ORIGINAL ARTICLE

Steam reforming of bio-ethanol over Ni on Ce-ZrO$_2$ support: Influence of redox properties on the catalyst reactivity

Wattana Singhto[1], Navadol Laosiripojana[2],
Suttichai Assabumrungrat[3] and Sumittra Charojrochkul[4]

Abstract

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The steam reforming of ethanol over Ni on Ce-ZrO$_2$ support, (Ni/ Ce-ZrO$_2$) were studied. The catalyst provides significantly higher reforming reactivity and excellent resistance toward carbon deposition compared to Ni/Al$_2$O$_3$ under the same conditions. At the temperature above 800ºC, the main products from the reforming processes over Ni/Ce-ZrO$_2$ were H$_2$, CO, and CO$_2$ with small amount of CH$_4$ depending on the inlet ethanol/steam and oxygen/ethanol ratios, whereas high hydrocarbon compounds i.e., C$_2$H$_4$ and C$_2$H$_6$ were also observed from the reforming of ethanol over Ni/Al$_2$O$_3$ in the range of conditions studied (700-1000ºC).

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[1]M.Sc. Student in Energy Technology, [2]Ph.D.(Chemical Engineering), The Joint Graduate School of Energy and Environment, King Mongkut's University of Technology Thonburi, Tungkru, Bangkok, 10140 Thailand. [3]Ph.D.(Chemical Engineering), Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, 10330 Thailand. [4]Ph.D.(Material Science), National Metal and Materials Technology Center (MTEC), Thailand Science Park, Klong Luang, Pathum Thani, 12120 Thailand.
Corresponding e-mail: navadol_l@jgsee.kmutt.ac.th

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These excellent ethanol reforming performances of Ni/Ce-ZrO$_2$ in terms of stability, reactivity and product selectivities are due to the high redox property of Ce-ZrO$_2$. During the ethanol reforming process, in addition to the reactions on Ni surface, the gas-solid reactions between the gaseous components presented in the system (C_2H_5OH, C_2H_6, C_2H_4, CH_4, CO_2, CO, H_2O, and H_2) and the lattice oxygen (O_x) on Ce-ZrO$_2$ surface also take place. Among these redox reactions, the reactions of adsorbed surface hydrocarbons with the lattice oxygen (O_x) ($C_nH_m + O_x \rightarrow nCO + m/2(H_2) + O_{x-n}$) can eliminate the formation of high hydrocarbons (C_2H_6 and C_2H_4), which easily decompose and form carbon species on Ni surface ($C_nH_m \rightarrow nC + m/2H_2$).

Key words : ethanol, steam reforming, autothermal reforming, solid oxide fuel cell

บทคัดย่อ

วัฒนะ สิงห์โต[1] นวดล เหล่าศิริพจน์[1] สุทธิชัย อัสสะบำรุงรัตน์[2] และ สุมิตรา จรสโรจน์กุล[3]

กระบวนการรีฟอร์มมิ่งของไบโอเอทานอลด้วยน้ำบนตัวเร่งปฏิกิริยาชนิด Ni/Ce-ZrO$_2$: ผลของคุณสมบัติรีด๊อกซ์ต่ออัตราการเกิดปฏิกิริยา

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การศึกษากระบวนการการรีฟอร์มมิ่งเอทานอลด้วยน้ำ โดยใช้ตัวเร่งปฏิกิริยาชนิด Ni/Ce-ZrO$_2$ (Ni บน Ce-ZrO$_2$) พบว่าตัวเร่งปฏิกิริยาชนิดนี้ให้ประสิทธิภาพการรีฟอร์มมิ่งที่ดี และมีความต้านทานต่อการเกิดคาร์บอน (carbon formation) สูงเปรียบเทียบกับตัวเร่งปฏิกิริยาชนิด Ni/Al$_2$O$_3$ ที่สภาวะเดียวกัน และ ณ ที่อุณหภูมิสูงกว่า 800°C พบว่าผลิตภัณฑ์หลักจากกระบวนการรีฟอร์มมิ่งด้วย Ni/Ce-ZrO$_2$ ได้แก่ H_2, CO, และ CO_2 โดยพบ CH_4 เพียงเล็กน้อยขึ้นอยู่กับสัดส่วนของการป้อน เอทานอล/น้ำ และสัดส่วนของการป้อน ออกซิเจน/เอทานอล อีกทั้งยังพบว่ามีสารประกอบไฮโดรคาร์บอนอื่น ๆ เช่น C_2H_4 และ C_2H_6 จากการทดลองทำการรีฟอร์มมิ่งเอทานอลด้วย Ni/Al$_2$O$_3$ ในช่วงอุณหภูมิที่ศึกษา (700-1000°C)

ประสิทธิภาพของตัวเร่งปฏิกิริยา Ni/ Ce-ZrO$_2$ ต่อการรีฟอร์มมิ่งของเอทานอลในเชิงของ stability, reactivity, and product selectivities นั้นต่างก็ขึ้นอยู่กับคุณสมบัติการ redox ที่สูงของ Ce-ZrO$_2$ จากกระบวนการรีฟอร์มมิ่งเอทานอลพบว่า ปฏิกิริยาบนพื้นผิวของ Ni ระหว่างก๊าซต่าง ๆ ที่ปรากฏในระบบ (C_2H_5OH, C_2H_6, C_2H_4, CH_4, CO_2, CO, H_2O และ H_2) กับ lattice oxygen (O_x) บนพื้นผิวของ Ce-ZrO$_2$ ได้เกิดขึ้น (gas-solid reactions) จากปฏิกิริยา redox เหล่านี้ ทำให้เกิดการดูดซับที่ผิวของ hydrocarbons โดย lattice oxygen (O_x) ($C_nH_m + O_x \rightarrow nCO + m/2(H_2) + O_{x-n}$) และสามารถกำจัดการก่อตัวของ high hydrocarbons (C_2H_6 และ C_2H_4) ซึ่งสามารถสลายตัวได้ง่ายและก่อให้เกิด carbon species บนพื้นผิวของ Ni ($C_nH_m \rightarrow nC + m/2H_2$)

Solid Oxide Fuel Cell (SOFC) is a promising energy conversion unit that produces electrical energy and heat with greater energy efficiency and lower pollutant emission than combustion processes. Hydrogen is a major fuel for SOFC. Nevertheless, the use of other hydrocarbon fuels such as methane, methanol, ethanol, gasoline and other oil derivatives is also possible when operated as an internal or in-stack reforming. As SOFC is operated at such a high temperature, these hydrocarbons can be internally reformed producing a H_2/CO rich gas, which is eventually used to generate the electrical energy and heat.

Regarding the global environmental problems and current fossil fuel crisis, the development of Internal Reforming Solid Oxide Fuel Cell (IR-

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[1] บัณฑิตวิทยาลัยร่วมด้านพลังงานและสิ่งแวดล้อม มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี บางมด ทุ่งครุ กรุงเทพฯ 10140 [2] ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย พญาไท กรุงเทพฯ 10330 [3] ศูนย์เทคโนโลยีโลหะและวัสดุแห่งชาติ อุทยานวิทยาศาสตร์แห่งประเทศไทย อำเภอคลองหลวง จังหวัดปทุมธานี 12120

SOFC) fed by biomass or renewable based fuels attracts more attention to be an alternative method for power generation in the near future. Among renewable sources, ethanol is a promising candidate, since it is readily produced by fermentation of biomasses and has reasonably high hydrogen content, in addition, ethanol is also safe to handle, transport and store (Cavallaro *et al.*, 1996; Athanasio *et al.*, 2004). The major difficulty to reform ethanol is the deactivation of the reforming catalyst due to the possible carbon deposition during ethanol decomposition, particularly at high temperature.

Previously, steam reforming of ethanol has been studied by several researchers (Garcia *et al.*, 2000; Srinivas *et al.*, 2003). Most of them have investigated the reforming of ethanol over noble metal catalysts (e.g. Rh, Ru, Pt, Pd) on several oxide supports (e.g. Al_2O_3, MgO, SiO_2, TiO_2) (Cavallaro *et al.*, 1996; Freni *et al.*, 2003). Verykios and coworkers (Fatsikostas *et al.*, 2002; Liguras *et al.*, 2003) reported that Rh-based catalyst provides significantly higher activity and stability toward the steam reforming of ethanol compared to Ru, Pt, Pd, and also Ni. Similarly, Freni *et al.* (Cavallaro *et al.*, 1996; Freni, 2001; Freni *et al.*, 2002) reported that Rh/Al_2O_3 provides the highest reforming reactivity among noble metal catalysts (e.g. Rh, Ru, Pt, Pd) on several oxide supports (e.g. Al_2O_3, MgO, SiO_2, TiO_2). Sobyanin and coworkers (Galvita *et al.*, 2002) studied the decomposition of ethanol in the presence of steam over Pd supported on a porous carbonaceous material, and reported that the catalyst exhibits a high activity and long-term stability. Burch and coworkers (Breen *et al.*, 2002) found that the order of ethanol steam reforming reactivity of the metals was Rh > Pd > Ni = Pt, and also reported the important role of the catalyst support. Verykios and coworkers (Fatsikostas *et al.*, 2002; Liguras *et al.*, 2003) also investigated the steam reforming of ethanol over Ni based catalyst on several oxide supports (e.g. La_2O_3, Al_2O_3, YSZ, and MgO). They revealed that Ni/La_2O_3 and Ni/La_2O_3/Al_2O_3 exhibit high activity and stability for hydrogen production.

According to the previous publications, under steam reforming conditions, an extensive formation of encapsulated carbon was always observed even if the noble metal catalysts were applied. This carbon formation was mainly due to the decomposition of ethanol forming high hydrocarbons (e.g. acetaldehyde, ethylene, and ethane), which easily formed the carbonaceous deposits. Adding oxygen as an autothermal reforming was proven to provide great benefits in terms of catalyst stability and coke suppression (Laosiripojana *et al.*, 2005); however, the yield of hydrogen production could be minimized due to the oxidation of hydrogen by oxygen added.

In this work, it was aimed to develop an alternative catalyst for steam and reforming of ethanol, which could provide high stability and activity toward this reaction at such a high temperature (700-1000ºC). According to the economical point of view, Ni was selected as a catalyst rather than other precious metals such as Pt, Rh and Ru. Although the precious metals have been reported to be active for the reforming reactions and resistant to the carbon formation than Ni (Mattos *et al.*, 2003; Roh *et al.*, 2003), 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 (Rostrup-Nielsen *et al.*, 1988). Selection of a support material is the major consideration of this work. It has widely been reported that metal catalysts are not very active for the steam reforming when supported on inert oxides (Wang *et al.*, 2002). Various supports have been investigated, for example, α-Al_2O_3 (Roh *et al.*, 2002), and γ-Al_2O_3 with alkali metal oxide and rare earth metal oxide (Miao *et al.*, 1997), and CeO_2 based supports (Dong *et al.*, 2002). A promising catalyst system for the reforming reactions appeared to be a metal on CeO_2-based supports, where metals can be Ni, Pt or Pd. Therefore, Ce-ZrO_2 was chosen as catalyst support over Ni in this work.

In the present work, the stability and activity toward the steam reforming of ethanol over Ni on

Ce-ZrO_2 support (Ni/Ce-ZrO_2) was studied and compared to conventional Ni/Al_2O_3. The resistance toward carbon formation and the product selectivities over these catalysts were also studied.

Experimental

1. Catalyst preparation and characterization

$Ce_{1-x}Zr_xO_2$ supports with different Ce/Zr molar ratios were prepared by co-precipitation of cerium nitrate ($Ce(NO_3)_3 \cdot H_2O$), and zirconium oxychloride ($ZrOCl_2 \cdot H_2O$) (from Aldrich). 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. The ratio between each metal salt was altered to achieve nominal Ce/Zr molar ratios: $Ce_{1-x}Zr_xO_2$, where x = 0.25, 0.50, and 0.75 respectively. This solution was stirred by magnetic stirring (100 rpm) for 3 h, and the precipitate was filtered and washed with deionised water and ethanol to prevent an agglomeration of the particles. It was dried overnight in an oven at 110ºC, and then calcined in air at 1000ºC for 6 h.

Ni/Ce-ZrO_2 was prepared by impregnating Ce-ZrO_2 with a $Ni(NO_3)_2$ solution (from Aldrich). The catalyst was reduced with 10%H_2/Ar for 6 h before use. For comparison, Ni/Al_2O_3 (5wt% Ni) were also prepared by impregnating α-Al_2O_3 (from Aldrich) with $Ni(NO_3)_2$. After reduction, the catalysts were characterized by several physicochemical methods. The weight content of Ni in Ni/Al_2O_3 and Ni/Ce-ZrO_2 (with different Ce/Zr ratio) were determined by X-ray fluorescence (XRF) analysis. The reducibility and dispersion percentages of nickel were measured from temperature-programmed reduction (TPR) with 5% H_2 in Ar and temperature-programmed desorption (TPD) respectively. The catalyst specific surface areas were obtained from BET measurement.

2. Apparatus and Procedures

An experimental reactor system was constructed as shown in Figure 1 The feed gases including the components of interest (ethanol and steam from the evaporator, and oxygen as the additive gas) and the carrier gas (helium) were

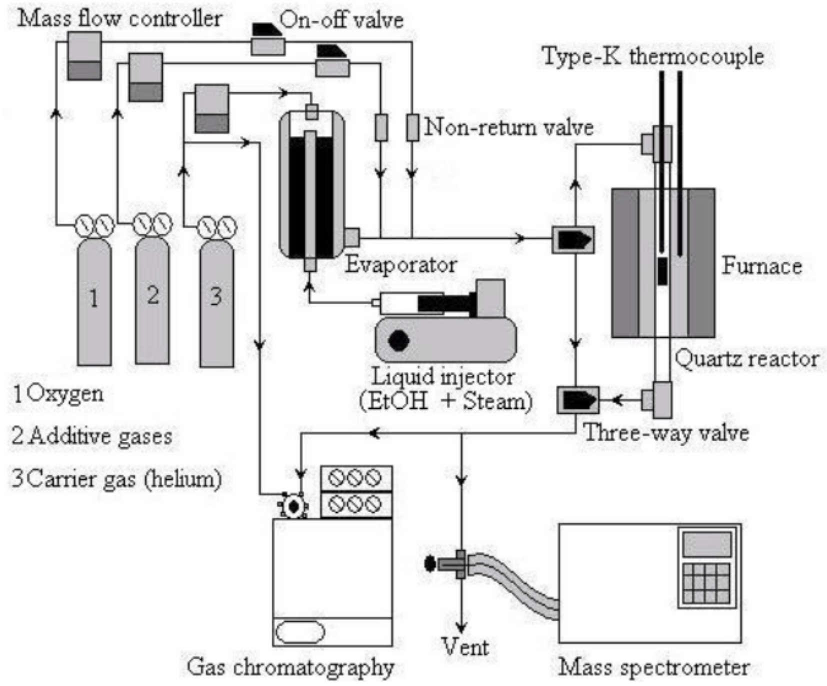

Figure 1. Schematic diagram of the experimental set-up.

introduced to the reaction section, in which an 10-mm diameter 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 (Laosiripojana *et al*., 2005; Laosiripojana, 2003), in order to avoid any limitations by intraparticle diffusion, the weight of catalyst loading was kept constant at 50 mg, while the total gas flow rate was 100 cm^3 min^{-1} under a constant residence time of 5 x 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 in order to re-check the possible temperature gradient. The record showed that the maximum temperature fluctuation during the reaction was always ±0.75ºC or less 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 consists of a Porapak Q column Shimadzu 14B gas chromatograph (GC) and a mass spectrometer (MS). The gas chromatography was applied in order to investigate the steady state condition experiments, whereas the mass spectrometer in which the sampling of the exit gas was done by a quartz capillery and differential pumping was used for the transient carbon formation experiment. In order to study the formation of carbon species on catalyst surface, Temperature Programmed Oxidation (TPO) was applied by introducing 10% oxygen in helium (100 cm^3 min^{-1}) into the system, after purging with helium. The operating temperature increased from room temperature to 1000ºC by the rate of 20ºC/min. The calibrations of CO and CO$_2$ productions were performed by injecting a known amount of these calibration gases from a loop, in an injection valve in the bypass line. The response factors were obtained by dividing the number of moles for each component over the respective areas under peaks. The amount of carbon formations on the surface of catalysts were determined by measuring the CO and CO$_2$ yields from the TPO results (using Microcal Origin Software) assuming a value of 0.026 nm^2 for the area occupied by a carbon atom in a surface monolayer of the basal plane in graphite (Ramirez *et al*., 2002). In addition to the TPO method, the amount of carbon deposition was confirmed by the calculation of carbon balance in the system. The amount of carbon deposited on the surface of the catalyst is theoretically equal to the difference between the inlet carbon containing components (C_2H_5OH) and the outlet carbon containing components (CO, CO_2, CH_4, C_2H_6, C_2H_4, and C_2H_4O). The amount of carbon deposited per gram of catalyst is given by the following equation:

$$C_{deposition} = \frac{mole_{carbon(in)} - mole_{carbon(out)}}{m_{catalyst}} \tag{1}$$

3. Kinetic parameters formulae

The results of ethanol decomposition were shown in terms of conversion (XEthanol), and the products selectivity (hydrogen, carbon monoxide, carbon dioxide, methane, ethane, ethylene, and acetaldehyde (Sproduct), which are calculated according to Eqs. (2) - (9):

$$X_{Ethanol} = \frac{100(\%Ethanol_{in} - \%Ethanol_{out})}{\%Ethanol_{in}} \tag{2}$$

$$S_{H_2} = \frac{100(\%H_2)}{3(\%Ethanol_{in} - \%Ethanol_{out}) + (\%H_2O_{in} - \%H_2O_{out})} \tag{3}$$

$$S_{CO} = \frac{100(\%CO)}{2(\%Ethanol_{in} - \%Ethanol_{out})} \tag{4}$$

$$S_{CO_2} = \frac{100(\%CO_2)}{2(\%Ethanol_{in} - \%Ethanol_{out})} \tag{5}$$

$$S_{CH_4} = \frac{100(\%CH_4)}{2(\%Ethanol_{in} - \%Ethanol_{out})} \tag{6}$$

$$S_{C_2H_6} = \frac{100(\%C_2H_6)}{2(\%Ethanol_{in} - \%Ethanol_{out})} \tag{7}$$

$$S_{C_2H_4} = \frac{100(\%C_2H_4)}{2(\%Ethanol_{in} - \%Ethanol_{out})} \qquad (8)$$

$$S_{C_2H_4O} = \frac{100(\%C_2H_4O)}{2(\%Ethanol_{in} - \%Ethanol_{out})} \qquad (9)$$

Results

1. Homogenous (non catalytic) reaction

Before studying performances of the catalysts, homogeneous (non-catalytic) steam reforming and autothermal reforming of ethanol were primary investigated. Regarding the steam reforming testing, inlet C_2H_5OH/H_2O in helium with the molar ratio of 1.0/3.0 was introduced to the system, while the temperature increased from 100ºC to 950ºC. As shown in Figure 2, it was observed that ethanol was converted to acetaldehyde, and hydrogen at the temperature above 200ºC. Methane and carbon monoxide productions were initially observed at the temperature around 250-300ºC. The selectivity of acetaldehyde significantly dropped at the temperature of 550ºC and approached zero at the temperature of 650ºC. In this range of temperature, the formations of ethane and ethylene were observed. The selectivities of carbon monoxide, carbon dioxide, methane, ethane and ethylene remained almost constant at temperatures higher than 650ºC.

According to the testing, ethanol homogenously converts to acetaldehyde, hydrogen, methane, and carbon monoxide via the dehydrogenation of ethanol and simultaneous fast decomposition of acetaldehyde at low temperature (300-500ºC) (Eqs. 10 and 11).

$$C_2H_5OH \rightarrow C_2H_4O + H_2 \qquad (10)$$

$$C_2H_4O \rightarrow CH_4 + CO \qquad (11)$$

When the temperature increases, the methane steam reforming and water-gas shift reactions (Eqs. 12 and 13) then take place. Ethylene is also formed by the dehydration of ethanol (Eq. 14) whereas the production of ethane is from ethylene hydrogenation (Eq. 15). This phenomenon is confirmed by the observation of lower H_2 selectivity compared to CO selectivity.

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad (12)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (13)$$

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \qquad (14)$$

$$C_2H_4 + H_2 \rightarrow C_2H_6 \qquad (15)$$

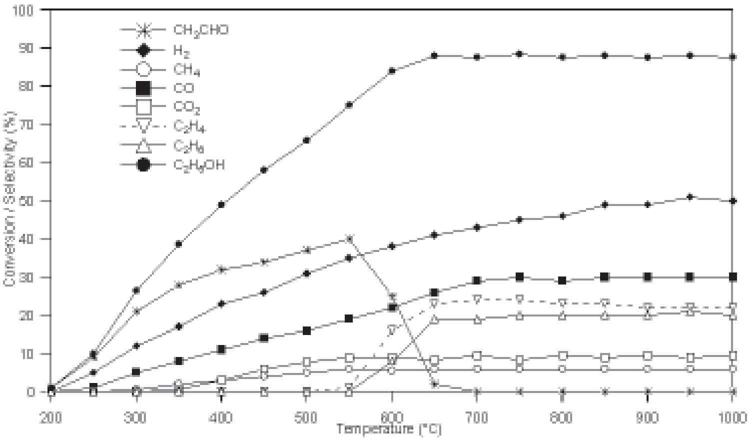

Figure 2. Homogenous (in the absence of catalyst) reactivity of ethanol steam reforming (4 kPa C_2H_5OH, and 12 kPa H_2O)

The formations of ethylene and ethane by the homogeneous decomposition of ethanol are the major difficulties for the catalytic reforming of ethanol at high temperature. It has been widely established that ethane and ethylene act as very strong promoters of carbon formation. Moreover, ethanol and methane can also be decomposed and converted to coke. Although the formations of ethylene and ethane can be reduced by adding oxygen, significant amount of these high hydrocarbons remains observed from the reaction. Eqs. 16-21 below present the most probable reactions that could lead to carbon deposition from the reforming of ethanol:

$$C_2H_6 \leftrightarrow 3H_2 + 2C \qquad (16)$$

$$C_2H_4 \leftrightarrow 2H_2 + 2C \qquad (17)$$

$$CH_4 \leftrightarrow 2H_2 + C \qquad (18)$$

$$2CO \leftrightarrow CO_2 + C \qquad (19)$$

$$CO + H_2 \leftrightarrow H_2O + C \qquad (20)$$

$$CO_2 + 2H_2 \leftrightarrow 2H_2O + C \qquad (21)$$

C is the carbonaceous deposits. At low temperature, Eqs. (20-21) are favorable, while Eqs. (16-19) are thermodynamically unflavored (Lwin *et al.*, 2000). The Boudard reaction (Eq. 19) and the decomposition of hydrocarbons (Eqs. 16-18) are the major pathways for carbon formation at such a high temperature as they show the largest change in Gibbs energy. According to the range of temperature in this study, carbon formation would be formed via the decomposition of hydrocarbons and Boudard reactions. By increasing inlet steam to ethanol molar ratio, the degree of carbon formation from the steam reforming of ethanol decreases, as the equilibrium of water-gas shift reaction moves forward producing more CO_2 rather than CO and eventually avoids carbon deposition via the Boudard reaction. However, significant amount of carbon remains detected due to the decomposition of ethane, ethylene, and methane (Eqs. 8-10).

2. Ratio Selection of Ce/Zr supported on Ni/Ce-ZrO$_2$

After preparation, all physicochemical properties of the synthesized catalysts are characterized as presented in Table 1. For Ce-ZrO$_2$, XRD testing was carried out to confirm the formation of Ce-ZrO$_2$ as shown in Figure 3. To determine the suitable ratio of Ce to Zr for the preparation of Ni/Ce-ZrO$_2$, the activity testing from using different ratios was conducted at 750ºC. The feed was C_2H_5OH/H_2O in helium with the molar ratios of 1.0/3.0. The ratios of Ce/Zr were 0:1, 1:3, 1:1, 3:1 and 1:0. The result in Figure 4 shows that the Ce/Zr ratio = 1:3 demonstrates the highest selectivity of hydrogen when testing at 750ºC.

3. Reactivity toward ethanol steam reforming

The steam reforming of ethanol over Ni/Ce-ZrO$_2$ and conventional Ni/Al$_2$O$_3$ were studied at

Table 1. Physicochemical properties of the catalysts after reduction

Catalyst	Ce/Zr Ratio	Ni-load[a] (wt.%)	BET Surface Area (m^2 g^{-1})	Ni-reducibility[b] (Ni%)	Ni-dispersion[c] (Ni%)
Ni/Ce-ZrO$_2$	1/3	5.0	20	90.4	4.24
Ni/Ce-ZrO$_2$	1/1	4.7	18	89.8	4.13
Ni/Ce-ZrO$_2$	3/1	4.8	19	88.1	4.37
Ni/Al$_2$O$_3$		4.9	40	92.1	4.87

[a] **Measured from X-ray fluorescence analysis.**
[b] **Measured from temperature-programmed reduction (TPR) with 5% hydrogen.**
[c] **Measured from temperature-programmed desorption (TPD) of hydrogen after TPR measurement.**

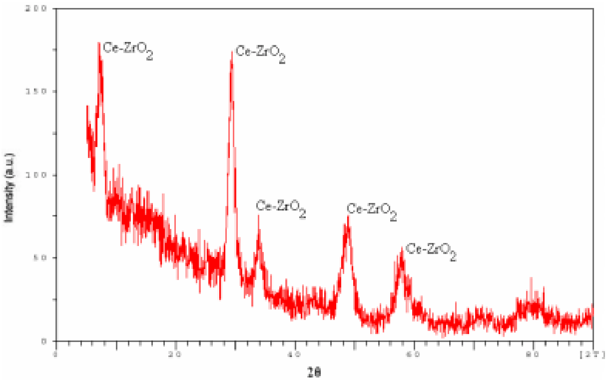

Figure 3. XRD pattern of synthesized Ce-ZrO$_2$

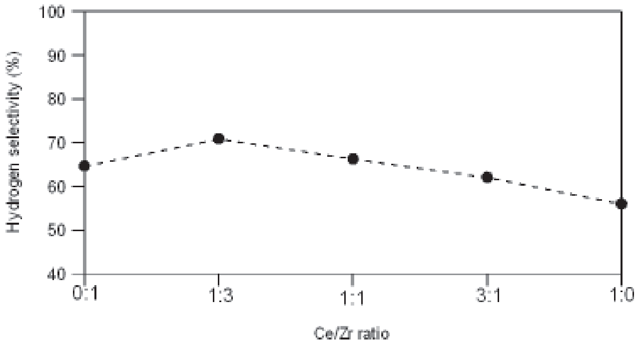

Figure 4. The percentage of hydrogen selectivity from ethanol steam reforming by varying ratio of Ce/Zr on Ni/Ce-ZrO$_2$ at 750ºC

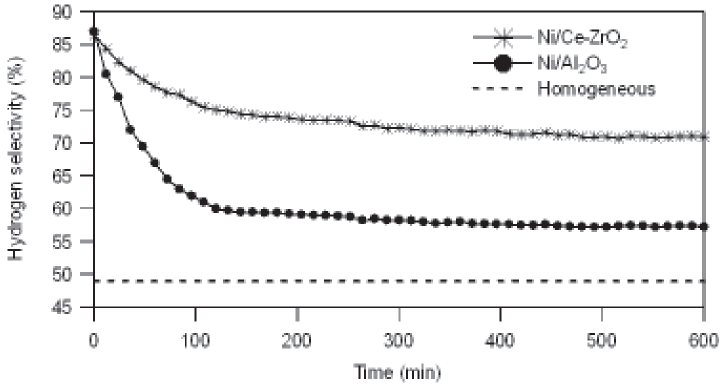

Figure 5. Steam reforming of ethanol at 750ºC for Ni/Ce-ZrO$_2$ (Ce/Zr = 3/1) and Ni/Al$_2$O$_3$

750ºC. The feed was C_2H_5OH/H_2O in helium with the molar ratios of 1.0/3.0. The variations in hydrogen selectivities (%) with time at 750ºC for different catalysts are shown in Figure 5 During 10 h operation, the hydrogen selectivities of Ni/Ce-ZrO$_2$ were significantly higher than Ni/Al$_2$O$_3$, the hydrogen selectivity of Ni/Ce-ZrO$_2$ at steady state is approximately 70-75%. However, the

Table 2. Physicochemical properties of the catalysts after exposure in ethanol steam reforming at 750ºC for 10 h

Catalyst	C_2H_5OH/H_2O ratio	Deactivation (%)	BET surface ($m^2 g^{-1}$)	Ni-load [a] (wt.%)	Ni-red.[b] (Ni%)	Ni-disp.[c] (Ni%)
Ni/Al_2O_3	1.0/3.0	17.1	17.1	4.9	90.2	4.18
(Ce/Zr = 3/1)	1.0/2.0	19.8	17.2	4.9	90.0	4.13
	1.0/1.0	24.6	17.1	4.7	90.2	4.17
Ni/Ce-ZrO_2	1.0/3.0	33.2	~ 40.0	4.9	92.0	4.85
	1.0/2.0	34.6	39.5	4.9	91.7	4.87
	1.0/1.0	39.5	~ 40.0	4.8	91.8	4.87

[a] **Measured from X-ray fluorescence analysis**
[b] **Nickel reducibility (measured from temperature-programmed reduction (TPR) with 5% hydrogen)**
[c] **Nickel dispersion (measured from temperature-programmed desorption (TPD) after TPR)**

Table 3. The dependence of inlet C_2H_5OH/H_2O ratio on the amount of carbon formation remaining on the catalyst surface after exposure in ethanol steam reforming at 750ºC for 10 h

C_2H_5OH/H_2O ratio	Total carbon formation (monolayers)	
	Ni/Ce-ZrO_2	Ni/Al_2O_3
1.0/3.0	1.52 [a] (1.47) [b]	4.52 [a] (4.54) [b]
1.0/2.0	1.69 (1.72)	4.76 (4.78)
1.0/1.0	1.84 (1.84)	4.81 (4.79)

[a] **Calculated using CO and CO_2 yields from temperature-programmed oxidation (TPO) with 10% oxygen.**
[b] **Calculated from the balance of carbon in the system.**

deactivations were also observed in both catalysts. Results of the catalyst stabilities expressed as deactivation percentages and the post reaction characterizations are given in Table 2.

The post-reaction temperature-programmed oxidation (TPO) experiments were then carried out after a helium purge by introducing 10% oxygen in helium in order to determine whether the observed deactivation is due to the carbon formation. From the TPO results shown in Figure 6, small peaks of carbon dioxide and carbon monoxide were observed for Ni/Ce-ZrO_2, whereas huge amount of carbon dioxide and carbon monoxide formations were detected for Ni/Al_2O_3. The amount of carbon formations can be determined by measuring the CO and CO_2 yields from these TPO results. Using a value of 0.026 nm^2 for the area occupied by a carbon atom in a surface monolayer of the basal plane in graphite (Ramirez *et al.*, 2002), the quantities of carbon deposited over Ni/Ce-ZrO_2 and Ni/Al_2O_3 were observed to be approximately 1.52 and 4.52 monolayers, respectively, for the inlet C_2H_5OH/H_2O ratio of 1.0/3.0. The degree of carbon formation was found to decrease with increasing inlet H_2O concentration as shown in Table 3.

The high resistance toward carbon deposition for Ni/Ce-ZrO_2 was reported in our previous publications (Laosiripojana *et al.*, 2005) and is mainly due to the high oxygen storage capacity (OSC) of this material. Ce-ZrO_2 contains a high concentration of highly mobile oxygen vacancies and thus acts as a local source or sink for oxygen on its surface. It has been reported that at high

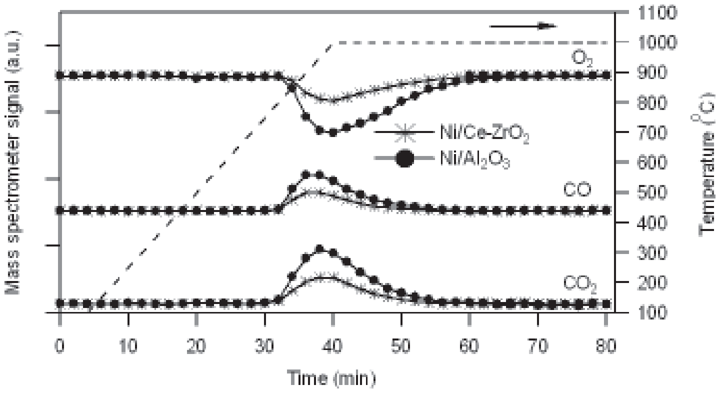

Figure 6. Temperature Programmed Oxidation (TPO) of Ni/Ce-ZrO$_2$ and Ni/Al$_2$O$_3$ after exposure in steam reforming of ethanol (4 kPa C_2H_5OH, and 12 kPa H_2O) for 10 h.

temperature the lattice oxygen (O_x) at the Ce-ZrO$_2$ surface can oxidize gaseous hydrocarbons (methane (Laosiripojana *et al.*, 2005), ethane (Laosiripojana *et al.*, 2006) and propane (Laosiripojana *et al.*, 2006). By using Ni/Ce-ZrO$_2$ as the catalyst, in addition to the reaction on Ni surface, the possible carbon depositions could be inhibited by the gas-solid reactions between these hydrocarbons and the lattice oxygen (O_x) at Ce-ZrO$_2$ surface forming hydrogen and carbon dioxide, which are thermodynamically unfavored to form carbon species, as illustrated schematically below.

$$C_2H_6 + 2S \leftrightarrow 2(CH_3\text{-}S) \quad (22)$$

$$C_2H_4 + 2S \leftrightarrow 2(CH_2\text{-}S) \quad (23)$$

$$CH_4 + 2S \leftrightarrow CH_3\text{-}S + H\text{-}S \quad (24)$$

$$CH_3\text{-}S + S \leftrightarrow CH_2\text{-}S + H\text{-}S \quad (25)$$

$$CH_2\text{-}S + S \leftrightarrow CH\text{-}S + H\text{-}S \quad (26)$$

$$CH\text{-}S + S \leftrightarrow C\text{-}S + H\text{-}S \quad (27)$$

$$C\text{-}S + O_x \leftrightarrow CO + O_{x-1} + S \quad (28)$$

$$2H\text{-}S \leftrightarrow H_2 + 2S \quad (29)$$

S is the catalyst surface site and CH_x-S is an intermediate surface hydrocarbon species. S can be considered to be a unique site, or the same site as the lattice oxygen (O_x) (Laosiripojana *et al.*, 2003). During the steam reforming, hydrocarbons are adsorbed on either a unique site (S) or the lattice oxygen (O_x). The lattice oxygen is regenerated by reaction with oxygen containing compounds (steam) present in the system.

$$H_2O + O_{x-1} \leftrightarrow O_x + H_2 \quad (30)$$

4. Influence of operating temperature on the product selectivities

The influence of operating temperature on the product selectivities over Ni/Ce-ZrO$_2$ and Ni/Al$_2$O$_3$ at the inlet C_2H_5OH/H_2O molar ratio of 1.0/3.0 were further studied by varying temperature from 700ºC to 1000ºC. As shown in Figure 7, it was found that the main products from the ethanol steam reforming over Ni/Ce-ZrO$_2$ were H_2, CO, CO_2, and CH_4, with small amounts of C_2H_4 and C_2H_6 depending on the operating temperature. In contrast, significant amounts of C_2H_4 and C_2H_6 were also observed as well as other chemical components from the ethanol steam reforming over Ni/Al$_2$O$_3$ in the range of conditions studied. Consequently, less H_2, CO, and CO_2 selectivities were achieved over these catalysts. Table 4 presents the quantities of carbon deposited on both catalysts after operated at several temperatures.

For comparison, the conversions and the product selectivities at equilibrium state were

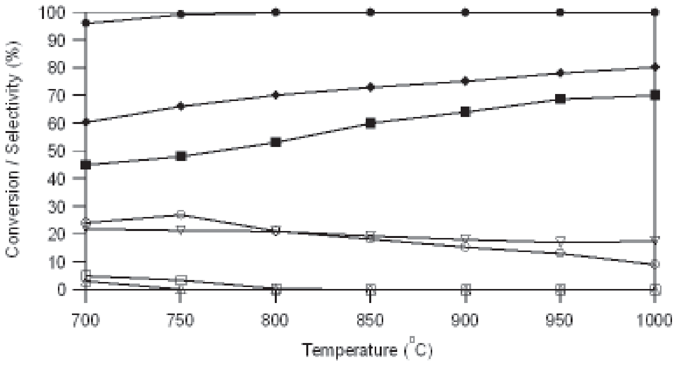

Figure 7(A)

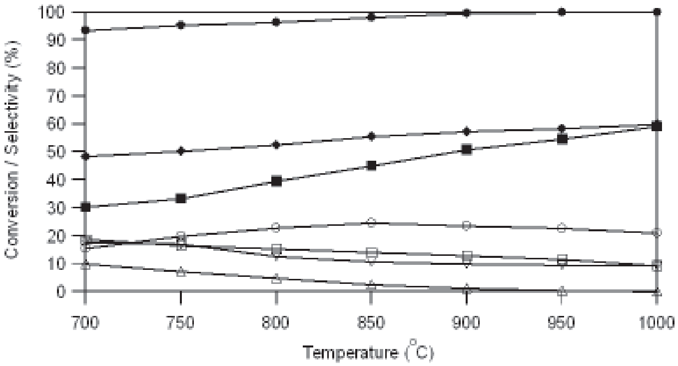

Figure 7(B)

Figure 7. **Effect of temperature on the conversion and product selectivities (C_2H_5OH(●), H_2(◆), CO(■), CO_2(∇), CH_4(O), C_2H_4(□), C_2H_6(Δ)) from ethanol steam reforming over Ni/Ce-ZrO$_2$ (Figure 7a) and Ni/Al$_2$O$_3$ (Figure 7b) with inlet C_2H_5OH/H_2O ratios of 1/3.**

Table 4. **The quantities of carbon deposited on catalysts after operated at several temperatures.**

Temperature (ºC)	The quantities of carbon deposited (monolayers)	
	Ni/Al$_2$O$_3$	Ni/Ce-ZrO$_2$
700	5.78a (5.77)[b]	2.08 a (2.04)[b]
750	5.39 (5.31)	1.89 (1.91)
800	5.01 (5.07)	1.66 (1.68)
850	4.74 (4.71)	1.58 (1.55)
900	4.52 (4.54)	1.52 (1.47)
950	4.33 (4.36)	1.37 (1.34)
1000	4.21 (4.20)	1.11 (1.14)

[a] **Calculated using CO and CO$_2$ yields from temperature-programmed oxidation (TPO) with 10% oxygen.**

[b] **Calculated from the balance of carbon in the system.**

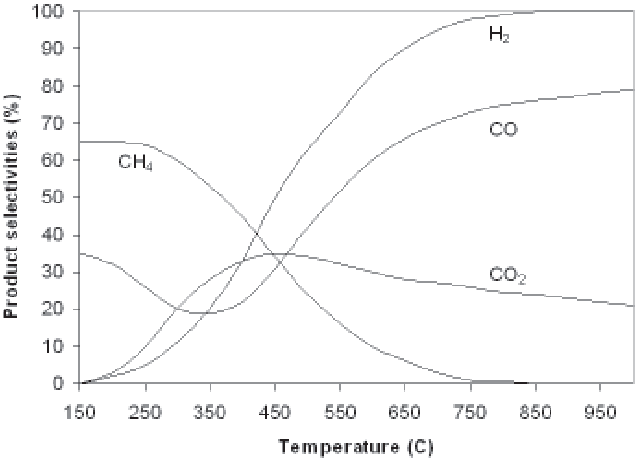

Figure 8. The product selectivities from ethanol steam reforming at the equilibrium level (4 kPa C_2H_5OH, and 12 kPa H_2O).

calculated using AspenPlus10.2 simulation program as shown in Figure 8. Regarding the simulation, the conversions of ethanol at equilibrium level are 100% in the range of temperature between 700-1000ºC. The selectivity of hydrogen at equilibrium are slightly higher than those achieved from the experiments over Ni/Ce-ZrO$_2$, in addition, neither C_2H_6 nor C_2H_4 formation was observed at the equilibrium state in this range of temperature due to the complete reforming of this component to CH_4, CO, and CO_2.

Conclusion

Ni on Ce-ZrO$_2$ support (Ni/Ce-ZrO$_2$) provides excellent reactivity toward the steam reforming of ethanol with high resistance toward carbon deposition and better product selectivities compared to Ni/Al$_2$O$_3$. The main products from these reforming processes over Ni/Ce-ZrO$_2$ were H_2, CO, and CO_2 with small amount of CH_4, whereas the formations of C_2H_4 and C_2H_6 were also observed together with the above gas components from the reactions over Ni/Al$_2$O$_3$ in the range of conditions studied. These high hydrocarbon compounds are easily formed by the homogenous decomposition of ethanol at high temperature (above 550ºC) without the catalyst requirement. The great benefits of Ni/Ce-ZrO$_2$ in terms of stability and reactivity toward ethanol reforming, high resistance toward carbon deposition, and good product selectivities are due to the high redox property of Ce-ZrO$_2$.

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References

Aguiar, P., Chadwick, D. and Kershenbaum, L. 2002. Modelling of an indirect internal reforming solid oxide fuel cell, Chem. Eng. Sci., 57: 1665-1677.

Athanasios, N. Fatsikostas and Xenophon, E. Verykios 2004. Reaction network of steam reforming of ethanol over Ni-based catalysts, J. Catal., 225: 439ñ452.

Breen, J.P., Burch, R. and Coleman, H.M. 2002. Metal-catalysed steam reforming of ethanol in the production of hydrogen for fuel cell applications, Appl. Catal. B: Environ., 39: 65-74.

Cavallaro, S., Chiodo, V., Freni, S., Mondello, N. and Frusteri, F. 2003. Performance of Rh/Al$_2$O$_3$ catalyst in the steam reforming of ethanol: H_2 production for MCFC, Appl. Catal. A: Gen., 249: 119-128.

Cavallaro, S., Chiodo, V., Vita, A. and Freni, S. 2003. Hydrogen production by auto-thermal reforming of ethanol on Rh/Al$_2$O$_3$ catalyst, J. Power Sour., 123: 10-16.

Cavallaro, S., Freni, S. 1996. Ethanol steam reforming in a molten carbonate fuel cell: A preliminary kinetic investigation, Int. J. Hydrogen Energy., 21(6): 465-469.

Dong, W.S., Roh, H.S., Jun, K.W., Park, S.E. and Oh, Y.S. 2002. Methane reforming over Ni/Ce-ZrO$_2$ catalysts: effect of nickel content, Appl. Catal. A., 226: 63-72.

Fatsikostas, A., Kondarides, D., and Verykios, X. 2002. Production of hydrogen for fuel cells by reformation of biomass-derived ethanol, Catal. Today., 75: 145-155.

Fierro, V., Klouz, V., Akdim, O. and Mirodatos, C. 2002. Oxidative reforming of biomass derived ethanol for hydrogen production in fuel cell applications, Catal. Today., 75: 141-144.

Fishtik, I., Alexander, A., Datta, R. and Geana, D. 2000. A thermodynamic analysis of hydrogen production by steam reforming of ethanol via response reactions, Int. J. Hydrogen Energy., 25: 31-45.

Freni, S. 2001. Rh based catalysts for indirect internal reforming ethanol applications in molten carbonate fuel cells, J. Power Sour., 94: 14-19.

Freni, S., Cavallaro, S., Mondello, N., Spadaro, L. and Frusteri, F. 2002. Steam reforming of ethanol on Ni/MgO catalysts: H$_2$ production for MCFC, J. Power Sour., 108: 53-57.

Freni, S., Cavallaro, S., Mondello, N., Spadaro, L. and Frusteri, F. 2003. Production of hydrogen for MC fuel cell by steam reforming of ethanol over MgO supported Ni and Co catalysts, Catal. Commun., 4: 259-268.

Freni, S., Maggio, G. and Cavallaro, S. 1996. Ethanol steam reforming in a molten carbonate fuel cell: a thermodynamic approach, J. Power Sour., 62: 67-73.

Galvita, V.V., Belyave, V.D., Frumin, A.V., Demin, A.K., Tsiakaras, P.E. and Sobyanin, V.A. 2002. Performance of a SOFC fed by ethanol reforming products, Solid State Ionics. 152-153: 551-554.

Garcia, L., French, R., Czernik, S. and Chornet, E. 2000. Catalytic steam reforming of bio-oils for the production of hydrogen: effects of catalyst composition, Appl. Catal. A: Gen., 201: 225-239.

Laosiripojana, N. 2003. Reaction engineering of indirect internal steam reforming of methane for application in solid oxide fuel cells, PhD Thesis, University of London, UK.

Laosiripojana, N. and Assabumrungrat, S. 2005. Catalytic dry reforming of methane over high surface area ceria, Appl. Catal. B: Environ., 60: 107-116.

Laosiripojana, N. and Assabumrungrat, S. 2005. Methane steam reforming over Ni/Ce-ZrO$_2$ catalyst: Influences of Ce-ZrO$_2$ support on reactivity, resistance toward carbon formation, and intrinsic reaction kinetics, Appl. Catal. A: Gen., 290: 200-211.

Laosiripojana, N., Sangtongkitcharoen, W. and Assabumrungrat, S. 2006. Catalytic steam reforming of ethane and propane over CeO$_2$-doped Ni/Al$_2$O$_3$ at SOFC temperature: Improvement of resistance toward carbon formation by the redox property of doping CeO$_2$, Fuel., 85: 323-332.

Laosiripojana, N., Sutthisripok, W. and Assabumrungrat, S. 2005. Synthesis gas production from dry reforming of methane over CeO$_2$ doped Ni/Al$_2$O$_3$: Influence of the doping ceria on the resistance toward carbon formation, J. Chem Eng., 112: 13-22.

Liguras, D., Kondarides, D., and Verykios, X. 2003. Production of hydrogen for fuel cells by steam reforming of ethanol over supported noble metal catalysts, Appl. Catal. B: Environ., 43: 345-354.

Llorca, J., Homs, N., Sales, J. and Ramirez de la Piscina, P. 2002. Efficient Production of Hydrogen over Supported Cobalt Catalysts from Ethanol Steam Reforming, J. Catal., 209: 306-317.

Llorca, J., Ramirez de la Piscina, P., Dalmon, J.-A., Sales, J. and Homs, N. 2003. CO-free hydrogen from steam-reforming of bioethanol over ZnO-supported cobalt catalysts: Effect of the metallic precursor, Appl. Catal. B: Environ., 43: 355-369.

Lwin, Y., Daud, W.R.W. and Mohamad, A.B., Yaakob, Z. 2000. Hydrogen production from steam± methanol reforming: thermodynamic analysis, Int. J. Hydrogen Energy., 25: 47-53.

Marino, F., Baronetti, G., Jobbagy, M. and Laborde, M. 2002. Cu-Ni-K/α-Al$_2$O$_3$ supported catalysts for ethanol steam reforming Formation of hydrotalcite-type compounds as a result of metal-support interaction, Appl. Catal. A: Gen., 238: 41-54.

Marino, F., Cerrella, E.G., Duhalde, S., Jobbagy, M. and Laborde, M.A. 1998. Hydrogen from steam reforming of ethanol. Characterization and performance of copper-nickel supported catalysts, Int. J. Hydrogen Energy., 23: 1095-1101.

Mattos, L.V., Rodino, E., Resasco, D.E., Possos, F.B. and Noronha, F.B. 2003., Partial oxidation and CO$_2$ reforming of methane on Pt/Al$_2$O$_3$, Pt/ZrO$_2$, and Pt/Ce-ZrO$_2$ catalysts, Fuel Proc. Technol. 83: 147-161.

Miao, Q., Xiong, G., Sheng, S., Cui, W., Xu, L. and Guo, X. 1997. Partial oxidation of methane to syngas over nickel-based catalysts modified by alkali metal oxide and rare earth metal oxide, Appl. Catal. A, 154: 17-27.

Ramirez, E., Atkinson, A. and Chadwick, D. 2002. Reactivity of ceria, Gd- and Nb-doped ceria to methane, Appl. Catal. B, 36: 193-206.

Roh, H.S., Jun, K.W. and Park, S.E. 2003. Methane-reforming reactions over Ni/Ce-ZrO$_2$/α-Al$_2$O$_3$ catalysts, Appl. Catal. A 251: 275-283.

Roh, H.S., Jun, K.W., Dong, W.S., Chang, J.S., Park, S.E. and Joe, Y.I. 2002. Highly active and stable Ni/Ce-ZrO$_2$ catalyst for H$_2$ production from methane, J. Molecul. Catal. A 181: 137-142.

Rostrup-Nielsen, J.R., Christiansen, L.J. and Bak-Hansen, J.-H. 1988. Activity of steam reforming catalysts: Role and assessment, Appl. Catal. 43: 287-303.

Sfeir, J., Philippe, A.B., Mockli, P., Xanthopoulos, N., Vasquez, R., Hans, J.M., Jan, V.H. and Thampi, K.R. 2001. Lanthanum Chromite Based Catalysts for Oxidation of Methane Directly on SOFC Anodes, J. Catal., 202: 229-244.

Srinivas, D., Satyanarayana, C.V.V., Potdar, H.S. and Ratnasamy, P. 2003. Structural studies on NiO-CeO$_2$-ZrO$_2$ catalysts for steam reforming of ethanol, Appl. Catal. A: Gen. 246: 323-334.

Takeguchi, T., Furukawa, S.N. and Inoue, M. 2001. Hydrogen Spillover from NiO to the Large Surface Area CeO$_2$-ZrO$_2$ Solid Solutions and Activity of the NiO/CeO$_2$-ZrO$_2$ Catalysts for Partial Oxidation of Methane, J. Catal., 202: 14-24

Terribile, D., Trovarelli, A., Llorca, J., Leitenburg, C. de. and Dolcetti, G. 1998. The preparation of high surface area CeO$_2$-ZrO$_2$ mixed oxides by a surfactant-assisted approach, Catal. Today. 43: 79-88

Wang, X. and Gorte, R.J. 2002. A study of steam reforming of hydrocarbon fuels on Pd/ceria, Appl. Catal. A., 224: 209-218.