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RAPID COMMUNICATION

Effects of water vapor and temperature upon combustion stability of $CeZrO_2$-modified Pd-Pt/Al_2O_3 catalyst

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Abstract−Two bimetallic Pd-Pt catalysts were prepared by wash-coating the composites of Pd-Pt/$CeZrO_2$-Al_2O_3 onto cordierite monolith and they were evaluated in a tubular reactor for stability in combustion of SOFC stack flue gas at GHSV 29,280 h^{-1} and 1 atm. The Pd-rich catalyst showed better stability than the Pt-rich catalyst for combustion of the wet feed. Water vapor in the stack flue gas affected the catalyst activity adversely via the formation of inactive $Pd(OH)_2$ species at the reaction temperatures of 723 and 823 K, but this effect was eliminated by raising the temperature to 923 K or above. Catalyst properties such as specific surface area, pore size and metal dispersion did not deteriorate significantly after combustion of the wet feed in the temperature range of 723-1,023 K. The presence of $CeZrO_2$ in Al_2O_3 material was considered to affect the support properties favorably, leading to a kind of metal-support interaction beneficial for the combustion of the wet feed. This interaction helped to enable the Pd-Pt catalysts to maintain good stability for combusting the wet SOFC stack flue gas with the stoichiometric air-to-fuel ratio at 923 K or above.

Keywords: SOFC Stack Flue Gas Combustion, Bimetallic Pd-Pt Catalyst, $CeZrO_2$-Al_2O_3 Support, Water Vapor and Temperature Effects, Catalyst Stability

INTRODUCTION

For the solid oxide fuel cell (SOFC) equipped with a steam-methane reformer, stack flue gas contains combustible components such as hydrogen, carbon monoxide and methane in residual concentrations, oxidation products such as water vapor and carbon dioxide, and air as the oxidant. In the SOFC system, the stack flue gas is combusted in the catalytic burner with the highest thermal efficiency possible in order to meet the heat requirement. The catalysts used for the combustion are usually comprised of active ingredient crystallites of precious group metal(s) dispersed onto a refractory support material [1,2]. Al_2O_3 is probably the most important material used as catalyst support for automotive application due to excellent textural properties and acid/base characteristics. Its hydrothermal stability and textural properties can be controlled by varying the synthesis route, depending on the severity of its use [3]. Stability of the combustion catalyst is an important factor for the long-term operation of the SOFC system, because the support material as well as the active ingredients affects the catalyst stability significantly. Although Al_2O_3 possesses good support properties, its surface tends to deteriorate gradually in a hydrothermal environment. The properties of Al_2O_3 support can be altered or modified by adding promoters such as ceria and zirconia, and the catalyst performance can be enhanced as these promoters function favorably. Ceria provides extra oxygen from the lattice during oxygen deficiency, whereas zirconia working as temperature-resistant promoter helps to improve oxygen storage capacity of ceria [4].

The advantage of incorporating $CeZrO_2$ into Al_2O_3 can be found in the literature [5-7]. Although the presence of $CeZrO_2$ tends to improve the oxygen storage capacity and thermal resistance of alumina, an optimum content of zirconia must be selected to maintain the surface area of $CeZrO_2$-Al_2O_3 to the highest value possible. Excess zirconia may lead to the growth of $CeZrO_2$ crystallites, causing the deterioration of support properties. In this context, the catalyst consisting of noble metal crystallites deposited onto $CeZrO_2$-Al_2O_3 support is a good candidate for catalyzing the combustion of the SOFC stack flue gas with the extended stability [5,8]. Based on the background described above, catalytic combustion of the SOFC stack flue gas was studied in this work by using the bimetallic Pd-Pt catalysts supported on Al_2O_3 modified with $CeZrO_2$. Our purpose was to investigate the effects of water vapor in the feed and reaction temperature upon the catalyst stability. In our previous work [9], bimetallic Pd-Pt catalysts supported on Al_2O_3 only were tested for the purpose of catalyst screening to address the synergistic effect of Pd and Pt upon the catalyst activity. In this work, we anticipated that combustion of the SOFC stack flue gas would be enhanced by the Pd-Pt catalyst supported on $CeZrO_2$-Al_2O_3 in the hydrothermal environment.

EXPERIMENTAL

Table 1 lists the chemical composition (nominal) of catalytic composites used for the bimetallic Pd-Pt catalysts, i.e., HM-1 and HM-2 catalysts which are Pd-rich and Pt-rich, respectively. A detailed experimental procedure is described in the supplementary information. Nominal flow rate and composition of the feeds, i.e., Gas-1 with no water vapor and Gas-2 with water vapor, are listed in Table 2. Gas-1 was used to simulate the SOFC stack flue gas containing H_2, CO and CH_4 with no water vapor, while Gas-2 was used to assess the effect of water vapor in the feed to be combusted. Results of this work were discussed principally for the HM-1 catalyst in comparison with the HM-2 catalyst. Additional runs for combusting

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Table 1. Chemical composition of the catalytic composites wash-coated onto the cordierite monolithic support

Pd-Pt bimetallic catalysts	Chemical composition, wt%
HM-1 (Pd-rich catalyst)	Pd(1.8), Pt(0.9), $CeZrO_2$(14.0), Al_2O_3(balance)
HM-2 (Pt-rich catalyst)	Pd(1.0), Pt(1.7), $CeZrO_2$(14.0), Al_2O_3(balance)

Table 2. Flow rate, composition and space velocity (GHSV) of the feeds (Gas-1 and Gas-2)

Components	Flow rate, ml/min (composition, vol%)	
	Gas-1	Gas-2
H_2	17.3(3.54)	17.3(3.54)
CO	17.3(3.54)	17.3(3.54)
CH_4	17.4(3.56)	17.4(3.56)
N_2	188(38.52)	-
Air	248(50.84)	248(50.84)
Steam	-	188(38.52)
Total	488	488
GHSV, h^{-1}	29,280	29,280

the feeds containing H_2, CO or CH_4 individually as well as their mixture were also conducted to check the competing reactions and evaluate the effect of H_2 and/or CO upon CH_4 combustion, which was discussed in the supplementary information. Fresh and used catalyst samples were characterized by XPS and XRD analyses and BET and CO chemisorption measurements.

RESULTS AND DISCUSSION

1. Catalyst Characterization

Binding energy of the active metal phase on the catalyst was analyzed by XPS in order to observe the change of chemical state of the active phase versus reaction temperature. The results are shown in Fig. 1 as XPS spectra of the palladium phase, which were compared between its fresh state and used states after twenty hours of combustion run in Gas-2 at 723, 823, 923 and 1,023 K, respectively. Palladium phase on the fresh HM-1 (Pd-rich) catalyst was identified as mostly Pd^0 by the $Pd^0(3d_{5/2})$ peak at 335.0 eV as well as Pd^{2+} by the weak $Pd^{2+}(3d_{5/2})$ peak at 336.3 eV [10,11]. As the catalyst was used in the combustion run in the hydrothermal condition, Pd^0 phase was replaced by Pd^{4+} phase identified by the $Pd^{4+}(3d_{3/2})$ peak at 343.5 eV [12] and an evidence for increasing Pd^{2+} peak intensity was also observed. These spectra indicate that three kinds of Pd species, i.e., Pd, PdO and PdO_2, coexisted on the catalyst, and Pd phase was oxidized to PdO phase and then to PdO_2 phase in the combustion run. As the run was extended, Pd and Pd/PdO mixture phases became more active than PdO_2 phase [13]. Thus, Pd phase changed in the various states in response to the reaction temperature and oxidizing environment, forming active sites favored by the reaction. Change of the chemical state of the platinum phase on the catalyst could not be detected as XPS binding energy of platinum was overlapped with Al_2O_3 existing in abundance on the catalyst. The presence of Ce and Zr on the catalyst was identified by XRD analysis, as shown in Fig. 2(a) and 2(b) for the fresh and 1,023 K-tested catalysts. The crystallographic planes of Pd and Pt were difficult to assign due to the dominant Al_2O_3 phase, although the $CeZrO_2$ phase could be clearly resolved in the XRD pattern [14].

Metal dispersion, specific surface area and average pore size of the HM-1 catalyst are listed in Table 3, which indicates that Al_2O_3 support is principally responsible for the decrease in surface area and metal dispersion resulting from the combustion runs. Compared with 29.6% metal dispersion, 21.1 m^2/g surface area and 4 nm average pore size for the fresh catalyst, metal dispersion decreased to 18.7% and then to 17.4%, surface area decreased to 18.4±0.2 and then to 18.1±0.7 m^2/g, and average pore size increased to 8.6 nm and then to 10.5 nm as the reaction temperature increased to 723 K

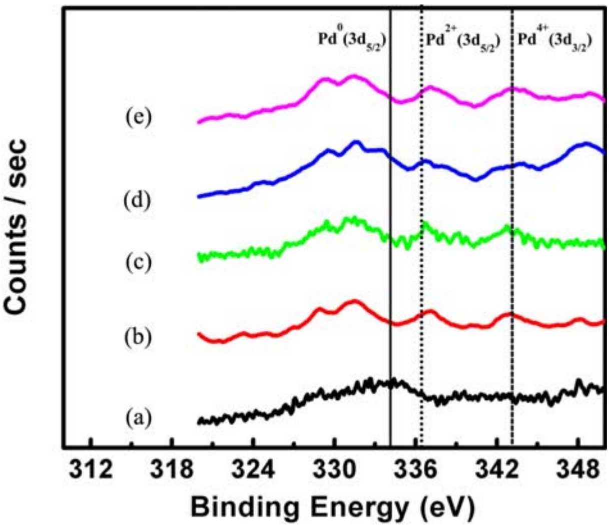

Fig. 1. XPS binding energy spectra of the palladium phase on the Pd-rich catalyst ((a) fresh catalyst, (b) after 723 K-operation, (c) after 823 K-operation, (d) after 923 K-operation, (e) after 1,023 K-operation).

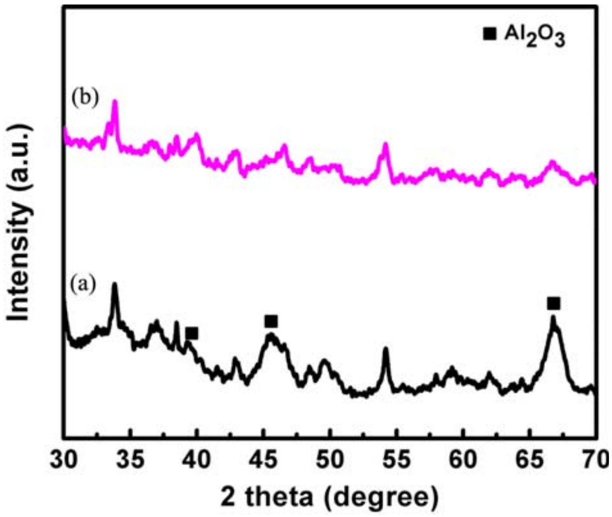

Fig. 2. XRD patterns of the Pd-rich catalyst ((a) fresh catalyst, (b) after 1,023 K-operation). Full squares denote the peaks for alumina phase and all other peaks are associated with $CeZrO_2$ phase.

Table 3. Metal dispersion, BET surface area and average pore size of the Pd-rich catalyst used in the 20 h stability test conducted at various temperatures in the wet feed (Gas-2)

Catalyst samples	Fresh catalyst	Used catalyst after the test at 723 K	Used catalyst after the test at 823 K	Used catalyst after the test at 923 K	Used catalyst after the test at 1,023 K
Metal dispersion (%)	29.6	18.7	17.9	17.5	17.4
BET surface area (m^2/g)	21.1	18.4±0.2	18.2±0.4	18.1±0.5	18.0±0.7
Average pore size (nm)	4.0	8.6	9.5	10.0	10.5

and then to 1,023 K for the used catalysts. Because Al_2O_3 is susceptible to agglomeration in the hydrothermal condition, it can block and capture the active sites of the catalyst, resulting in the decrease of surface area and metal dispersion, and the increase of pore size. High reaction temperature and extended run time can make the situation aggravated, thus the catalyst supported on Al_2O_3 only can be deactivated by restructuring of alumina phase, which was described in our previous work [9]. However, in the present work, $CeZrO_2$ was incorporated into Al_2O_3 in the fraction of 14 wt%, as $CeZrO_2$ can modify the surface of Al_2O_3 to reduce the above-mentioned susceptibility or it can alter electronic structure of the active ingredients deposited on the support. Such modification of Al_2O_3 with $CeZrO_2$ can lead to a kind of metal-support interaction beneficial for the combustion reaction. Characterization data shown in Table 3 supported this anticipation as the catalyst properties did not significantly change in the temperature range of 723-1,023 K. The trend of stability for the physical properties of the Pd-rich catalyst is further illus-

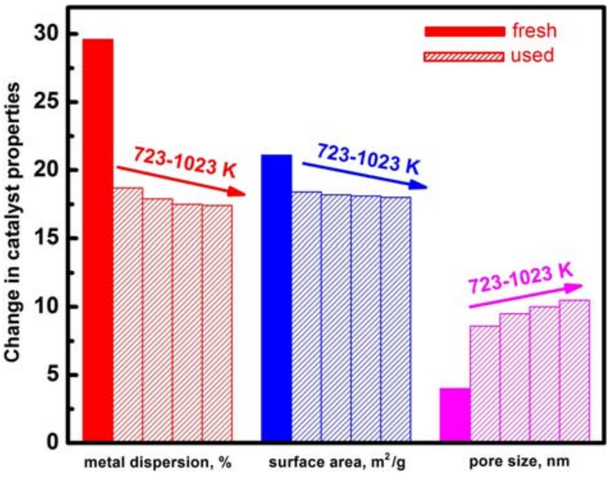

Fig. 3. Change in the physicochemical properties of the Pd-rich catalyst tested in the wet feed (Gas-2).

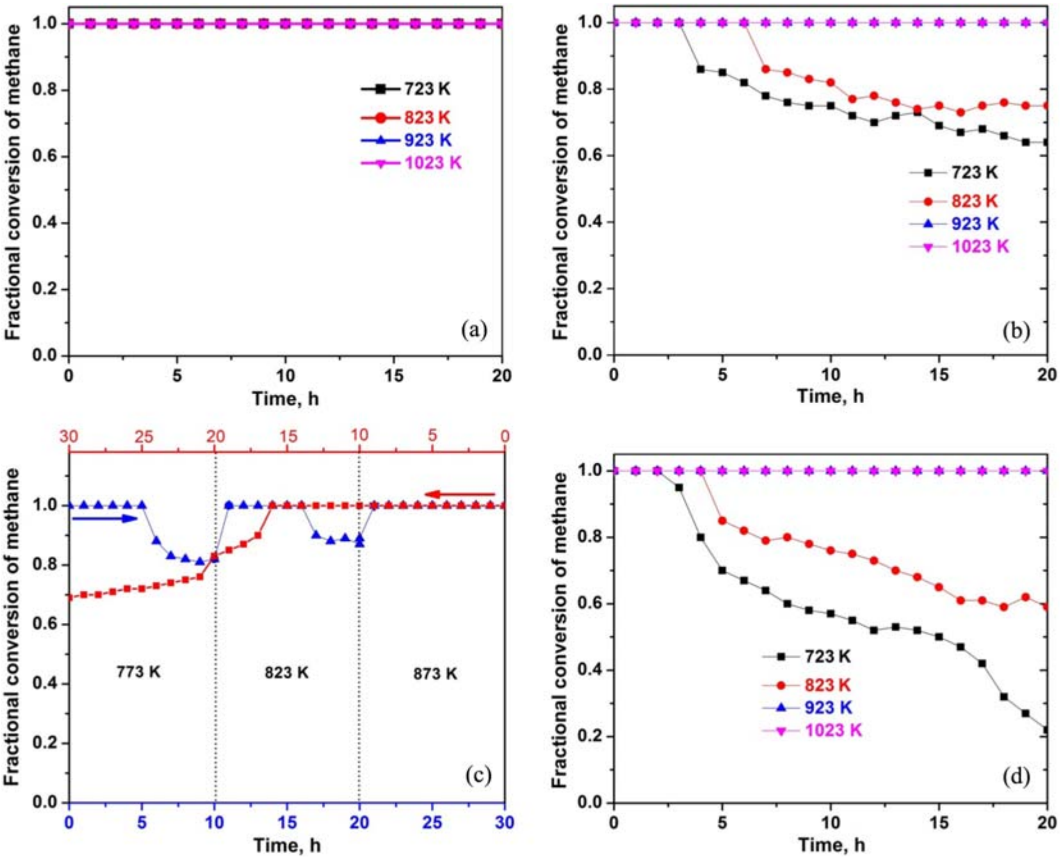

Fig. 4. Catalytic combustion of the dry feed ((a) Gas-1) and wet feed ((b), (c) and (d) Gas-2): (a), (b) and (c) depict the results obtained for the Pd-rich catalyst, and (d) depicts the results obtained for the Pt-rich catalyst.

trated in Fig. 3. Reductions of the catalyst surface area from combustion of the dry feed (Gas-1) and wet feed (Gas-2) were compared and discussed in the supplementary information.

2. Catalyst Stability in the Combustion Runs

Fig. 4(a) shows the catalyst stability observed for each twenty on-stream hours in combustion of the dry feed (Gas-1) at 723-1,023 K. At each temperature tested, the Pd-rich catalyst maintained complete conversion of CH_4 throughout the combustion run, supporting that the Pd-rich catalyst was not deactivated significantly in the dry feed, although its specific surface area was reduced a little as shown in the supplementary information (Table S1). This result suggests that the catalyst stability maintained in the dry feed was due to the metal particles on the catalyst which were not agglomerated to a serious extent. As the feed was changed to the wet Gas-2 containing the water vapor, a remarkably different trend was obtained from the combustion runs as shown in Fig. 4(b). At each temperature tested, the Pd-rich catalyst exhibited complete conversion of CH_4 in the beginning. In the 723 K-run, however, noticeable reduction of CH_4 conversion occurred within five on-stream hours of the run. After twenty on-stream hours, CH_4 conversion dropped to 0.66, indicative of serious catalyst deactivation. In the 823 K-run, the Pd-rich catalyst began to be deactivated after six on-stream hours, and CH_4 conversion decreased to 0.75 after twenty on-stream hours, exhibiting another evidence of catalyst deactivation. However, in the 923 K-run and 1,023 K-run, the Pd-rich catalyst maintained complete conversion of CH_4 throughout the combustion run, supporting that the catalyst was not deactivated in combustion of the wet feed conducted at 923 K or above. Considering that the Pd-rich catalyst did not undergo significant reduction of specific surface area after combustion of the wet feed (see Table S1), the catalyst stability in combustion of the wet feed at 923 K or above may be explained as follows: the interaction between the active ingredient and support material plays an important role in performance enhancement of the catalyst. Although alumina is a well-known support material for oxidation catalysts, its stabilization is still necessary for improvement of the catalyst performance for methane combustion. Owing to advantages such as oxygen storage capacity and thermal resistivity claimed for $CeZrO_2$-Al_2O_3 support, activity and stability of the catalyst were anticipated to increase [15]. Researchers have shown that $CeZrO_2$ helps to reduce the activation energy of the combustion reaction due to the presence of zirconia introducing Zr^{4+} ions into the ceria lattice [16].

It is noteworthy that stability of the Pd-rich catalyst was maintained in the dry feed for twenty on-stream hours of combustion run conducted at 723 and 823 K, whereas the catalyst stability considerably deteriorated in the wet feed used for the same operation. This contrast indicates that the deactivation of the Pd-rich catalyst is related to the adverse effect of water vapor: water vapor in the wet feed resulted in the formation of inactive $Pd(OH)_2$ species on the catalyst via the following reaction or adsorption route which is favored by the high moisture content and lower reaction temperature [17,18]:

$$PdO(s)+H_2O(g)=Pd(OH)_2(s); \qquad \Delta H=-13.9\ \text{kcal/mol}$$

The formation of $Pd(OH)_2$ species corresponds to the deactivation of the Pd-Pt catalyst and its dehydration reactivates the deactivated catalyst. The not so much distinct but still discernible peaks of Pd(II) and Pd(IV) states shown in the XPS data indicate the presence of inactive $Pd(OH)_2$ species as well as active PdO phase and unstable hydrated palladium (IV) oxide species on the deactivated catalyst. For the Pd-Pt catalyst used in the combustion of the wet feed at 723 or 823 K, surface density of the active PdO phase decreased due to the formation of the inactive $Pd(OH)_2$ species, resulting in the catalyst deactivation as evidenced by the decrease of CH_4 conversion versus time. However, the effect of water vapor could be alleviated by the effect of temperature, as the formation of inactive $Pd(OH)_2$ species was suppressed by raising the reaction temperature to 923 K or above, and the catalyst was not deactivated in the combustion runs conducted at those temperatures as evidenced by the steady CH_4 conversion versus time. This phenomenon indicates that there was a temperature threshold of 923 K above which the catalyst deactivation caused by water vapor was reversed or neutralized by the effect of temperature.

The reversibility of catalyst deactivation by temperature change in the reaction condition is illustrated in Fig. 4(c), which shows that the catalyst deactivation occurring in combustion of the wet feed (Gas-2) below 923 K could be reversed by increasing the temperature in the cyclic hold-and-ramp sequence of 773-823-873 K. At each temperature increasing by 50 K increment from 773 to 873 K, the activity of the Pd-rich catalyst was monitored by means of CH_4 conversion versus on-stream duration of ten hours. At 773 K, the catalyst activity was maintained at the level of complete CH_4 conversion for the initial five on-stream hours, which was followed by the catalyst deactivation leading to CH_4 conversion of 0.83 at the end of the next five on-stream hours. As the temperature was increased to 823 K, the catalyst activity readily recovered to the level of complete CH_4 conversion lasting for six on-stream hours and then declined again to the level of CH_4 conversion of 0.88 at the end of temperature-hold at 823 K. As the temperature was further increased to 873 K, the catalyst activity readily recovered again to the level of complete CH_4 conversion, which lasted with no decay for ten on-stream hours at 873 K. The activity data for the increasing temperature cycle are shown in Fig. 4(c) as the full triangles strung by blue line and directed by a blue arrow. Following the sequence of temperature rise, the reaction temperature was then decreased in the cyclic hold-and-ramp sequence of 873-823-773 K, and the catalyst activity was monitored in the same manner as described above. The catalyst activity did not decay from CH_4 conversion of 1.00 for the entire ten hours at 873 K. After the temperature was decreased to 823 K, the catalyst activity was still steady for six hours before decaying to CH_4 conversion of 0.83 at the end of temperature-hold at 823 K. As the temperature was further decreased to 773 K, the catalyst activity continued to decline monotonically before it reached CH_4 conversion of 0.69 at the end of temperature-hold at 773 K. The continuous decay of catalyst activity in the duration of temperature-hold at 773 K was attributed to the catalyst deactivation accumulated at the end of the cycle at 823 K. The activity data for the decreasing temperature cycle are shown in Fig. 4(c) as the full squares strung by red line and directed by a red arrow. While the catalyst deactivation in the increasing temperature cycle was reversible, the catalyst deactivation in the decreasing temperature cycle was irreversible. Meanwhile, as shown in Fig. 4(d), deactivation of the Pt-rich catalyst in combustion of the wet feed below 923 K was earlier and worse than the Pd-rich catalyst. At 923 K or above, however, the Pt-rich catalyst exhibited good stability, virtually indistinct from the Pd-rich catalyst. Pd is known to be more active and stable than Pt for methane combustion [19], and the role of Pt in the bimetallic Pd-Pt catalyst was to help to maintain adequate CH_4 conversion which could not be obtained by the monometallic Pd catalyst [9].

CONCLUSIONS

Bimetallic Pd-Pt catalysts supported on $CeZrO_2$-Al_2O_3 exhibited good catalytic stability in combustion of the wet SOFC stack flue gas at 923 K or above. Oxygen storage capacity and thermal endurance of $CeZrO_2$ played an important role in the stabilization of $CeZrO_2$-Al_2O_3 support material, thus contributing to lower the activation energy of combustion reaction and maintain its textural properties in the rigorous hydrothermal environment. For the dry feed containing no water vapor, the Pd-rich catalyst did not exhibit any deterioration of combustion activity in the temperature range of 723-1,023 K during the 20 h stability test. For the combustion of the wet feed containing water vapor, the catalyst activity versus time deteriorated below 923 K: at GHSV 29,280 h^{-1}, catalyst deactivation started in three hours at 723 K and in approximately six hours at 823 K, respectively. The Pt-rich catalyst showed earlier and worse deterioration of the catalyst activity than the Pd-rich catalyst at those temperatures. Deterioration of catalyst activity at the temperatures below 923 K is attributed to the formation of inactive $Pd(OH)_2$ species on the catalyst in the wet feed. This deactivation phenomenon is reversible and dependent on the presence of water vapor in the feed as well as reaction temperature. At 923 K or above, water vapor in the feed did not affect catalyst activity for combustion of the SOFC stack flue gas as the formation of inactive $Pd(OH)_2$ species was suppressed on the catalyst.

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Supporting Information

Effects of water vapor and temperature upon combustion stability of $CeZrO_2$-modified Pd-Pt/Al_2O_3 catalyst

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EXPERIMENTAL

1. Catalyst Synthesis

In order to apply the typical catalyst synthesis procedure, cylindrical cordierite monoliths in diameter of 50 mm, length of 50 mm and channel wall thickness of 0.18 mm were used for wash coating of $CeZrO_2$-Al_2O_3 followed by impregnation of the active ingredients. Size of each channel opening of the cordierite monolith was 1.5×1.5 mm. Pore size of the monolith was not measured because it was known to be far less porous as compared with the $CeZrO_2$-Al_2O_3 wash-coat. Pretreatment of the monoliths included washing in dilute HNO_3 solution (0.5 M) at room temperature for 24 h and then calcining at 973 K for 4 h to remove impurities from the monoliths. Al_2O_3 powder was purchased from Sigma Aldrich and $CeZrO_2$ was synthesized by a conventional procedure [1]. To synthesize $CeZrO_2$, an aqueous solution of cerium (IV) ammonium nitrate and zirconium nitrate was prepared with a Ce/Zr atomic ratio of 3. Then, cerium hydroxide and zirconium hydroxide were co-precipitated by the addition of an excess of ammonium hydroxide solution. Finally, the precipitates were washed with doubly-deionized (DDI) water and then were calcined to $CeZrO_2$ at 1,073 K for 4 h in a muffle furnace. The slurry of Al_2O_3 and $CeZrO_2$ was prepared by wet milling in a 1.5 M HNO_3 aqueous solution and then a dried monolith was immersed in the slurry for several minutes. Subsequently the monolith was removed from the slurry and then was flushed by air to remove excess liquid from the channels of the monoliths. The monolith was then consolidated overnight at room temperature and then was calcined at 1,073 K overnight in order to stabilize the $CeZrO_2$-promoted Al_2O_3 coat. The coating process can be repeated to obtain the desired contents of $CeZrO_2$-Al_2O_3. Aqueous solution of palladium chloride and chloroplatinic acid were used to deposit palladium and platinum on the $CeZrO_2$-Al_2O_3-coated monolith. In the wet impregnation process, palladium was deposited first and then platinum was deposited to obtain the desired loading of active ingredients. The monolithic catalysts were washed by DDI water until no Cl^- was detected and then were dried in an oven at 423 K for 30 minutes followed by calcination at 873 K for 2 h [2].

2. Catalyst Characterization

The catalytic composites consisting of noble metals and $CeZrO_2$-promoted alumina were collected by carefully scraping them from the surface of cordierite monolith, using a clean and sharp spatula. The catalyst samples thus prepared were used for characterization runs including the BET measurement. BET surface area of the fresh and used catalysts was measured by nitrogen adsorption at 77 K (Micromeritics Gemini 2375). Prior to the BET analysis, catalyst samples were degassed by helium for at least 2 h at 473 K to remove the impurities from the samples. Binding energy of the metal phase on the catalyst was analyzed by X-ray photoelectron spectroscopy using a VG ESCALAB MK2 Electron Spectrometer (Al Kα radiation; hν=1,486.6 eV). The XPS data were calibrated using the binding energy of C1s (284.6 eV) as the standard. XRD patterns were collected using a RIGAKU diffractometer with a Cu Kα radiation. Noble metal dispersion was measured by CO pulse chemisorption at 313 K using CO pulses of 0.5 ml (10% CO in He) injected into helium flow of 50 ml/min. Prior to the dispersion measurement, catalyst samples were reduced for 60 minutes at 523 K in hydrogen flow of 20 ml/min followed by helium purge of 20 ml/min for 90 minutes at 533 K. Porosity of the samples was measured by Autosorb-1 sorption system (Quantachrome Corporation). Before the porosity measurement, the samples were degassed by helium at 523 K for 3 h.

3. Catalyst Stability Measurement

In order to simulate the SOFC stack flue gas with or without water vapor, H_2, CO and CH_4 were mixed together with [air+water vapor] or [air+nitrogen] to prepare the wet feed or dry feed. Throughout the temperature range of this study, the effect of CO_2 in the feed or product stream may be neglected because combustion of CH_4 is thermodynamically more favorable than the competing reactions such as methanation, WGS or RWGS reaction, and CO_2 reforming of methane [3,4], given the feed containing so much oxygen in it. Nominal flow rate and composition of the feeds (Gas-1 and Gas-2) used for combustion of the SOFC stack flue gas are listed in Table 2. For the Gas-1 and Gas-2, oxygen (actually air) was present in the stoichiometric ratio of the combustible components at the GHSV of 29,280 h^{-1}. The catalyst stability test was carried out at each of four reaction temperatures: 723, 823, 923 and 1,023 K. The bimetallic Pd-Pt catalyst was exposed to the Gas-1 and Gas-2, respectively for 20 on-stream hours of combustion run and the fractional conversion of combustible components in the feed was monitored continuously. For the purpose of examining the reversibility of catalyst deactivation with respect to temperature, an additional catalyst stability test was conducted in the Gas-2 for the Pd-rich catalyst with the cyclic hold-and-ramp sequence of 773-823-873 K. For each temperature-hold of the sequence, the fractional conversion of combustible components in the feed was monitored for ten on-stream hours of combustion. Composition of the stream at the inlet and outlet of the reactor was measured by using a gas chromatograph

Table S1. BET surface area of the HM-1 (Pd-rich) catalyst in its fresh state and used states after combustion of the dry feed (Gas-1) or wet feed (Gas-2)

Catalysts	BET surface area, m^2/g					
	Fresh catalyst	After 20 h run at 723 K	After 20 h run at 823 K	After 20 h run at 923 K	After 20 h run at 1,023 K	After cyclic 773-823-873 K sequential run[a]
HM-1 in Gas-1*	21.1	18.4±0.2	18.3±0.3	18.2±0.5	18.0±0.7	n/a
HM-1 in Gas-2*	21.1	18.4±0.2	18.2±0.4	18.1±0.5	18.0±0.7	18.1±0.6

[a]Total 30 on-stream hours of combustion by the hold-and-ramp sequence of 773-823-873 K (10 on-stream hours of combustion at each temperature-hold)

*Gas-1: dry feed with no water vapor; Gas-2: wet feed with water vapor (flow rate and composition are given in Table 2)

Table S2. Flow rate, composition and space velocity of the feeds containing H_2, CO or CH_4 individually and their mixture

Components	Flow rate, ml/min (composition, vol%)			
	Gas-S1	Gas-S2	Gas-S3	Gas-S4
H_2	70(23)	-	-	17.3(5.77)
CO	-	70(23)	-	17.3(5.77)
CH_4	-	-	17.4(5.80)	17.4(5.80)
N_2	-	-	34.6(11.50)	-
Air	230(77)	230(77)	248(82.70)	248(82.66)
Total	300	300	300	300
GHSV, h^{-1}	18,000	18,000	18,000	18,000
Remark	With H_2 only	With CO only	With CH_4 only	With H_2, CO and CH_4

(Donam Systems 6200) equipped with a TCD detector.

RESULTS AND DISCUSSION

1. Catalyst Characterization

Table S1 lists the BET measurement data for the Pd-rich catalyst used in combustion of the Gas-1 (containing nitrogen in addition to combustibles and air) and combustion of the Gas-2 (containing water vapor in addition to combustibles and air) to address the hydrothermal effect upon catalyst surface structure in the temperature range of 723-1,023 K. At each temperature, the Pd-rich catalyst was tested for twenty on-stream hours of combustion run. Specific surface area of the used catalyst exhibited a similar extent of reduction at different temperatures, indicating an evidence for stable surface structure of the Pd-Pt catalyst. Compared with the fresh catalyst, approximately 12.8, 13.2, 13.7 and 14.6% reduction of BET surface area occurred to the used catalysts after combustion of the Gas-1 at 723, 823, 923 and 1,023 K, respectively while the extent of surface area reduction after combustion of the Gas-2 at the same sequence of temperatures were 12.8, 13.6, 14.2 and 14.6%, respectively. These results indicate that water vapor in the feed did not affect the reduction of surface area but water vapor could be adsorbed onto ceria and/or it could alter the acidity of alumina, which affects the surface area and/or catalyst activity. Thus, $CeZrO_2$ incorporated into Al_2O_3 can not only improve the properties of support material but also introduce a kind of metal-support interaction favorable for combustion reaction. As a result, the catalyst surface was stabilized even after combustion run at 1,023 K. BET surface area of the used catalyst after combustion of the Gas-2 by the cyclic hold-and-ramp sequence of 773-823-873 K was also measured: compared with the fresh catalyst, approximately 14.2% reduction of surface area occurred to the Pd-rich catalyst. This extent of surface area reduction corresponds closely to the average of surface area reductions after 823 K and 923 K combustion.

2. Effect of H_2 and CO Upon CH_4 Combustion in the Feed

CH_4 conversion in this study corresponds to the means of evaluating the catalyst activity for combusting the feed, because CH_4 was the feed component most difficult to combust. Other reactants such as H_2 and CO were readily and completely oxidized to H_2O and CO_2 by catalytic combustion at the temperatures well below the

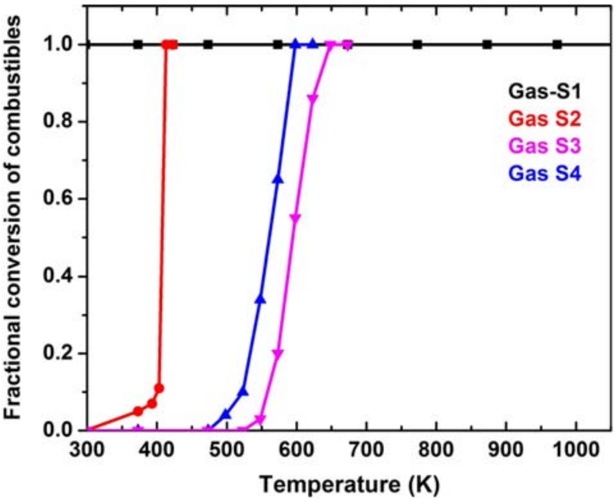

Fig. S1. Combustion profiles of the feed Gas-S1 to Gas-S4 over the Pd-rich catalyst as a function of temperature.

temperature at which the reactant CH_4 began to be oxidized. In Fig. S1, it is shown that over the Pd-rich catalyst, H_2 and CO were completely combusted at room temperature and at 413 K, respectively. Thus, the catalyst activity was evaluated just by CH_4 conversion via combustion reaction. From combustion of the feed simulating the SOFC stack flue gas, no other products but CO_2 and H_2O were observed, eliminating the need of considering the product selectivity or competing reactions to consume the reactant CH_4. In fact, H_2 and CO in the feed containing CH_4 (Gas-S4) provided the effect of shifting the profile of CH_4 conversion versus temperature to the left, i.e., to the direction of lower light-off temperature as compared with the feed containing CH_4 only (Gas-S3). Also, from the supplemental runs, it was found that methanation did not occur from a feed containing H_2 and CO with air, because catalytic combustion is thermodynamically more favorable. In fact, as even trace amount of O_2 in the feed inhibits methanation at any temperature in the methanation process [5], it is unlikely that methanation may occur from the feed containing so much oxygen in this study.

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