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Effect of catalytically active $Ce_{0.8}Gd_{0.2}O_{1.9}$ coating on the heterogeneous combustion of methane within MgO stabilized ZrO_2 porous ceramics

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ABSTRACT

Within this work, a MgO stabilized ZrO_2 (MSZ) porous media with and without a gadolinia doped ceria ($Ce_{0.8}Gd_{0.2}O_{1.9}$, GDC) catalyst coating has been evaluated in heterogeneous combustion of mixtures of methane and air at different equivalence ratios inside of a porous combustor. The temperature distribution within the combustion chamber along with optical and acoustic emissions profiles from the exhaust side of the combustion chamber has been analyzed to characterize performance of the combustor. It was shown that enhancement of MgO–ZrO_2 ceramic surfaces with up to 5 wt% GDC ceramic coating provides a significant enhancement to the chemical reactions occurring during heterogeneous combustion. The placement of the GDC catalyst enables (i) higher temperatures through the combustion chamber; (ii) increases in maximum heating rates for fixed reactant flow rates; as well as (iii) extending the operating limits of the combustor.

1. Introduction

Important considerations in the development of modern energy conversion technologies are decreasing in ecological impact, increased efficiency, while decreasing or at least maintaining operational costs. Combustion of hydrocarbons has become a worldwide standard energy source which is both reliable and cost effective. At the same time however, hydrocarbon combustion produces CO, NO_x, and volatile organic compounds (VOCs) which are hazardous byproducts of hydrocarbon combustion [1]. In addition, hydrocarbon combustion is also a major source of CO_2—a greenhouse gas [2]. However, if future combustion technologies operated using a greater fraction of hydrocarbons with higher hydrogen content, such as C_3H_8, C_2H_6, or even CH_4, the environmental impact of combustion based energy conversion could be significantly reduced as these fuels have a lower potential for CO_2 production and have also been shown to burn cleaner [3,4].

One modern approach to combustion is heterogeneous combustion [5,6], which utilizes a highly porous ceramic media placed within the combustion chamber to support and regulate the flame, as well as to redistribute heat released during combustion throughout the combustion chamber, providing heat recuperation and thus enabling superadiabatic combustion where local flame temperatures are in excess of the adiabatic flame temperature [7–10]. Enhanced flame stability for momentary reactant flow rate disruptions, along with stable burning under ultra-rich and ultra-lean fuel/oxidizer mixtures, are all easily achieved in heterogeneous combustion occurring inside of the porous media. Porous ceramic materials, such as alumina (Al_2O_3), silicon carbide (SiC), or magnesia partially stabilized zirconia (MgO stabilized ZrO_2, MSZ) are thermally stable in high temperature environments. This materials exhibit high heat capacity, which make them perfect candidates to be used as the support for heterogeneous combustion [11]. It was found that, among these three porous ceramics, MSZ promoted combustion most effectively [12]. Therefore, among these three materials, MSZ is of special interest as a porous media with enhanced catalytic properties for heterogeneous combustion. MSZ shows oxygen-ion transport as it possesses a certain amount of oxygen vacancies in the lattice, Zr^{4+} ions are substituted by Mg^{2+} ions causing the formation of O^{2-} ion vacancies, while maintaining its charge neutrality [13]. Through the vacancy transport, the MSZ lattice facilitates the oxidation of

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adsorbed compounds, by enabling the transport of O^{2-} ions to adsorbates which bind to the weak acid base sites of the MSZ surface [14,15].

Heterogeneous combustion inside of the porous MSZ media can be enhanced even further if the media surface is coated with a suitable catalytically active material [16–18]. Such coating can further promote combustion reactions by facilitating an increase in lattice oxygen mobility and reactivity with different molecular species in the gas phase, which are formed during hydrocarbon combustion. CeO_2 based ceramics are well known and important catalysts for the oxidations of hydrocarbons [19]. The catalytic behavior may be attributed to the ceria lattice, which contains a high concentration of highly mobile oxygen vacancies and can therefore act as a local source or sink for oxygen involved in combustion reactions taking place on the ceria surface [19,20]. The doping of CeO_2 with Gd_2O_3 generates a significant number of oxygen vacancies presented by defect formation reaction $Gd_2O_3 = 2Gd'_{Ce} + \ddot{V}_o + 3O_o^x$ in Kröger–Vink notation [21], which increases the turnover frequency of the catalyst even further [22]. Detailed studies of adsorption and interaction of light hydrocarbons, such as methane, with CeO_2 have been published [23–25]. It was established that the activation of methane occurs over CeO_2 surfaces through either surface coordinatively unsaturated (cus) oxygen or surface lattice oxygen anions, which both are surface active oxygen species [19,23]. In addition to surface active oxygen species, acid-base sites are also important in the adsorption and reactions of hydrocarbons on ceria surfaces [26]. Crystallographic imperfections, such as steps, terraces, and kinks; which are considered low coordination sites on CeO_2 surfaces, and are where the formation of acid-base pairs are strongly favored. The presence of such defects significantly promotes the abstraction of H atoms from the hydrocarbons' C–H bonds, enabling the formation of active CH^{3-} and H^+ ions on the CeO_2 lattice surface [24]. Formation of such ions lead to the subsequent adsorption of hydrocarbon radicals from the gas phase and unsaturated hydrocarbons bonding predominately with strong acid sites on the ceria surface which may then undergo reactions with adsorbed O^{2-} and O^- ions, promoting complete methane oxidation [19].

The deposition of catalytically active Gd doped CeO_2 on ZrO_2 based porous ceramic supports can improve the stability of CeO_2 nanopowders for powder loadings less than 15 wt% on the support surface [27]. Under such low catalyst concentrations, the support will prevent loosely distributed powders from sintering and coarsening at high operational temperatures [28] and, thus, the high catalytic activity of CeO_2 during methane combustion will be preserved. It is also well know that a combination of CeO_2 and ZrO_2 oxides can create a rather stable ionically conductive ceramic material which itself could act as a catalyst for the combustion of methane [29,30].

Therefore, in this paper we report a comparative analysis of heterogeneous methane combustion at fixed air flow rates and varying equivalence ratios using a MSZ ceramic porous media with and without $Ce_{0.8}Gd_{0.2}O_{1.9}$ (GDC) ceramic nanopowder coatings. To perform the experiments CH_4 and air mixtures are delivered to a heterogeneous combustor, described in extensive detail elsewhere [31]. The temperature profiles are measured within the combustion chamber using thermocouples while an external microphone is used to collect and characterize acoustic signatures of combustion along with a CCD camera which is used to photograph light emitted from the porous media which is visible through the combustion chamber exhaust [31,32]. Both microstructural and phase characterization of the catalyst and substrate are reported, along with the temperature profiles within combustion chamber and photographs and acoustic emission signals from the exhaust during operation.

2. Experimental procedures

The combustion experiments were performed where the flame was contained within $MgO–ZrO_2$ porous media either with or without GDC catalytic enhancement with simultaneous measurements of temperature profiles within combustion chamber as well as optical photograph and acoustic emission signals coming from the combustion chamber exhaust. Deposition of $Ce_{0.8}Gd_{0.2}O_{1.9}$ powder on the surface of porous $MgO–ZrO_2$ ceramic media was performed by dip coating.

2.1. Characterization of catalyst powders and substrate

Commercially available $Ce_{0.8}Gd_{0.2}O_{1.9}$ (Praxair: Danbury, USA) ceramic powders were used for the deposition on the 3 wt% MgO partially stabilized ZrO_2 (MSZ) porous matrix (ASK Chemicals: Hilden, DE). The phase compositions of MSZ and GDC powders were characterized by Powder X-Ray diffraction (Rigaku Miniflex, $Cu_{k\alpha}$ radiation: Tokyo, JP). For XRD experiment, the as-received GDC powders were used for collection of diffractogram, while MSZ powder for powder diffraction with and without GDC coating were obtained by grinding a small 5 g piece of solid MSZ ceramic into powder using a standard alumina mortar and pestle. The particle size and morphologies of the powders were evaluated using a Scanning Electron Microscope (Zeiss: Oberkochen, DE) equipped with EDS detector (IXRF Systems: Austin, USA), which allowed for evaluation of chemical compositions of the powder.

2.2. Dip coating of the catalyst onto the surface of porous ceramic media

A simple dip coating technique [33] was utilized to deposit the GDC catalyst's powder onto the surface of MSZ porous ceramic media. The media has dimensions of 50.4 mm in length and 50.0 mm in diameter. It was cleaned in ultrasonically excited acetone bath before catalyst deposition to remove possible contamination and make the surface of the media clean. An ultrasonically excited suspension of GDC in 2-propanol was prepared and, subsequently, the MSZ media was immersed in the suspension. The media dwelled in the suspension for 1 h and then, after drying in air to allow 2-propanol on the media surface to evaporate, the MSZ media was placed into a furnace for calcination. The MSZ media with deposited GDC coating was calcined at 1100 °C for 4 h with 2 °C/min heating/cooling rate. The calcination step was performed for another time after the media was dip coated with GDC for a second time after the first calcination. It is estimated that up to 5 wt% of GDC loading was achieved on the surface of MSZ as a result of the performed dip coating procedure.

2.3. Experimental apparatus and procedures

Design of the combustion chamber is described in details elsewhere [31]. A schematic representation of the combustion chamber and key labeled dimensions is presented in Fig. 1. As one can see from Fig. 1, that the thermocouple TC0 (0.0 mm) is placed at the location at the combustion chamber inlet before the porous media. Thermocouples TC1 (44.1 mm), TC2 (64.7 m), and TC3 (85.4 mm), are placed just after the beginning of the porous media, the middle of the porous media, and just before the end of the media, respectively; while the thermocouple TC4 (112.9 mm) is located at the end of the combustion chamber and is the last axial thermocouple within the combustion chamber. All axially mounted thermocouples are located in close proximity to 316 stainless steel mesh, used to wrap the porous media to avoid direct contact of the porous media with a combustion chamber walls [31]. Uncoated