :0.39eV, E_a:0.95eV) obtained from pure Rh(111) surface.³⁰ Nonetheless, considering that Mn^{δ+} and O^{δ-} sites are mostly populated with the adsorbed OH* and H* respectively, MnO₂ are less likely to serve as primary active sites for ethanol activation.

Moreover, the adsorption mode of CH₂CH₂O* at the interface (Figure 5d) resembles the five-member ring oxametallacycle obtained on Rh(111) surface,²⁵ suggesting a minimum number of Rh

ensemble size is mandatory for $\text{CH}_2\text{CH}_2\text{O}^*$ formation. The same ensemble-size requirement can be also found in elementary step of C-C bond scission: $\text{CHCO}^* \rightarrow \text{CH}^* + \text{CO}^*$ ($\Delta E: -0.53\text{eV}$, Figure 6), which was predicted to be the RDS for C-C bond breaking in ethanol decomposition.¹⁹ Similar results were obtained on pure Rh(111) surface ($\Delta E: -0.66\text{eV}$ and $E_a: 0.69\text{eV}$).³⁰ Here, we should note that the initial structures for optimization of initial-state CHCO^* and final-state $\text{CH}^* + \text{CO}^*$ were arranged in space as close to MnO_2 chain as possible, and reasonably in connected mode, but all were pushed back to Rh empty sites after optimization, where the dissociated CH^* and CO^* fragments occupy the 3-fold hollow site and adjacent atop site, respectively. This clearly indicates that C-C bond scission requires large ensemble size of Rh on catalyst surface, consistent with our previous experimental results,⁵⁵ and in this case, at least five surface atoms on Rh (111) facet are critically needed.

One can also see that no direct role of pre-adsorbed OH^* can be identified from these reactions though initial structures were arranged reasonably in connected mode, suggesting hydroxylated MnO_2 mainly act as oxidizer for removing over-binding CO^* , CH_x^* , and C^* species after being formed on Rh surface.

Fig.6. C-C bond scission of CHCO^* forming CH^* and CO^* at $\text{MnO}_2/\text{Rh}(111)$ interface.

On the other hand, ethanol dehydrogenation at $\text{MgO}/\text{Rh}(111)$ interface can be complex and varied depending on whether the geometry of MgO chain is fixed or allowed to relax during the optimization (Figure 7). In either case, hydroxyl group of ethanol interacts noticeably with MgO chain deposited on $\text{Rh}(111)$ surface. In initial dehydrogenation step, hydroxyl H of ethanol can interact with OH^* pre-adsorbed at $\text{Mg}^{\delta+}$ site to form H_2O and $\text{CH}_3\text{CH}_2\text{O}^*$ in the fixed MgO chain setup (Figure 7a), and further dehydrogenation via $\text{C}_\alpha\text{-H}$ bond scission leads to CH_3CHO^* adsorbed at $\text{Mg}^{\delta+}$ site through carbonyl O in a substantially exothermic process ($\Delta E: -0.83\text{eV}$). By contrast, in the relaxed MgO chain setup (Figure 7b), hydroxyl O of ethanol can interact spontaneously with both Rh and $\text{Mg}^{\delta+}$ site to form

$\text{CH}_3\text{CH}_2\text{O}^*$ and H^* adsorbed at adjacent $\text{O}^{\delta-}$ site via O-H bond scission (ΔE : -1.66eV), followed by α -H abstraction to form CH_3CHO^* interacting with both Rh and $\text{Mg}^{\delta+}$ site through carbonyl O. During the optimization, however, the integrity of MgO chain is broken. It seems that under reaction stress, MgO chain is more flexible than MnO_2 chain at interface due to its ionic nature. Our calculated results agree well with our recent experimental study that MgO is actively involved in ethanol activation.⁵⁶

Fig.7. Dehydrogenation of ethanol forming acetaldehyde at the interface of OH-preadsorbed MgO/Rh(111) via ethoxy pathway $\text{CH}_3\text{CH}_2\text{OH}^* \rightarrow \text{CH}_3\text{CH}_2\text{O}^* + \text{H}^* \rightarrow \text{CH}_3\text{CHO}^* + 2\text{H}^*$. (a) with fixed MgO chain, and (b) with relaxed MgO chain.

In summary, ethanol dehydrogenation at $\text{MO}_x/\text{Rh}(111)$ interface can be varied depending on the nature of MO_x . Our results suggest that MO_x as well as pre-adsorbed OH^* plays a less significant role in C-C bond breaking, which, in particular, requires large-size ensemble on Rh surface, e.g., at least five Rh surface atoms on (111) facet needed for $\text{CHCO}^* \rightarrow \text{CH}^* + \text{CO}^*$ to proceed. Nonetheless, the large-size ensemble is concomitant with the deposition of overbinding CO^* , CH_x^* , and C^* surface species, which lead to the deactivation of metal catalyst. Meanwhile, MO_x pre-occupied with dissociated H_2O is less likely to be poisoned by these surface species.

3.3 Forming Rh_1M_3 ($M = Ir, Ru, Cu, Pd, Au$) alloy to mitigate deposition of carbon residues

As discussed above, one commonly used strategy for designing highly active catalysts is to introduce oxophilic metal into the catalyst, probably in the form of MO_x , such that the role of oxidizer OH^* can be realized efficiently in the removal of CO^* , CH_x^* , and C^* deposits which are strongly adsorbed at adjacent metal sites. The prerequisite for such a bifunctional effect to be effective is the weaker binding of adsorbed OH^* at $M^{\delta+}$ sites of MO_x , which is probably the main working mechanism for improved electro-catalytic performance of SnO_2 -based EOR catalyst observed in experiment.^{7, 12-17} On the other hand, it's highly desirable for developing a metal catalyst that can alleviate the adverse effect of these strongly-bound residues while maintaining the activation of ethanol. In this direction, theoretical studies have established that severe deposition of atomic adsorbates (e.g., C^* , H^* , O^*) on metal surface can be altered by designing the structure of surface alloy (SA) or near surface alloy (NSA) catalyst.⁵⁷⁻⁵⁸

We further investigated two Rh_1M_3 ($M = Ir, Ru$) SAs and three Rh_1M_3 ($M = Cu, Pd, Au$) NSAs for their binding strength towards C^* and CO^* . It has been predicted that CO^* is the most abundant surface species in the process of ethanol decomposition on most metal surfaces.¹⁹ Figure 8a exhibits a nearly linear correlation between C^* and CO^* binding energy, an indicative of 'scaling relations'¹⁹ that is also held for modified metal surface. Among alloyed models studied, Rh_1Au_3 NSA has the weakest C^* and CO^* binding, followed by Rh_1Cu_3 and Rh_1Pd_3 NSAs. This agrees well with the previous studies that Au and Cu are excellent components for inhibiting C^* depositions and for enhancing catalytic performance in steam reforming reactions.⁵⁹⁻⁶¹ In contrast, the formation of Rh_1Ir_3 and Rh_1Ru_3 SAs has almost no effect on mitigating C^* and CO^* depositions with respect to pure Rh. As restricted by 'scaling relations', the binding strengths of certain adsorbates (e.g., CO^* , CH_x^* , and C^*) cannot be freely tuned without affecting the others. This consequently affects the activation of chemical bonds (e.g., C-H, O-H, C-C and C-O) of key reaction intermediates associated with these adsorbates,⁶²⁻⁶⁴ dictated by Sabatier Principle that the binding of the key reaction intermediates should be neither too strong nor too weak for optimal catalytic activity and selectivity. Clearly, designing alloyed structure which has weakened C^* and CO^* binding is an effective approach for boosting EOR and SRE activity.

Fig.8. (a) Binding energy of CO (BE-CO) on Rh₁M₃ alloy surface (M = Cu, Ru, Pd, Ir, and Au) as a function of binding energy of C (BE-C). Triangle: fcc 3-fold hollow site; dot: top site. (b) Binding energy of OH (BE-OH) on Rh₁M₃ alloy surface as a function of dissolution potential of pure M in bulk form⁶⁵. Empty square: abnormality.

One of the major challenges to practical application of DEFC technology is to maintain the durability of electrodes due to the extreme working conditions, such as strong acidic media and high potential. Under these conditions, the surface atoms of metal or alloy electrodes tend to be oxidized even down to the bulk) and thereby are dissolved as cations into the strong acidic media. This can lead to the disintegration of pre-synthesized catalyst structure together with deactivation. We thus examined the stability of Rh₁M₃ alloys against oxidation using OH-binding energy as a descriptor. As shown in Figure 8b, the OH-binding energy (BE-OH) on Rh₁M₃ (M=Cu, Pd, Ru, and Au) alloy surfaces is linearly correlated with the dissolution potential of their corresponding bulk metals (except Ir).⁶⁵ This suggests that ability of Rh₁M₃ (M=Cu, Pd, Au) NSAs and Rh₁Ru₃ SAs against dissolution in acidic media can be estimated from OH-binding strength, i.e., the higher OH-binding strength is, the lower ability against dissolution would be. As expected, Rh₁Au₃ NSAs has the weakest OH-binding (0.98eV) and hence the highest dissolution potential (1.5V), whereas Rh₁Cu₃ NSAs has the strongest OH-binding (-0.37eV) and hence the lowest dissolution potential (0.345V). The variation in binding strength of OH* and other O-containing species is essentially associated with the oxophilic tendency of metals and thus, it's predicted that early dehydrogenation of ethanol prefers alkoxy route via CH₃CH₂O* intermediate on oxophilic

surface (e.g., Cu, Ru), in contrast to hydroxyl route via CH_3CHOH^* intermediate on non-oxophilic metal surface (e.g., Au, Pd).

4. Conclusions

We employed first-principles DFT simulations to investigate ethanol activation at metal oxide/Rh(111) interface and the alloying effect on mitigating the deposition of carbon-containing species on metal surface by forming Rh_1M_3 alloy. Our calculated results show that charge transfer is a two-way process: charge can transfer from Rh(111) substrate to MO_x chain (e.g., MoO_3 and MnO_2), or from MO_x chain (e.g., MgO , SnO_2 , ZrO_2 , and TiO_2) to Rh(111) substrate. The OH-binding strength at $\text{M}^{\delta+}$ site is increased exponentially with $\text{M}^{\delta+}$ charge, wherein MnO_2 and MgO chains bind with OH^* weakly resulting in high surface mobility of OH^* . This renders MnO_2 and MgO chains high capability of removing CO^* , CH_x^* , and C^* residues deposited on Rh surface and potentially the good candidates for DEFC anode or SRE catalysts. Ethanol dehydrogenation at $\text{MO}_x/\text{Rh}(111)$ interface can be varied depending on the nature of MO_x . It seems that MO_x as well as pre-adsorbed OH^* plays a less important role in C-C bond breaking which requires large-size ensemble on Rh surface. This however leads to the potential deposition of CO^* , CH_x^* , and C^* surface species on empty Rh surface being inevitable. We further investigated two Rh_1M_3 ($\text{M} = \text{Ir}, \text{Ru}$) SAs and three Rh_1M_3 ($\text{M} = \text{Cu}, \text{Pd}, \text{Au}$) NSAs for their binding ability towards C^* and CO^* . Our results suggest that Rh_1Au_3 NSA has the weakest C^* and CO^* binding. The general implication of this study is that by engineering alloyed structure of weakened C^* and CO^* binding augmented with metal oxides of weakened OH-binding, high-performance DEFC anode or SRE catalysts can be identified.

Supporting Information. Calculated lattice constant and surface segregation energy of Rh in Rh_1M_3 alloy.

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