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Effects of CeZrO₂–Al₂O₃ support composition of metal-foam-coated Pd–Rh catalysts for the steam-biogas reforming reaction

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ABSTRACT

Biogas conversion to syngas by steam reforming was studied over metal-foam-coated Pd–Rh catalysts with variable CeZrO₂–Al₂O₃ support compositions. Catalysts with a higher CeZrO₂/Al₂O₃ ratio exhibited greater CH₄ and CO₂ conversions and higher H₂/CH₄ yields, while displaying lower H₂/CO ratios and reduced coke formation. Catalytic stability tests over 200 h showed CH₄ and CO₂ conversion rates of 93–97% and 0–5%, respectively. CeZrO₂-modification of the catalyst leads to reduction in the BET area and metal dispersion. Sintering was observed in used catalysts; however there was no clear correlation between the extent of morphological deterioration and the CeZrO₂/Al₂O₃ ratio of the catalyst support.

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Introduction

Biogas is an important renewable resource that is often left unused due to its distributed nature and the high cost of development for commercial use. Direct biogas emissions to the atmosphere cause significant harm due to methane's role as a short lived climate pollutant (SLCP). Therefore, biogas development and utilization for energy production can considerably reduce net greenhouse gas (GHG) emissions [1]. Methane in the biogas can either be combusted directly as a fuel or can be converted into syngas through the steam-biogas reforming (SBR or bi-reforming) process which combines steam-methane reforming with dry (or CO₂) reforming of methane [2]. The benefits of the later approach have been detailed in previous studies by the authors. Syngas consists of H₂ and CO and is a versatile feedstock that can be used for fuels, chemicals and power production [3,4].

Biogas typically consists of 35–75% CH₄ and 15–50% CO₂ along with moisture. Additional water in the form of steam has to be added to the SBR system since coke formation is a serious problem

encountered when CH₄ is reformed with CO₂ without sufficient steam or in the absence of steam. The steam to carbon ratio is also a critical parameter affecting CH₄ and CO₂ conversion during the SBR reaction. Major reactions involved in the SBR process are listed below [5–7]:

Commercial SMR catalysts for syngas production are mostly nickel-based and are supported on alumina [8]. Dry reforming and bi-reforming are not commercial technologies and the catalysts are still under development for these processes [2,9–11]. Jakobsen

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et al. studied SMR and DRM reactions over a Ru/ZrO₂ catalyst in the low temperature range (700–850 K), reporting CH₄ conversions below 35% [7]. Angeli et al. studied CH₄ bi-reforming over Ni–Rh on La₂O₃–ZrO₂ and La₂O₃–CeO₂–ZrO₂ catalysts at 673–823 K with a feed CH₄/CO₂ ratio of unity and a relatively large steam/CH₄ ratio (S/C = 3), reporting 5–10% less CH₄ conversions than the equilibrium values [12]. The stability tests, conducted for over 50 h, showed a trend of decreasing methane conversions. Other materials that have been evaluated for steam/dry reforming of methane include Ni–La₂O₃ [13], Ni–In/SiO₂ [14], Ni/MgO [15], Ni–MgO–Al₂O₃ [16], Ni/MgO–CeO₂ [17], Fe₂O₃–Al₂O₃–CuO catalyst with Ba, Ca, Mg and Sr [18], Cu–CeO₂–ZrO₂ [19], Co–MgO [20], Co/CeO₂ [21], Fe, Mn, Co and Cu supported on Al₂O₃ [22].

Research has shown that CeO₂-modification of the SBR catalyst support material significantly improves catalytic performance and as an active ingredient, performance of Rh is superior to that of Ni [12]. Compared with nickel, noble metals lead to reduced coke formation in biogas reforming. However, due to the cost factor of noble metals, research has focused on improving catalysts by adding small quantities of noble metal(s) to nickel or by modifying the catalyst support material with promoters such as CeO₂ or CeZrO₂ [23,24].

A number of studies focusing on noble metal catalysts for methane reforming are available in the literature, including evaluation of bimetallic catalysts prepared by adding a small portion of rhodium, the most active ingredient for activating methane, to another noble metal [25–36]. Our previous publications detailed the performance of substrate-coated Pd–Rh catalysts developed for the SBR process [2,9–11]. We demonstrated that a certain extent of CeZrO₂-modification of the Al₂O₃ support altered the physical characteristics and improved the SBR activity of a 1.31 wt% Pd–Rh catalyst having the optimum bimetallic composition of Pd(7)–Rh(1) by weight [2]. Our present study focuses on how different CeZrO₂–Al₂O₃ support compositions affect the surface structure and SBR performance of the Pd(7)–Rh(1) catalyst coated on a metal foam substrate. The results of this study can be used to design a suitable bimetallic noble metal catalyst for the SBR process.

Experimental

Catalyst preparation and characterization

Each Pd–Rh catalyst was prepared by coating 7.6 g of catalytic composites, which consist of active metal ingredients and metal oxide(s) support, onto 0.1 l metal foam substrate (foam density 1 g/cm³, surface area 13.68 m²/l, cell diameter 450 μm, porosity 78.5%) made of Al–Ni–Cr alloy. The catalytic composites were made by loading 1.31 wt% Pd(7)–Rh(1) clusters on CeZrO₂-modified Al₂O₃ powder having 6 different Al₂O₃/CeZrO₂ ratios: 100/0, 85/15, 75/25, 50/50, 25/75, 0/100 by weight. Catalyst preparation procedure has been described in detail in an earlier study [11]. A slurry containing Pd–Rh, alumina, and ceria–zirconia was made by

impregnating the mixed powder of alumina and ceria–zirconia with palladium nitrate and rhodium nitrate solutions, then dispersing the impregnated powder in de-ionized water, and then wet-milling the dispersed powder. The volumes of palladium nitrate and rhodium nitrate solutions were calculated so that the impregnated powder had palladium and rhodium contents of 1.15 wt% and 0.16 wt%, respectively. The slurry was coated onto Al–Ni–Cr alloy foam substrate by the wash-coating method, and excess slurry was blown away from the substrate by an air-knife. The coated substrate was dried at 393 K in an oven for three hours, and then was calcined at 873 K in a muffle furnace for three hours. For each one liter volume of the alloy substrate, nominally 76 g (dry basis) of the impregnated powder was coated. Noble metals loading in the wash-coat composite is 1.31 wt%, and their overall loading value in the metal foam catalyst is reduced to 0.093 wt% when the weight of metal foam is included. The noble metals/metal foam catalysts were used in this study without further pretreatments.

Chemical compositions of the (Pd–Rh)/(CeZrO₂–Al₂O₃) catalysts were measured by the ICP (inductively-coupled plasma) (Agilent Technologies, 5100) method, after scraping catalytic composites from the coated alloy substrate. Catalytic composites of the fresh and used catalysts were characterized for BET surface area and pore structure by nitrogen adsorption and porosimetry (Micromeritics, ASAP 2010) and active metal dispersion was measured by CO chemisorption at 313 K using CO pulse technique (BEL, BelCat Analyzer). Catalyst morphology was examined by scanning electron microscope (JEOL, JSM-5610). Chemical compositions of the catalytic composites are listed in Table 1.

SBR reaction experiments

For evaluating the activity and stability of the metal-foam-coated Pd–Rh/(CeZrO₂–Al₂O₃) catalysts, SBR reaction runs were conducted at atmospheric pressure in a microchannel heat exchanger platform (HEP) reactor (Catacel/Johnson-Matthey), as described previously [11]. Nine pieces of the substrate-coated Pd–Rh catalyst strips (1 cm width × 1 mm thickness) were inserted into the reformer side of the reactor where the reforming feed was passed at GHSV (Gas Hourly Space Velocity) of 1400 h^{−1}. The reactant (biogas + steam) flow was 380 sccm and the amount of catalyst used is about 17.5 g, which results in a GHSV of 1400 h^{−1}. Several K-type thermocouples were used to measure the catalyst bed temperature at different axial positions inside the reactor. The alternate chambers of the HEP reactors were used to conduct combustion over a Pd–Pt catalyst in order to supply the energy necessary for the reforming reaction. Details are reported in our previous study [11]. Thermocouples were also installed in the combustor side of the reactor, where a mixture of methane and air was passed over a different set of substrate-coated Pd–Pt catalyst strips to enable combustion. The HEP reactor was enclosed inside a temperature-programmed furnace which was interfaced with a data acquisition system. A schematic diagram of the HEP reactor

Table 1

The catalytic composites of the Pd–Rh catalysts.

Catalytic composites	Catalyst name	Active ingredients ^a (wt%)	Oxides support (wt%)
[Pd(7)–Rh(1)]/[Al ₂ O ₃ (100)–CeZrO ₂ (0)]	mfc (100/0)	Pd 1.15, Rh 0.16	Al ₂ O ₃ 98.7, CeZrO ₂ 0.0
[Pd(7)–Rh(1)]/[Al ₂ O ₃ (85)–CeZrO ₂ (15)]	mfc (85/15)	Pd 1.15, Rh 0.16	Al ₂ O ₃ 83.9, CeZrO ₂ 14.8
[Pd(7)–Rh(1)]/[Al ₂ O ₃ (75)–CeZrO ₂ (25)]	mfc (75/15)	Pd 1.15, Rh 0.16	Al ₂ O ₃ 74.0, CeZrO ₂ 24.7
[Pd(7)–Rh(1)]/[Al ₂ O ₃ (50)–CeZrO ₂ (50)]	mfc (50/50)	Pd 1.15, Rh 0.16	Al ₂ O ₃ 49.3, CeZrO ₂ 49.3
[Pd(7)–Rh(1)]/[Al ₂ O ₃ (25)–CeZrO ₂ (75)]	mfc (25/75)	Pd 1.15, Rh 0.16	Al ₂ O ₃ 24.7, CeZrO ₂ 74.0
[Pd(7)–Rh(1)]/[Al ₂ O ₃ (0)–CeZrO ₂ (100)]	mfc (0/100)	Pd 1.15, Rh 0.16	Al ₂ O ₃ 0.0, CeZrO ₂ 98.7

^a The active metal composition in the composite material is 1.31 wt%. The active metal loading is 0.093 wt% when the weight of the metal foam support is considered.

with the substrate-coated catalysts is shown in Fig. 1. Catalyst sample placed inside the reactor was heated from room temperature to the reaction temperature at a rate of 5 K/min in reactant gas flow. Gas mixtures were supplied from the manifold consisting of gas cylinders, mixer/vaporizer, and water source. Gas components and water were mixed together and were heated to 433 K in the mixer/vaporizer before entering the reactor. The model biogas feed consisted of 60% CH₄ and 40% CO₂. Product gas composition was analyzed on a dry basis by using a residual gas analyzer (RGA, Cirrus-MKS Technologies). SBR reaction runs were conducted using a steam/CH₄ (S/C) ratio of 1.50 in the temperature range of 923–1123 K. Prior to each reaction run, the catalyst strips were

$$\text{H}_2/\text{CH}_4\text{yield} = \left(\frac{(\text{H}_2)_{\text{out}}}{(\text{CH}_4)_{\text{in}}} \right)_{\text{reformer}}$$

Coke formation during the SBR reaction

Coke formation during the SBR reaction is a serious concern since solid carbon (coke) deposition on the catalyst surface leads to deactivation. Two different methods were used to calculate the extent of coke formation; i.e., the fraction of carbon in the feed that turned into solid carbon:

$$\text{Coke formation} = \frac{(\text{moles of gaseous carbon in the feed} - \text{moles of gaseous carbon in the product gas})}{\text{moles of gaseous carbon}(\text{CH}_4 \text{ and CO}_2) \text{ in the feed}}_{\text{reformer}} \quad (1)$$

$$\text{Coke formation} = \frac{\text{moles of CO}_2 \text{ in the exhaust during oxidation of used catalyst oxidation over a 10h period}}{\text{moles of CH}_4 \text{ and CO}_2 \text{ fed to the reformer for 200h}} \quad (2)$$

pretreated at 873 K in [10% H₂+90% N₂] flow of 200 ml/min for 60 min followed by [40% steam+60% N₂] flow of 380 ml/min for 30 min in order to remove the deposited coke and oxygen from catalyst surface. Catalytic stability was tested at 1073 K and atmospheric pressure with a S/C ratio of 1.50 for 200 on-stream hours. The reaction temperature was maintained for at least 2.5 h after the target temperature was achieved. Each experiment was repeated at least three times for each catalyst. The standard deviation was measured and was negligible (<2.5%). Catalytic activity was evaluated using the following equations:

$$\text{CH}_4\text{conversion} = \left(\frac{(\text{CH}_4)_{\text{in}} - (\text{CH}_4)_{\text{out}}}{(\text{CH}_4)_{\text{in}}} \right)_{\text{reformer}}$$

$$\text{CO}_2\text{conversion} = \left(\frac{(\text{CO}_2)_{\text{in}} - (\text{CO}_2)_{\text{out}}}{(\text{CO}_2)_{\text{in}}} \right)_{\text{reformer}}$$

$$\text{H}_2/\text{CO ratio of syngas product} = \left(\frac{(\text{H}_2)_{\text{out}}}{(\text{CO})_{\text{out}}} \right)_{\text{reformer}}$$

The first equation (method 1) has been reported in our previous articles and is straightforward, based on the molar flow rates of CH₄, CO₂ and CO at reformer inlet and outlet [2,9–11]. Oxidation of the used catalyst sample can also be used to estimate coke formation from the SBR reaction in an alternate manner. The used catalyst was subjected to oxidation in a separate packed bed reactor for 10 h: catalyst samples of approximately 1 g each were taken from the catalysts used for the 200 h stability test, and then were placed individually in the packed bed reactor for 10 h under an air flow of 200 sccm at 973 K, which is high enough to burn the coke off from the sample. The reactor exhaust was connected to an RGA throughout the course of the oxidation process and the CO₂ concentration in the product gas stream was measured live. The total number of moles of CO₂ produced during the oxidation reaction was used to calculate the total coke deposited on the catalyst using the second equation (method 2). The results from the second method are more reliable than the first method since it is a direct measurement of the deposited carbon and is also not influenced by the accuracy of the RGA.

Results and discussion

Catalyst activity

Active metals loading of 1.31 wt% Pd–Rh on CeZrO₂–Al₂O₃ support is converted to 0.093 wt% Pd–Rh on the metal oxides support plus metal foam substrate, since 7.6 g of catalytic composites was coated onto 0.11 metal foam of 1.0 g/cm³ density. Despite the small quantity of active metals loading, most of the substrate-coated Pd(7)–Rh(1) catalysts are quite active in view of CH₄ conversion and syngas product yield as observed from the SBR reaction results. The metal-foam-coated (mfc) Pd–Rh catalysts are referred to using the phrase ‘mfc (Al₂O₃ weight percentage/CeZrO₂ weight percentage)’. Based on this system, the catalyst sample names are: mfc (100/0), mfc (85/15), mfc (75/25), mfc (50/50), mfc (25/75), and mfc (0/100) based on the relative abundance of CeZrO₂ in the Al₂O₃ support (Table 1).

Catalytic activity of the alloy substrate for the SBR reaction, shown in Fig. 2, is considered to be minimal. This is due to the substrate being made via heat treatment at 1473 K and its specific surface area being quite small due to the large extent of sintering caused by the heat treatment. At 923 K–1123 K, the substrate itself,

Fig. 1. Experimental setup of the SBR reaction process inside the HEP reactor [2].

Fig. 2. CH₄ conversion during the SBR reaction over the blank metal foam support.

without the catalytic material, exhibited merely 3–11% CH₄ conversion from the SBR reaction at the same GHSV that was used for the Pd–Rh catalysts. As shown in Fig. 3, CH₄ conversion from the SBR reaction increased with temperature for all of the Pd–Rh catalysts. However, the CeZrO₂-modified Pd–Rh catalysts (mfc (85/15), mfc (75/25), mfc (50/50), mfc (25/75), and mfc (0/100)), exhibited higher CH₄ conversion than the unmodified catalyst (the mfc (100/0)) at each reaction temperature, indicating that CeZrO₂-modification of the Al₂O₃ support has a positive effect upon CH₄ activation. The CH₄ conversion over the mfc (100/0) catalyst was 5–20% less than the CeZrO₂ modified catalysts' values, although the differences were attenuated above 1098 K. At or below 1098 K, CH₄ conversion improvement was most remarkable when CeZrO₂ was introduced to the catalyst support (mfc (85/15)). Further increase in the CeZrO₂ percentage maintained CH₄ conversion improvement trend but the improvement margins were significantly smaller. The CeZrO₂ modified catalysts exhibited CH₄ conversions greater than 90% at 998 K and above, whereas the mfc (100/0) catalyst did the same only at 1048 K and above. The CH₄ conversion from the SBR reaction over the mfc Pd–Rh/(CeZrO₂–Al₂O₃) catalyst was in the order of mfc (0/100) > mfc (25/75) > mfc (50/50) > mfc (75/25) > mfc (85/15) > mfc (100/0), consistent with the order of

Fig. 3. CH₄ conversion during the SBR reaction over the Pd–Rh catalysts.

Fig. 4. CO₂ conversion during the SBR reaction over the Pd–Rh catalysts.

relative CeZrO₂ abundance in the Al₂O₃ support. Similar CH₄ conversion improvements during SMR and DRM reactions due to CeO₂- or CeZrO₂-modification of supported Ni catalysts have been reported in the literature [37–39].

Fig. 4 exhibits a complicated pattern of CO₂ conversion versus temperature from the SBR reaction: the CO₂ conversion values decreased with temperature from 923 to 973 K in a negative range, and then reached negative minima at 973 K, above which temperature they turned to increase. This pattern may indicate that from 923 K to 973 K, CO₂ consumption by the DRM and/or RWGS route was far less selective than CO₂ production by the SMR route coupled with WGS route, and then from 973 K and upward, the CO₂ consumption route(s) began to be selective. At temperatures below 1073 K, for all of the mfc Pd–Rh catalysts except for the mfc (0/100) catalyst, CO₂ conversion was negative, evidencing that net CO₂ production occurred from the SBR reaction as the result of competition between the DRM and [SMR + WGS] reaction routes [10]. However, at 1073 K and above, all of the mfc Pd–Rh catalysts showed positive CO₂ conversion, e.g., 5.06% at 1073 K and 7.67% at 1123 K for the mfc (0/100) catalyst (supported on CeZrO₂) as well as 0.13% at 1073 K and 5.22% at 1123 K for the mfc (100/0) catalyst (supported on Al₂O₃), demonstrating meaningful achievement of net CO₂ consumption from the SBR reaction. The mfc (0/100) catalyst began to show positive CO₂ conversion (2.10%) at 1048 K, while the rest of the mfc catalysts did the same at 1073 K. The CO₂ conversion trends of the catalysts followed the same trends as CH₄ conversion described above, illustrating the positive effect of CeZrO₂-modification upon CO₂ activation. The CO₂ conversion improvement was most pronounced as the catalyst support changed from 75% CeZrO₂–25% Al₂O₃ (the mfc (25/75)) to 100% CeZrO₂ (the mfc (0/100)) in the range of 998–1098 K. The CeZrO₂-modification of the catalyst is thought to have a positive effect on CH₄ and CO₂ activation through oxygen storage and oxide reducibility improvement abilities, leading to the improvement of CH₄ and CO₂ conversions [27]. A notable difference in the CH₄ and CO₂ conversion trends is that the effect on CH₄ conversion was most remarkable as the support composition changed from 100% Al₂O₃ (the mfc (100/0)) to 15% CeZrO₂–85% Al₂O₃ (the mfc (85/15)) whereas the effect on CO₂ conversion was most remarkable as the support composition changed from 75% CeZrO₂–25% Al₂O₃ (the mfc (25/75)) to 100% CeZrO₂ (the mfc (0/100)). One possible explanation for this difference is that the threshold of the CeZrO₂-modification for CO₂ conversion improvement is higher than that for CH₄ conversion improvement, because CO₂ conversion

Fig. 5. H_2/CO ratio of the syngas product from the SBR reaction over the Pd-Rh catalysts.

Fig. 6. H_2/CH_4 yield from the SBR reaction over the Pd-Rh catalysts.

improvement requires the formation of larger ensembles of active sites on the $CeZrO_2-Al_2O_3$ support.

The mfc (0/100) catalyst exhibited lower H_2/CO ratio of the syngas product and higher H_2/CH_4 yield than the other catalysts, as shown in Figs. 5 and 6. This feature is consistent with the significantly higher comparative CO_2 conversion of the mfc (0/100) catalyst than the comparative CH_4 conversion (Figs. 3 and 4), resulting in increased CO production and a lower H_2/CO ratio. Over the temperature range of 1023–1098 K in which the mfc (0/100) catalyst achieved meaningful conversions of both CH_4 and CO_2 , its

H_2/CO syngas ratio and H_2/CH_4 yield were 3.19–2.93 and 2.91–2.94, respectively. Both mfc (0/100) and mfc (75/25) catalysts exhibited nearly identical H_2/CO syngas ratio over this temperature range, whereas the syngas ratio for the other catalysts was higher, with mfc (100/0) exhibiting a significantly higher ratio at lower temperatures.

Coke formation values in mol% calculated using method 1 are shown in Table 2. For all the catalysts, coke formation increased with temperature until a peak temperature and then decreased. The peak temperature was in the order of mfc (0/100) = mfc (25/75) < mfc (50/50) = mfc (75/25) = mfc (85/15) < mfc (100/0): 948 K for the mfc (0/100) and mfc (25/75) catalysts, 998 K for the mfc (50/50), mfc (75/25) and mfc (85/15) catalysts, and 1023 K for the mfc (100/0) catalyst. Peak value (mol%) of coke formation was in the order of mfc (0/100) (2.79) < mfc (25/75) (3.46) < mfc (50/50) (4.02) < mfc (75/25) (4.23) < mfc (85/15) (4.33) < mfc (100/0) (8.21). The trends show that higher $CeZrO_2$ content in the Al_2O_3 support resulted in reduced coke formation over the same temperature range. A similar coke formation tendency was observed for CH_4 reforming over $Ni/\alpha-Al_2O_3$ catalyst with CeO_2 - and/or ZrO_2 -modification by Pompeo et al. [37]. $CeZrO_2$ in the Al_2O_3 support of the mfc Pd-Rh catalyst is thought to suppress the coke formation during the SBR reaction through the following sequence [2]:

The extent of reaction was calculated for each of the following routes involved in the SBR reaction using the molar balance based on biogas conversion and syngas yield:

As shown in Fig. 7, ξ_1 , ξ_2 , ξ_3 and ξ_4 are the extents of reaction for the reaction routes (1), (2), (3) and (4), respectively, which were evaluated in mol/h for the model biogas and steam fed at GHSV of $1400 h^{-1}$ and S/C ratio of 1.50. In view of $321.2 \times 10^{-3} mol/h$ CH_4 and $214.2 \times 10^{-3} mol/h$ CO_2 in the biogas feed, sum of the extents of reaction for the routes (1), (2) and (4) draws good agreement with CH_4 conversion shown in Fig. 3, and the difference of those for the routes (2) and (3) reasonably accounts for CO_2 conversion shown in Fig. 4. Coke removal routes such as $2C + CO_2 \rightarrow 2CO$ and/or $C + H_2O \rightarrow CO + H_2$ were excluded from the molar balance because

Table 2
Coke formation (mol%) from the SBR reaction over the Pd-Rh catalysts.

T (K)	mfc (100/0)	mfc (85/15)	mfc (75/25)	mfc (50/50)	mfc (25/75)	mfc (0/100)
923	5.82	3.11	3.29	3.51	3.27	2.08
948	6.33	3.84	3.73	3.88	3.46	2.79
973	7.02	3.89	3.77	3.84	3.36	2.57
998	7.40	4.33	4.23	4.02	3.25	1.95
1023	8.21	3.65	3.97	3.78	2.15	1.71
1048	7.76	3.36	3.31	2.97	2.16	1.31
1073	5.45	2.96	2.27	2.12	1.69	1.17
1098	3.26	2.79	2.72	2.11	1.65	1.20
1123	3.01	2.29	2.30	1.86	1.62	1.82

Fig. 7. Extents of the reaction for the SBR reaction routes (inlet flow rates: CH_4 $321.1 \times 10^{-3} \text{ mol/h}$, CO_2 $214.2 \times 10^{-3} \text{ mol/h}$; GHSV 1400 h^{-1} ; S/C ratio 1.50).

Fig. 8. Catalytic stability of the Pd-Rh catalysts for the SBR reaction at 1073 K: (a) CH_4 conversion; (b) CO_2 conversion; (c) H_2/CO ratio of syngas product; (d) H_2/CH_4 yield.

Table 3

Coke formation (mol%) during the SBR reaction stability test at 1073 K.

Catalyst	Coke formation (mol%)	
	Method 1	Method 2
mfc (100/0)	5.45	2.82
mfc (85/15)	2.96	2.40
mfc (75/15)	2.27	2.40
mfc (50/50)	2.12	2.35
mfc (25/75)	1.69	2.10
mfc (0/100)	1.17	1.97

these routes could not be deconvoluted from the coke formation route (4).

Catalytic stability for 200 on-stream hours

Fig. 8 shows the SBR performance of each Pd–Rh/(CeZrO₂–Al₂O₃) catalyst for 200 on-stream hours at 1073 K. The temperature value of 1073 K was selected for the catalytic stability test since the CO₂ conversion became positive at this temperature regardless of the CeZrO₂/Al₂O₃ ratio of the catalyst. All of the catalysts maintained steady performances with negligible changes during the stability test, indicating that the extent of CeZrO₂-modification of the Al₂O₃ support did not affect the resistance to catalyst deactivation for at least 200 on-stream hours. As shown in Fig. 8(a), CH₄ conversion was steady in the range of 92.8–96.0% respectively for the mfc (100/0), mfc (85/15), mfc (75/25), mfc (50/50), mfc (25/75), and mfc (0/100) catalysts. The CO₂ conversion, shown in

Fig. 8(b), was also steady from 0.13 to 5.06% for the mfc (100/0), mfc (85/15), mfc (75/25), mfc (50/50), mfc (25/75), and mfc (0/100) catalysts. As shown in Fig. 8(c) and (d), H₂/CO ratio of the syngas product was steady at 2.96–3.12, while H₂/CH₄ yield was also steady at 2.73–2.91, respectively for the mfc (100/0), mfc (85/15), mfc (75/25), mfc (50/50), mfc (25/75), and mfc (0/100) catalysts.

Each of the Pd–Rh catalysts used for the 200 h stability test was oxidized at 973 K in another packed bed reactor for evaluating coke formation from the SBR reaction by the second method described in Section “Coke formation during the SBR reaction”. The results for coke formation calculated by method 2 are presented in Table 3. The coke formation data from the two methods clearly show that CeZrO₂ in the catalyst support played an important role of providing oxygen storage capacity to the Pd–Rh catalyst, and consequently suppressed coke formation from the SBR reaction. The CeZrO₂ only supported mfc (0/100) catalyst was least prone to coke deposition whereas the Al₂O₃ supported mfc (100/0) catalyst was most prone to coke deposition.

Catalyst characterization

Although all the Pd–Rh/(CeZrO₂–Al₂O₃) catalysts maintained steady activity for the SBR reaction for 200 on-stream hours, their thermal stability needed to be examined through catalyst characterization. BET surface area, pore structure and active metal dispersion of the catalytic composites are presented in Table 4 for the fresh as well as the used catalysts sampled after 200 h catalytic stability test described above. CeZrO₂-modification of the Al₂O₃ support in the fresh catalysts showed the

Table 4Characterization of the [Pd(7)–Rh(1)]/(CeZrO₂–Al₂O₃) composites.

Properties	BET surface area (m ² /g)		Pore volume (cm ³ /g)		Pore size (nm)		Active metal dispersion (%)	
Catalyst	Fresh	Used	Fresh	Used	Fresh	Used	Fresh	Used
mfc (100/0)	126.3	106.3	0.62	0.53	22.1	23.8	52.1	37.3
mfc (85/15)	94.9	81.5	0.46	0.38	18.1	18.9	40.7	30.9
mfc (75/15)	88.3	76.1	0.43	0.36	17.3	17.9	33.1	28.6
mfc (50/50)	84.1	74.3	0.34	0.31	13.5	15.7	30.2	20.4
mfc (25/75)	79.5	72.4	0.36	0.23	9.5	14.4	26.2	18.5
mfc (0/100)	69.8	58.7	0.10	0.12	7.2	13.9	21.0	16.8

Fig. 9. XPS data for coke formation: (a) results of the XPS analysis for used Pd(7)–Rh(1)/[Al₂O₃(100)CeZrO₂(0)] catalyst; (b) peak intensity for carbon from XPS results with varying ratio of Al₂O₃/CeZrO₂.

Fig. 10. SEM images of the fresh Pd-Rh catalysts.

tendency to decrease BET surface area and active metal dispersion by adversely affecting the catalyst pore structure. Compared to fresh catalysts, significant reduction of BET surface area was observed in the used catalysts, a tendency also observed by Pompeo et al. in a similar catalyst support modification study [37,40]. The BET surface area was reduced approximately 9–16% in the used catalysts in our study, with no clear correlation between the extent of reduction and the extent of CeZrO₂-modification of the Al₂O₃ support. Pore sizes and pore volumes of the used catalysts increased and decreased in concurrence with the reduction of BET surface area. The exception was the mfc (0/100) catalyst which showed only an increase in the pore size, without pore volume decrease due to its usage by the catalytic stability test. Accompanying these changes, active metal dispersion decreased for the used catalysts by approximately 4–15%, again without a clear correlation to the extent of CeZrO₂-modification of the Al₂O₃ support.

X-ray Photoelectron Spectroscopy (XPS) analysis of the spent catalysts were performed and the results are presented in Fig. 9. Fig. 9(a) shows the XPS analysis of mfc (100/0) for coke deposited over the catalyst. Fig. 9(b) shows the change in peak intensity of coke formation over the spent catalysts for the different Al₂O₃/CeZrO₂ ratios. The results show the same trend as estimated using the two coke formation calculation methods presented in Table 3.

Considering that the catalytic activity for the SBR reaction did not degrade during the 200 h catalytic stability test for any of the catalysts, it can be postulated that the catalyst sintering described above is not detrimental enough to negatively affect the catalytic activity. However, it must be acknowledged that the catalytic stability test must be extended to a period much longer than 200 on-stream hours in order to conclusively understand catalyst sintering and its effect on catalyst activity. Scanning electron microscopic images of fresh and used Pd-Rh/(CeZrO₂-Al₂O₃) catalysts are shown in Figs. 10 and 11, respectively. The

Fig. 11. SEM images of the Pd–Rh catalysts used in the 200 h catalytic stability test at 1073 K.

SEM images show that morphological changes occurred on the catalyst surfaces due to the 200 h catalytic stability test: sintering of the catalyst surface was evidenced by small pebbles which tend to form on the used catalyst surface exposed to high temperature for an extended period. Cross-sectional SEM images of the catalysts were taken to further assess the sintering. The cross-sectional SEM image in Fig. 12 shows large, smooth pieces on the surface, thus providing evidence to the sintering phenomenon.

Conclusions

Six metal-foam-coated 1.31 wt% [Pd(7)–Rh(1)]/(CeZrO₂–Al₂O₃) catalysts were studied to evaluate the effects of the support composition upon their performances for the SBR reaction. The catalytic activity was measured from 923 to 1123 K at atmospheric pressure in a Heat Exchanger Platform

reactor operated under an S/C ratio of 1.50 and GHSV of 1400 h^{–1}. The key results are summarized below.

1. Increasing the extent of CeZrO₂-modification of the catalyst support resulted in CH₄ and CO₂ conversion improvements for steam reforming of a model biogas consisting of 60% CH₄ and 40% CO₂.
2. The CH₄ and CO₂ conversion improvements were accompanied by a decrease in the H₂/CO ratio of the syngas product and an increase in the H₂/CH₄ yield. This allows the SBR process to be potentially configured to meet the needs of downstream processes.
3. Increased relative abundance of CeZrO₂ in the catalyst support suppressed coke formation from the SBR reaction due to oxygen storage and ability to improve oxide reducibility.
4. Regardless of the CeZrO₂–Al₂O₃ composition of the catalyst support, all of the metal-foam-coated Pd–Rh catalysts maintained catalytic stability for the SBR reaction steadily for

Fig. 12. Cross-sectional SEM images of the catalysts were taken to further assess the sintering.

200 on-stream hours. Some catalyst sintering was observed without a clear correlation to the extent of CeZrO_2 modification of the Al_2O_3 support of the catalyst.

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