Dalton Transactions

PAPER

Cite this: Dalton Trans., 2014, 43, 2079

Received 2nd September 2013, Accepted 3rd November 2013 DOI: 10.1039/c3dt52404c www.rsc.org/dalton

1. Introduction

Ionic noble metal catalysts continue to receive attention because they can provide a means to achieve enhanced reactivity. Substituting noble metals into oxide hosts is an attractive alternative to supporting noble metal nanoparticles on oxides, with substitution allowing the use of very small amounts of expensive, precious metals while still accessing their reactivity for CO oxidation, NO_x reduction, and hydrocarbon conversion.¹ Hegde *et al.* have shown that Pd-substituted binary oxides are superior CO oxidation catalysts to the traditional metal nanoparticle catalyst on an oxide support.^{2,3} Recently, our group has reported that Pd-substituted CeO₂ can be used as a methane partial oxidation catalyst, and determined that CeO_2 as a host oxide is not able to maintain the stability of ionic Pd under strongly reducing reaction conditions.⁴ However, it has been previously demonstrated that Pd ions can be substituted into pervoskites and stabilized in complex oxides.⁵⁻⁸ With this in mind, we now consider Pd-substitution in perovskite hosts.

Rapid microwave-assisted sol-gel preparation of Pd-substituted $LnFeO_3$ (Ln = Y, La): phase formation and catalytic activity[†]

Lauren M. Misch, Alexander Birkel, C. Adrian Figg, Brett P. Fors, Craig J. Hawker, Galen D. Stucky and Ram Seshadri

We present a rapid microwave-assisted sol-gel approach to Pd-substituted LnFeO₃ (Ln = Y, La) for applications in C-C coupling reactions. These materials could be prepared in household microwave ovens in less than 15 minutes of reaction time with the final materials displaying well-defined structure and morphology. Phase evolution was studied using time-dependent microwave heatings and then compared with the results obtained from thermogravimetric analyses. Materials were confirmed to be phase pure by laboratory and synchrotron X-ray diffraction. Substituted Pd is ionic as shown by the binding energy shift from X-ray photoelectron spectroscopy. The short heating periods required for phase purity allow these materials less time for sintering as compared to conventional solid state preparation methods, making relatively high surface areas achievable. These materials have been successfully used as catalyst precursor materials for C-C coupling reactions in which the active species is Pd⁰. Pd-substituted LnFeO₃ (Ln = Y, La) provides Pd⁰ in solution which can be complexed by the ligand SPhos, allowing for aryl chloride coupling.

> Perovskites have long been studied for catalytic purposes. First reports of perovskites as automotive emissions catalysts date back to the 1970s.9,10 The utility of these materials lies in their ability to be reduced and subsequently re-oxidized multiple times. Structurally, the large A site, usually occupied by an alkaline earth or rare earth ion, and corner-sharing B site octahedra make the perovskite amenable to ion substitution on both cation sites. For this reason, perovskites can be prepared with various substituents, notably noble metals.¹¹ Although primarily studied as catalysts for CO oxidation and NO_x reduction, these materials have also been considered as catalysts for coupling reactions in organic chemistry.12 Although LaFeO₃ and YFeO₃ have very similar crystal structures, the significant size difference of the A site cation results in the much smaller Y³⁺ creating significantly tilted and rotated octahedra in YFeO3. This subtle difference is shown in Fig. 1. It was of interest to understand whether these differences in the structure would result in distinct behavior.

> We have prepared Pd-substituted (La,Y)FeO₃ in order to better understand the contribution of inductive effects from the A site cations and the role this plays in dopant ion stabilization. Pd compounds are of particular interest as catalysts for cross-coupling reactions (*i.e.* Suzuki–Miyaura,¹³ Negishi,¹⁴ Stille,¹⁵ Sonogashira,¹⁶ Buchwald–Hartwig,¹⁷ Heck,¹⁸ Hiyama,¹⁹ *etc.*). More specifically, Pd-substituted perovskites have the ability to provide Pd⁰ under reducing conditions, as



View Article Online

Department of Chemistry and Biochemistry, Materials Department, and Materials Research Laboratory University of California, Santa Barbara, CA 93106, USA †Electronic supplementary information (ESI) available. See DOI: 10.1039/c3dt52404c



Fig. 1 Crystal structures for (a) LaFeO₃ and (b) YFeO₃. The A site cations are displayed as grey spheres and FeO₆ octahedra in blue.

well as to regenerate with Pd cations formed in an oxidative environment, thus providing a fully recyclable Pd source.^{11,20,21} Previous success with Pd-perovskites as recyclable catalysts¹² in Suzuki–Miyaura reactions has further prompted our study of Pd-substituted (La,Y)FeO₃ for these reactions.^{22,23} Here we utilize the Suzuki–Miyaura reaction to compare and understand the catalytic activity of materials with various substitution levels of Pd (0, 5, 10 mol%), differing A site cations and varying surface areas, which can all be easily controlled using our rapid and facile microwave preparation method.

One very interesting approach to rapidly prepare uniform and phase pure materials is the use of microwave-assisted reactions.^{24–27} Recently, it has been demonstrated that with simple modification and optimization, household microwave ovens can be employed to obtain high quality materials that enable various types of reactions, including conventional solid-state reactions to yield phosphors with high quantum yields,^{28,29} the heating of air-sensitive materials in evacuated fused silica tubes to access intermetallics for thermoelectrics^{30,31} and the use of sol–gel based preparations.³² Along with providing stable, stoichiometric, complex compounds, the microwave preparation routes are also appropriate for preparing complex substituted oxides, in which a dopant ion resides on a metal cation site.

In the present study we report a rapid microwave-assisted combustion/sol-gel preparation as a method to produce noble metal-substituted perovskites. Unsubstituted materials as well as various synthetic pathways leading to them have been investigated previously.^{6,33–37} The specific approach followed here allows for the careful investigation of the phase formation process due to the very short and controllable heating times. We have applied the materials prepared using microwave-assisted techniques to Suzuki-Miyaura coupling reactions and determined that the substituted perovskites are actually precursor catalysts and provide a Pd source for coupling catalysis. The La containing pervoskites, and it has been established

unambiguously through the use of the ligand 2-dicyclohexylphosphine-2',6'-dimethoxybiphenyl (SPhos) that any catalytic activity does not stem from the perovskite itself, but from the reduced Pd^0 that is released and then bound by the ligand. We have demonstrated that these materials are appropriate for the coupling of aryl chlorides under more mild conditions than has previously been reported.

2. Experimental methods

Sample preparation

All samples were prepared *via* a microwave-assisted reaction pathway, employing a citric acid based sol–gel reaction.³² In a typical synthesis, to 15 mL of MilliPore water (18 M Ω cm) and 5 mL ethanol (in a 50 mL beaker), a two-fold excess (in terms of metal cations) of citric acid was added and the solution was stirred until clear, which usually took about 5 minutes. Subsequently, the pH was adjusted to neutral through the addition of several drops of aqueous ammonia.

For the preparation of $Ln_{1-x}Pd_xFeO_{3-\delta}$ (with Ln = La, Y), stoichiometric amounts of the metal nitrates Ln(NO₃)₃·6H₂O, Fe(III) acetylacetonate and Pd(II) acetylacetonate (all obtained from Sigma-Aldrich) were dissolved and the solution was vigorously stirred. After the addition of either La(NO₃)₃·6H₂O or $Y(NO_3)_3 \cdot 6H_2O$, a milky precipitate formed. The other reagents were added after the dissolution of this precipitation. In the case of $Y_{1-x}Pd_xFeO_{3-\delta}$, a small excess (between 5 mol% and 10 mol%) of Fe(III) acetylacetonate had to be used to limit the amount of Y₂O₃ impurities. The temperature of the reaction mixture was held at 65 °C to slowly evaporate the solvent until a gel was formed, which usually happened between 8 h and 10 h. This gel is then dried at 125 °C overnight and eventually finely ground. A batch size of about 250 mg of dried gel is then heated in a so-called hybrid microwave (Panasonic NN-SN667B, 1250 W) setup, as described in previous studies.28,29,38

Many iterations with various heating profiles and power levels were attempted. The reaction time and power level were adjusted to optimize the crystallinity, phase purity, and surface area of the investigated samples. A time-dependent study of the phase formation was carried out at various reaction times, using a power setting of 100%, 1250 W. The optimized reaction time was 150 seconds at a power level setting of 70% for $La_{1-x}Pd_xFeO_{3-\delta}$ and a multi-step heating profile (2 minutes at a power settings) for $Y_{1-x}Pd_xFeO_{3-\delta}$. The temperature was measured in various intervals during and after the reaction was finished using a portable infrared pyrometer (PalmerWahl DHS235XEL).

Sample characterization

Laboratory powder X-ray diffraction (XRD) data were obtained using Cu K α radiation (Philips X'Pert) over the angular range $15^{\circ} \leq 2\theta \leq 90^{\circ}$ with a step size of 0.016°. High resolution synchrotron powder diffraction data were collected using

beamline 11-BM at the Advanced Photon Source (APS), Argonne National Laboratory using an average wavelength of 0.413893 Å. Discrete detectors covering an angular range from -6° to $16^{\circ} 2\theta$ were scanned over a $34^{\circ} 2\theta$ range, with data points collected every $0.001^{\circ} 2\theta$ at a scan speed of $0.01^{\circ} \text{ s}^{-1}$. Rietveld fits³⁹ of the data were obtained using the TOPAS Academic program suite.⁴⁰ TGA was carried out using a METTLER TGA/sDTA851e ThermoGravimetric Analyzer in air in the temperature range between 25 °C and 900 °C at a heating rate of 10 °C per minute. X-ray photoelectron spectra were obtained on a Kratos Axis Ultra Spectrometer with a monochromatic Al-K α source (E = 1486.61 eV). Samples were mounted on a stainless steel holder using double-sided carbon tape. The residual pressure inside the sample analysis chamber was below 7×10^{-9} Torr. Survey spectra were collected with an analyzer pass energy of 80 eV and high-resolution Pd 3d spectra were acquired at a pass energy of 20 eV. Spectra were calibrated to the C 1s peak from adventitious hydrocarbons, expected at a binding energy of 285.0 eV. For peak fitting of the spin-orbit doublets in high resolution scans, the $d_{3/2}$ to $d_{5/2}$ peak area was constrained to a ratio of 2/3 with the use of CasaXPS software. Field-emission scanning electron microscopy was performed on a FEI XL40 Sirion FEG microscope with an Oxford Inca X-ray system attached for chemical analysis. SEM samples were mounted on aluminum stubs using double-sided conductive carbon tape and coated with a thin layer of Au/Pd in order to avoid charging effects. The images were recorded with an acceleration voltage of 5 kV. Energy-dispersive X-ray spectroscopy was performed using an acceleration voltage of 20 kV. The samples were not sputtered with conductive coatings. Transmission electron microscopy was performed on a FEI Tecnai G2 Sphera Microscope with an acceleration voltage of 200 kV. TEM samples were prepared by dispersing a small amount of the powder in ethanol and subsequent ultrasonication for about 15 minutes. Then, 2 to 3 drops were administered onto copper grids (lacey carbon, Type-A, Ted Pella) and the solvent was allowed to evaporate overnight. Brunauer-Emmett-Teller (BET) surface area measurements were performed on a MicroMeritics TriStar 3000 porosimeter using N2 as a probe gas.

Catalytic activity

All reactions were carried out under an argon atmosphere. The isopropanol was purchased from Fischer Scientific and was degassed before use (three freeze-pump-thaw cycles). Aryl halides, aryl boronic acids, SPhos and potassium carbonate were purchased from Sigma-Aldrich and were used as received. All compounds were characterized by ¹H NMR, ¹³C NMR, IR spectroscopy, and high-resolution mass spectrometry. Nuclear Magnetic Resonance (NMR) spectra were recorded on a Varian 600 MHz instrument. ¹H NMR experiments are reported in δ units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm) in the deuterated solvent. ¹³C NMR spectra are reported in δ units, ppm, relative to deuterochloroform (77.23 ppm) and all were obtained with ¹H decoupling. FT-IR spectra were obtained

with a Thermo-Nicolet Avatar-330 IR spectrometer with a single-bounce attenuated total reflection (ATR) accessory with a Ge crystal. Gas chromatography (GC) analyses were performed on a Shimadzu GC-2014 instrument with a flame ionization detector (FID) using a Restek SHRXI-5MS column. High-resolution mass spectrometry was conducted with a Micromass QTOF2 Quadrupole/Time-of-Flight Tandem mass spectrometer. Flash chromatography was performed using a Biotage SP4 instrument with prepacked silica cartridges.

General procedure for a Suzuki–Miyaura reaction with different (La,Y)FeO perovskites. An oven-dried test tube, which was equipped with a magnetic stir bar and fitted with a teflon septum, was charged with SPhos (0–1 mol%), the perovskite (0–0.04 mol% Pd), phenylboronic acid (171 mg, 1.4 mmol) and K_2CO_3 (193 mg, 1.4 mmol). The vessel was evacuated and backfilled with argon (this process was repeated a total of 3 times) and then the 3-chloropyridine (95 μ L, 1.0 mmol) and the degassed solvent mixture (1:1 i-PrOH–H₂O, 2 mL) were added *via* a syringe. The solution was heated at 80 °C for 20 h and then cooled to room temperature, diluted with ethyl acetate (20 mL) and washed with water (5 mL). Decane was added to the solution as an internal standard and the yield was determined by GC analysis.

General procedure for a Suzuki–Miyaura reaction with $LaFe_{0.95}Pd_{0.05}O_{3-\delta}$. An oven-dried test tube, which was equipped with a magnetic stir bar and fitted with a teflon septum, was charged with SPhos (4.1 mg, 1 mol%), $LaFe_{0.95}Pd_{0.05}O_{3-\delta}$ (2 mg, 0.04 mol% Pd), aryl boronic acid (1.4 mmol) and K_2CO_3 (193 mg, 1.4 mmol). The vessel was evacuated and backfilled with argon (this process was repeated a total of 3 times) and then the aryl halide (1.0 mmol) and the degassed solvent mixture (1:1 i-PrOH-H₂O, 2 mL) were added *via* a syringe. The solution was heated at 80 °C for 20 h and then cooled to room temperature, diluted with ethyl acetate (20 mL), washed with water (5 mL) and concentrated *in vacuo*. The crude product was purified using a Biotage SP4 flash purification system.

Results and discussion

Evolution of perovskite products

Thermogravimetric analysis including differential thermal analysis of $(La,Y)Fe_{0.95}Pd_{0.05}O_{3-\delta}$ gels was conducted after the drying step at 125° and before the sample was subjected to any microwave heating (Fig. 2). This offers insight into product formation during the microwave heating steps with two significant heat losses being observed during the TGA analysis. The first occurs between room temperature and 200 °C, when the samples loses about 10% of their respective masses, due to evaporation of re-adsorbed water and surface hydroxyl groups as well as thermal decomposition of ammonium nitrate. The second major weight loss occurs in the temperature range between 200 °C and 400–500 °C. Here, the samples lose another 70% of their mass. As described in the Experimental section, the gels contain a two-fold excess (in terms of total



Fig. 2 Thermogravimetric analysis of the decomposition of the dried precursor gels. Panel (a) shows the decomposition for LaFe_{0.95}Pd_{0.05}O₃- $_{\delta}$ and panel (b) shows YFe_{0.95}Pd_{0.05}O_{3- δ}. A 10% mass loss is observed between room temperature and 200 °C which can be attributed to water and surface hydroxyls while a much larger weight loss is observed between 200 °C and 500 °C as a result of the citric acid combustion and burning of residual organics.

metal cations) of citric acid which combusts at temperatures exceeding 200 °C. The DTA for both samples indicates two sharp exothermic events at this temperature. The combustion process is completed at about 500 °C, and only a small weight loss after 500 °C is observed, which is mostly due to the burning of residual organics. Our findings agree well with the results found by Qi et al.35 who prepared LaFeO3 using combustion synthesis. Conventional solid-state preparation of these materials usually starts from a mixture of oxides, generally requires temperatures of 1000 °C and above, involves multiple regrinding steps in between multi-day heatings and yields very low surface area products. Even most sol-gel based preparation methods require several hours of heating at temperatures well above 500 °C, proving again the time- and energy-saving nature of this microwave-assisted reaction pathway.

Taking advantage of the short heating and reaction times, the microwave-assisted sol-gel (or combustion) preparation allows us to study the phase formation process of the perovskites in more detail. It should be noted that although the microwave heating times are very short, the sol-gel preparation that precedes microwave heating is completed over the course of two full days. The shortened heating time allowed by the microwave does significantly reduce the total time usually required for a sol-gel preparation, in which the final heating step may take up to several hours or days. The microwaveassisted heating method can be applied to a more conventional solid-state preparation in which precursor oxides can be ground with a mortar and pestle in a matter of minutes followed by very short microwave heating times. We chose to



Fig. 3 Phase evolution of LaFe_{0.95}Pd_{0.05}O_{3- δ} after 30 s intervals of the reaction, using laboratory X-ray powder diffraction data. The indicated temperatures were measured using the infrared pyrometer, aimed at the center of the inner crucible, immediately after the microwave irradiation has stopped. Formation begins after 650 °C and becomes more crystal-line at higher temperatures.

pursue sol-gel preparation because we were able to achieve more phase pure samples and higher surface areas than with the ceramic preparation.

Here we make use of the short heating and cooling times facilitated by the microwave and we focus on the evolution of reactants in the formation of $LaFe_{0.95}Pd_{0.05}O_{3-\delta}$. Fig. 3 shows the laboratory X-ray diffraction data of different stages of the reaction, starting from the dried gel until 2 minutes, with 30 second steps. In both, the dried gel before subjecting to microwave radiation as well as the sample being subjected to microwave radiation for 30 s (a temperature of about 250 °C was measured after that time with fume/smoke starting to evolve from the specimen), weak reflections of NH_4NO_3 can be found. These originate from the reaction of the nitrate precursor with the aqueous ammonia solution used to adjust the pH of the precursor solution.

After 60 s of microwave irradiation (and a temperature of 475 °C), the NH₄NO₃ decomposed. Also, the sample's color changed from light brown to black with the evolution of additional smoke. At this point of the reaction, the X-ray data showed only an amorphous material, consisting of the citrate complexes of the dissolved precursors. After another 30 seconds (90 s total heating time), a temperature of about 650 °C was reached and the X-ray diffraction data showed that the phase formation is completed, as only reflections of LaFe_{0.95}Pd_{0.05}O_{3- δ} are visible in the trace. These reflections are very broad and of rather low intensity, pointing to the fact that small crystallites have been formed. Crystallite size analysis using TOPAS Academic showed an average size of about 30 nm. At this point, the sample body color changed from black to brown and the sample exhibited some fluffiness.



Fig. 4 Synchrotron X-ray powder diffraction data of (a) $LaFe_{1-x}Pd_xO_{3-\delta}$ and (b) $YFe_{1-x}Pd_xO_{3-\delta}$ with various amounts of Pd substituted into the host (various x values).

Further heating increases the temperature to about 800 $^{\circ}$ C, leading to a larger crystallite size (about 75 nm) and therefore sharper reflections. These findings correspond very well with the thermal decomposition behavior observed from the TGA data.

Laboratory and synchrotron X-ray powder diffraction data were collected to confirm the phase purity of all the investigated materials. Rietveld fits of high-resolution synchrotron powder X-ray diffraction data collected at beam line 11-BM confirm that especially the substituted YFeO₃ samples contain at least some detectable crystalline metallic palladium (Pd⁰), as summarized in Fig. 4. Although the amount estimated from a quantitative Rietveld fit does not exceed 2.5%, it is worth considering this when interpreting catalytic reactivity results. In addition, LaO(OH) can be found in small quantities (less than 5 wt%) as a secondary phase in the LaFe_{0.9}Pd_{0.1}O_{3- δ} perovskites. We did observe some small changes in lattice parameter with various levels of Pd-substitution. However, no significant trend, such as a steady increase or decrease in the cell lengths as a function of increasing Pd content, was observed. This is not entirely unexpected, as this is an aliovalent substitution. As Pd²⁺ substitutes onto a 3+ site, an oxygen vacancy is subsequently created for neutrality. This was observed previously with Pd-substitution in YFeO3.6

Scanning electron micrographs, as presented in Fig. 5, for typical 5% Pd-substituted LaFeO₃ and YFeO₃ samples show that both substituted materials exhibit very similar morphologies. Near spherical particles that are 100 nm and smaller in size were observed and these agglomerate to form larger chunks. The micrographs shown here are representative of all perovskite materials prepared using the optimized heating profile, detailed in the Experimental section. Surface area is a critical parameter for materials for catalytic





Fig. 5 Scanning electron micrographs of (a) LaFe_{0.95}Pd_{0.05}O_{3- δ} and (b) YFe_{0.95}Pd_{0.05}O_{3- δ}. Representative samples prepared using the optimized heating profiles show 100 nm crystallites agglomerated together.

applications. High surface area materials allow access to many active sites at once and are more efficient in catalytic conversion of reactants to products than the same materials having lower surface area. With this in mind, the microwave heating profiles were adjusted through duration and power level to ensure that the materials possessed the highest attainable surface area with this method. Materials that were heated for longer times and at higher power levels were subjected to sintering and showed fewer small particles and larger chunks. This phenomenon is directly related to surface area. Energy dispersive X-ray spectroscopy and mapping (shown in the ESI[†]) confirmed increasing Pd content with Pd concentration during preparation and a homogeneous dispersion of Pd ions in as-prepared materials. Upon closer inspection with transmission electron microscopy (Fig. 6), crystallinity anticipated from the X-ray diffraction data was observed. Similar to observations with the scanning electron micrographs, materials subjected to more strenuous heating profiles were not comprised of small enough particles to observe uniform crystallinity in the TEM.



Fig. 6 Transmission electron micrographs of (a) $LaFe_{0.95}Pd_{0.05}O_{3-\delta}$ and (b) $YFe_{0.95}Pd_{0.05}O_{3-\delta}$ show uniform crystallinity.

With many iterations of various microwave heating profiles, intermittent XRD analysis, and the TGA result in mind, we were able to achieve phase-pure, crystalline materials, with surface areas near 25 $m^2\ g^{-1}$ for $LaFeO_3$ materials and near 5 m² g⁻¹ for YFeO₃ materials. The sol-gel microwave-assisted preparation method for substituted oxide catalysts has been proven to produce superior materials in an extremely timeefficient manner compared to traditional solid-state methods. Due to different heating profiles required for La and Y containing oxides, their surface areas differ slightly. The lower surface area that is achieved for the Y analogue is attributed to the longer reaction time required for achieving phase purity. Though these surface areas are less than those of high surface area microporous catalysts, such as zeolitic materials, a 20-fold increase in surface area (in the La perovskite) over conventionally prepared solid-state materials is appreciable and suggests that this microwave-assisted method may be amenable to further modification for surface area enhancement.

X-ray photoelectron survey spectra and high-resolution spectra for the Pd 3d region were collected over the range of 1000 eV to 0 eV and 350 eV to 330 eV, respectively. Survey



Fig. 7 X-ray photoelectron spectroscopy data of (a) $LaFe_{0.95}Pd_{0.05}O_{3-\delta}$ and (b) $YFe_{0.95}Pd_{0.05}O_{3-\delta}$. There are two contributions observed in the case of the La perovskite and only one contribution observed for the Y perovskite. Both materials show the Pd 3d peaks shifted to higher binding energy than metallic Pd or PdO. Dashed reference lines are taken from ref. 41.

scans did not show evidence for any elements aside from the anticipated La/Y, Fe, Pd, O, and C. Quantification of the survey scans using CasaXPS software indicated that materials expected to contain 10% Pd were closer to 8% Pd, along with 51% La and 40% Fe. Materials expected to contain 5% Pd were shown to contain 5% Pd with 52% La and 43% Fe. It is expected that there is some inherent error in quantifying the survey spectra as peak areas and background type are selected manually within the software. High-resolution scans of the Pd 3d region shown in Fig. 7 indicate that the Pd 3d peaks are shifted to a slightly higher binding energy than the expected position for Pd²⁺ in PdO, 336.8 eV for the 3d_{5/2} peak, and Pd⁰ in which the 3d_{5/2} appears at 335.4 eV.⁴¹ This suggests that Pd is in a very ionic environment, more so than if PdO domains are forming along with the perovskite host.

It is clear that Pd substituted into LaFeO₃ is different from Pd substituted into YFeO3. In the case of La as the A-site cation, we see two distinct Pd species. This is in contrast to the single Pd species observed when Y is on the A-site. This anomaly may be a result of differing inductive contributions from La and Y or Pd occupying more than one site in the case of La. The difference in catalytic behavior, discussed below, may be a result of the difference in Pd occupation in the two perovskites. We hypothesize that the La perovskite may make the Pd more accessible for catalysis and cycling to metallic Pd, while the Pd in the Y perovskite may be less accessible. This may explain the difference in catalytic reactivity for the two perovskites, as the difference in surface area is not significant enough to cause a noticeable effect. One future application of this work is to probe ionic Pd catalysis, which requires the preparation of materials that stabilize ionic Pd under various

reaction conditions. It was shown in our previous work⁴ that a binary oxide like CeO_2 is not a sufficient ion stabilizing host to maintain Pd ions under reducing reaction conditions. Here we show that Pd ions substituted onto the B-site of a perovskite host may experience increased ion stabilization as a result of A-site cation induction. The fact that dopant ionicity is affected by differing A-site cations further advances this stabilizing host oxide concept.

4. Catalytic activity

The Suzuki–Miyaura coupling was chosen as a model reaction to demonstrate the potential of Pd-substituted (La,Y)FeO₃ perovskites as catalyst precursors in cross-coupling reactions. Of equal importance, this reaction was selected to understand the effects of Pd-substitution levels, the contribution of the A-site cation and the particle surface area of our microwave synthesized perovskites on the catalytic activity of these systems.

Recently, Martin and coworkers demonstrated that Pd-containing perovskites are suitable catalysts for Suzuki–Miyaura reactions.^{22,23} They elegantly demonstrated that under their reaction conditions, Pd species desorb from the perovskite to give a soluble active catalyst. However, aryl and heteroaryl chlorides were poor substrates using this method, requiring harsh reaction conditions (*i.e.* 135 °C) and resulting in modest yields. Currently, the most general catalyst systems for coupling these difficult substrates are based on discrete phosphine ligated Pd⁰ complexes.¹³ In order to demonstrate that perovskites can be general catalysts for cross-coupling reactions, we set out to develop a method that would efficiently couple aryl and heteroaryl chlorides under mild conditions.

We commence with the reaction of a heteroaryl chloride with an aryl boronic acid using LaFe_{0.95}Pd_{0.05}O_{3- δ} as the catalyst. We hypothesized that by adding a biarylphosphine ligand developed by Buchwald for Suzuki-Miyaura couplings, SPhos,⁴² to the reaction mixture, the Pd⁰ species would be ligated as it is desorbed from the perovskite, leading to the formation of a highly active catalyst. In support of this, using LaFe_{0.95}Pd_{0.05}O_{3- δ} (0.04 mol% Pd), SPhos (1 mol%), and K₂CO₃ in i-PrOH-H₂O at 80 °C, 3-chloropyridine was reacted with phenylboronic acid to give the desired biaryl product in 93% yield (Table 1, entry 2). Interestingly, removing SPhos from this same reaction gave no product, demonstrating that the ligand is playing a critical role in the reaction and suggesting that the Pd⁰ is indeed being ligated as it is desorbed from the LaFe_{0.95}Pd_{0.05}O_{3- δ}.

We next investigated the impact of surface area, Pd-substitution levels, as well as the contribution of the A-site cation in the perovskite, on the catalyst activity of this system. Reducing the surface area of the particles from 28.5 m² g⁻¹ to 3.4 m² g⁻¹ led to a decrease in yield from 93% to 50% (Table 1, entry 3); this result suggests that surface area has some influence on catalysis for this system. We hypothesize that the increased surface area enables more efficient desorption of the Pd from the perovskite leading to higher concentrations of active

 Table 1
 Impact of the perovskite surface area, Pd-substitution levels

 and A-site cation identity in Suzuki–Miyaura cross-coupling reactions



Reaction conditions: perovskite (0.04 mol% Pd), SPhos (0 to 1 mol%), 3-chloropyridine (1.0 mmol), phenylboronic acid (1.4 mmol), K_2CO_3 (1.4 mmol), 1:1 i-PrOH-H₂O (2 mL), 80 °C for 20 h. There was no yield for reactions in which the ligand (SPhos) was omitted. ^{*a*} For perovskites with 0% Pd substitution the same mass was used in the reaction as the materials with 5% substitution.

catalyst. Further, increasing the Pd-substitution from 5% to 10% in these materials substantially decreased the yield to 23% (Table 1, entry 4). This trend is similar to what was observed for Pd-substituted in CeO₂, where 5% Pd-substitution is more active than 2.5% Pd and 7.5% Pd substitution.⁴ Moreover, using a material with no Pd-substitution, LaFeO₃, provided no desired product (Table 1, entry 1), confirming that Pd is responsible for catalysis. Lastly, substituting La for Y in these materials caused nearly complete loss in activity (Table 1, entries 6–8). We postulate that the differing A-site cation will contribute a varying inductive effect in the perovskite, influencing the stability of the Pd ions in the material, as well as the rate of desorption under reducing conditions.

The scope of this process was further examined utilizing the high surface area LaFe_{0.95}Pd_{0.05}O_{3- δ} as the Pd source and SPhos as a supporting ligand (Fig. 8). Employing only 0.04 mol% Pd, heteroaryl chlorides and bromides were coupled with aryl boronic acids in good to excellent yields (Fig. 8a-d). Moreover, heteroaryl boronic acids proved to be proficient coupling partners under these conditions. For example, 2-thienylboronic acid was reacted with 2-bromopyridine to give the desired product in 78% isolated yield (Fig. 8). Aryl chlorides that did not contain any heteroatoms proved to be acceptable substrates under these conditions (Fig. 8e-g); however, they resulted in moderately decreased yields compared to heteroaryl chlorides. The above results clearly demonstrate that Pd-containing LaFeO₃ perovskites can be effective Pd sources in challenging cross-coupling reactions and can provide general and efficient catalytic activity when used in combination with supporting ligands. We envisage that this strategy will be applicable to a wide range of processes and has the potential to afford highly active, long-lived and recyclable catalysts.



Fig. 8 Substrate scope for Suzuki–Miyaura cross-coupling reactions using $LaFe_{0.95}Pd_{0.05}O_3$ as the Pd source (isolated yields).

5. Conclusions

A rapid microwave-assisted sol-gel preparation method yields Pd-substituted perovskite materials $Ln_{1-x}Pd_xFeO_{3-\delta}$ (with Ln =La, Y). The very short heating times in microwave reactions help us elucidate the phase formation process and have shown that the reaction for forming LaFeO3 is completed after 90 s. In contrast to furnace-based sol-gel or combustion methods, the microwave heating method has allowed the easy and reproducible tuning of material parameters such as crystallite size and surface area. Using a combination of characterization methods, we have shown that materials prepared with this method are phase pure and contain well-dispersed ionic Pd. We have also shown that changing the A site cation affects the structure and properties of the perovskite hosts. The applicability of the prepared perovskites as Pd⁰ catalyst sources in Suzuki cross-coupling reactions has been demonstrated for aryl chlorides. This method is amenable to further tuning of the reaction parameters and may allow for the preparation of materials with even higher surface areas, thereby impacting their properties.

Acknowledgements

This work is supported by the Department of Energy through DE-FG02-10ER16081. L.M.M. acknowledges support from the ConvEne IGERT Program (NSF-DGE 0801627). B.P.F. thanks the California NanoSystems Institute for the Elings Prize Fellowship in Experimental Science. The research carried out here made extensive use of shared experimental facilities of the Materials Research Laboratory supported by the NSF-MRSEC Program (DMR 1121053). The MRL is a member

of the NSF-funded Materials Research Facilities Network (http://www.mrfn.org). The use of the Advanced Photon Source at Argonne National Laboratory was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under contract no. DE-AC02-06CH11357. We thank Dr Christina Birkel for help with the TGA analysis.

References

- 1 M. S. Hegde, G. Madras and K. C. Patil, *Acc. Chem. Res.*, 2009, **42**(6), 704–712.
- 2 A. Gupta, A. Kumar, U. V. Waghmare and M. S. Hegde, *Chem. Mater.*, 2009, **21**(20), 4880–4891.
- 3 T. Baidya, A. Gupta, P. A. Deshpandey, G. Madras and M. S. Hegde, *J. Phys. Chem. C*, 2009, **113**(10), 4059–4068.
- 4 L. M. Misch, J. A. Kurzman, A. R. Derk, Y.-I. Kim, R. Seshadri, H. Metiu, E. W. McFarland and G. D. Stucky, *Chem. Mater.*, 2011, 23(24), 5432–5439.
- 5 U. Singh, J. Li, J. Bennett, A. Rappe, R. Seshadri and S. Scott, *J. Catal.*, 2007, 249(2), 349–358.
- 6 J. Li, U. G. Singh, T. D. Schladt, J. K. Stalick, S. L. Scott and R. Seshadri, *Chem. Mater.*, 2008, **20**(3), 6567–6576.
- 7 J. A. Kurzman, X. Ouyang, W. B. Im, J. Li, J. Hu, S. L. Scott and R. Seshadri, *Inorg. Chem.*, 2010, **49**(10), 4670–4680.
- 8 J. A. Kurzman, J. Li, T. D. Schladt, C. R. Parra, X. Ouyang, R. Davis, J. T. Miller, S. L. Scott and R. Seshadri, *Inorg. Chem.*, 2011, **50**(17), 8073–8084.
- 9 W. F. Libby, S. Url and S. Levine, *Science*, 1971, 171(3970), 499–500.
- 10 D. B. Meadowcroft, Nature, 1970, 226, 847-848.
- 11 Y. Nishihata, J. Mizuki, T. Akao, H. Tanaka, M. Uenishi, M. Kimura, T. Okamoto and N. Hamada, *Nature*, 2002, **418** (6894), 164–167.
- 12 S. P. Andrews, A. F. Stepan, H. Tanaka, S. V. Ley and M. D. Smith, *Adv. Synth. Catal.*, 2005, 347(5), 647–654.
- 13 R. Martin and S. L. Buchwald, *Acc. Chem. Res.*, 2008, **41**(11), 1461–1473.
- 14 E. Negishi, Q. Hu, Z. Huang, M. Qian and G. Wang, *Aldrichimica Acta*, 2005, **38**, 1–48.
- 15 K. Fugami and M. Kosugi, *Top. Curr. Chem.*, 2002, **219**, 87–130.
- 16 R. Chinchilla and C. Nájera, *Chem. Soc. Rev.*, 2011, 40(10), 5084.
- 17 D. S. Surry and S. L. Buchwald, Chem. Sci., 2010, 2(1), 27.
- 18 I. P. Beletskaya and A. V. Cheprakov, *Chem. Rev.*, 2000, 100, 3009–3066.
- 19 T. Hiyama and E. Shirakawa, *Top. Curr. Chem.*, 2002, 219, 61–85.
- 20 I. Hamada, A. Uozumi, Y. Morikawa, A. Yanase and H. Katayama-Yoshida, J. Am. Chem. Soc., 2011, 133(46), 18506–18509.
- 21 S. Yanagisawa, A. Uozumi, I. Hamada and Y. Morikawa, J. Phys. Chem. C, 2013, 117(3), 1278–1286.
- 22 M. D. Smith, A. F. Stepan, C. Ramarao, P. E. Brennan and S. V. Ley, *Chem. Commun.*, 2003, 2652.

- 23 S. P. Andrews, A. F. Stepan, H. Tanaka, S. V. Ley and M. D. Smith, *Adv. Synth. Catal.*, 2005, **347**(5), 647–654.
- 24 R. Roy, S. Komarneni and L. Yang, J. Am. Ceram. Soc., 1985, 68(7), 392–395.
- 25 J. D. Katz, Annu. Rev. Mater. Sci., 1992, 22, 153-170.
- 26 D. Baghurst, A. Chippindale and D. M. P. Mingos, *Nature*, 1988, **332**, 311.
- 27 K. Biswas, S. Muir and M. Subramanian, *Mater. Res. Bull.*, 2011, 46(12), 2288–2290.
- 28 A. Birkel, L. E. Darago, A. Morrison, L. Lory, N. C. George, A. A. Mikhailovsky, C. S. Birkel and R. Seshadri, *Solid State Sci.*, 2012, 14(6), 739–745.
- 29 A. Birkel, K. A. Denault, N. C. George, C. E. Doll, B. He, A. A. Mikhailovsky, C. S. Birkel, B.-C. Hong and R. Seshadri, *Chem. Mater.*, 2012, 24, 1198–1204.
- 30 C. S. Birkel, W. G. Zeier, J. E. Douglas, B. R. Lettiere, C. E. Mills, G. Seward, A. Birkel, M. L. Snedaker, Y. Zhang, G. J. Snyder, T. M. Pollock, R. Seshadri and G. D. Stucky, *Chem. Mater.*, 2012, 24(13), 2558–2565.
- 31 C. S. Birkel, J. E. Douglas, B. R. Lettiere, G. Seward, N. Verma, Y. Zhang, T. M. Pollock, R. Seshadri and G. D. Stucky, *Phys. Chem. Chem. Phys.*, 2013, 15(18), 6990– 6997.

- 32 A. Birkel, N. A. DeCino, N. C. George, K. A. Hazelton, B.-C. Hong and R. Seshadri, *Solid State Sci.*, 2013, 19, 51–57.
- 33 Z. Zhong, K. Chen, Y. Ji and Q. Yan, *Appl. Catal.*, A, 1997, 156, 29–41.
- 34 P. Ciambelli, S. Cimino, L. Lisi, M. Faticanti, G. Minelli, I. Pettiti and P. Porta, *Appl. Catal.*, *B*, 2001, **33**(3), 193–203.
- 35 X. Qi, J. Zhou, Z. Yue, Z. Gui and L. Li, *Mater. Chem. Phys.*, 2002, **78**, 25–29.
- 36 X. Zhang, Y. Li, H. Li and W. Shen, J. Nat. Gas Chem., 2012, 21(2), 113–118.
- 37 J. Zhang and H. Li, *Perovskite: Crystallography, Chemistry and Catalytic Performance*, Nova Science Pub Incorporated, 2013.
- 38 P. D. Ramesh, D. Brandon and L. Schächter, *Mater. Sci. Eng.*, A, 1999, 266(1-2), 211–220.
- 39 H. M. Rietveld, J. Appl. Crystallogr., 1969, 2(2), 65-71.
- 40 A. A. Coelho, *Topas Academic V4.1 Software*, Coelho Software, Brisbane, Australia, 2007.
- 41 M. Brun, A. Berthet and J. Bertolini, J. Electron Spectrosc. Relat. Phenom., 1999, 104(1-3), 55–60.
- 42 T. E. Barder, S. D. Walker, J. R. Martinelli and S. L. Buchwald, J. Am. Chem. Soc., 2005, 127(13), 4685– 4696.