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**Endothermic Reforming Using Novel Catalysts Prepared by Exsolution**

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1. T. Cao, R. Huang, R.J. Gorte, and J.M. Vohs, "Endothermic Reactions of 1-Propanamine on a Zirconia Catalyst", *Applied Catalysis A*, **590**, 117372 (2020).
2. T. Cao, O. Kwon, R.J. Gorte, and J.M. Vohs, "Metal Exsolution to Enhance the Catalytic Activity of Electrodes in Solid Oxide Fuel Cells," *Nanomaterials*, **10**, 2445 (2020).
3. A.S. Raman and A. Vojvodic, "Modeling Exsolution of Pt from  $\text{ATiO}_3$  Perovskites (A=Ca/Sr/Ba) using First-principles Methods", *Chemistry of Materials* **32**, 9642-9649 (2020).
4. T. Cao, O. Kwon, J.M. Vohs, and R.J. Gorte, "Substrate Structure Directs the Growth of ALD Perovskite Films," *Journal of Green Energy*, <https://doi.org/10.1080/15435075.2021.1946815> (2021).
5. T. Cao, O. Kwon, J. M. Vohs, and R. J. Gorte, "Two-Dimensional Perovskite Crystals Are Formed by Atomic Layer Deposition of  $\text{CaTiO}_3$  on  $\gamma\text{-Al}_2\text{O}_3$ ", *Nanomaterials*, **11**, 2027 (2021).
6. "Liquid-Organic Hydrogen Carriers as Endothermic Fuels", Tianyu Cao; WooJae Lee; Renjing Huang; Raymond Gorte; John M. Vohs, *Fuel*, 313 (2022) 123063.
7. "Ni ingress and egress in  $\text{SrTiO}_3$  single crystals of different facets", B. Alayyoub, T. Cao, O. Kwon, J. M. Vohs, R. J. Gorte, and A. Vojvodic, submitted.
8. "Investigation into Support Effects for Pt and Pd on  $\text{LaMnO}_3$ ", Tianyu Cao, Ching-Yu Wang, Kai Shen, J. M. Vohs, and R. J. Gorte, *Applied Catalysis A*, accepted.
9. "Metal Exsolution to Enhance the Catalytic Activity of Electrodes in Solid Oxide Fuel Cells", T. Cao, O. Kwon, J. M. Vohs, and R. J. Gorte, *Nanomaterials*, **10** (2020) 2445, doi:10.3390/nano10122445

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10. X. Mao, B. Alayyoub, A.C. Foucher, Z.Yu, A. Vojvodic, E.A. Stach, J.M. Vohs, and R.J. Gorte, "A Comparison of Rh, Pd, and Pt Catalysts Supported on  $\text{LaFeO}_3$  Films Prepared by Atomic Layer Deposition".
11. B. Alayyoub, C. Lin, J. M. Vohs, R.J. Gorte, and A. Vojvodic, "Host, Facet, and Temperature Dependence of Atomic Platinum Migration Through  $\text{ATiO}_3$  (A = Ca/Sr/Ba) Perovskites Using DFT and ALD".

12. B. Alayyoub, A.S. Raman, A. Vojvodic, “Segregation-Trends of 4d Metals from Doped  $\text{ATiO}_3$  (A= Ca/Sr/Ba) Host Perovskites”.

### **Project Summary**

Cooling of critical engine parts in hypersonic aircraft (above Mach 5) is challenging since air cooling is not practical at such high velocities. While the fuel itself can be used to provide some cooling before it enters the combustion chamber, this approach is not sufficient to supply the required cooling load since the temperature to which the fuel can be heated is limited by gas phase pyrolysis reactions that have appreciable rates above  $650^\circ\text{C}$  and produce tars that will foul the fuel lines.

In the present contract period, we have explored two approaches aimed at achieving practical cooling using endothermic reactions. First, we have explored alternative fuels, demonstrating high heats and coking resistance for dehydrogenation of amines to nitriles over a zirconia catalyst and dehydrogenation of 1,2,3,4-tetrahydroquinoline to quinoline over a Pd/alumina catalyst. Second, since enhancing catalyst stability, especially preventing deactivation by coking resulting from decomposition of fuel molecules, will be required for endothermic reforming reactions, we also explored, both experimentally and computationally, the properties of metal catalysts prepared by ex-solution from perovskite supports which have been shown to exhibit tolerance against coking in previous work. In these studies, we explored the synthesis of this type of catalyst with high-surface-area perovskites prepared using Atomic Layer Deposition on stable supports and demonstrated that these materials maintain their high coking resistance. Computationally, we demonstrated that ex-solution processes are highly dependent on the composition of both the metal catalyst and the perovskite, as well as the crystallographic orientation of the perovskite.

### **Synopsis of Research Findings**

#### **“Endothermic Reactions of 1-Propanamine on a Zirconia Catalyst” [see Publication 1 above]**

Here, we propose using alkylamines that dehydrogenate to nitriles and  $\text{H}_2$  over  $\text{ZrO}_2$  catalysts as the endothermic fuel. Temperature programmed desorption (TPD) revealed that 1-propanamine on  $\text{ZrO}_2$  undergoes dehydrogenation at temperatures below 600 K. At 723 K and below, the selectivity to form  $\text{H}_2$  and propionitrile is greater than 90%. Heat measurements at 60 bar show heat uptakes as large as  $2000 \text{ kJ kg}^{-1}$  of fuel reacted could be achieved at 723 K. Side reactions at higher conversions and temperatures lowered this value but values above  $1000 \text{ kJ kg}^{-1}$  were still obtained at nearly 100% conversion of the amine. The observation of a significant endothermic effect suggests that the unconventional functional groups in the fuels merit further investigation to achieve a more profound chemical heat sink. Possible ways to apply this approach are discussed.

#### **“The Use of Hydrogen-Storage Compounds for Endothermic Reforming Applications” [see Publication 6 above]**

Ring-containing hydrocarbons with nitrogen in the ring have been proposed for use in hydrogen storage because of their stability against coke formation and favorable dehydrogenation equilibrium constants. In this study, we examined whether these compounds could also be used in endothermic reforming conditions. To demonstrate the concept, dehydrogenation of 1,2,3,4-tetrahydroquinoline to quinoline over a Pd/alumina catalyst was studied under conditions relevant

to endothermic reforming. First, we demonstrated high conversions (>65% at 723 K and >80% at 873 K) and high endothermicity (>1000 kJ/kg) for the reaction at 60 bar total pressure. Furthermore, the activity of the catalyst was stable for hours, even at 873 K. By contrast, attempts to use methylcyclohexane dehydrogenation to toluene led to rapid coking at 873 K and also cause the overall reactions to be exothermic. The results suggest that alternative fuels could be useful in endothermic-reforming applications in hypersonic flight.

**“Two-Dimensional Perovskite Crystals Are Formed by Atomic Layer Deposition of CaTiO<sub>3</sub> on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>” [see Publication 5 above]**

CaTiO<sub>3</sub> films with an average thickness of 0.5 nm were deposited onto  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> by Atomic Layer Deposition (ALD) and then characterized by a range of techniques, including X-Ray Diffraction (XRD) and High-Resolution, Transmission Electron Microscopy (HRTEM). The results demonstrate that the films form two-dimensional crystallites over the entire surface. Lattice fringes from HRTEM indicate that the crystallites range in size from 5 to 20 nm and are oriented in various directions. These results help explain why the thin perovskite films exhibit diffraction patterns in XRD, even though the films are thinner than the coherence length of the x-rays. Interestingly, films of the same thickness on SiO<sub>2</sub> remained amorphous, indicating that the support plays a role in forming the crystallites. This also suggests that there may be opportunities for directing the crystallographic orientation of perovskite films through the use of an appropriate support.

**“Substrate Structure Directs the Growth of ALD Perovskite Films” [see Publication 4 above]**

LaFeO<sub>3</sub> films were deposited to a thickness of 0.5 nm onto amorphous SiO<sub>2</sub> by Atomic Layer Deposition and used as supports for Pt. Uniform coverage of the SiO<sub>2</sub> was demonstrated by Scanning Transmission Electron Microscopy (STEM) and Temperature Programmed Desorption (TPD) of 2-propanol. The films were found to be amorphous to X-Ray Diffraction but the reducibility of the Fe in the films and the ability of the films to maintain high Pt dispersions following harsh redox treatments suggested that the perovskite phase was formed on a short length scale. Similar to results found on Pt/LaFeO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub>, Pt/LaFeO<sub>3</sub>/SiO<sub>2</sub> catalysts maintained a high Pt dispersion following redox cycling at 1073 K and showed high activity for CO oxidation following high-temperature reduction. The implications for using these materials as endothermic-reforming catalysts is discussed.

**“Modeling Exsolution of Pt from ATiO<sub>3</sub> Perovskites (A=Ca/Sr/Ba) using First-principles Methods” [see Publication 3 above]**

To understand the factors that control the substitution of the catalytic metal ions into and out of the perovskite lattice, we have used modeling including Density Functional Theory (DFT) calculations and molecular dynamics simulations in parallel with the experimental work also enabled by this funding. Our computational approach is targeting to map out both the thermodynamics and kinetics of the ion substitution and migration process of ions from the subsurface to the surface as a function of the perovskite composition and dopant catalytic metal for well-defined thin films of oxide systems.

Using accurate first-principles DFT simulations coupled with an *ab-initio* steered molecular dynamics and umbrella sampling framework, we rationalize both the energetics as well as the dynamics of the exsolution process of a quintessential system: Pt-doped ATiO<sub>3</sub> (A = Ca/Sr/Ba) perovskites and identify the major driving forces for Pt exsolution. From the developed *ab initio*

thermodynamic framework, we find that Pt exsolution from  $\text{ATiO}_3$  ( $A = \text{Ca/Sr/Ba}$ ) perovskites has a distinct host-perovskite facet dependence and likely proceeds through subsurface vacancy formation followed by diffusion of the doped Pt to the surface of the host perovskite. The molecular dynamics simulations reveal that the exsolution process has a clear temperature and host-perovskite dependence, establishing that only specific dopant-host perovskite combinations at favorable thermophysical conditions result in the catalyst with the novel properties. This opens new paths for the predictive synthesis of intelligent catalysts.

### **“Host, Facet, and Temperature Dependence of Atomic Platinum Migration Through $\text{ATiO}_3$ ( $A = \text{Ca/Sr/Ba}$ ) Perovskites Using DFT and ALD” [see Publication 11 above]**

This atomic scale computational effort build off our findings in Publication 3 above and focuses on modeling both the existence and migration of metal ions in the near surface (sub-surface) and direct surface region (surface layer) of metal doped thin perovskite films. We initially modelled the thermodynamics of segregation of Pt from the bulk of three different  $\text{ATiO}_3$  perovskite oxides with  $A = \text{Ca, Sr, and Ba}$ , to different surface facets using DFT. We found that the segregation energies are highly dependent on the surface orientation [*e.g.* (001), (110), (111)] as well as the surface termination [*e.g.* AO- or  $\text{BO}_2$ -terminated (001)]. Our results indicate that Pt would prefer to segregate (move from the bulk or sub-surface to the surface *i.e.* exsolve as ions from the perovskite) onto specific surfaces (negative  $E_{\text{seg}}$ ) and not others (positive  $E_{\text{seg}}$ ). Still, a thermodynamically possible segregation event might be kinetically prohibited, affecting the overall metal exsolution process by the existence of a high activation energy barrier for segregation.

To study these potential kinetic effects, we developed a new computational framework encompassing *ab-initio* steered molecular dynamics and umbrella sampling to model the dynamics and temperature dependence of the ion migration phenomena. Modeling Pt migration from the bulk of the CTO, STO and BTO to the surface showed that the exsolution activation energy barrier for Pt migration is highly temperature dependent for all the considered host. Importantly, in addition to the chemical composition of the oxide, the exposed surface facet and termination play a crucial role in determining the exact temperature dependence of the ion migration from the bulk to the surface. Furthermore, we explored the effects of surface oxygen non-stoichiometry, altering the thermodynamic driving force for Pt migration, alluding to potential design and synthesis considerations. Experimentally, we used CO oxidation to probe the extent of exsolved metal to the oxide surface, which is constituted by the reduction temperature. We found a correlation between a high reduction temperature corresponding to more metal on the surface and a higher CO oxidation activity.

### **“Segregation-Trends of 4d Metals from Doped $\text{ATiO}_3$ ( $A = \text{Ca/Sr/Ba}$ ) Host Perovskites” [see Publication 12 above]**

This study focuses on identifying possible metal-dopant/host perovskite combinations that could be considered as potential suitable starting candidate systems to study the exsolution phenomena (*i.e.* a stable metal/host oxide solid-solution). We performed DFT simulations and calculated the segregation energies of different 4d transition-metals (Zr, Nb, Mo, Ru, Rh, Pd, Ag) doped in three archetypal host perovskite oxides:  $\text{CaTiO}_3$ ,  $\text{SrTiO}_3$ , and  $\text{BaTiO}_3$ . We modeled different facet terminations and level of strain to better understand their effects on the segregation properties of the metal ions. The results show that the thermodynamic tendency of 4d metal-dopants towards remaining in the sub-surface/bulk layers, forming a dilute metal/host solid-

solution, or segregating to the surface is (i) predominantly facet dependent, (ii) has a weak to no dependence on the considered hosts perovskite (i.e. is independent on the type of considered A metal of the titanate), and (iii) doesn't vary significantly with strain of the host perovskite. This computational screening study delineated the surface segregation energies of metal-doped perovskites which help in a better understanding of the exsolution process.

#### **“Exsolution from Ni-doped SrTiO<sub>3</sub> Single Crystals” [see Publication 7 above]**

In addition to the studies of metal-support interactions on thin perovskite films, we investigated metal-ion migration using SrTiO<sub>3</sub> single crystals with different exposed surfaces. This study was motivated by our computational results that showed migration of transition metal ions in perovskites has a directional dependency (see Publications 3, 7 and 9). NiO films were deposited onto SrTiO<sub>3</sub>(110) and SrTiO<sub>3</sub>(100) single crystals and annealed at 1073 K. After etching the remaining NiO from the surfaces, the samples were reduced at 1073 K to force back to the surface any Ni<sup>2+</sup> that had migrated into the perovskite. The results revealed that Ni particles formed on the (110) surface, while exsolution onto the (100) surface did not occur because Ni did not migrate into this surface. This result is consistent with our DFT calculations of Ni ion migration of the different STO surfaces where we find crystal-plane dependency on metal ion migration in the near surface region.

#### **“A Comparison of Rh, Pd, and Pt Catalysts Supported on LaFeO<sub>3</sub> Films Prepared by Atomic Layer Deposition” [see Publication 10 above]**

Metal-support effects were studied for Rh, Pd, and Pt deposited onto 1-nm LaFeO<sub>3</sub> (LFO) films prepared by Atomic Layer Deposition (ALD) on MgAl<sub>2</sub>O<sub>4</sub>. Significant differences were observed for how the three metals interact with LFO. Although Scanning Transmission Electron Microscopy (STEM) showed that Rh remained well-dispersed after multiple oxidation and reduction steps at 1073 K, both reduced and oxidized catalysts showed low activity for CO oxidation. STEM data for the Pd/LFO showed reversible formation of larger Pd particles and evidence for Pd-Fe alloy upon high-temperature reduction. CO-oxidation rates on Pt/LFO could be cycled between inactive and active states by oxidation or reduction at 1073 K. In the absence of metal catalysts, reduction of LFO at 1073 K was negligible but between 1.5 and 2 oxygens per metal atom could be removed on the supported catalysts. Coulometric titrations demonstrated that each of the metals was more difficult to reduce when supported on LFO. We performed a complementary DFT study showing that the bonding interaction between metal atoms and LFO are unique for each of the studied system with a similar trend among the metals as the experimental observation.

#### **“Metal Exsolution to Enhance the Catalytic Activity of Electrodes in Solid Oxide Fuel Cells” [see Publication 9 above]**

Exsolution is a novel technology for decorating metal catalyst particles onto ceramic anodes in the solid oxide fuel cells (SOFCs). The exsolved metal particles in the anode exhibit unique properties for reaction and have demonstrated remarkable stabilities under conditions that normally lead to coking. Despite extensive investigations, the underlying principles behind exsolution are still under investigation. In this review, the present status of exsolution materials for SOFC applications was reported, including a description of the fundamental concepts behind metal incorporation in oxide lattices, a listing of proposed mechanisms and thermodynamics of the exsolution process, and a discussion on the catalytic properties of the resulting materials. Prospects and opportunities to use materials produced by exsolution for SOFC are discussed.

### **“Investigation into Support Effects for Pt and Pd on LaMnO<sub>3</sub>” [See publication 8]**

The catalytic properties of Pt and Pd supported on thin-film LaMnO<sub>3</sub> were investigated. The LaMnO<sub>3</sub> film consisted of an ALD-grown 0.5-nm-thick film supported on a high-surface-area MgAl<sub>2</sub>O<sub>4</sub>. Pt and Pd were added to the LaMnO<sub>3</sub> films by Atomic Layer Deposition (ALD) and then aged by repeated oxidation and reduction cycles at 1073 K. X-Ray Diffraction (XRD), together with Scanning Transmission Electron Microscopy (STEM)/Energy Dispersive Spectroscopy (EDS) showed that Pt underwent extensive sintering during these redox treatments and formed a Pt-Mn alloy following reduction at 1073 K. Consistent with this, the activity of the supported Pt catalysts for CO oxidation decreased progressively with the number of redox cycles. In contrast to the results for Pt, STEM/EDS results indicated that Pd remained well dispersed on LaMnO<sub>3</sub>, even after five redox cycles. The Pd catalyst showed high activity for CO oxidation at lower temperatures due to a low activation energy and positive reaction order in CO. XRD results with Rietveld analysis for the Pd catalyst indicated the presence of very large crystallites for PdO on the oxidized catalyst and metallic Pd on the reduced catalyst, inconsistent with the high dispersions measured by STEM and the high CO-oxidation rates. Possible explanations for these observations are discussed.

### **Summary**

Going forward, we would like to continue our studies of the fundamental properties of perovskite-supported metal catalysts for application to endothermic reforming in hypersonic aircraft. Experimentally, most of the work will focus on metals supported on thin-film perovskites synthesized by Atomic Layer Deposition (ALD) on high-surface-area oxides. Computationally, our work will focus on first-principles modeling of the complex metal-perovskite systems including systems with stark modifications from the typically perfect crystals encountered in traditional computational studies. The mechanisms underlying metal-ion migration in and out of the perovskite films will be studied at the atomic level to the point where we can harvest and tailor the unique catalytic properties of these metal particles. In addition to examining the dependence of perovskite composition, we will study how the support used for the perovskite film can influence the crystallographic orientations and other properties of the perovskite and how this in turn affects the catalytic activities of metals on their surface. To link the experimental and computational results, the thermodynamics of metal oxidation will be used as a descriptor of catalytic activity. Model studies of metals on perovskite single crystals will be used to determine the relationship between bulk and thin-film perovskites as supports for metal catalysts. The overall goal of the program will be to understand and control three interactions within the system: metal with the reactants, metal with the thin film perovskite, and thin film perovskite with the high-surface-area support.