Catalytic hydrogen combustion for treatment of combustible gases from fuel cell processors

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ABSTRACT

Catalytic combustion of H_2 was carried out over combustion synthesized noble metal (Pd or Pt) ion-substituted CeO_2 based catalysts using a feed stream that simulated exhaust gases from a fuel cell processor. The catalysts showed a high activity for H_2-combustion and complete conversion was achieved below 200 °C over all the catalysts when O_2 was used in a stoichiometric amount. With higher amounts of O_2, the reaction rates increased and complete conversions were possible below 100 °C. The reaction was also carried out over Pd-impregnated CeO_2. The conversions of H_2 with stoichiometric amount of O_2 were found to be higher over Pd-substituted compound. The mechanism of the reaction over noble metal-substituted compounds was proposed on the basis of X-ray photoelectron spectroscopy studies. The redox couples between Ce and metal ions were established and a dual site redox mechanism was proposed for the reaction.

1. Introduction

Fuel cell technology for energy systems is attractive both from energy as well as environmental viewpoints. Due to the direct conversion of the chemical energy to electrical energy, the efficiency of such systems is not limited by the Carnot efficiency [1]. The performance of the conventional thermal heat engine systems becomes inferior compared to that of a fuel cell system due to highly irreversible nature of the combustion reaction [2]. The products of the reaction from a fuel cell processor are cleaner as compared to those from thermal engine systems, which inherently produce hazardous gases like CO and NO_x. Fuel cell processors have a wide range of potential applications including those in automobile and propulsion systems, domestic and industrial supply [3], and such systems are also seen as systems for cogeneration of heat and electricity [4].

Fuel cells utilizing H_2 have several advantages like high energy density, low operating temperature and fast response to load changes [5]. However, the use of H_2 poses a potential environmental hazard because all H_2 supplied to the fuel cell is not consumed. In some cases, excess H_2 has to be supplied to maintain a stable voltage [6], which results in a higher amount of unreacted H_2 in the system. One of the strategies to overcome this problem is the recycling of the exhaust gases from the fuel cell processor. However,

this increases the complexity of the system and recycling becomes practical only for large systems [7]. Even in the case of systems with recycle, the exhaust gas cannot be made completely free from H_2 and some residual H_2 is always observed in the outlet stream. Accumulation of H_2 can result in the formation of combustible or explosive mixtures. Such accidents have indeed been observed in the past [8]. Therefore, it is very important process the exhaust gases for the removal of residual H_2.

The combustion of H_2 is a highly exothermic reaction with an enthalpy of reaction of −286 kJ/mol. Therefore, the reaction is accompanied by a large increase in temperature. H_2 has a wide flammability range of 4–75% [9]. Direct flame combustion of H_2 has been investigated by several investigators [10–12]. However, catalytic combustion offers several advantages over flame combustion. According to Vlachos and co-workers [13–15], homogeneous flame combustion is the preferred mode of combustion of hydrocarbons only for large scale operations and with reduction in system volume, the coated wall reactors show better and more stable performance. Due to the highly exothermic nature of the reaction, it is desirable to carry out the reaction in microcombustors. Kaisare et al. [16,17] have studied the catalytic combustion in wall coated microcombustors. Structured monolithic reactors have also been used to study the catalytic combustion of H_2 and hydrocarbons [18].

As pointed out by Ladacki et al. [19], in spite of the importance of H_2–O_2 reaction for energy and environmental applications, this reaction has not been well explored. Whereas the catalytic combustion of CH_4 has been widely studied over different noble metals and different supports [20–24], there have been a few reports of

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H_2-O_2 combination over a number of metals including Ni, Cu, Pd, Ag and Au [25–29] and over supported catalysts like Al_2O_3 and Fe_2O_3 [26,30]. In this study, we have carried out the catalytic combustion of H_2 in a H_2-lean gas mixture that simulated typical fuel cell processor conditions. We have synthesized a series of Pd and Pt ion-substituted CeO_2 compounds and the related solid solutions. We have previously reported high catalytic activity of these compounds for CO oxidation and NO_x reduction [31,32]. We have tested the activity of the catalysts for catalytic H_2-combustion. The use of a reducible support is expected to enhance rate of reaction by the involvement of the lattice oxygen.

2. Experimental

2.1. Catalyst synthesis

Noble metal (Pd and Pt) ion-substituted CeO_2 solid solutions were prepared using the solution combustion technique. Three different modifications of the support were used. Apart from pure CeO_2, 15% Zr and Ti ions were substituted in the support CeO_2 to obtain $Ce_{0.85}Zr_{0.15}O_2$ and $Ce_{0.85}Ti_{0.15}O_2$, respectively. 2 at.% substitution of the noble metal was carried out. Therefore, the compounds synthesized were $Ce_{0.98}Pd_{0.02}O_{2-\delta}$, $Ce_{0.98}Pt_{0.02}O_{2-\delta}$, $Ce_{0.83}Zr_{0.15}Pd_{0.02}O_{2-\delta}$, $Ce_{0.83}Zr_{0.15}Pt_{0.02}O_{2-\delta}$, $Ce_{0.83}Ti_{0.15}Pd_{0.02}O_{2-\delta}$ and $Ce_{0.83}Ti_{0.15}Pt_{0.02}O_{2-\delta}$, where δ represents the oxide ion vacancy created due to substitution of the metal in ionic form. For the synthesis of the compounds, the precursor nitrates of all the elements were dissolved in a solution in a stoichiometry given by the chemical formula and a fuel (glycine) was added. The amount of glycine required was calculated by making a balance over the oxidizing and the reducing valences in the solution [33]. The solution was made to undergo combustion in a furnace at 350 °C. Further details on the synthesis of the compounds can be found elsewhere [31,33]. Pd-impregnated CeO_2 was also prepared using wet impregnation technique for comparing the activity of metal ion-substituted catalysts. 2 at.% substitution of Pd in CeO_2 corresponds to 1.25 wt% of Pd in Pd-impregnated CeO_2 and, therefore, 1.25 wt% Pd/CeO_2 was synthesized. CeO_2 was synthesized by the solution combustion technique. A slurry of CeO_2 and $PdCl_2$ was made and a dilute solution of hydrazine hydrate in water was added slowly to the slurry to reduce Pd salt to Pd nanoparticles, which got deposited over support CeO_2. The solids were filtered and washed with ethanol and solicited for 15 min. The wet solids obtained were heated at 150 °C for 4 h to obtained Pd-impregnated catalyst.

2.2. Catalyst characterization

The compounds were characterized by powder X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). XRD patterns of all the compounds were recorded on a Phillips X'pert diffractometer in 2θ range of 20–90° with a step size of 0.067°. The XPS of all the elements in the compounds were recoded on Thermo Fisher Multilab ESCA with AlKα radiations of energy 1486.6 eV. All the peaks were calibrated with respect to graphitic of C1 s peak with a binding energy of 284.5 eV and confirmed with the binding energy of O1s.

2.3. Catalytic reactions

The gas phase catalytic combustion reactions were carried out in glass tube reactors of 9 mm I.D. The catalyst granules of size 300–600 μm size were diluted with silica granules of the same size. Due to highly exothermic nature of the reaction, the catalyst weight was minimal (10 mg) and diluted with silica to make a total bed weight of 1 g and bed length of 1.5 cm. Uniform dispersion of the catalyst particles in the diluent was ensured for each catalyst bed. The catalyst bed was made between two plugs of ceramic wool. A thermocouple was placed in the catalyst bed to measure the temperature of the bed. The reactor was heated from outside by an electric heater and the temperature was controlled using a PID temperature controller. The reactions were carried out under isothermal conditions. Due to exothermicity of the reaction, a gradual increase in the bed temperature was indeed observed but the increase of the temperature was very small such that the reaction can be considered to be taking place essentially under isothermal conditions. The reactant gas mixture consisted of H_2, O_2 and N_2 (Shri Vinayaka Gases, Bangalore, India). In all the reactions, a total flow rate of 200 ml/min was maintained. The concentration of H_2 was fixed at 2.75 mol%. The amount of O_2 in the mixture was varied. Reactions with 1.38 mol% and 2.75 mol% of O_2 were carried out, which corresponded to the O_2 stoichiometry of 1 and 2, respectively, required for the combustion reaction. The gases were sent through control valves to obtain the required composition. The reactions were also carried out using simulated air conditions in which the amount of O_2 in the reactant gas corresponded to the composition of air. Typically, the reaction mixture had a composition of H_2:O_2:N_2 = 5.5:41.5:153. The reactions were also carried out in the presence of CO to observe the effect and co-oxidation of CO. For the reactions in the presence of CO, 2.75 mol% H_2, 2.75 mol% CO and 2.75 mol% O_2, balanced with N_2, were used. The composition of the products and the unreacted gas mixture was determined using an online gas-chromatograph (Mayura Analyticals, Bangalore, India) using a combination of Hayesep – A and molecular sieve columns. The detection was accomplished by a thermal conductivity detector and a flame ionization detector.

3. Results and discussion

3.1. Catalyst characterization

The crystal structure of the catalysts was established using XRD. Fig. 1 shows the XRD of unsubstituted and noble metal ion-substituted catalysts. Fig. 1(a) shows the XRD of CeO_2, $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ and $Ce_{0.98}Pt_{0.02}O_{2-\delta}$. The lines in the XRD of CeO_2 correspond to the cubic structure with a space group of F$m3m$. On comparing the XRD of metal ion-substituted CeO_2 with unsubstituted CeO_2, it can be seen that all the compounds have the same structure and the metal ions were substituted in the lattice. However, this exclusively may not show the substitution of the ions in the lattice. A very fine dispersion of Pd/Pt nanoparticles in CeO_2 matrix may not result in any appreciable peak in the XRD pattern. However, the substitution of the metals in the lattice results in the changes in the lattice parameters owing to the differences in the ionic radii of Ce^{4+} and M^{2+} (M = Pd/Pt). Therefore, Rietveld refinement of the patterns was carried out. It was found that changes in the lattice parameter occurred on substitution [34]. Further, we have previously established the structure of the compounds using several techniques including XRD, FT-Raman, TEM, and EXAFS and have found that the metal ions were indeed substituted in the lattice and were not present as oxides (PdO or PtO) and also not as a fine dispersion of metal [31].

Bulk substitution of Zr^{4+} and Ti^{4+} ions in Ce^{4+} sites was carried out with 15 at.% substitution. The XRD of $Ce_{0.85}Zr_{0.15}O_2$ and $Ce_{0.85}Ti_{0.15}O_2$ are shown in Fig. 1(b) and (c), respectively, and the patterns match with the cubic structure. Therefore, the parent CeO_2 structure was retained on bulk substitution and the compounds were indeed solid solutions. The Rietveld refinement of $Ce_{0.85}Zr_{0.15}O_2$-based compounds showed the difference in the lattice parameter compared to that of the parent compound showing the substitution of the compounds [34]. The superior values of the