PEROVSKITE CATALYSTS ENHANCED COMBUSTION ON POROUS MEDIA

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ABSTRACT

The effects of La-Sr-Fe-Cr-Ru based perovskite catalysts, on matrix stabilized combustion in a porous ceramic media are explored. Highly porous silicon carbide ceramics are used as a porous media for a catalytically enhanced superadiabatic combustion of a lean mixture of methane and air. The direct observation of the flame during the combustion becomes possible due to a specially designed stainless steel chamber incorporating a quartz window where the initiation and propagation of the combustion reaction/flame was directly visible. Perovskite catalytic enhancement of SiC porous matrix with $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.6}\text{Cr}_{0.35}\text{Ru}_{0.05}\text{O}_3$, $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.6}\text{Cr}_{0.4}\text{O}_3$, $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.95}\text{Ru}_{0.05}\text{O}_3$, $\text{La}_{0.75}\text{Sr}_{0.05}\text{Cr}_{0.95}\text{Ru}_{0.05}\text{O}_3$, and $\text{LaFe}_{0.95}\text{Ru}_{0.05}\text{O}_3$ were used to enhance combustion. The flammability limits of the combustion of methane and air were explored using both inert and catalytically enhanced surfaces of the porous ceramic media. By coating the SiC porous media with perovskite catalysts it was possible to lower the minimum stable equivalence ratio and achieve more efficient combustion.

Keywords: Porous-media burner; low-calorific fuel; perovskite catalysts; catalytic combustion.

1. INTRODUCTION

Matrix stabilized porous burner technology is an advanced combustion method in which a mixture of fuel and oxidizer is burned within a solid porous medium, as opposed to open, burner-stabilized flames such as that on a Bunsen burner. The advantages of porous burners over that of burner-stabilized flames is mainly due to the thermal feedback effect provided by the solid medium through which heat conduction in the upstream direction results in preheating the incoming reactants, [1-3], where a review article of combustion within porous media is provided in Ref.[1], a paper describing a porous media burner for heat-exchanger/boiler application is presented in Ref. [2], design and operation of a reciprocal flow porous burner achieving super adiabatic combustion is described in Ref. [3]. The process yields a flame temperature higher than the equilibrium adiabatic value achievable by the fuel-oxidizer mixture in the absence of a porous medium, which is called superadiabatic combustion [4-8]. The heat transfer can be further enhanced by increasing the surface area to volume ratio of the porous medium [6, 9, 10] and by the increased mixing due to turbulence generated in the porous structure [7, 11]. Therefore porous burners help to sustain lean flames of fuel-oxidizer mixtures lower than the conventionally known lean flammability limit, and can also be used for burning low-calorific gases [12-14]. Applications of porous burner technology include power generation via thermoelectric devices [8, 12, 15-17], small scale heating purposes [18], and combustion of low-calorific value landfill-seepage gases [2, 19]. Due to increasing levels of environmental concerns and conservation of energy resources, burning low-calorific value gases and lean mixtures are desirable.

To extend the lean burning limits using the porous burner, catalysts can be coated on the surfaces of the porous medium. This is particularly advantageous because the porous structure possesses large surface to volume ratio, providing the much needed surface area for applications of heterogeneous catalysts. This study presents the results of coating five different types of perovskite catalysts $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.6}\text{Cr}_{0.35}\text{Ru}_{0.05}\text{O}_3$, $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.6}\text{Cr}_{0.4}\text{O}_3$, $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.95}\text{Ru}_{0.05}\text{O}_3$, $\text{La}_{0.75}\text{Sr}_{0.05}\text{Cr}_{0.95}\text{Ru}_{0.05}\text{O}_3$, and $\text{LaFe}_{0.95}\text{Ru}_{0.05}\text{O}_3$ to the surface of an articulated silicon carbide (SiC) porous structure. The use of such catalytically active materials as a coating for the porous media could have the further benefit of increased flame stability and control of the flame location within of the porous matrix. By employing perovskite catalysts, the activation energy of combustion reactions are reduced, this lowers the amount of heat recirculated required for stable combustion within the media. Allowing the flame of a lean mixture to stabilize closer from the inlet of the catalytically enhanced porous structure, at any given flow rate and lean equivalence ratio, this will increase the range of locations where a flame can be stabilized within the media and, simultaneously, decrease its possible minimum stable equivalence ratio, (Φ), which is defined as the actual ratio of fuel to oxidant over the ideal ratio of fuel to oxidant where all the fuel has reacted with no excess air, thus being at stoichiometry [20].

It is generally accepted that alumina (Al_2O_3) porous matrix is catalytically inert and does not participate in the enhancement of the combustion reaction inside of the porous media [21]. Some attempts were used to investigate the effect of silicon carbide (SiC) ceramic to verify if the lean limit can be extended in the combustion inside of the SiC porous matrix [22]. Our previous work on superadiabatic combustion in Al_2O_3 and SiC coated porous media was devoted to the investigation of temperature and lean limits for combustion reactions and comparison of the

performance of these two materials [22, 23]. In that work the porous burner was built utilizing porous alumina foam with 85% of porosity, 2-3 mm average pore size, as a combustion chamber. Two honey comb alumina flame arresters were located at both sides of the porous matrix to ensure the efficient gas mixture delivery to the combustion zone, and the three alumina parts were enclosed inside of the stainless steel casing. One thermoelectric module was attached to the hot surface of the steel casing allowing power to be generated from the temperature difference between the hot combustion chamber and the cold side of the thermoelectric module. It was established that SiC surfaces of the porous combustion matrix might be a good promoter of the combustion for the stoichiometric fuel to air ratio, which performed in a better way in comparison with inert Al_2O_3 surfaces [23]. However, SiC coated porous media did not outperform the inert Al_2O_3 matrix when the lean mixtures were used. The microscopy analysis of the surfaces of the porous media within the zones where combustion occurred revealed that while the carbon deposits were formed on catalytically inert Al_2O_3 surfaces, there were no deposits found on the SiC coated surfaces in the case where stoichiometric mixtures were used. Thus SiC helps to promote the complete combustion reactions, however it is possibly prone to the oxidation itself during combustion and, once the significant amounts of SiO_2 phase forms on the surface of SiC, the catalytic properties of the ceramic will degrade. Therefore new and more active catalysts should be explored which would be better suited to promote combustion, reduced the recirculated energy requirement needed to stabilize the flame, and facilitate the superadiabatic combustion to generate cheap and efficient heat [23].

Noble metals, such as platinum (Pt) or palladium (Pd), show high methane combustion activity at low temperature, and they, indeed, are very promising candidates to facilitate combustion reactions [24, 25]. However, while catalytic activity of noble metals is high, their

cost is also very high, and their possible sublimation and/or sintering can occur in a catalytic burner at high temperatures in the presence of water and CO₂ gasses [26]. Another problem in the catalytic combustion of methane and other hydrocarbons is carbon deposition and, as a result, catalyst deactivation [27].

Transition metals are considered excellent catalysts for many applications. Transition metals' perovskite based ceramics with a crystal structure ABO₃, wherein the large cation A has a dodecahedral co-ordination and the smaller B cation, usually a transition metal, has a six-fold co-ordination are also considered as excellent catalytic material in many reduction and oxidation reactions [27]. LaFeO₃ or LaCrO₃, based perovskites are attractive materials because their crystal structure serves as the support for the transition metal ions due to its high thermal stability, high electronic conductivity, as well as other properties. To inhibit carbon deposition, which can lead to deactivation of the catalysts, such promising strategies as reduction of perovskite oxide phase to precipitate small metal particles at the surfaces of ceramics resulting in high activity and sustainability against coke formation can be done [28, 29]. Some of the perovskites with appropriate doping, called mixed ionic electronic conducting (MIEC) perovskites exhibit both ionic and electronic conductivities, thus can even further enhance the reduction and oxidation combustion reactions [30]. The promising MIEC perovskites contain rare earth cations located on the A-site of perovskite lattice where large A³⁺ cations (such as lanthanum La³⁺ ion) were substituted with different A²⁺ cations (such as strontium Sr²⁺, calcium Ca²⁺, or barium Ba²⁺) introducing oxygen vacancies in the lattice and at the same time inducing the mixed valence state in B-site cations such that cobalt (Co³⁺), manganese (Mn³⁺), or iron (Fe³⁺) become a mixture of Co³⁺/Co⁴⁺; Mn³⁺/Mn⁴⁺, and Fe³⁺/Fe⁴⁺ ions [31-33]. Oxidation reactions over the perovskite materials have been found to follow two routes, either incorporating surface absorbed oxygen

species or enhancing the mobility of lattice oxygen and a redox cycle of the B-ion [34]. Additionally perovskites showed promising performance toward methane oxidation, even in gasified biomass testing [35].

Pure LaCoO_3 was investigated as a catalyst toward CO_2 reforming of CH_4 in comparison with LaNiO_3 perovskite and La_2NiO_4 and La_2CoO_4 ceramic materials, where La_2NiO_4 showed the highest activity and stability for dry CH_4 reforming reactions [36]. Pure LaCoO_3 , LaMnO_3 , and LaFeO_3 perovskites were also investigated as promoters for methane oxidation and the nature of the active sites on the surfaces of these oxides were also studied. It was established that the significant quantities of carbonated species were formed on the surfaces of perovskites after methane oxidation [37]. The addition of carbonates to rare earth oxides is known to improve the selectivity for the oxidative coupling of methane [38], which is the process of converting methane into value added chemicals through catalysts, a hard process due to methane's strong covalent bonding and, thus, high chemical stability.

It was established that the catalytic performance of pure perovskites, such as LaFeO_3 or LaCoO_3 , were significantly improved by doping La^{3+} with Sr^{2+} ion on the A site of the perovskite lattice. It was shown that $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ and $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ showed similar catalytic activity in methane combustion, but $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ perovskites were much more easily reduced by H_2 or CH_4 in comparison with $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ perovskites [26]. It was also reported that $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ catalysts achieved better than Pt performance in treating NO_x in fuel-efficient diesel engines [39]. Other substitutions of A and B sites in perovskite structures, such as with silver ions (Ag^{3+}) [40], cerium ions (Ce^{4+}) [41], praseodymium (Pr^{3+}), samarium (Sm^{3+}), europium ions (Eu^{3+}) [42], as well as the addition of precious metals, such as Pd, and their regeneration [43], provide a significant synergistic effect for enhancement of catalytic activity of the perovskites

and are proposed to be an effective tool of catalyst design and customization [44]. Several studies were performed on ruthenium (Ru) containing perovskites where oxidation of CO were performed over $\text{La}_{0.7}\text{Sr}_{0.3}\text{Cr}_{1-x}\text{Ru}_x\text{O}_3$ ($0.025 \leq x \leq 0.100$) perovskite type catalysts. Improved catalytic activity of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Cr}_{1-x}\text{Ru}_x\text{O}_3$ reported along with decreased surface resistivity when it was established that the concentration of Ru^{4+} in the surface region and its stability are both determining factors for the CO oxidation activity [45]. Another Ru ion containing compositions, such as $\text{La}_{0.6}\text{Sr}_{1.4}\text{Fe}_{0.8}\text{Ru}_{0.2}\text{O}_{4\pm\delta}$, $\text{La}_{0.4}\text{Sr}_{1.6}\text{Fe}_{0.7}\text{Ru}_{0.3}\text{O}_{4\pm\delta}$, and $\text{La}_{0.2}\text{Sr}_{1.8}\text{Fe}_{0.6}\text{Ru}_{0.4}\text{O}_{4\pm\delta}$ were shown to exhibit promising electrical properties at high temperature and therefore might also potentially be considered as a good catalyst [46]. LaRuO_3 was shown to be very catalytically active with ruthenium in 3+ oxidation state. $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ was then synthesized with an oxidation state of 4+, an oxidation state that it is more stable for ruthenium, which increase the thermal stability of the perovskite [47].

Here the study of superadiabatic combustion of methane inside of the porous matrices with catalytic enhancement by perovskites is reported. Five different perovskite compositions were used for methane combustion, different equivalence ratios were used and the obtained results were compared to the methane combustion in the SiC porous matrix where no perovskite promoter was present. The lean limit was established depending on the perovskite composition, as well as temperature profile measurements and determination of the combustion zone locations at the given lean limit was recorded. The perovskite composition that showed the best results for lean superadiabatic combustion was established.

2. EXPERIMENTAL DESIGN

Fig. 1 shows a schematic diagram of the experimental setup used in this work. The combustion chamber is composed of two types of porous media: two alumina honeycomb at each end of the combustion chamber and an articulated SiC or alumina foam in the middle. The images of the cylindrical articulated foam are shown in Fig. 2; the foam is highly porous consisting of 85% of porosity, has a diameter of 20.32 mm, a length of 50.8 mm, and an average pore size of 2-3 mm. The lower porosity (38%) alumina honeycomb ceramic cylinders that are placed at the inlet and at the exhaust of the combustion chamber, between the reticulated foam, has 8 pores per centimeter, a diameter of 20.32 mm, and a length of 25.4 mm. The average pore size of the honeycomb alumina is much lower than the articulated foam's, which allows the flame to propagate along the axis of the articulated foam ceramic but to quench at top surface of the honeycomb. Therefore, the honey comb ceramic modules acts as a flame arrestor due to their lower average pore size, forcing the combustion zone to be stabilized in articulated ceramic foam section of the burner.

Eight K-Type thermocouples were placed along the axis of the cylindrical SiC reticulated foam, equidistantly spaced 7.2 mm apart (see Fig. 1) to measure the temperature distribution within the combustion chamber. The thermocouples have an uncertainty of 0.75% from 0 to 1250 °C. The thermocouples were connected to a National Instruments data acquisition system (NI USB-6210) and then logged into the LabView virtual instrument for data collection.

High grade methane (99% purity) and dry laboratory compressed air were used in the combustion experiment. The mixture of methane and air was formed in a line of sufficient length to allow proper mixing after the two reactant streams meet at a T-junction (Fig. 1). The air and methane flows were each controlled with Omega (FMA 3200) mass flow controllers. The flow

controllers have an uncertainty of $\pm 1.5\%$ of their full scale range of 0-5 L/min and 0-10 L/min for the methane and air flow meters, respectively.

The combustion chamber enclosing the porous burner was composed of stainless steel and featured a quartz transparent window that allowed observation of the flame behavior during ignition (see a movie in an annex). In this study the assembly featured a casing that was insulated on every side with a 25.4 mm thick ceramic fiber board insulation as seen in Fig. 3 (the panel covering the window during combustion experiments is not shown in Fig. 3 to better showcase additional details), to reduce heat loss from the burner, to increase the repeatability of the experiments, and to ensure the measurable effects of the catalysts activity in the chemical reactions of combustion.

Multiple samples of articulated foam ceramics were used in this work. In addition to the uncoated SiC articulated foams, perovskite catalyst $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.6}\text{Cr}_{0.35}\text{Ru}_{0.05}\text{O}_3$, $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.6}\text{Cr}_{0.4}\text{O}_3$, $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.95}\text{Ru}_{0.05}\text{O}_3$, $\text{La}_{0.75}\text{Sr}_{0.05}\text{Cr}_{0.95}\text{Ru}_{0.05}\text{O}_3$, and $\text{LaFe}_{0.95}\text{Ru}_{0.05}\text{O}_3$ coated SiC articulated foams were used inside the porous burner. Perovskite powders were produced by Praxair Inc, specialties ceramics by a spray pyrolysis method. By conducting several runs of both inert and catalytically enhanced articulated foams the run to run variation and repeatability was measured. The lattice parameters and crystal structure analysis of all five perovskite compositions were measured using a high resolution synchrotron X-ray at the Advanced Photon Source (Beamline11-BM), Argonne National Laboratory, with the US Department of Energy. Refinement of the structure was performed using the HighScore Plus software. The microstructures of five perovskite composition were characterized using Scanning Electron Microscope (SEM, VEGA II, TESCAN, USA).

The catalytically active perovskite coatings were deposited on the surface of the porous media using the dip coating method. Samples of SiC articulated foams were coated with five different compositions of perovskite catalysts. The dip coating process consisted of forming a suspension of the perovskite powders in isopropyl alcohol and placing the slurry mixture in a test tube submerged in a water bath within an ultrasound machine to ensure stability of the suspension. The articulated foam ceramic was then lowered into the slurry and held suspended for one minute, which allowed enough time for the coating to penetrate the pores and bond to the surface. Once coated the articulated foam was placed in a tray and allowed to dry overnight in the fume hood until all the isopropyl alcohol fully evaporated.

2.2 TESTING PROCEDURE

The reactants were allowed to enter the burner from the bottom of the combustion chamber as seen in Fig. 1. The burner was first ignited using a spark near the top of the articulated foam ceramic or at the thermocouple location T7, at $\Phi = 1.0$. Once ignited, the Φ is reduced to 0.7. At an equivalence ratio of 0.7, the flame is very stable given a cold combustion chamber, and the max temperature of the flame does not exceed 1200 °C during warm-up. The fuel flow rate was varied to obtain the desired Φ , and the air volumetric flow rate was held constant at 0.008 m³/min throughout the experiment. A summary of the experiment conditions is shown in Table 1. After ignition, at $\Phi = 0.7$, the premixed combustion wave propagated in the opposite direction of the flow. Through the quartz window, the combustion zone was observed as a highly luminescent zone (see a movie in an annex) slowly traveling upstream. The combustion wave was allowed to travel against the direction of the flow to record the eventual downstream movement of the wave once the Φ is further reduced. This initial value of $\Phi = 0.7$ was used to

warm-up the combustion chamber. If any of the eight thermocouples reached a temperature higher than 1200 °C, which is the higher limit of measurement for the thermocouples used in the experiments, the volumetric flow rate of methane was reduced while maintaining the air flow rate constant, reducing Φ . This caused the temperature to drop. The combustion chamber was never allowed to reach temperatures well above 1200 °C for prolonged periods of time to protect burner components such as the quartz window and thermocouple wires. Preheating was used as it has a significant effect on combustion in porous media [48]. It was important in this work that the burner was essentially “saturated” with the thermal energy before continuing with the minimum Φ measurement because by such saturation, the effect of catalysts could be accurately accessed.

The burner was determined to have reached the steady state if the temperature readings and the flame position had remained steady for 10 minutes. All the temperature data reported here are those measured during the steady state. It is noted that, when discussing the results of Fig. 4, this 10-minute criterion was applied whenever the Φ was changed, for example, to reach the condition near the flammability limit. The lean flammability limit was reached at the Φ for which the flame failed to maintain a steady location. The process was repeated for the articulated foams investigated to document the behavior of the different catalytically enhanced or articulated foam ceramics without perovskite coating.

3. RESULTS AND DISCUSSION

By decreasing the Φ in the burner in a step-wise manner, the flame started moving in a step-wise manner downstream. As the flame moved downstream, incoming reactants cooled down the upstream section of the solid ceramic core, increasing the temperature difference between the

solid closed to the inlet and the part of the solid downstream from the combustion wave, which enhanced the heat transfer within the solid, thus preheating the reactants. Eventually the heat loss, heat recirculated, and thermal energy reached a balance, and the combustion wave slowed to a stop and began to “stand” reaching steady state. As the step-wise downstream movement of the flames neared the end of the solid ceramic length, the radiation to the surroundings becomes a greater portion of the total heat loss [49]. Further, decreases in Φ will eventually cause the flame to blow off or exit the SiC articulated foam and be extinguished. The feedback of heat transfer from products to the reactants is, in part, a function of the porous media thickness and the axial position of the flame within the porous media, with respect to the media’s inlet and outlet [49-51].

Fig. 4 shows the typical time trace of temperature collected from the experiments using SiC porous media. During the preheating stage of the experiments, the flame propagated upstream and began to stand near thermocouple location T2, as seen at minute 0 in Fig. 4. Once steady state was reached, or the temperature approached 1200 °C, the amount of methane in the mixture was reduced. The Φ was reduced at minute $t = 19$, $t = 45$, $t = 78$, $t = 100$, $t = 145$, $t = 178$, and $t = 265$, shown by the dash lines in Fig. 4. The decrease in Φ would result in less heat generated to heat up the incoming fuel-air mixture, and therefore, there would be insufficient heat to sustain a stable combustion at a fixed position [48]. The combustion wave retreated to a downstream location until a balance between heat generation, increased heat recirculation, and heat loss was reestablished to stabilize the flame to stand again. This process is observed between the time intervals of $t = 0-19$, $t = 45-78$, $t = 78-100$, $t = 100-145$, $t = 145-178$, and $t = 178-265$ minutes in Fig. 4. The drop in temperature at the thermocouple location with the highest temperature after the dashed line and the increase in temperature of the next thermocouple location after the dash

line in Fig. 4 demonstrate how the combustion wave moved downstream as the Φ was reduced. For example, the temperature peak detected by thermocouple T4 occurred around $t = 220$ minutes, while that for T3 is around $t = 190$ minutes. One might conclude that as the Φ is reduced, the flame location moves in the downstream direction.

The downstream movement of the combustion wave due to lowering of the Φ is more apparent in Fig. 5. Where it is shown that the flame moved and stabilized at a downstream location once the equivalent ratio is reduced, the temperature profiles shown were taken when the burner had reached steady state and when the flame had begun to stand. Additionally, the magnitude of the flame displacement due to the change in Φ becomes apparent. The temperature distribution at $\Phi = 0.58$, taken at $t = 98$ minutes, shows that the flame stabilized at the thermocouple location T2 with a maximum temperature of $1,030^\circ\text{C}$. At $\Phi = 0.54$, the flame has propagated downstream from thermocouple location T2 and has begun to stand at thermocouple location T3 with a maximum temperature of 975°C . At $\Phi = 0.52$, the flame stabilized at thermocouple location T5 with a maximum temperature of 994.3°C . The flame moved downstream from the thermocouple location T2 to T5 as Φ was reduced from 0.58 to 0.52. Such controlled location of the flame inside of the porous media as a function of equivalence ratio is important because it allowed the flame to stabilize in a controlled manner thus increasing the homogeneity of temperature distribution, increasing the range of volumetric flow rates that the burner can support, and allowing more efficient combustion. The downstream shift of position of the flame due to the reduction of equivalence ratio observed agrees with previous research on combustion on porous media [52].

Fig. 6 shows the data with higher resolution from the same run as Fig. 4 for $t = 177$ -377 minutes, a shorter time range toward the end of the experiment. At $t = 177$ min, the wave is stabilized at thermocouple location T3, with a $T_{\max} = 1,004$ °C. After the Φ has been reduced the temperature at that location drops at $t = 185$ min, followed by an increase at thermocouple location T4 from $T = 976$ °C to $T = 1099$ °C. This is due to the downstream motion of the combustion wave. Eventually the downstream displacement motion of the combustion wave slows down and begins to stand, starting at 250 minutes, the temperature profile around minute 260 is the location of the temperature profile ($\Phi = 52$) in Fig. 5. Additionally it is evident that after reducing the Φ again at minute 270 of Fig. 6, the downstream motion of the wave continues to thermocouple location T6 and T7 until it is quenched by the lower porosity honey comb alumina ceramic. Thus the temperature profile at minute 260 of Fig. 6 and the line labeled ($\Phi = 52$) in Fig. 5 show the temperature profile of the lowest stabilized Φ where the combustion chamber can sustain a standing wave.

Multiple experiments were done to collect data for inert SiC articulated porous media and catalytically enhanced SiC. Table 2 shows the tabulated results, specifically the minimum stable Φ achieved, for inert uncoated SiC articulated ceramic foam and for the SiC catalytically enhanced with five different compositions of perovskite catalysts: $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.60}\text{Cr}_{0.35}\text{Ru}_{0.05}\text{O}_3$, $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.60}\text{Cr}_{0.40}\text{O}_3$, $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.95}\text{Ru}_{0.05}\text{O}_3$, $\text{LaFe}_{0.95}\text{Ru}_{0.05}\text{O}_3$, and $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.95}\text{Ru}_{0.05}\text{O}_3$. The $\pm$ sign in the table shows the standard deviation, or run-to-run variation, between the results of the multiple runs with the same configuration of coated or uncoated articulated foam ceramics. The trend of lowering Φ by doping mixed ionic electronic conducting perovskites can be observed from the results presented in Table 2, it shows that that

all five perovskite compositions yielded better results at lowering the minimum stable Φ compared with the uncoated SiC articulated foam.

The X-ray diffraction patterns of all five perovskite compositions are presented in Fig. 7. The lattice parameters along with the unit cell volume and the goodness of fit X^2 are presented in Table 3. All perovskites adopt the orthorhombic *Pbnm* (No—62) space group structure. All the powders are phase pure as no extra peaks were detected, which might indicate the presence of the secondary phases. The SEM micrographs of five perovskite compositions are shown in Fig. 8. As the perovskite powders were produced by the spray pyrolysis, the powders consisted of small particles with submicron average sizes, (Fig. 8: B, D, F, H, J), but these small particles were agglomerated into large and rather soft sphere with the diameter size of 20-200 μ m. These powders were used for the deposition of the catalyst on the articulated SiC foams for performing combustion experiments.

While all perovskite-coated porous media show improvement for lowering the Φ in comparison with uncoated SiC foam, the best results were achieved for perovskite composition where both La^{3+} ions substituted with Sr^{2+} ions and Fe^{3+} ions were present in addition to the existence of minute quantities of $\text{Ru}^{3+}/\text{Ru}^{4+}$ ions. It is known that Cr^{3+} ions in ABO_3 perovskite structure create rather stable and non-catalytically active ceramics, which can be well used as interconnect in solid oxide fuel cells [53] due to its stability in oxidizing and reducing environment and high electronic conductivity [54]. Therefore three compositions containing Cr^{3+} ions, $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.95}\text{Ru}_{0.05}\text{O}_3$, $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.60}\text{Cr}_{0.35}\text{Ru}_{0.05}\text{O}_3$, and $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.60}\text{Cr}_{0.40}\text{O}_3$ used in the present experiment did not show the best catalytic enhancement of combustion. However, despite the presence of non-active Cr^{3+} ions, the availability of catalytically active Fe^{3+} ions in

the perovskite lattice slightly improved the performance of $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.60}\text{Cr}_{0.35}\text{Ru}_{0.05}\text{O}_3$ and $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.60}\text{Cr}_{0.40}\text{O}_3$ even when Cr^{3+} ions were also present. The composition $\text{LaFe}_{0.95}\text{Ru}_{0.05}\text{O}_3$ did not show the best results even though the Cr^{3+} ions were not present. This can be explained by the fact that the A site of ABO_3 perovskite is presented by La^{3+} ion without any substitution of La^{3+} with Sr^{2+} , which leads to almost stoichiometric quantities of O^{2-} ions and reduced amount of oxygen vacancies in the lattice. As a result, both ionic and electronic conductivities, along with oxygen mobility and catalytic activity of $\text{LaFe}_{0.95}\text{Ru}_{0.05}\text{O}_3$ perovskite, are decreased in comparison with compositions where a certain quantity of La^{3+} ions are substituted with Sr^{2+} ions in the lattice. The $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.95}\text{Ru}_{0.05}\text{O}_3$ perovskite showed the most promising catalytic activity toward enhancement of superadiabatic combustion as it has both La^{3+} ions substituted with Sr^{2+} ions; Cr^{3+} ions are not present on B site of the perovskite lattice and, at the same time, a small number of Fe^{3+} ions were substituted with very active $\text{Ru}^{3+}/\text{Ru}^{4+}$ ions, bringing the best performance in catalytic enhancement of combustion inside of the porous media.

Fig. 9 shows the last minutes of a run with the SiC porous combustion chamber enhanced with $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.95}\text{Ru}_{0.05}\text{O}_3$. The data was collected with the same procedure as the data collected for the uncoated SiC foam run(s) shown in Fig. 4 and Fig. 6. At $t = 200$ minutes, of Fig.9, the Φ was changed to 0.5 causing the flame to propagate downstream and eventually begin to stand between $t = 213$ - 223 minutes at thermocouple location T6 with a T_{max} of 1039°C , where the temperature profile and Φ at steady state was recorded. At $t = 223$ minutes the Φ was reduced to 0.49, in this case the flame failed to stand any further and it was quenched by the alumina honeycomb. Experiments and data were collected that followed the methods shown in Figs. 4,6 and 9 for all of the SiC articulated foams coated with the five different types of

perovskites compositions and the results have been summarized in Table 2. The minimum average Φ achieved by an inert SiC articulated foams was 0.547 while the catalytically enhanced SiC porous media reduced the minimum stable Φ to 0.535-0.51; $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.95}\text{Ru}_{0.05}\text{O}_3$ perovskite provided the best results with a minimum average Φ of 0.51.

Fig. 10 shows an example of the contrast between the temperature profile of a flame stabilized within an inert SiC porous foam and a flame that has been stabilized within a $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.95}\text{Ru}_{0.05}\text{O}_3$ perovskite enhanced SiC porous foam at a matching Φ of 0.52. The perovskite-coated SiC stabilized at the thermocouple location T3, with a T_{max} of 1072 °C, while the non-coated SiC stabilized at the thermocouple location T5, with a T_{max} of 994 °C. It is a total of 1.45 cm of displacement difference of the flame location, while having both the same Φ and volumetric flow rate. The flame within the catalytic enhanced SiC needs less heat recirculation to be stabilized within the media, thus allowing it to be stabilized closer to the inlet for any given parameters when compared with a flame within an inert SiC foam. This can be explained by the decrease in activation energy of the reaction achieved by the perovskite catalyst.

Fig. 11 shows the temperature profile of the enhanced SiC with $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.95}\text{Ru}_{0.05}\text{O}_3$ at a stabilized standing wave with an Φ of 0.52 and 0.50. The minimum stable Φ was 0.5, which the flame stabilized to a standing wave located at T6 while at $\Phi = 0.52$, the flame successfully stabilized at T3. Thus, by examining results of Figs. 10 and 11, it is evident that by coating the porous SiC articulated foam with perovskite catalysts, the combustion wave can stabilize closer to the inlet at any given Φ , in the same way an increase in Φ (as seen in Fig. 5) or lowering of the flow rate [49] can help stabilize the flame upstream. For the flame to stabilize at a given position in the porous media, the right balance of chemical input, thermal energy recirculation,

and heat loss must occur. By enhancing the surface area of the porous media with high-temperature perovskite catalysts the activation energy required to release the chemical energy of the reactants is reduced. It effectively increases the minimum stable Φ that a catalyzed porous burner can achieve.

4. CONCLUSIONS

Various perovskite compositions were deposited on the surface of the SiC articulated foam used to stabilize the flame location in the combustion chamber. The performance of these compositions during combustion was tested and the conclusion can be made as follows.

- (1) The mixed ionic electronic conducting perovskite compositions proved to be adequate catalysts to lower the minimum equivalence ratio in the combustion chamber below the published lean flammability limits of the fuel used in this study. These results indicated that by coating the articulated foams with perovskite-type catalysts, the reaction rate of combustion was increased. The best perovskite composition tested was $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.95}\text{Ru}_{0.05}\text{O}_3$, which reduced the average minimum equivalence ratio to 0.51 ± 0.01 from 0.547 ± 0.018 when compared with tests of non-perovskite coated inert experiments.
- (2) It was established that while all five perovskite compositions of catalyst deposited on the surface of the SiC porous media improved the performance of the porous burner, the compositions $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.95}\text{Ru}_{0.05}\text{O}_3$, $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.60}\text{Cr}_{0.35}\text{Ru}_{0.05}\text{O}_3$, and $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.60}\text{Cr}_{0.40}\text{O}_3$, where Cr^{3+} ions were present in the ceramic structure did not performed in the best possible way. This might be explained by rather inert catalytic nature of Cr^{3+} ions.

(3) One composition ($\text{LaFe}_{0.95}\text{Ru}_{0.05}\text{O}_3$), where La^{3+} ions on the A site of the perovskite structure were not substituted by Sr^{2+} ions, also did not show the minimum equivalence ratio achieved during combustion, which could possibly be explained by not sufficient number of oxygen vacancies available for the oxygen reduction reaction in the combustion chamber in comparison with the compositions where Sr^{2+} ions have been present.

(4) The best enhancement of combustion was achieved with the composition $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.95}\text{Ru}_{0.05}\text{O}_3$, where Sr^{2+} ions were present creating significant number of oxygen vacancies in the lattice and only highly catalytically active Fe^{3+} and $\text{Ru}^{3+}/\text{Ru}^{4+}$ ions were present on the B site of the lattice.

Finally, it was demonstrated that due to the decrease in activation energy from catalytic enhancement, the minimum equivalence ratio that could be sustained in the combustion chamber was decreased. This can translate to an increase in stability in the combustion of lean mixtures, which is the most important merit of matrix-stabilized combustion on porous media.

NOMENCLATURE

Φ	Equivalence ratio
Ag	Silver
Al_2O_3	Alumina/Aluminum oxide
Ce	Cerium
Cr	Chromium
Eu	Europium
Fe	Iron
La	Lanthanum
MIEC	Mixed ionic electronic conducting
Pd	Palladium
Pr	Praseodymium
Pt	Platinum
Ru	Ruthenium
SEM	Scanning electron microscope
SiC	Silicon carbide
Sm	Samarium
Sr	Strontium
T	Temperature [Celsius]
t	Time [minutes]
T#	Thermocouple location
XRD	X-ray diffraction

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FIGURE CAPTIONS

Figure 1. Experimental setup schematic.

Figure 2. Silicon carbide articulated ceramic foams, used to stabilize the flame inside of the combustion chamber.

Figure 3. Porous burner, front insulation panel not shown to show additional details.

Figure 4. Temperature vs time of non-coated SiC experiment as the equivalence ratio of the mixture is reduced and steady state temperature profile measurements were taken.

Figure 5. Shows the temperature of the thermocouple locations versus axial distance, along the axis of the combustion chamber, of the stabilized standing combustion wave at 0.58, 0.54, and 0.52 equivalence ratios.

Figure 6. Temperature vs the range of time of non-coated SiC experiment where the minimum stable equivalence ratio temperature profile measurements were taken (between 250-270 minutes).

Figure 7. X-ray diffraction of the perovskite compositions.

Figure 8. SEM micrographs of A) $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.60}\text{Cr}_{0.35}\text{Ru}_{0.05}\text{O}_3$; B)

$\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.60}\text{Cr}_{0.35}\text{Ru}_{0.05}\text{O}_3$; C) $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.60}\text{Cr}_{0.40}\text{O}_3$; D) $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.60}\text{Cr}_{0.40}\text{O}_3$; E)

$\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.95}\text{Ru}_{0.05}\text{O}_3$; F) $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.95}\text{Ru}_{0.05}\text{O}_3$; G) $\text{LaFe}_{0.95}\text{Ru}_{0.05}\text{O}_3$; H) $\text{LaFe}_{0.95}\text{Ru}_{0.05}\text{O}_3$;

I) $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.95}\text{Ru}_{0.05}\text{O}_3$; J) $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.95}\text{Ru}_{0.05}\text{O}_3$ perovskite powders.

Figure 9. Temperature vs the range of time of $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.95}\text{Ru}_{0.05}\text{O}_3$ coated SiC experiment were the minimum stable equivalence ratio temperature profile measurements were taken (between 215-223 minutes).

Figure 10. Axial temperature profile comparison between a $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.95}\text{Ru}_{0.05}\text{O}_3$ perovskite coated and non-coated SiC under the the same equivalence ratio and volumetric flow rate.

Figure 11. Axial temperature profile of an experiment with SiC coated with $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.95}\text{Ru}_{0.05}\text{O}_3$ at $\Phi=0.25$ and $\Phi=0.50$.

Table 1. Summary of minimum equivalence ratio experimental conditions

Minimum Equivalence Ratio Experimental Conditions	
Dry laboratory air volumetric flow rate	Constant at 0.008 m³/min
Methane volumetric flow rate	Progressively reduced starting at stoichiometry
Steal casing insulation	25.4 mm of ceramic fiber board
Porous media in reactor	Inert or Perovskite coated porous SiC
SiC articulated foam porosity	85%
SiC articulated average pore size	2-3 mm
Output	8 K-type thermocouples
Input	Air/Methane flow controllers

Table 2. Minimum stable equivalence ratio results of multiple experiments of 5 types of perovskite coated and un-coated inert SiC articulated foam.

Coating Composition of SiC Articulated Foam	T_{max} at $\Phi = 0.58$, °C	T_{max} at Minimum Stable Φ, °C	Minimum Stable Φ	Number of Runs
Un-Coated (Inert)	1030.9	994.3	0.547±0.018	4
La_{0.75}Sr_{0.25}Fe_{0.60}Cr_{0.35}Ru_{0.05}O₃	1158.5	1081.4	0.525±0.021	2
La_{0.75}Sr_{0.25}Fe_{0.60}Cr_{0.40}O₃	989.4	1056.2	0.525±0.007	2
La_{0.75}Sr_{0.25}Cr_{0.95}Ru_{0.05}O₃	953.9	1041.5	0.535±0.007	2
LaFe_{0.95}Ru_{0.05}O₃	1033.7	1072.9	0.53	1
La_{0.75}Sr_{0.25}Fe_{0.95}Ru_{0.05}O₃	906.6	1039.2	0.51±0.01	3

Table 3. XRD refinement results

Composition	a, b, c [Å]	Volume	χ^2
La_{0.75}Sr_{0.25}Fe_{0.60}Cr_{0.35}Ru_{0.05}O₃	5.548, 5.514, 7.799	238.639	7.000
La_{0.75}Sr_{0.25}Fe_{0.60}Cr_{0.40}O₃	5.544, 5.508, 7.789	237.948	4.018
La_{0.75}Sr_{0.25}Cr_{0.95}Ru_{0.05}O₃	5.496, 5.461, 7.782	233.609	24.71
LaFe_{0.95}Ru_{0.05}O₃	5.562, 5.569, 7.863	243.624	4.076
La_{0.75}Sr_{0.25}Fe_{0.95}Ru_{0.05}O₃	5.533, 5.555, 7.853	241.421	5.676

Figure 1. Experimental setup schematic.

Figure 2. Silicon carbide articulated ceramic foams, used to stabilize the flame inside of the combustion chamber.

Figure 3. Porous burner, front insulation panel not shown to show additional details.

Figure 4. Temperature vs time of non-coated SiC experiment as the equivalence ratio of the mixture is reduced and steady state temperature profile measurements were taken.

Figure 5. Shows the temperature of the thermocouple locations versus axial distance, along the axis of the combustion chamber, of the stabilized standing combustion wave at 0.58, 0.54, and 0.52 equivalence ratios.

Figure 6. Temperature vs the range of time of non-coated SiC experiment were the minimum stable equivalence ratio temperature profile measurements were taken (between 250-270 minutes).

Figure 7. X-ray diffraction refinement of the perovskite compositions.

Figure 8. Scanning electron microscope images at magnification x500 (left) and x10k (right) where: A) $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.60}\text{Cr}_{0.35}\text{Ru}_{0.05}\text{O}_3$ at x500; B) $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.60}\text{Cr}_{0.35}\text{Ru}_{0.05}\text{O}_3$ at x10k; C) $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.60}\text{Cr}_{0.40}\text{O}_3$ at x500; D) $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.60}\text{Cr}_{0.40}\text{O}_3$ at x10k; E) $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.95}\text{Ru}_{0.05}\text{O}_3$ at x500; F) $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.95}\text{Ru}_{0.05}\text{O}_3$ at x10k; G) $\text{LaFe}_{0.95}\text{Ru}_{0.05}\text{O}_3$ x500; H) $\text{LaFe}_{0.95}\text{Ru}_{0.05}\text{O}_3$ x10k; I) $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.95}\text{Ru}_{0.05}\text{O}_3$ x500; J) $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.95}\text{Ru}_{0.05}\text{O}_3$ x10k perovskite powders.

Figure 9. Temperature vs the range of time of $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.95}\text{Ru}_{0.05}\text{O}_3$ coated SiC experiment were the minimum stable equivalence ratio temperature profile measurements were taken (between 215-223 minutes).

Figure 10. Axial temperature profile comparison between a $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.95}\text{Ru}_{0.05}\text{O}_3$ perovskite coated and non-coated SiC under the the same equivalence ratio and volumetric flow rate.

Figure 11. Axial temperature profile of an experiment with SiC coated with

$\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{0.95}\text{Ru}_{0.05}\text{O}_3$ at $\Phi=0.25$ and $\Phi=0.50$.