

Catalytic Steam and Autothermal Reforming of Used Lubricating Oil (ULO) over Rh- and Ni-Based Catalysts

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The steam reforming of used lubricating oil (ULO) over Ni- and Rh-based catalysts supported by Ce-ZrO₂ and Al₂O₃ is studied in the present work. Among all catalysts, Rh/Ce-ZrO₂ (5 wt % Rh) provides relatively higher reforming reactivity (in terms of ULO conversion and H₂ yield) with excellent resistance toward carbon deposition compared to the other three catalysts. At 850 °C after exposure in the steam reforming condition for 72 h, H₂ yield of 78.1% can be achieved from the reaction over Rh/Ce-ZrO₂. For Ni/Ce-ZrO₂ and Ni/Al₂O₃, significant deactivations with time are detected and H₂ yields of 55.3–58.7% are achieved after exposure for 72 h; in addition, considerable amounts of C₂H₄, C₂H₆ and C₃H₆ are also found in the product along with H₂, CO, CO₂, and CH₄. The effect of O₂ addition was further studied over Ni/Ce-ZrO₂ and Ni/Al₂O₃. It was found that this addition significantly reduces the degree of carbon deposition as well as promoting the conversion of hydrocarbons to CO and H₂. At a suitable amount of O₂, a high H₂ yield comparable to that of steam reforming over Rh-based catalysts can be achieved. Nevertheless, it must be noted that introducing too high an O₂ content resulted in lower H₂ production due to the combustion of H₂ and ULO by O₂ addition.

Introduction

Hydrogen-rich gas or synthesis gas is one of the promising clean fuels for the near future. Currently, the main existing process for synthesis gas production is catalytic steam reforming and partial oxidation of various hydrocarbons, e.g., natural gas, ethanol, methanol, and oils. Nevertheless, the use of these hydrocarbon feedstocks for hydrogen production always faces high competition for utilization with several applications, e.g., for petrochemical feedstock or for transportation fuel. On this basis, the production of hydrogen from wastes has great benefit in terms of energy and environmental aspects. Used lubricating oil (ULO) is known as an important hazardous waste that currently is generated in amounts more than 35 million tons from the industrial sector a year. It is one of the most serious materials for humans and the environment due to its toxicity and difficulty in management. It is classified as “F list designates”, which is hazardous wastes from certain common industrial or manufacturing processes (wastes from nonspecific sources). Polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) are main components in ULO; these compounds are highly toxic when released to the environment or contaminated in water, causing the obstruction of sunlight and oxygen from the atmosphere to water which consequently results in the harm to aquatic life. Considering these toxicities to the environment, the catalytic treatment of ULO to produce hydrogen would be a great promising technology for clean fuel generation and environmental treatment.

Recently, catalytic steam reforming of several hydrocarbons and oxygenated hydrocarbons, e.g., natural gas, LPG, methanol, acetic acid, ethanol, acetone, phenol, or cresol, has been widely

investigated. In addition, in recent years, many researchers have also investigated the addition of oxygen together with steam in a single process, called autothermal reforming. By this combination, exothermic heat from the partial oxidation can directly supply the energy required for the endothermic steam reforming reaction. Therefore, it is considered to be thermally self-sustaining and consequently more attractive than steam reforming. However, the main disadvantage of this reaction is the lower production of synthesis gas (H₂ and CO) from this reaction compared to steam reforming. Currently, the general process for the production of hydrogen and synthesis gas is based on the steam reforming reaction using nickel-based catalyst. It is noted that worldwide efforts are in progress to explore a novel catalyst with higher activity and stability for the reforming reactions. Various precious metals such as Pt, Rh, and Ru have been reported to be active for the reforming reactions and resistant to the carbon formation. However, the current prices of these metals are very high for commercial uses, and the availability of some precious metals such as ruthenium was too low to have a major impact on the total reforming catalyst market. It should also be noted that selection of catalyst support material is an important issue as there was evidence that metal catalysts are not very active when supported on inert oxides.¹ Various supports have been investigated, for example, α -Al₂O₃, γ -Al₂O₃, and γ -Al₂O₃ with alkali metal oxide and rare earth metal oxide, CaAl₂O₄ and Ce-ZrO₂. A promising catalyst system for the reforming reactions appeared to be a metal on Ce-ZrO₂ support, where the metal can be Ni, Pt, or Pd.^{2–9}

The aim of the present work is to develop the reforming catalysts that can convert ULO to hydrogen with high reforming activity and great resistance toward carbon formation. For economy, Ni was applied as a catalyst rather than precious metals such as Pt, Rh, and Ru, although it is more sensitive to carbon formation. Ni/Ce-ZrO₂ was selected as primary catalyst; its reforming performances were compared to conventional Ni/Al₂O₃. In addition, for comparison, Rh/Ce-ZrO₂ and Rh/Al₂O₃

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Table 1. Physical Properties of Synthesized Catalysts

catalyst	specific surface area (m ² g ⁻¹)	metal loading (%wt)	catalyst reducibility (%)	metal dispersion (%)
Rh/Ce-ZrO ₂	36.7	5.0	89.4	4.2
Rh/Al ₂ O ₃	42.3	4.9	94.5	4.4
Ni/Ce-ZrO ₂	38.1	5.1	91.3	4.8
Ni/Al ₂ O ₃	45.0	5.0	94.9	4.9

were also tested as the reforming catalysts; their steam and autothermal reforming reactivity were carried out compared to Ni-based catalysts.

Experimental Methodology

Catalyst Preparations and Characterizations. Ce_{1-x}Zr_xO₂ was prepared by coprecipitation of cerium nitrate (Ce(NO₃)₃·H₂O), and zirconium oxychloride (ZrOCl₂·H₂O) (from Aldrich). It should be noted according to our previous publication¹⁰ that Ce_{1-x}Zr_xO₂ with Ce/Zr molar ratio of 3/1 showed the best performance in terms of steam reforming activity and stability, therefore, the ratio between each metal salt that provides nominal Ce/Zr molar ratio of 3/1 was used in the present work. The starting solution was prepared by mixing 0.1 M of metal salt solution with 0.4 M of urea at a 2 to 1 volumetric ratio. This solution was stirred by magnetic stirring (100 rpm) for 3 h, and the precipitate was filtered and washed with deionized water and ethanol to prevent an agglomeration of the particles. The precipitate was dried overnight in an oven at 110 °C, and then calcined in air at 900 °C for 6 h.

Rh/Ce-ZrO₂ and Ni/Ce-ZrO₂ were prepared by dry impregnating Ce-ZrO₂ with Rh(NO₃)₃ and Ni(NO₃)₂ solutions (from Aldrich). The catalyst was reduced with 10% H₂/Ar at 500 °C for 6 h before use. For comparison, Rh/Al₂O₃ and Ni/Al₂O₃ were also prepared by impregnating γ -Al₂O₃ (from Aldrich) with Rh(NO₃)₃ and Ni(NO₃)₂. After reduction, the XRD study indicated the formation of crystalline phase over these synthesized catalysts. Furthermore, these catalysts were characterized with various physicochemical methods. The weight contents of Rh and Ni were determined by X-ray fluorescence (XRF) analysis. The reducibility percentage of rhodium was measured and calculated from the degree of H₂ uptake from the temperature-programmed reduction (TPR) test using 5% H₂ with a total flow rate of 100 cm³ min⁻¹ and temperature from room temperature to 500 °C, whereas the dispersion percentage of rhodium was identified from the volumetric H₂ chemisorption measurement using a chemisorption analyzer. The catalyst specific surface areas were obtained from BET measurement. All physicochemical properties of the synthesized catalysts are presented in Table 1.

According to these characterization results, the metal loadings are closed to 5 wt % as initially prepared, which indicates insignificant loss of metals during preparation. Furthermore, high catalyst reducibility and metal dispersion can be achieved for all synthesized catalysts. It is noted that the catalyst reducibility and metal dispersion are known to be important parameters for determining the catalyst activity; the good catalyst should have a high portion of reduced-form metal (i.e., Ni and Rh) compared to oxidized-form metal (i.e., NiO and RhO) as well as high dispersion of these metals on the surface of the support.

Apparatus and Procedures. To investigate the steam reforming of ULO and its associated reactions, an experimental reactor system was constructed. It is noted that the compositions of ULO used in the present work are 82.8% C, 15.2% H, 0.9% N, 0.53% O, and 0.57% S according to the ultimate analysis. The feed gases including the components of interest such as ULO, H₂O, helium, and O₂ were introduced to the reaction

section, in which an 8-mm i.d. and 40-cm length quartz reactor was mounted vertically inside a furnace. The catalyst was loaded in the quartz reactor, which was packed with a small amount of quartz wool to prevent the catalyst from moving. Regarding the results in our previous publications,^{10,11} to avoid any limitations by external mass transfer, the total gas flow was 1000 cm³ min⁻¹ under a constant residence time of 5×10^{-4} g min cm⁻³ in all experiments. A Type-K thermocouple was placed into the annular space between the reactor and the furnace. This thermocouple was mounted on the tubular reactor in close contact with the catalyst bed to minimize the temperature difference between the catalyst bed and the thermocouple. Another Type-K thermocouple was inserted in the middle of the quartz tube to recheck the possible temperature gradient, especially when O₂ was added along with ULO and H₂O as the autothermal reforming. The record showed that the maximum temperature fluctuation during the reaction never exceeded ± 1.90 °C from the temperature specified for the reaction. After the reactions, the exit gas mixture was transferred via trace-heated lines to the analysis section, which consisted of a Porapak Q column Shimadzu 14B gas chromatograph (GC) and a mass spectrometer (MS).

To study the formation of carbon species on catalyst surface, temperature programmed oxidation (TPO) was applied by introducing 10% O₂ in helium, after purging the system with helium. The operating temperature increased from 100 to 1000 °C at a rate of 20 °C min⁻¹. The amounts of carbon formation (mmol g_{cat}⁻¹) on the surface of catalysts were determined by measuring the CO and CO₂ yields from the TPO results (using Microcal Origin Software). In the present work, the reactivity was defined in terms of conversion and product distribution. The yield of H₂ production was calculated by hydrogen balance, defined as molar fraction of H₂ produced to total H₂ in the products. Distributions of other byproduct selectivities (e.g., CO, CO₂, CH₄, C₂H₄, C₂H₆, and C₃H₆) were calculated by carbon balance, defined as ratios of each mole of product to the moles of hydrocarbons in the product gas, accounting for stoichiometry; this information was presented in terms of (relative) fractions of these byproduct components, which are summed to 100%.

Results and Discussions

Reactivity toward the Steam Reforming of ULO. The catalytic steam reforming reactions over several catalysts were carried out under atmospheric pressure at 850 °C with H₂O/C ratio of 3. Figure 1 shows conversion of ULO (calculated by the carbon balance assumption), H₂ production, and carbon formation of all the catalysts after exposure in the steam reforming condition for 72 h.

It can be seen that the initial conversion for all catalysts is above 90%, while H₂ yields are in the ranges of 71.6–72.4% and 82.9–84.3% over Ni- and Rh-based catalysts, respectively. After 72 h of operation, H₂ yields drop by 19–22% over Ni-based catalysts and 7–10% over Rh-based catalysts. The deactivation is mainly related to the formation of carbon species on the surface of catalysts. After exposure to ULO steam reforming for 72 h, coke formation was investigated by TPO

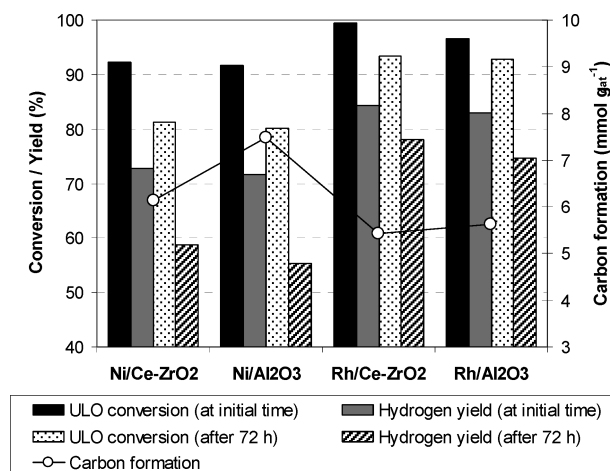


Figure 1. Effect of catalysts on ULO conversion, H₂ % yield, and carbon formation after exposure under steam reforming at 850 °C (with H₂O/C ratio of 3 for 72 h).

Table 2. Gaseous Byproduct Selectivities from the Steam Reforming of ULO at 850 °C (With H₂O/C Ratio of 3 for 72 h)

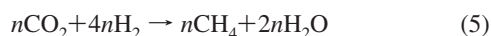
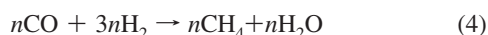
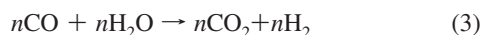
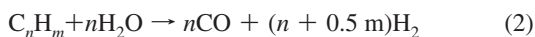
catalyst	gaseous byproduct selectivities (%)					
	CO	CO ₂	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆
Rh/CeZrO ₂	21.7	37.9	32.2	6.5	3.9	2.8
Rh/Al ₂ O ₃	23.9	32.6	27.4	14.4	4.1	2.6
Ni/Ce-ZrO ₂	19.2	29.7	23.3	24.1	5.3	3.4
Ni/Al ₂ O ₃	19.3	28.3	21.5	24.8	7.2	3.9

and was found to occur in all cases. The results show that Rh/Ce-ZrO₂ gave the best carbon formation resistance toward steam reforming whereas Ni/Al₂O₃ gave the least resistance (5.4 and 7.5 mmol/g-catalyst, respectively). Considering the gaseous product distribution, along with H₂ generated, CO and CO₂ as well as the light hydrocarbons (i.e., CH₄, C₂H₄, C₂H₆, and C₃H₆) were also observed in the product gas with different contents depending on the catalyst used, as presented in Table 2. It can be seen that relatively higher formation of hydrocarbons with less production of H₂, CO, and CO₂ was observed from Ni-based catalysts, particularly Ni/Al₂O₃, compared to Rh-based catalysts.

According to the mechanistic viewpoint, the overall reactions involved in the steam reforming of ULO are complex. At such a high operating temperature, the thermal decomposition of ULO takes place producing several gaseous products as well as coke from the following reaction:



When steam is introduced, the catalytic steam reforming of hydrocarbons (C_nH_m) occurs along with some side-reactions (e.g., water gas shift reaction and methanation).



The generations of saturated and unsaturated C₂₊ hydrocarbons (e.g., ethylene and ethane) are the major difficulties for the catalytic steam reforming, as these components act as very strong promoters for carbon formation. Based on these studies, it can be indicated that Rh-based catalysts efficiently convert

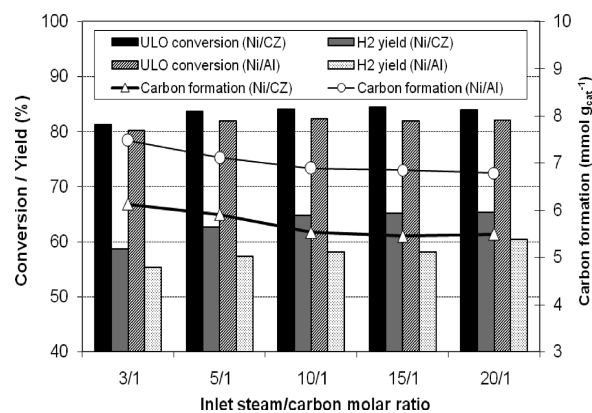


Figure 2. Effect of steam to carbon ratio over Ni-Al₂O₃ and Ni-Ce/ZrO₂ toward steam reforming at 850 °C in terms of ULO conversion, H₂ % yield, and carbon formation

ULO to H₂ with less formation of hydrocarbon byproduct compared to Ni-based catalysts. Rh is well-known as the most active catalyst toward several types of steam reforming reactions and also exhibits the highest resistance toward deactivation by carbon formation.¹² On comparison of supports, it was found that Ce/ZrO₂ gave higher ULO conversion and higher H₂ % yield compared to Al₂O₃ due to its higher oxygen storage capacity (OSC).¹³ It is noted according to our studies that the OSC values over Rh/Ce-ZrO₂ and Ni/Ce-ZrO₂ (determined by the TPR) are 2539–2572 μmol g_{cat}⁻¹, which are close to the OSC of Ce-ZrO₂ (2649 μmol g_{cat}⁻¹). In general, Ce-ZrO₂ and Rh render better coke resistance; the former provides higher OSC, which is crucial for combustion of deposited coke, while the latter is well known to provide high resistance toward carbon formation during the reforming of hydrocarbons.

Effect of Steam to Carbon Ratio. The steam to carbon (H₂O/C) ratio was varied in the range of 3:1 to 20:1 to investigate its effect on catalytic performance over Ni-Al₂O₃ and Ni-Ce/ZrO₂. The H₂O/C ratio was maintained at ratios of 3, 5, 10, 15, and 20. Again, ULO conversion, H₂ production, and carbon deposition after exposure were observed over Ni-doped catalysts toward steam reforming of ULO at 850 °C under atmospheric pressure as shown in Figure 2. For both catalysts, the result shows that higher amounts of steam help to improve catalyst performance to a small degree. However, there was no significant difference for ULO conversions at all ratios of H₂O/C to produce 80–85% conversion. H₂ production was found to increase significantly with increasing H₂O/C ratio for both catalysts. This is presumably due to more H₂O molecules in the feed reactant stoichiometrically. Nevertheless, the amount of H₂ production at H₂O/C ratios higher than 10 showed no increase.

It was found that carbon formation decreases with increasing steam to carbon ratio. It might well be possible that increased quantities of oxygen were available. Among the same catalysts, the carbon formation started to drop and remained constant at steam to carbon ratios higher than 10 indicating that excess steam beyond this ratio did not improve coke resistance to ULO steam reforming. The optimal steam to carbon ratio for ULO steam reforming over Ni-Al₂O₃ and Ni-Ce/ZrO₂ is 10. At the same steam to carbon ratio, Ni-Ce/ZrO₂ showed better performance compared to Ni-Al₂O₃ regarding ULO conversion, H₂ % yield, and coke resistance possibly due to its higher OSC. It should be noted that the use of high H₂O/C ratio strongly affected the CO and CO₂ selectivities. The production of CO₂ increased gradually with increasing this ratio, whereas the production of CO decreased, which is mainly due to the effect

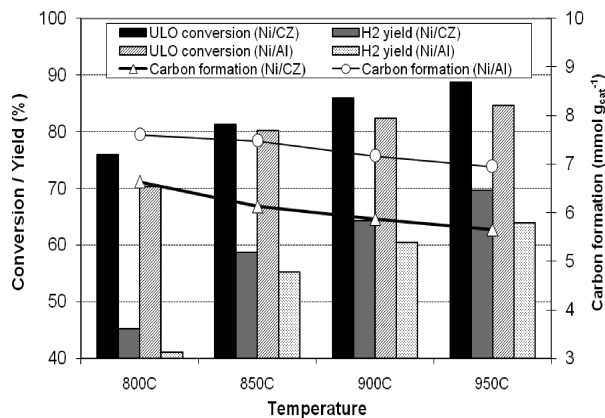


Figure 3. Effect of temperature over Ni–Al₂O₃ and Ni–Ce/ZrO₂ toward steam reforming (with H₂O/C ratio of 3) in terms of ULO conversion, H₂ % yield, and carbon formation

of water gas shift reaction. Nevertheless, the H₂O/C ratio shows only slight impact on the CH₄, C₂H₄, C₂H₆, and C₃H₆ selectivities; significant amounts of these hydrocarbons remain even by using the inlet H₂O/C ratio of 20.

Effect of Temperature. The effects of operating temperatures on ULO steam reforming were studied over Ni-doped catalysts. The temperature was kept constant at 800, 850, 900, and 950 °C. Figure 3 shows ULO conversion, H₂ production, and carbon deposition after exposure of Ni–Ce/ZrO₂ and Ni–Al₂O₃ at different temperatures to ULO steam reforming. Both catalysts show some ULO conversion and H₂ % yields at low temperature. For instance, at 800 °C, ULO conversions of Ni–Ce/ZrO₂ and Ni–Al₂O₃ are 76 and 70, while their H₂ productions are 45 and 41% yield, respectively. Higher operating temperature improved ULO conversion and H₂ production. At temperature higher than 900 °C, the ULO conversions for both catalysts are higher than 80%. There is a large improvement in H₂ productions also as they turn out to be higher than 60% yield. The highest ULO conversion and H₂ % yield occurred in both catalysts at 950 °C. Carbon formation was found to decrease on increasing the temperature for both catalysts. The lowest carbon formation for both catalysts was detected at 950 °C at 5.7 and 7.0 mmol/g, respectively.

Apart from the benefits in terms of H₂ yield production improvement and carbon formation reduction, the use of high operating temperature also reduced the formation of hydrocarbons in the product gas. By increasing the operating temperature from 850 to 950 °C, the CH₄, C₂H₄, C₂H₆, and C₃H₆ selectivities from the steam reforming over Ni/Ce–ZrO₂ decreased from 23.3%, 24.1%, 5.3%, and 3.4% to 22.1%, 16.3%, 1.9%, and 0.1%, respectively. This is mainly due to the higher conversion of these hydrocarbons to H₂, CO, and CO₂ at high operating temperature.

Effect of Oxygen Addition. Lastly, the dependence of oxygen on the yield of hydrogen production over Ni/Ce–ZrO₂ was tested, as shown in Figure 4.

Figure 4 illustrates the effect of O₂ inlet to carbon ratio on ULO conversion, H₂ % yield, and carbon deposition of Ni-doped catalyst systems. It can be seen that the amount of carbon deposition linearly decreases with increasing O₂ adding content; nevertheless, the effect of oxygen addition on hydrogen yield is nonmonotonic. Hydrogen production yield was observed to increase with increasing O₂ partial pressures until a ratio of 2:1 and 2.5:1 was reached for Ni–Ce/ZrO₂ and Ni–Al₂O₃, respectively. Above that ratio, oxygen was found to negatively affect the hydrogen yield. At low O₂ addition, O₂ adding helps

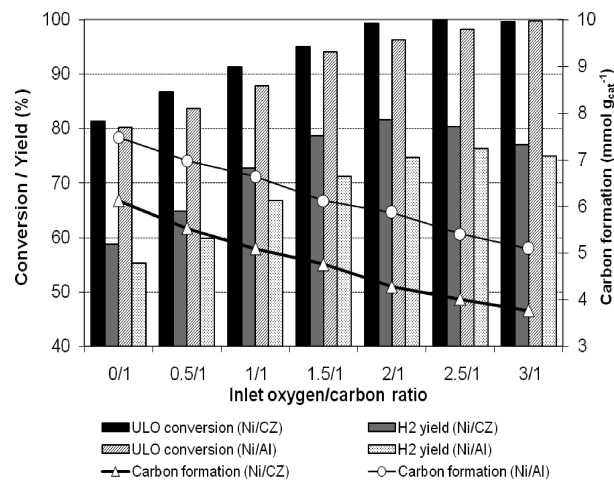


Figure 4. Effect of O₂ inlet to carbon ratio over Ni–Al₂O₃ and Ni–Ce/ZrO₂ toward steam reforming at 850 °C (with H₂O/C ratio of 3) in terms of ULO conversion, H₂ % yield, and carbon formation

oxidizing the surface carbon species; hence, the steam reforming can occur efficiently and H₂ yield increases with increasing O₂ addition content. Nevertheless, by adding too much O₂, H₂ yield oppositely decreases, which could be due to the oxidation of ULO as well as H₂ to H₂O. Importantly, by adding O₂ along with the feed, the formation of hydrocarbons in the product gas can be reduced considerably. By adding O₂ at the inlet O₂/C ratio of 2, the CH₄, C₂H₄, C₂H₆, and C₃H₆ selectivities from the steam reforming over Ni/Ce–ZrO₂ decreased to 15.3%, 2.1%, 0.2%, and 0%, which could be due to the prevention of ULO thermal decomposition by adding O₂.

Conclusions

Rh/Ce–ZrO₂ exhibits excellent reactivity toward the steam reforming of ULO in terms of its high H₂ yield and a high resistance toward carbon deposition. It is predicted that Ce–ZrO₂ support plays an important role in improving the reforming performance due to its high oxygen storage capacity (OSC). Addition of O₂ with ULO and H₂O can reduce the degree of carbon deposition and promote the conversions of CH₄, C₂H₄, and C₂H₆ to CO and H₂. The major consideration was the suitable co-fed reactant/ULO ratio since the presence of too high an O₂ concentration could reduce the yield of H₂ production.

Acknowledgment

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Literature Cited

- (1) Wang, X.; Gorte, R. J. A study of steam reforming of hydrocarbon fuels on Pd/ceria. *Appl. Catal., A* **2002**, 224, 209.
- (2) Martínez-Arias, A.; Coronado, J. M.; Cataluña, R.; Conesa, J. C.; Soria, J. Influence of Mutual Platinum-Dispersed Ceria Interactions on the Promoting Effect of Ceria for the CO Oxidation Reaction in a Pt/CeO₂/Al₂O₃ Catalyst. *J. Phys. Chem. B* **1998**, 102, 4357.
- (3) Skarmoutsos, D.; Tietz, F.; Nikolopoulos, P. Structure - property relationships of Ni/YSZ and Ni/(YSZ+TiO₂) cermet. *Fuel Cells* **2001**, 1, 243.
- (4) Takeguchi, T.; Furukawa, S. N.; Inoue, M. Hydrogen spillover from NiO to the large surface area CeO₂-ZrO₂ solid solutions and activity of the NiO/CeO₂-ZrO₂ catalysts for partial oxidation of methane. *J. Catal.* **2001**, 202, 14.

(5) Sfeir, J.; Philippe, P. A.; Moseki, P.; Xanthopoulos, N.; Vasquez, R.; Hans, J. M.; Jan, V. H.; Thampi, K. R. Lanthanum chromite based catalysts for oxidation of methane directly on SOFC anodes. *J. Catal.* **2001**, *202*, 229.

(6) Mamak, M.; Coombs, N.; Ozin, G. Mesoporous Yttria-Zirconia and Metal-Yttria-Zirconia Solid Solutions for Fuel Cells. *Adv. Mater.* **2000**, *12*, 198.

(7) Mamak, M.; Coombs, N.; Ozin, G. Self-assembling solid oxide fuel cell materials: Mesoporous yttria-zirconia and metal-yttria-zirconia solid solutions. *J. Am. Chem. Soc.* **2000**, *122*, 8932.

(8) Mamak, M.; Coombs, N.; Ozin, G. A. AC Impedance Measurements on Mesoporous Nickel-Yttria-Zirconia Solid Oxide Fuel Cell Materials. *Chem. Mater.* **2001**, *13*, 3564.

(9) Bera, P.; Mitra, S.; Sampath, S.; Hegde, M. S. Promoting Effect of CeO₂ in a Cu/CeO₂ Catalyst: Lowering of Redox Potentials of Cu Species in the CeO₂ Matrix. *Chem. Commun.* **2001**, *10*, 927.

(10) Laosiripojana, N.; Chadwick, D.; Assabumrungrat, S. Effect of high surface area CeO₂ and Ce-ZrO₂ supports over Ni catalyst on CH₄ reforming with H₂O in the presence of O₂, H₂, and CO₂. *Chem. Eng. J.* **2008**, *138*, 264.

(11) Laosiripojana, N.; Assabumrungrat, S. Catalytic dry reforming of methane over high surface area ceria. *Appl. Catal., B* **2005**, *60*, 107.

(12) Rostrup-Nielsen, J. R.; Bak-Hansen, J.-H. CO₂-reforming of Methane over Transition Metals. *J. Catal.* **1993**, *144*, 38.

(13) Laosiripojana, N.; Assabumrungrat, S. Hydrogen Production from Steam and autothermal reforming of LPG over High Surface Area Ceria. *J. Power Sources* **2006**, *158*, 1348.

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