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# Inverse bimetallic RuSn catalyst for selective carboxylic acid reduction

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#### Abstract

Inverse bimetallic catalysts (IBCs), synthesized by sequential deposition of noble and oxophilic metals, offer potential reactivity enhancements to various reactions, including the reduction of carboxylic acids for renewable fuels and chemicals. Here, we demonstrate that an IBC comprising of RuSn exhibits high selectivity for propionic acid reduction to 1-propanol, while Ru alone results in cracking. On RuSn, Xray absorption spectroscopy identified Ru<sup>0</sup> nanoparticles with a near-surface bimetallic Ru<sup>0</sup>Sn<sup>0</sup> alloy and small SnO<sub>x</sub> domains. Corresponding model surfaces were examined with density functional theory to elucidate the observed selectivity difference. Only selective hydrogenation is predicted to be favorable on SnO<sub>x</sub>/Ru, with the SnO<sub>x</sub> clusters facilitating C-OH scission and Ru enabling hydrogen activation. Intrinsic barriers along non-selective pathways suggest that the RuSn alloy and SnO<sub>x</sub> resist cracking. SnO<sub>x</sub>/Ru hydrogenation activity was supported experimentally by inhibiting hydrogenation with phenylphosphonic acid, differentiating the system from fully-alloyed RuSn metallic nanoparticles. Overall, this work demonstrates a plausible mechanism for selective reduction of carboxylic acids and proposes a roadmap for rational design of IBCs.

keywords: propionic acid; 1-propanol; selective hydrogenation; aqueous phase catalysis; ruthenium; ruthenium-tin alloy; tin oxide

#### Introduction

Understanding the structure and performance-enhancing mechanism of industrially-relevant bimetallic catalysts remains a critical challenge for rational catalyst design, especially in the context of emerging renewable processes.<sup>1, 2</sup> Aqueous phase reduction of biologically-derived carboxylic acids is one such transformation,<sup>1, 3-7</sup> capable of producing alcohols that are suitable as fuel additives,<sup>8, 9</sup> precursors to acrylonitrile,<sup>10, 11</sup> or polymer precursors with potential for lower overall greenhouse gas emissions.<sup>1, 8, 12-15</sup> Typical catalyst candidates for selective reduction of carboxylic acids involve combinations of noble (e.g. Pd, Pt, or Ru) and oxophilic, promoting metals (e.g. Re, Ti, or Sn),<sup>1, 16-25</sup> but the precise nature of their sites remains unresolved.<sup>26</sup> Some investigations attributed unique reactivity to the synergy of metal and metal oxide functionalities,<sup>2, 16, 18, 20, 21, 27-37</sup> analogous to CO<sub>2</sub> hydrogenation observed over inverse catalysts, with inverse catalyst defined as the sequential deposition of metal oxide on top of a noble metal, or metal-supported metal oxides (Scheme 1, left).<sup>38-40</sup> Other studies point to bimetallic alloys being responsible for catalyst enhancement.<sup>17, 22-24, 41, 42</sup> The possibility of alloying distinguishes inverse bimetallic catalysts (IBCs) from inverse catalysts and complicates the ability to interpret the active sites (Scheme 1, right). Accordingly, in-depth characterization and computational modeling of distinct surface sites are needed to develop a holistic view of these materials.

In this work, we examined IBCs supported on activated carbon for selective propionic acid (PA) hydrogenation to 1-propanol (1-PrOH). We identified the most promising catalyst to be RuSn with Ru-to-Sn molar ratio of 1:1. We subsequently characterized the RuSn catalyst and performed density functional theory (DFT) calculations to elucidate its active species and catalytic mechanism. Phenylphosphonic acid (PPA) was co-fed to inhibit Lewis acidic domains on Ru and RuSn, distinguishing catalytic roles in hydrogenation pathways. Extended X-ray absorption fine structure (EXAFS) spectroscopy of reduced catalysts was performed to obtain electronic and structural information. Mimicking EXAFS results, Ru(0001), Sn<sup>0</sup>/Ru(0001), and Sn<sub>4</sub>O<sub>4</sub>/Ru(0001) surfaces were constructed for DFT investigation and the computed energetics enabled the interpretation of observed selectivity trends. As a result, we propose a reaction scheme consistent with DFT calculations, characterization, and observed reactivity that provides a basis for rational IBC design.



**Scheme 1**. Representations of inverse-prepared catalysts, with inverse defined as a metal oxide sequentially deposited on top of a noble metal. In this figure,  $M_1$  represents Ru and  $M_2O$  represents  $SnO_x$ . Alloying of the metal oxide and noble metal phase can occur to from a distinct  $M_1M_2$  alloy phase, resulting in an inverse bimetallic catalyst.

#### Results

**Catalyst activity and selectivity.** Batch reactor catalyst screening identified that the RuSn catalyst, prepared as an IBC with Ru-to-Sn molar ratio of 1:1, is selective not only in succinic acid,<sup>1</sup> but also propionic acid hydrogenation, performing better than PdRe, PtSn, or their monometallic counterparts supported on powder activated carbon (PAC) (see **Fig S1-3**). While sparse literature is available on the aqueous phase reduction of propionic acid, a comparison of RuSn to other catalysts for succinic acid reduction can found in our previous work.<sup>1</sup> The addition of Sn to Ru markedly reduced the formation of non-selective reduction and cracking products observed with monometallic Ru, indicative of over-reduction pathways to propane and cracking to form ethane and methane (**Fig S2**). CO was not detected during the analysis of gas-phase reaction products, though it may be readily converted to  $CO_2$  via the water gas shift reaction over Ru.<sup>43,44</sup>

The high performance of RuSn-PAC led to the testing of RuSn supported on granular activated carbon (GAC) in a trickle bed flow reactor, as it is necessary to assess a more industrially relevant pellet-supported catalyst for stability at high conversions and high yield conditions. The results from the high-conversion time-on-stream run in this reactor are shown in **Fig 1**. At a WHSV of 0.3 h<sup>-1</sup>, RuSn-GAC demonstrated excellent selectivity for PA hydrogenation, achieving 1-PrOH yields of  $94 \pm 2$  mol% at 100% PA conversion while remaining stable for over 100 hours on stream.



Fig 1. Propionic acid hydrogenation in a trickle bed flow reactor with RuSn-GAC. Conditions: 160°C, 100 bar  $H_2$  at 200 sccm, 1.0 g RuSn-GAC, propionic acid 25 g L<sup>-1</sup>, WHSV 0.3 h<sup>-1</sup>.

To discern RuSn-GAC reactivity, we measured PA hydrogenation rates and selectivities using low-conversion timeon-stream (<10%) experiments, with the results provided in Table 1. The rate of PA hydrogenation was 10 times higher on Ru-GAC than on RuSn-GAC. Alongside rate changes, chemisorption experiments showed a 14-fold higher hydrogen uptake on Ru-PAC compared with RuSn-PAC, suggesting that Sn blocks H<sub>2</sub> adsorption and that the active sites involve Ru<sup>0</sup>. In addition, negligible CO uptake was previously observed on RuSn-PAC.<sup>1</sup> While CO is known to poison Ru hydrogenation sites,<sup>45</sup> the high activity observed over monometallic Ru would suggest that significant surface sites remain available and active for propionic acid reduction. However, product selectivities were vastly different with PA mainly converted to light products (CO<sub>2</sub>, methane, ethane, and propane) with Ru-GAC and to 1-PrOH with RuSn-GAC, implying that Sn influences the nature of the active site.

In unraveling the role of Sn, PPA was introduced to the mobile phase during PA hydrogenation over Ru-GAC and RuSn-GAC to target and inhibit surface metal oxide species. The change in PA hydrogenation rate upon PPA exposure is shown in Fig 2. Effectively, no change in the rate was observed on Ru-GAC, but an 80% reduction in the rate took place on RuSn-GAC. Interestingly, selectivity to 1-PrOH was maintained on RuSn-GAC during inhibition, implying that the residual activity is not due to Ru<sup>0</sup> sites but rather is related to the reversibility of deactivation (Fig S4). Previous work demonstrated that PPA selectively binds to Lewis acidic oxides,<sup>46-49</sup> including self-assembled monolayers of phosphonic acids on SnO<sub>2</sub>.<sup>50, 51</sup> Additionally, these catalysts have been shown to exhibit weak Lewis-acidic character and X-ray photoelectron spectroscopy (XPS) demonstrated evidence of Sn oxide formation.1 Thus, the activity inhibition experiments suggest that oxidic Sn constitutes part of the RuSn IBC active site.

**Table 1.** Propionic acid hydrogenation rates on Ru-GAC and RuSn-GACcatalysts in a flow reactor at 160°C and 100 bar H2. \*Measured from totalPA consumption, conversion <10%, bmeasured via HPLC quantification,</td>°calculated from the difference in the overall rate and 1-PrOH productionrate, and <sup>d</sup>determined from H2 chemisorption on powder catalysts.

Catalant	Overall rate <sup>a</sup>	Individual rate	H <sub>2</sub> uptake <sup>d</sup>		
Catalyst	(mmol g <sup>-1</sup> h <sup>-1</sup> )	1-Propanol <sup>b</sup>	Lights <sup>c</sup>	(µmol g <sup>-1</sup> )	
Ru-GAC	27.2 (± 0.2)	2.6 (10%)	24.6 (90%)	47.5	
RuSn-GAC	$2.6 (\pm 0.1)$	2.5 (95%)	0.1 (5%)	3.3	



**Fig 2**. Change in the overall propionic acid conversion rate (listed in **Table 1** as a function of time during exposure of the catalysts to a feed of 2 g<sup>-1</sup> L<sup>-1</sup> PPA, 100 g<sup>-1</sup> L<sup>-1</sup> propionic acid; Conditions: 160°C, 200 sccm H<sub>2</sub>, 100 bar H<sub>2</sub>, propionic acid WHSV 4 h<sup>-1</sup>.

**X-ray absorption spectroscopy.** With a previous report pointing to oxide formation<sup>1</sup> and reactivity testing suggesting oxidic species to be active, further characterization was achieved by employing X-ray absorption spectroscopy (XAS) to probe the structure of RuSn IBC. Fresh and spent Ru-PAC and RuSn-PAC catalysts were examined under ambient and reducing conditions via controlled-atmosphere EXAFS at both Ru and Sn K edges. X-ray absorption near edge structure (XANES) and k<sup>2</sup>-weighted Fourier transform spectra results, shown in **Fig 3** and summarized in **Table 2**, reveal that the spent, air-exposed catalysts contained oxidized metals Ru<sup>3+</sup> and Sn<sup>4+</sup>, while the fresh, air-exposed Ru-PAC contained some Ru<sup>0</sup>. Treatment of all materials in H<sub>2</sub> at 160°C led to reduction of Ru<sup>3+</sup> to Ru<sup>0</sup> and Sn<sup>4+</sup> to Sn<sup>2+</sup> (see **Table S1**, **Figs S5-6** for more details).

The low-intensity of the Ru-Ru peak in the Ru EXAFS of Ru-PAC (Fig 3C) indicates that Ru formed small nanoparticles; this was true for fresh and spent Ru-PAC and RuSn-PAC catalysts, with particle sizes ranging from 2.5 to 4.5 nm, consistent with previous studies of these materials.<sup>1</sup> There were no significant differences between fresh and spent catalysts, except for spent RuSn-PAC, which exhibited a smaller particle size upon treatment with H<sub>2</sub> at 160°C. This suggests that the bimetallic catalyst rearranges under reaction-like conditions. The Ru edge energy in the XANES region for RuSn-PAC (Fig 3A) was similar to that of Ru-PAC; however, the shape of the edge was shifted to slightly lower energy and white line intensity was also slightly lower, similar but not identical to the spectra of a Ru<sub>3</sub>Sn<sub>7</sub> standard (Fig S5). This suggests that addition of Sn to Ru-PAC led to the formation of a nanoparticle partially comprised of a RuSn bimetallic phase. Direct evidence for this formation was difficult to observe by EXAFS analysis, since Ru and Sn have a similar number of electrons and scatter similarly. Further, near surface allov formation cannot be confirmed from this bulk particle analysis. The nearly identical edge energy of the Ru-PAC and RuSn-PAC catalysts suggests that most of the Ru was present as Ru nanoparticles, implying that the bimetallic RuSn phase may be present at the nanoparticle surface.

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Table 2. EXAFS results for Ru-PAC and RuSn-PAC catalysts. \*Unused, as made catalyst; \*catalyst after 15 h of batch reaction, 100 bar H2, 160°C, 25 g L-1 propionic acid.

Catalyst	Condition	Treatment	XANES energy (keV)		Ru-O		Ru-Ru		Sn-O		Oxidation state		Estimated
			Ru	Sn	Ν	R (Å)	Ν	R (Å)	Ν	R (Å)	Ru	Sn	size (nm)
	Fresh <sup>a</sup>	Air, RT	22.1264	n.d.	3.4	2	5.3	2.68	n.d.	n.d.	III	n.d.	n.d.
Ru-PAC	Fresh <sup>a</sup>	H <sub>2</sub> , 160°C	22.1181	n.d.	n.d.	n.d.	9.1	2.65	n.d.	n.d.	0	n.d.	4
	Spent <sup>b</sup>	Air, RT	22.1280	n.d.	5.8	2	n.d.	n.d.	n.d.	n.d.	III	n.d.	n.d.
	Spent <sup>b</sup>	H <sub>2</sub> , 160°C	22.1171	n.d.	n.d.	n.d.	9.3	2.65	n.d.	n.d.	0	n.d.	4
	Fresh <sup>a</sup>	Air, RT	22.2128	29.2040	5.5	2	n.d.	n.d.	5.8	2.04	III	IV	n.d.
RuSn- PAC	Fresh <sup>a</sup>	H <sub>2</sub> , 160°C	22.1171	29.0010	n.d.	n.d.	9.5	2.66	2.5	2.06	0	II	4.5
	Spent <sup>b</sup>	Air, RT	22.1285	29.2040	5.8	2	n.d.	n.d.	6	2.05	III	IV	n.d.
	Spent <sup>b</sup>	H <sub>2</sub> , 160°C	22.1172	29.2000	n.d.	n.d.	7.1	2.65	1.9	2.05	0	II	2.5



**Fig 3**. (A) Ru K edge spectra of Ru-PAC and RuSn-PAC treated in H<sub>2</sub> at 160°C, and (B) Sn K edge spectra of fresh RuSn-PAC air-exposed and treated in H<sub>2</sub> at 160°C compared to Sn<sup>2+</sup>O standard. (C) Ru k<sup>2</sup>-weighted Fourier transformed spectra for Ru foil standard and Ru-PAC treated in H<sub>2</sub> at 160°C. The low intensity of Ru-Ru scattering for reduced Ru-PAC, in contrast to the Ru foil, indicates small Ru nanoparticles, and (D) Sn k<sup>2</sup>-weighted Fourier transformed spectra of RuSn-PAC treated in H<sub>2</sub> at 160°C compared to Sn<sup>2+</sup>O standard.

Sn K edge spectra (**Fig 3B**) showed that, after treatment with  $H_2$  at 160°C, most of the Sn in RuSn-PAC was reduced from Sn<sup>4+</sup> to Sn<sup>2+</sup>, with an edge energy similar to Sn<sup>2+</sup>O. The k<sup>2</sup>-weighted Fourier transform spectrum (**Fig 3D**) of RuSn-PAC after treatment with  $H_2$  at 160°C showed fewer high shell Sn-O-Sn peaks than bulk Sn<sup>2+</sup>O and Sn<sup>4+</sup>O<sub>2</sub>, indicating that Sn<sup>2+</sup>O and Sn<sup>4+</sup>O<sub>2</sub> domains were quite small.

From the EXAFS results, we conclude that at 160°C under H<sub>2</sub>, the Ru-PAC catalyst consisted of <5 nm Ru<sup>0</sup>. Under the same conditions, the RuSn-PAC catalyst surfaces consisted of <5 nm Ru<sup>0</sup> nanoparticles with a surface that was enriched with Sn<sup>0</sup>, as well as small Sn<sup>2+</sup>O domains that were randomly dispersed on the surface (e.g. both on the activated carbon itself and on RuSn bimetallic nanoparticles). Observation of Sn oxide supports the above assertion that RuSn-GAC inhibition was due to PPA binding to Sn<sup>2+</sup>O sites. Previous characterization by chemisorption and temperature programmed reduction showed negligible hydrogen and CO uptake with the same RuSn catalyst, in stark contrast to its monometallic Ru counterpart.<sup>1</sup> XPS was also performed to confirm the presence of predominantly Ru<sup>0</sup> with mixed Sn oxidation states  $(Sn^0, Sn^{2+}, Sn^{4+})$  on the reduced RuSn catalyst, which would support the presence of alloy Sn/Ru at the near-surface along with an oxide phase.<sup>1</sup> Collectively, these results would suggest that the working RuSn catalyst is an inverse bimetallic. However, since the mechanism of the RuSn bimetallic active surface could not be deciphered from characterization and reaction testing alone, we then turned to DFT to provide further insight. Based on these characterization results, we constructed computational models to further probe reactivity by examining the main features of inverse bimetallic catalysts, namely  $\mathrm{Sn}^0$  in the alloyed phase and  $\mathrm{Sn}^{2+}\mathrm{O}$  domains.

Modeling inverse bimetallics. We used periodic DFT calculations to examine surface-adsorbate interactions over representative models, chosen to emulate EXAFS results. We modeled Ru<sup>0</sup> with Ru(0001),<sup>1, 52, 53</sup> constructed near-surface Ru<sup>0</sup>Sn<sup>0</sup> alloys by replacing surface Ru(0001) with Sn atoms,1, 17, 54, 55 and optimized a small Sn<sub>4</sub>O<sub>4</sub> cluster on Ru(0001) to represent Ru-supported Sn<sup>2+</sup>O domains (Table S2 and Fig S7). The latter model was chosen to investigate the specific role of the Sn2+O domains in facilitating selective carboxylic acid hydrogenation, rather than study the effects on adjacent Ru sites. DFT-based equilibrium phase diagrams,<sup>56, 57</sup> addressing hydrogen adsorption and shown in Fig 4, revealed that Sn<sup>0</sup> species inhibit Ru sites, resulting in lower coverage (see also Fig S8). Hydrogen dissociation barriers also increased from 0 kJ·mol<sup>-1</sup> on Ru(0001) to 11 and 15 kJ·mol<sup>-1</sup> on 25% Sn/Ru(0001) and 50% Sn/Ru(0001) (Fig S9). Hydrogen is predicted to exhibit stronger affinity to SnO/Ru(0001), but the associated dissociation barrier was 99 kJ·mol<sup>-1</sup>, signifying kinetic limitations. Consistent with previous reports, we conclude that Ru sites are essential for H<sub>2</sub> dissociation while both Sn<sup>0</sup> and oxidic Sn<sup>2+</sup> species contribute to lower H<sub>2</sub> uptake.<sup>58</sup> In the alloy models, we found that hydrogen interacts preferentially with Ru, suggesting that Sn<sup>0</sup> solely isolates Ru sites without fundamentally altering their function. While site isolation was proposed for RhSn<sup>59</sup> and RuSn<sup>35</sup> catalysts and reflected in PtSn alloy computational studies,<sup>54, 55</sup> this alone cannot explain the observed selectivity changes, requiring mechanistic understanding.



**Fig 4.** Phase diagrams showing hydrogen coverage on model surfaces as a function of temperature and pressure. Yellow rectangles represent the reaction conditions typical of propionic acid hydrogenation (i.e.  $100-200^{\circ}$ C and 30-130 bar H<sub>2</sub>). The insets show the equilibrium binding modes at these conditions, with the top layer represented with spheres.

To gauge the role of Sn in RuSn IBCs, we evaluated PA reactivity on Ru(0001), 25% Sn/Ru(0001), and Sn<sub>4</sub>O<sub>4</sub>/Ru(0001) (Fig S7 A, C, and E), referring to them hereafter as Ru, Sn/Ru and SnO/Ru, respectively. On each model surface, we identified the likely mechanism by means of intrinsic energetics, i.e. surfacespecific energies and barriers. Reactions were deemed kinetically accessible on a given surface if the activation energy was below 110 kJ • mol<sup>-1</sup>, reflecting typical barriers that can be overcome under reaction conditions (T =  $160^{\circ}$ C and P<sub>H2</sub> = 100 bar). The results of this analysis in Fig 5 highlight the surfaces capable of promoting each reaction cycle, suggesting that both selective and non-selective reaction paths are accessible on metallic Ru and bimetallic Sn/Ru alloys while SnO/Ru is only capable of the desired, selective PA hydrogenation to 1-PrOH, consistent with our PPA inhibition experiments (see also Tables S10-12, Figs S16-26).

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**Desired reduction to 1-PrOH.** The desired reaction, PA hydrogenation to 1-PrOH, follows PA deoxygenation to propanal and its subsequent reduction to 1-PrOH. Analogous to acetic acid hydrogenation studies,<sup>41, 52, 60</sup> we considered three main paths to propanal: (*i*) direct C-OH scission to propionyl followed by C-H

formation, (*ii*) C-H formation to propane-1-ol-1-olate followed by C-OH scission, and (*iii*) O-H scission to propionate followed by C-O scission to propionyl and C-H formation. Propanal reduction to 1-PrOH was found to be relatively facile on all model surfaces irrespective of O-H or C-H formation first.

All three deoxygenation paths (Fig S16) exhibited barriers lower than 88 kJ •mol<sup>-1</sup> on Ru, in line with previous studies involving hydrogenation of acetic<sup>52</sup> and propionic acids.<sup>61</sup> On Sn/Ru, only the propane-1-ol-1-olate deoxygenation path to propanal (reactions 2A and 2B) was found to be kinetically accessible, while direct C-OH scission and C-O scission along the propionate path were 64 and 16 kJ ·mol<sup>-1</sup> more endothermic with substantially higher barriers. We did not attempt to discern the dominant paths beyond kinetic accessibility, since microkinetic modeling assumptions and extrinsic parameters can alter such conclusions.<sup>52</sup> Instead, we stress the existence of only one lowbarrier path for PA deoxygenation on Sn/Ru, whereas multiple such paths likely contribute to the overall activity on Ru. The elevated deoxygenation barriers and fewer accessible paths leading to 1-PrOH on Sn/Ru suggest that alloying lowers IBC activity, as observed on RuSn-GAC.



**Fig 5.** Overall mechanism for propionic acid hydrogenation to propanol via direct C-OH scission (pathway 1) and hydrogenation first (pathway 2), propanol over-hydrogenation to propane (pathway 3), initial steps in propanol decarbonylation (pathway 4) and decarboxylation (pathway 5). The inset images show catalytic functionalities with accessible barriers (below 110 kJ  $\cdot$  mol<sup>-1</sup>) along each catalytic cycle.





**Fig 6. (A)** C-H scission and **(B)** O-H scission BEP relations based on literature results for Ru(0001) (grey dots) and values obtained in this work for reactions at Ru(0001) (blue dots), 25% Sn/Ru(0001) (yellow diamonds), the interface of SnO cluster and Ru(0001) (green squares), and SnO/Ru(0001) (orange triangles). The results from this work are ZPE-corrected.

In assessing SnO/Ru, we considered both the SnO cluster on its own and the reaction at the SnO-Ru interface. On SnO clusters, only the direct C-OH scission path to propanal was found to be kinetically accessible (reactions 1A and 1B). Interestingly, the high-barrier C-H formation steps (reactions 2A and 2C) were responsible for shutting down the propane-1-ol-1-olate deoxygenation path, which was accessible on both Ru and Sn/Ru. We attributed this and lower O-H formation barriers to the fundamental difference between metallic Ru and oxidic SnO/Ru, evidenced by significant shifts in Brønsted-Evans-Polanyi (BEP) relations in Fig 6. In fact, these distinctions may be responsible for synergistic effects between metallic Ru and oxidic SnO functionalities. In examining the SnO-Ru interface, we found that C-H formation can take place on Ru next to SnO (reaction 2A), resulting in propane-1-ol-1-olate adsorbed on SnO (Fig S21). This intermediate can then undergo C-OH scission to propanal on SnO (reaction 2B). The subsequent propanal hydrogenation also benefits from the dual functionality, showing facile O-H formation on SnO followed by C-H formation on Ru (reactions 1C and 1D, Fig S22). These results suggest that oxidic domains proximal to Ru can facilitate carboxylic acid hydrogenation to 1-PrOH as RuSn IBC active sites.

Assessing selectivity. To better understand selectivity trends, we assessed 1-PrOH over-reduction to propane and initial steps leading to PA cracking via decarbonylation and decarboxylation

(Table S10). On Ru, all side reactions were found to be accessible. Propanol easily converts to propane starting with C-H scission (Fig 5C, Fig S19), consistent with results for ethanol decomposition.53 Similarly, PA decarbonylation (Fig 5D) and decarboxylation (Fig 5E, Fig S20) had barriers lower than 80 kJ· mol<sup>-1</sup>, aligning with Ru-GAC being non-selective. Sn<sup>0</sup> incorporation into Ru resulted in higher C-OH, C-O, and C-H scission barriers, also observed on Sn-modified Pt and Ru surfaces for acetic acid hydrogenation.<sup>17, 24</sup> We attributed this to the weaker binding of intermediates and related like-binding fragments, namely CH<sub>3</sub>, CH<sub>2</sub>, H, OH, and O (Table S13). These surface species bind weaker on Sn/Ru, causing the final states, which constitute C-Ru bonded fragments co-adsorbed with H, OH, or O, to destabilize relative to the initial states. With destabilized final states, C-H and C-OH activation exhibit greater reaction energies and higher barriers consistent with the BEP principle, leading to slower, yet still accessible, reactions on Sn/Ru.

In contrast to either Ru or Sn/Ru, no side reactions were energetically favored over SnO/Ru. Based on the BEP trend found in this work (Fig 6, Fig S13), over-reduction to propane was hindered by C-H scission/formation (reactions 3A and 3D) with barriers exceeding 120 kJ·mol<sup>-1</sup> (Fig S19). Similarly, C-H and C-C scission barriers along decarbonylation and decarboxylation exceeded 130 kJ · mol<sup>-1</sup>, suggesting SnO/Ru is incapable of cracking. As with the above arguments, simple binding may explain this behavior. CO binds considerably weaker on SnO/Ru compared with Ru or Sn/Ru (Table S13), effectively destabilizing the final state in decarbonylation and increasing barriers associated with it. To summarize the computational findings, reflected in Fig 5 and Fig S26, Ru is predicted to have low barriers along all paths, providing an explanation for its high activity but poor selectivity. Sn/Ru is predicted to exhibit barriers that are higher or comparable to those on Ru, supporting the notion that Sn<sup>0</sup> inhibits and slows down reactions. The SnO/Ru model showed the greatest contrast between barriers along selective and non-selective paths, suggesting this functionality is responsible for enhancing selectivity of RuSn IBCs.

#### Discussion

Previous studies of bimetallic catalysts employed for selective hydrogenation of C=O moieties, be they carboxylic acids, esters, or aldehydes, have identified two possible active sites: (i) fully reduced M<sub>1</sub>M<sub>2</sub> alloys of varying primary (M<sub>1</sub>) and secondary (M<sub>2</sub>) metal compositions, <sup>17, 22-24, 41, 42</sup> and (ii)  $M_1M_2O_x$  involving an oxidized secondary component.<sup>2, 16, 18, 20, 21, 27-37</sup> It is unsurprising that conclusions about the active site depend heavily on catalyst preparation and its resulting phases,<sup>1, 62</sup> their characterization,<sup>22, 37</sup> and theoretical backing.<sup>17, 24, 41</sup> For instance, in the absence of information about the oxidation state of the catalyst, binary phase diagrams prompted the assertion that Ru<sub>3</sub>Sn<sub>7</sub> alloys are responsible for selective hydrogenation of levulinic<sup>22</sup> and butyric<sup>23</sup> acids. Similarly, XPS evidence for the alloying of Ru and Sn led Luo et al. to propose M1M2 active species for other carboxylic acids.24 Yet, there was no evidence discounting the participation of SnO<sub>v</sub> species.<sup>23, 24</sup> In fact, XPS of CoSn and RuSn catalysts revealed the presence of Sn<sup>2+</sup> and Sn<sup>4+</sup> species, suggesting M<sub>1</sub>M<sub>2</sub>O<sub>x</sub> may be responsible for improved selectivity in hydrogenation of fatty esters<sup>32-34, 63</sup> and carboxylic acids.<sup>1, 24</sup> For related PtSn catalysts, Alcala et al. identified PtSn alloy as the most abundant phase using Mössbauer spectroscopy and used DFT to show that Sn<sup>0</sup> incorporation into Pt(111) increases barriers for ethanol dehydroxylation more so than for acetic acid dehydroxylation, suggesting  $M_1M_2$  active species for selective acetic acid hydrogenation.<sup>17</sup> Yet, the less abundant SnO<sub>x</sub> was not assessed despite being observed in the same samples, likely because of computational limitations. Meanwhile, single crystal studies of

PtSn(111) pointed to  $M_1M_2O_x$  as the likely active species, stemming from observations that  $Sn^0$  incorporation lowers activity without altering selectivity in crotonaldehyde hydrogenation.<sup>36</sup>

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In this work, we aimed to discern the structure-selectivity relationship by employing an IBC formulation associated with highly selective and process-relevant RuSn catalysts.<sup>1</sup> We found that these catalysts exhibit high selectivity of PA to 1-PrOH and contain both M1M2 and M1M2Ox surfaces. The RuSn near-surface alloy, observed by EXAFS and modeled with DFT, energetically hinders hydrogenation to light products, largely shutting off the multiple pathways favored on monometallic Ru, yet still provides sites for H<sub>2</sub> dissociation. Meanwhile, domains of SnO located near Ru<sup>0</sup> were implicated as active sites by both PPA inhibition experiments and DFT, providing low energy barriers to 1-PrOH formation while also shutting off undesired cracking pathways. Thus, both bimetallic arrangements are beneficial in constructing this highly selective IBC, a conclusion reached only through the integrated experimental and computational approach herein. Experimental evidence alone could not rule out either of the proposed bimetallic sites while DFT relied on characterization to inform model surfaces. The resulting active site mechanism is consistent with models proposed previously,<sup>33, 34</sup> wherein a fully reduced primary metal and an oxidized secondary metal work in concert. Our findings are also in line with the proposed Sn<sup>0</sup> poisoning effect,35,59 wherein Sn<sup>0</sup> slows down the reactions leading to undesired, cracking products. Similar trends were seen in DFT calculations for C-O,<sup>17, 24</sup> C-C,<sup>17</sup> and C-H<sup>54, 55</sup> scission on PtSn<sub>x</sub> and Ru<sub>3</sub>Sn<sub>7</sub> surfaces.

Based on our findings, we can establish key design criteria for selective hydrogenation catalysts involving an interplay of M<sub>1</sub>,  $M_1M_2$ , and  $M_1M_2O_x$  sites. An optimal catalyst for this type of reaction would consist of (1) a reduced metal capable of activating  $H_{2}$ , (2) a secondary metal that can form a bimetallic phase to shut off non-selective hydrogenation pathways yet still be capable of H<sub>2</sub> dissociation, and (3) a Lewis acid oxide vicinal to the reduced metal to facilitate selective hydrogenation. Optimizing IBCs to further increase the overall rate or reduce their cost will be crucial in the adoption of these catalysts. One possible approach involves computational screening of metallic and oxidic functionalities by utilizing a set of energetic descriptors, such as atomic binding energies coupled with BEP relations. Tailored synthesis and characterization strategies can then be employed to validate their composition and performance. In this work, the BEP relations developed for monometallic Ru could be readily applied to bimetallic alloys because of similarities in the binding of intermediates, hinting at potential for reducing computational needs. Meanwhile, metal oxide clusters represent a significant shift from alloyed materials, suggesting future catalyst formulations can be inspired by in silico tuning of C-H, O-H, and C-OH bond activations. Furthermore, these relations may apply beyond carboxylic acid chemistry. For instance, the increase in C-H formation barriers on Sn2+O domains supports the trends in selective crotonaldehyde hydrogenation over PtSn and RuSn, where SnO<sub>x</sub> participation has been suggested.<sup>36, 37, 42</sup> While their applicability to other oxides remains to be explored, the implications for IBCs may be used more broadly to improve the carbon economy in CO<sub>2</sub> reduction or natural gas processing, where the same elementary steps are involved.

It is important to note that this work focused on discerning the active sites for a single working catalyst with a specific Ru:Sn ratio of 1:1, which performed best for the aqueous phase hydrogenation of succinic acid<sup>1</sup> and propionic acid. SnO/Ru was found to be a dominant driver for this chemistry based on PPA inhibition experiments that demonstrate the need for surface Lewis acidity (**Fig 2, Fig S4**) and DFT calculations that show the SnO/Ru has the greatest impact on selectivity. Still, alloy Sn/Ru may

contribute to selective hydrogenation. Further efforts are needed to understand the influence of varying concentrations of alloy Sn/Ru and oxidic SnO/Ru sites that can result when varying the Ru:Sn ratio, synthesis conditions, and catalyst pretreatment procedures that were beyond the scope of this work. As highlighted in this work, careful synthetic control with extensive material characterization and surface-specific catalytic performance measurements would be needed to elucidate the relative impact and co-dependency when varying the amount of surface exposed SnO/Ru and Sn/Ru alloy.

In considering future directions, extrinsic factors such as temperature, pressure, and condensed water can also affect catalyst surface coverage and hence the underlying energetics.<sup>64, 65</sup> For instance, microkinetic modeling has the potential to more precisely identify the contributions of each type of site,<sup>52</sup> but will require additional information about coverage effects on binding energies and intrinsic kinetics. Similarly, reaction conditions (*operando*) can provide structural information otherwise unavailable under reducing conditions (*in situ*). Accordingly, understanding how these dynamic effects impact computational and characterization results, as well as coupling the behavior to reaction kinetics, remains a worthy pursuit for screening and evaluating promising IBCs.

#### **Materials & Methods**

**Catalyst synthesis.** Catalyst synthesis details have been described previously using a sequential metal deposition procedure.<sup>1</sup> Generally, primary metals were loaded onto the support at approximately 4 wt% and dried and reduced in H<sub>2</sub> for 4h at 450°C. Secondary metals were then loaded onto these materials at approximately 4 wt% and dried and reduced in H<sub>2</sub> for 4h at 450°C. Unless noted otherwise, the catalysts denoted as "metal"-PAC (e.g. Ru-PAC or RuSn-GAC) refer to catalysts on the powder support, whereas catalysts denoted as "metal"-GAC refer to catalysts on the granular support.

**Propionic acid hydrogenation**. Batch reactor catalyst screening experiments were performed in a Parr multi-batch reactor system (Parr Instrument Company). Powder catalyst and reaction solution (20 mL of 25 g L<sup>-1</sup> aqueous propionic acid) were loaded into the reactors, sealed, and purged with pressurized helium three times to remove ambient air. The reactors were then pressurized to 100 bar of H<sub>2</sub> and heated to 160°C. After 15 hours at temperature the reactors were quenched in a water bath, cooled to room temperature, and the solution was filtered and collected for product analysis.

Trickle bed flow reactor experiments were performed with the equipment and protocol described previously.<sup>1</sup> The reactions were performed at 160°C, 100 bar H<sub>2</sub>, 0.2 mL min<sup>-1</sup> liquid feed, at varying concentrations of aqueous PA. Reactor effluent was collected periodically for analysis. More detailed descriptions can be found in the SI.

Inhibition of catalysts with phenylphosphonic acid (PPA) was performed in the flow reactors as described above. Once catalysts had reached steady state for propionic acid hydrogenation (fed at 0.2 mL min<sup>-1</sup>, 100 g L<sup>-1</sup> propionic acid) the liquid feed bottle was changed to include PPA (fed at 0.2 mL min<sup>-1</sup>, 2 g L<sup>-1</sup> PPA, 100 g L<sup>-1</sup> propionic acid). Reactor effluent was collected periodically for analysis.

Liquid reaction products for both batch and flow experiments were analyzed with an Agilent 1100 series HPLC equipped with a Bio-Rad Aminex HPX-87H column and cation H+ guard column, operating at 85°C, a refractive index detector, with dilute sulfuric acid (0.01 N) as the mobile phase at 1.0 mL min<sup>-1</sup>. Reactant and product concentrations were measured using authentic calibration standards prior to each use of the HPLC. The only compounds detected were propionic acid and 1-propanol, there were no peaks suggesting formation of any other condensed product (e.g. ethanol or 2-propanol).

**EXAFS.** X-ray absorption spectroscopy (XAS) experiments were performed at the Materials Research Collaborative Access Team (MRCAT) and CMC beamlines of the Advanced Photon Source at Argonne National Laboratory. Powder catalyst samples were loaded as self-supporting wafers in a 6-sample stainless steel sample holder. For samples requiring pre-treatment, the sample holder itself was loaded in a quartz sample tube equipped with gas and thermocouple ports and sealed at

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both ends by Kapton windows. The samples were heat-treated to 160°C under flowing H<sub>2</sub> (4% H<sub>2</sub>/He at 100 sccm) in a tube furnace for 30 minutes, then cooled under flowing He (100 sccm) to room temperature, sealed, and then placed in the beamline for XAS spectra collection. The XAS spectra were collected in transmission mode at the Ru (22.1172 keV) and Sn K edges (29.2001 keV). The XAS data was fit using standard procedures based on WINXAS software, and k2-weighted Fourier transform data was used to obtain the EXAFS coordination parameters with least-squares fits in q- and r-space of the isolated nearest neighbor.

Hydrogen Chemisorption. H<sub>2</sub> chemisorption of Ru-PAC and RuSn-PAC materials was performed on an Autochem II (Micrometrics) using a 10 temperature-programmed desorption (TPD) method. Prior to analysis samples were reduced under flowing H<sub>2</sub> (50 sccm, 10% H<sub>2</sub> in Ar) at 250°C 11 (2°C min<sup>-1</sup>) for two hours, then cooled to 40°C under inert flow. The 12 materials were then heated to 450°C (2°C min<sup>-1</sup>) and the desorbed H<sub>2</sub> was 13 detected by TCD.

Computational Modeling. Periodic DFT calculations were used to 14 analyze thermodynamics and intrinsic kinetics associated with propionic 15 acid reactions on Ru(0001), Sn/Ru(0001), and Ru(0001)-supported Sn<sub>4</sub>O<sub>4</sub> 16 domains. For selective PA hydrogenation to 1-PrOH, transition states for 17 each elementary step were computed explicitly using DFT. For nonselective routes, we used BEP relations for crude estimates, followed by 18 DFT refinement. The details of our calculations are available in the 19 Computational Modeling section of the SI. 20

Supporting Information. catalyst synthesis method, catalyst batch reactor screening, gas-phase hydrogenation products, catalyst inhibition experiment, x-ray absorption spectroscopy, computational modeling, Brønsted-Evans-Polanyi (BEP) relations, reaction mechanism, reaction energetics, adsorption energetics

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Conflict of Interest Disclosure. T.R.E., A.E.S., and D.R.V. are inventors on a patent application submitted by the Department of Energy on synthesis and use of bimetallic catalysts for selective carboxylic acid reduction (U.S. non-provisional patent application No. 15/828,658 filed on December 1, 2017).

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