Catalysis Letters Vol. 101, Nos. 3–4, June 2005 (© 2005)
DOI: 10.1007/s10562-005-4901-7

Low-temperature reforming of ethanol over CeO_2-supported Ni-Rh bimetallic catalysts for hydrogen production

Junichiro Kugai, Subramani Velu, and Chunshan Song*

Department of Energy and Geo-Environmental Engineering, Clean Fuels and Catalysis Program, The Energy Institute, The Pennsylvania State University, 209 Academic Projects Building, University Park, PA 16802, USA

Received 08 October 2004; accepted 02 February 2005

A new series of Ni-Rh bimetallic catalysts with different Ni and Rh loadings on a high-surface-area CeO_2 was developed for the reforming of bio-ethanol at low-temperature (below 450 °C) to produce H_2-rich gas for on-site or on-board fuel cell applications. Oxidative steam reforming of ethanol (OSRE) over a Ni-Rh/CeO_2 catalyst containing 5 wt% Ni and 1 wt% Rh was found to be more efficient offering about 100% ethanol conversion at 375 °C with high H_2 and CO_2 selectivity and low CO selectivity compared to the steam reforming of ethanol (SRE) reaction which required a higher temperature of about 450 °C to achieve 100% ethanol conversion. The high temperature SRE reaction favors the formation of large amount of CO, which would make the downsteam CO cleanup more complicated for polymer electrolyte membrane fuel cell (PEMFC). The presence of O_2 in the feed gas was found to greatly enhance the conversion of ethanol to produce H_2 and CO_2 as major products. Increase in Ni content above 5 wt% in the catalyst formulation decreased the H_2 selectivity while the selectivity of undesirable CH_4 and acetaldehyde increased. The 1 wt% Rh/CeO_2 catalyst was twice as active as 10 wt% Ni/CeO_2 catalyst in terms of ethanol conversion and acetaldehyde selectivity and this indicated that Rh was more effective in C–C bond cleavage than Ni. The reaction was found to proceed through the formation of acetaldehyde intermediate, which subsequently underwent decomposition to produce a mixture of CO and CH_4 or reforming with H_2O and O_2 to produce CO, CO_2 and H_2. The role of Rh is mainly to cleave the C–C and C–H bonds of ethanol to produce H_2 and COx while Ni addition helps converting CO into CO_2 and H_2 by WGS reaction under the conditions employed.

KEY WORDS: bio-ethanol; reforming; catalyst; Ni-Rh; ethanol hydrogen.

1. Introduction

Recent developments in fuel cell technology offer the potential to reduce the consumption of energy resources and the emissions of environmental pollutants from automobiles and electric power plants [1–3]. Owing to its high efficiency, high current density, and low operating temperature, the polymer electrolyte membrane fuel cell (PEMFC) is considered to be one of the most promising candidates for automotive applications. However, PEMFC uses pure H_2 or H_2-rich gas as a fuel, which needs to be stored or produced on-board a vehicle. Due to the lack of H_2 storage and distribution infrastructure, the catalytic on-board production of H_2-rich gas from a suitable hydrocarbon or alcoholic fuel is attracting increasing attention.

Owing to the ease of reforming and ready availability, methanol has been considered recently as a candidate primary fuel for the production of H_2 for fuel cells in mobile applications. Thus, an extensive research has been devoted in recent years on the methanol reforming and much improvement has been made [1,4–6]. However there are also health and safety issues and environmental impacts of methanol utilization. In the event of spills or leaks, methanol is also an environmental concern due to its toxicity.

On the other hand, bio-ethanol, which is a mixture of ethanol and water, is gaining increasing interest as a promising primary fuel for producing H_2 for fuel cells [7–12]. Some of the advantages of using bio-ethanol as a primary fuel to produce H_2 for fuel cell applications include the following: (1) It is a renewable raw material and can be obtained from the fermentation of biomass such as sugarcane, corn, or cellulosic feedstock like wood chips. (2) Bio-ethanol-based H_2 production is considered to be a CO_2-neutral process because CO_2 produced by the fermentation and the reforming process can be utilized for the biomass growth. Thus a closed carbon cycle could be established. (3) Unlike methanol, bio-ethanol is non-toxic. (4) Unlike gasoline, bio-ethanol does not contain any sulfur that might poison the reforming and the electrode catalysts.

Steam reforming of ethanol (SRE) has been performed over Ni, Co, Ni/Cu and noble metals such as Pd, Pt, Rh on various supports [8,12–15]. However, the reaction is highly endothermic and better performance has been observed only in the temperature range 600–750 °C. The high temperature reforming favors the thermodynamic equilibrium for the formation of large amount of CO, which is a poison to the PEMFCs, and this would require a more complicated

---

* To whom correspondence should be addressed.
E-mail: csong@psu.edu

1011-372X/05/0600–0255/0

gas clean up process downstream before feeding into the fuel cell. In addition, the reaction produces a wide range of undesirable liquid and gaseous byproducts such as CH_3CHO, CH_3COOH, $C_2H_5OC_2H_5$,CO, CH_4, ethylene, etc. depending upon the nature of the metal and support used. Catalysts containing Cu favor the dehydrogenation leading to the formation of large amount of acetaldehyde. On the other hand, catalysts containing Ni and Co reform ethanol more effectively, but lead to the formation of considerable amount of CH_4 due to ethanol decomposition and CO/CO_2 hydrogenation reactions and this results in significant loss of H_2 yield. Carbon deposition is an additional problem with these catalysts. In additions, Co-based catalysts severely suffer from the oxidation of active phase [16]. Noble metal catalysts, on the other hand, are highly efficient for the reforming of ethanol to produce quantitatively H_2 and CO/CO_2 [9,10,12]. However, they are very expensive and sufficient supply may not exist to meet large amount of reforming catalysts required in the future. The nature of support also plays a role in the selectivity of H_2 formation. Generally, acidic supports such as Al_2O_3 are known to prefer dehydration, whereas basic supports such as MgO favor dehydrogenation and condensation reactions [12,14]. Better catalytic performance with high selectivity of H_2 and low selectivity of undesirable byproducts can be expected over redox supports such as CeO_2 and ZrO_2.

$$CH_3CH_2OH(l) + 3H_2O(l) \rightarrow 6H_2(g) + 2CO_2(g) \quad (1)$$

$$\Delta H^{o}_{298} = +347.4\,\text{kJ mol}^{-1}$$

$$CH_3CH_2OH\ (l) + 1.5O_2(g) \rightarrow 3H_2(g) + 2CO_2(g) \quad (2)$$

$$\Delta H^{o}_{298} = -554.0\,\text{kJ mol}^{-1}$$

$$CH_3CH_2OH\ (l) + (3-2\delta)H_2O\ (l) + \delta O_2(g) \rightarrow (6-2\delta)H_2(g) + 2CO_2(g); \quad (3)$$

$$\text{If } \delta = 0.6, \Delta H^{o}_{298} = +4.4\,\text{kJ mol}^{-1}$$

Partial oxidation of ethanol (POE) reaction (equation (2)) has also been reported recently over Ni–Fe catalysts as a method for H_2 production [17]. Although the reaction could be performed at relatively lower temperature (around 300 °C), the high exothermicity of the reaction (equation (2)) would lead to hot-spot operation. In addition, there is about 50% reduction in the theoretical yield of H_2 compared to a steam reforming reaction. Lately, steam reforming in the presence of oxygen, which is termed as an oxidative steam reforming of ethanol (OSRE; see equation (3)) or autothermal reforming (ATR), has been reported to significantly improve ethanol conversion and H_2 selectivity [7,9–11]. The reaction is thermally neutral and avoids external heat supply.

The C–C bond cleavage is a very important step in the ethanol reforming to produce H_2 and carbon oxides. Both Ni and Rh are known to cleave the C–C bond effectively [18]. The combination of two metals may result in beneficial synergistic effects. In addition, Ni is known to participate in the water–gas shift (WGS) reactions to convert CO into CO_2 [19]. Redox supports such as CeO_2 are known to enhance the reducibility and the dispersion of the supported metal in addition to their role in WGS reactions [20]. Thus, it is anticipated that catalysts containing Ni with small amount of Rh supported on CeO_2 will offer a new catalyst for the efficient reforming of ethanol to H_2-rich gas with low selectivity towards undesirable byproducts such as CH_3CHO, CH_4, CO, etc.

The objective of the present study therefore was to develop a new, highly efficient, more stable and cost effective catalyst for the on-board reforming of bio-ethanol at relatively lower temperature to produce H_2 with high selectivity and low CO in the outlet gas, which will make the downsteam CO clean-up relatively easier for PEMFC applications. To further our understanding of the compositional and the mechanistic factors that affect the catalytic reaction, a series of Ni-Rh bimetallic catalysts with different Ni loadings (by keeping the Rh content constant at 1 wt%) have been synthesized [21]. In order to achieve a high metal dispersion, a high-surface-area CeO_2 having a BET surface area of about 148 $m^2\ g^{-1}$ (obtained from Rhodia Chemical Company) has been used as a support. The effects of metal loadings, and the reaction operating conditions on the catalytic performance in the ethanol reforming were investigated and the results are reported here.

2. Experimental

2.1. Catalyst preparation and characterization

Ni-Rh bimetallic catalysts supported on CeO_2 with four different Ni and Rh loadings, namely 1 wt% Rh without Ni, [Ni(0)Rh(1)/CeO_2], 1 wt% Rh-5 wt%Ni [Ni(5)Rh(1)/CeO_2], 1 wt% Rh-10 wt% Ni [Ni(10)Rh(1)/CeO_2], and 10 wt% Ni without Rh [Ni(10)Rh(0)/CeO_2] were prepared using an incipient wetness impregnation method [21]. Rh (III) chloride solution and nickel (II) nitrate solutions were used for the Rh and Ni sources, respectively. Commercially available CeO_2 (BET surface area = 148 $m^2\ g^{-1}$) obtained from Rhodia Chemical Company was used as a support. The impregnated samples were dried at 100 °C for 6–8 h, calcined at 450 °C for 3 h in a temperature programmed muffle furnace using a heating rate of 2 °C min^{-1}.

Temperature programmed reduction (TPR) data were collected using a Micromeritics 2910 TPD/TPR instrument. About 150 mg of the sample was loaded in a quartz reactor and heated at the heating rate of 10 °C min^{-1} in a stream of 5% H_2 in Ar with a flow rate of about 25 cc min^{-1} up to 800 °C. The outlet gas was passed through a liquid N_2 condenser to remove the moisture produced by the reduction. The hydrogen consumption due to the reduction of relevant cations was then monitored by a thermal conductivity detector and computer data acquisition system equipped with the instrument. N_2 adsorption–desorption experiments were conducted at liquid N_2 temperature on a Quantachrome Autosorb 1 instrument to evaluate the BET surface area and pore size distribution of the calcined catalysts.

2.2. Catalytic studies

Steam reforming (SR) and oxidative steam reforming (OSR) of ethanol reactions were conducted using a fixed bed stainless-steel down-flow reactor having an ID 0.245 inch. The powder catalysts were pelletized, crushed and sieved to 18–35 mesh. About 0.5 g of catalyst was loaded into the middle of the reactor tube with glass beads and quartz wool placed on both sides of the catalyst bed. A thermocouple was located in the catalyst bed to measure the reaction temperature (catalyst bed temperature) accurately. The reactor was mounted vertically and heated using an electric furnace in a temperature programmed manner. A premixed ethanol–water mixture with a water/ethanol molar ratio of 4:1 was fed into the reactor through a vaporizer using a pre-calibrated HPLC pump. The flow rate of ethanol (21.6 mL min^{-1}) was set to 1:10 of the total flow rate (216 mL min^{-1}), in which ethanol, water, air, and the carrier gas Ar were taken into account, by adjusting the Ar flow rate. The total gas hourly space velocity (GHSV) was varied between 44,000 and 244,000 h^{-1} (unless otherwise mentioned). This corresponds to the average contact time of gas between 82 and 15 ms. Prior to the catalytic reaction, the catalysts were reduced *in situ* in H_2 flow (10% H_2 in Ar) at 435 °C for 2 h, cooled down to the reaction temperature. The effluent of the reactor was analyzed using two on-line gas chromatograph (MRI Model 8610C). One GC was equipped with Molecular Sieve 5A and Silica gel packed columns, and TCD detector for the analysis of gaseous products such as H_2, CO, CO_2, CH_4, ethylene, etc. while the GC was equipped with a 7% Carbowax/Carbograph packed column, and FID detector for the analysis of liquid products such as ethanol, acetaldehyde, acetone, diethyl ether, etc.

3. Results

3.1. Physicochemical properties of catalysts

The BET surface area and pore size distribution values of all the Ni-Rh/CeO_2 catalysts are summarized in table 1. The BET surface area of the CeO_2 support before impregnation was 148 m^2 g^{-1}. The value decreases gradually with increasing metal loadings. Thus, the catalyst Ni(10)Rh(1)/CeO_2 with the highest metal loading showed the lowest BET surface area of 103 m^2 g^{-1}. The pore volume also decreases with increasing metal loadings.

The redox properties of the catalysts have been investigated by temperature programmed reduction (TPR) experiments and the results are shown in figure 1. The catalyst containing only Rh without Ni [Ni(0)Rh(1)/CeO_2] exhibits a sharp reduction peak at 138 °C together with a small shoulder at 108 °C. This peak can be attributed to the reduction of Rh^{3+} in Rh_2O_3 supported on CeO_2. Several authors have reported that in CeO_2-based supported catalysts, the reduction of surface CeO_2 occurs below 300 °C while the bulk CeO_2 is reduced above 700 °C [22–24]. Thus, surface reduction of CeO_2 can also contribute to H_2 consumption in this temperature range (below 300 °C). In fact, the H_2 uptake calculated from integration of peak area is significantly higher than the amount actually needed to reduce 1 wt% of Rh^{3+} in Rh_2O_3. Fornasiero *et al.* [22] and Rogemond *et al.* [23] have also observed a strong reduction peak between 100 and 200 °C in the TPR of Rh/CeO_2 catalyst and the peak has been attributed to the reduction of both Rh^{3+} as well as surface CeO_2. Addition of Ni to the Rh/CeO_2 catalyst in the present study shifts the peaks corresponding to the reduction of Rh^{3+} and the surface CeO_2 towards high temperature and a new peak for the reduction of NiO occurs above 300 °C, whose position also shifts towards high temperature with increasing Ni content. It is likely that the presence of NiO chemically affects the reducibility of Rh^{3+} in these catalysts. NiO in Ni(5)Rh(1)/CeO_2 is easier to reduce than that in Ni(10)Rh(1)/CeO_2 probably because the Ni particle in

Table 1
Textural properties of NiRh/CeO_2 catalysts measured by N_2 adsorption–desorption method

Catalyst	BET surface area (m^2 g^{-1})	Pore volume (cc g^{-1})	Average pore diameter (Å)
Ni(0)Rh(1)/CeO_2	141	0.129	36.6
Ni(5)Rh(1)/CeO_2	122	0.112	36.7
Ni(10)Rh(1)/CeO_2	103	0.099	38.6
Ni(10)Rh(0)/CeO_2	113	0.114	40.6

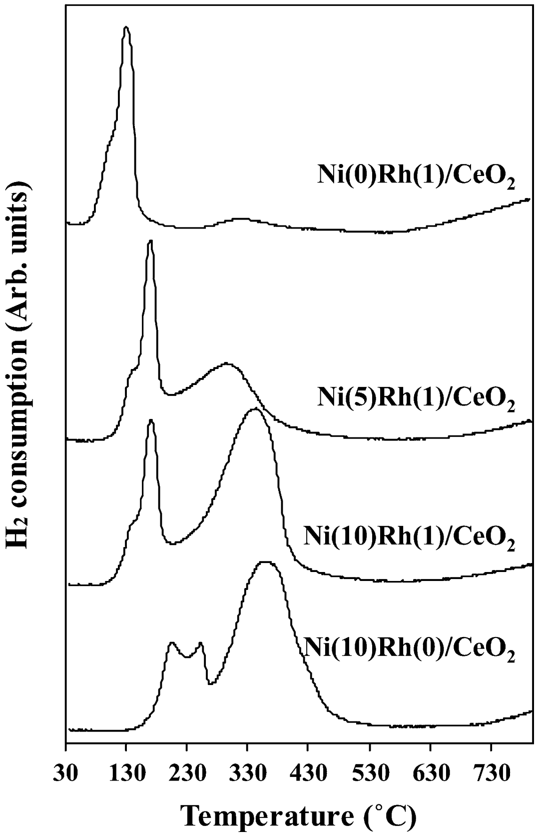


Figure 1. TPR profiles of Ni-Rh/CeO_2 catalysts.

the former sample is smaller and in closer contact with the CeO_2 support than in the latter sample.

The catalyst containing 10 wt% Ni without Rh [Ni(10)Rh(0)/CeO_2] also shows peaks at least in two different reduction regions. Reduction begins around 140 °C and completes around 500 °C. Earlier studies on the TPR of NiO supported CeO_2 catalysts indicated that the NiO reduction begins at 220 °C with a first peak around 250 °C and the second peak around 300 °C [19]. Another study showed an intense reduction peak around 360 °C together with a weak peak around 510 °C [25]. On the other hand, Shan *et al.* [24] in the TPR study of $Ce_{1-x}Ni_xO_2$ mixed oxide catalysts have observed a main peak around 370 °C together with two shoulders in the low temperature region, one around 240 °C and the other around 300 °C. These low temperature shoulders have been attributed to the reduction of adsorbed oxygen formed due to the formation of NiO solid solution in CeO_2. Taking all these results into account, the high temperature peak centering around 370 °C in the present study could be attributed to the reduction of bulk-like NiO phase while the doublet centering around 208 and 257 °C could be assigned to the reduction of well dispersed NiO together with reduction of adsorbed oxygen and surface CeO_2. The peak related to the reduction of the bulk CeO_2 is not observed in these catalysts, suggesting that the bulk CeO_2 is reduced at a temperature higher than 800 °C.

3.2. Catalytic ethanol reforming

3.2.1. Effect of reaction temperature

In order to demonstrate the beneficial effect of OSR over the conventional SR on the catalytic performance, these two reactions were conducted under comparable conditions at different temperatures over Ni(5)Rh(1)/CeO_2 catalyst. The ethanol conversion and product distribution in the SRE and OSRE are shown in figures 2 and 3, respectively. In both cases, the ethanol conversion increases with increasing temperature and the conversion reaches about 100% around 450 °C in SRE. On the other hand, about 100% ethanol conversion could be reached around 375 °C in the OSRE. In both cases, the H_2 also increases from about 50% at low temperature to over 60% around 100% ethanol conversion. H_2 yield in OSRE at 375 °C reached about 2.3 mol mol^{-1} of EtOH.

In the steam reforming, acetaldehyde decreases gradually from about 20% at low temperature with concomitant increase of CO_2 with increasing temperature. The CO remains at 15 mol% in the entire temperature range studied. On the other hand, the CO in the OSRE decreases to below 5 mol% around 100% ethanol conversion with consequent increase of CO_2. It appears that under the OSR conditions the CO formed is subsequently converted into CO_2 by CO oxidation and/or WGS reactions since both reactions are thermodynamically favorable at low temperature. The CH_4 remains almost constant around 15 mol% in both SRE and OSRE reactions.

It is known in the literature that CH_4 formation is thermodynamically favored at low temperature, below 500 °C due to the decomposition of acetaldehyde [11,13]. At high temperatures, above 500 °C, the CH_4 formed from ethanol is subsequently reformed to a mixture of H_2 and CO [26–28]. It is probably due to this

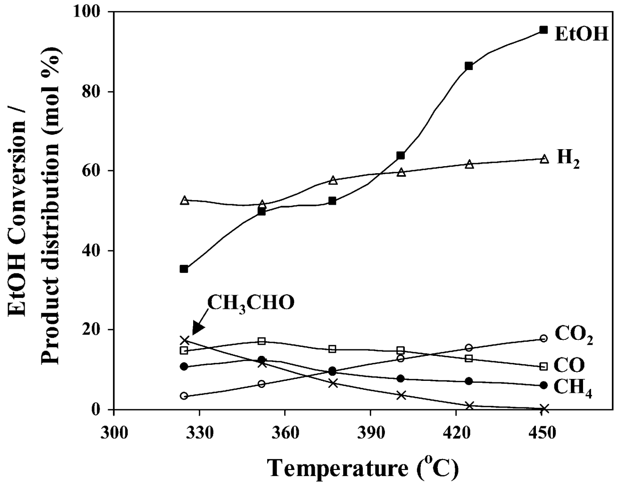


Figure 2. Effect of temperature on catalytic performance in the steam reforming of ethanol over Ni(5)Rh(1)/CeO_2 catalyst. GHSV = 44,000 h^{-1}; H_2O/EtOH molar ratio = 4.

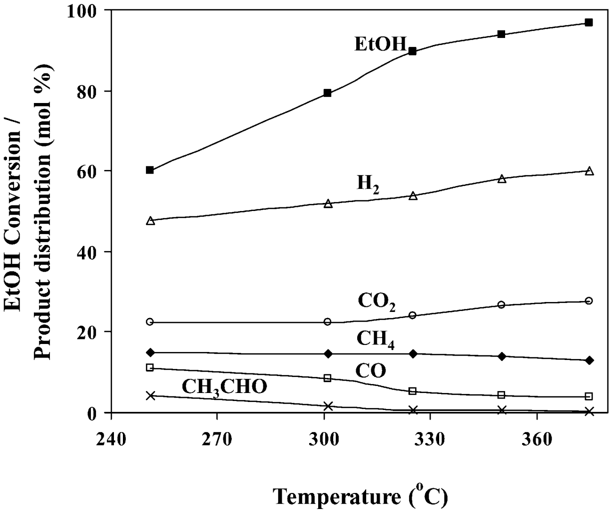


Figure 3. Effect of temperature on catalytic performance in the oxidative steam reforming of ethanol over Ni(5)Rh(1)/CeO_2 catalyst. GHSV = 44,000 h^{-1}; H_2O/EtOH molar ratio = 4; O_2/EtOH molar ratio = 0.4.

reason, ethanol reforming in most of the earlier studies have been performed at high temperatures, around 700 °C [26–28]. However, at this temperature, the thermodynamics favor the formation of large amount of CO, which would make the CO cleaning more complicated in order to use the reformed gas for PEMFCs. Recent reports by Velu *et al.* [11], Llorca *et al.* [8], and Wang *et al.* [17] have shown the low temperature reforming of bio-ethanol (below 400 °C) to produce H_2-rich gas with very low amounts of undesirable by products such as CO, CH_4 and acetaldehyde.

Another interesting observation is that the acetaldehyde production is very small in the OSRE reaction even when the ethanol conversion is low at low temperature, while a significant amount of acetaldehyde is produced in the SRE reaction. This implies that C–C bond cleavage can take place more effectively in the OSRE reaction than that in the SRE reaction and that this step is faster than the preceding steps such as dehydrogenation.

3.2.2. *Effect of Ni and Rh contents*

Since the above study indicated that the OSRE reaction is more efficient, occurring at relatively lower temperature to produce H_2 with high selectivity comparable to that obtained in the SRE reaction at high temperature, the former reaction was used to optimize the metal loadings and reaction operating conditions in order to achieve a high H_2 selectivity with low selectivity for undesirable byproducts. The effect of Ni and Rh loadings on the ethanol conversion and product selectivity has been investigated in the OSRE reaction at 300 °C and the results are shown in figures 4 and 5, respectively. Under the present experimental conditions, the catalyst containing only Rh without Ni [Ni(0)Rh(1)/CeO_2] exhibits over 80% ethanol conversion. Addition of Ni further increases the conversion and the conversion increases to 92% over the catalyst containing 10 wt% Ni and 1 wt% Rh [Ni(10)Rh(1)/CeO_2]. On the other hand, the Ni-rich catalyst without Rh [Ni(10)Rh(0)/CeO_2] shows only about 40% ethanol conversion. These results indicate that, Rh is more effective in reforming of ethanol compared to Ni [21].

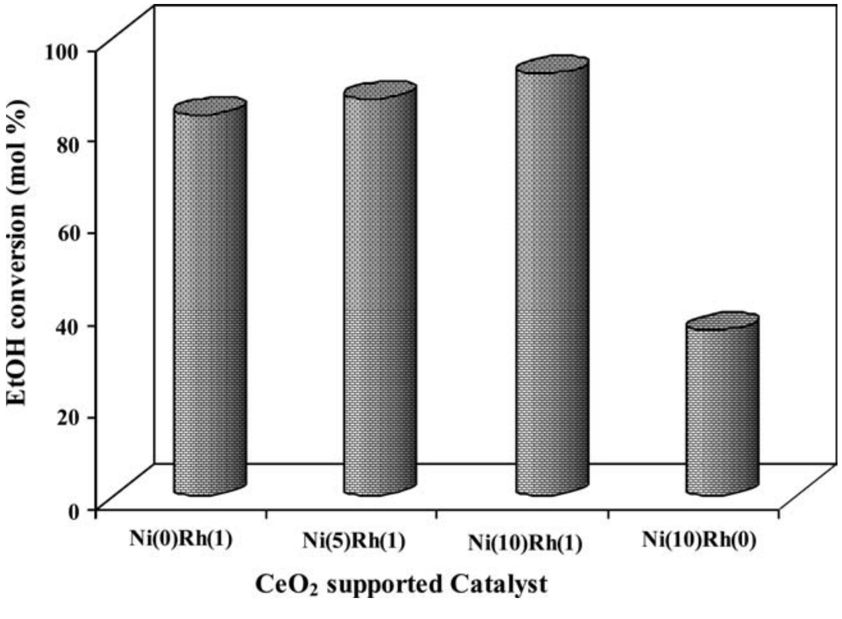


Figure 4. Effect of Ni and Rh loadings on ethanol conversion in the oxidative steam reforming of ethanol over Ni-Rh/CeO_2 catalysts. GHSV = 44,000 h^{-1}; H_2O/EtOH molar ratio = 4; O_2/EtOH molar ratio = 0.4.

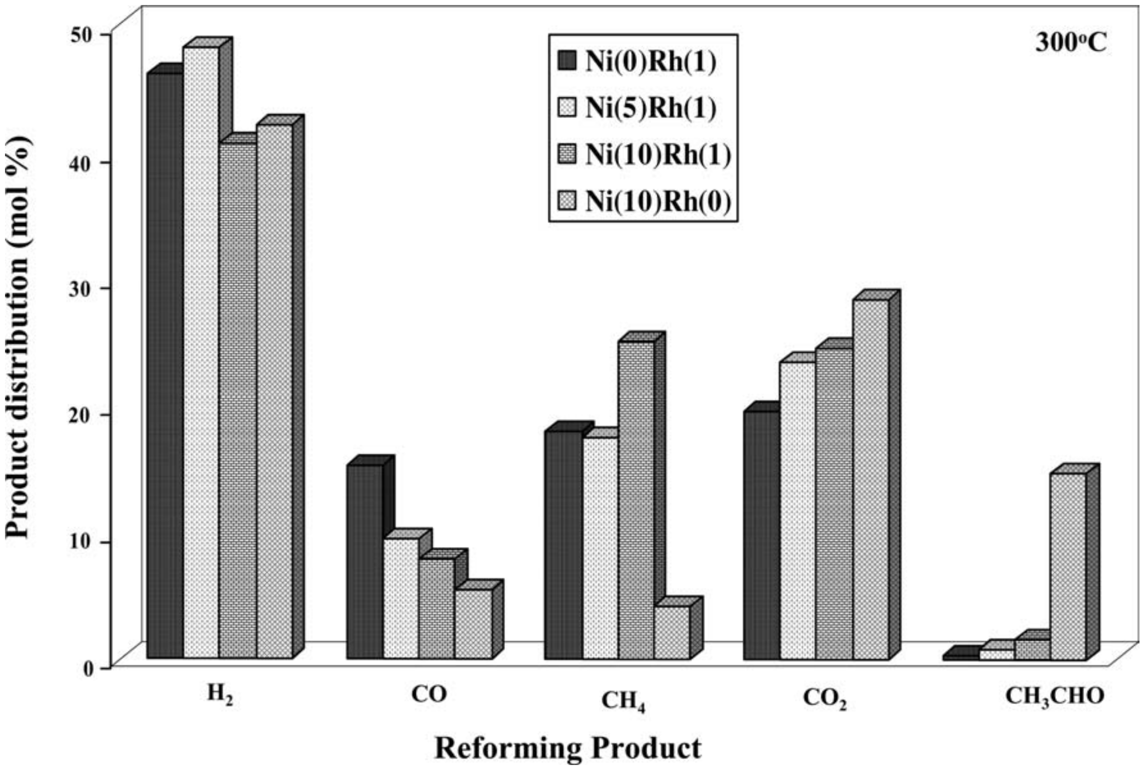


Figure 5. Effect of Ni and Rh loadings on product distribution in the oxidative steam reforming of ethanol over Ni-Rh/CeO_2 catalysts. GHSV = 44,000 h^{-1}; H_2O/EtOH molar ratio = 4; O_2/EtOH molar ratio = 0.4.

The product distribution shown in figure 5 also shows some interesting results. The catalyst, Ni(5)Rh(1)/CeO_2 exhibits a maximum H_2 selectivity. The CO selectivity decreases and CO_2 selectivity increases with increasing Ni content. This implies that Ni efficiently converts CO to CO_2, probably via WGS reaction or CO oxidation. The selectivity between CH_4 and acetaldehyde also seems to have some relation. CH_4 selectivity remains almost the same for the catalyst without Ni and that containing 5% Ni. However the acetaldehyde selectivity increases with further increase in the Ni content to 10 wt%. A dramatic drop in CH_4 selectivity has been observed over the catalyst containing 10 wt% Ni without Rh. However, the same catalyst shows the highest selectivity for acetaldehyde. These results indicate that Ni favors dehydrogenation to acetaldehyde. Acetaldehyde is further converted into H_2 and carbon oxides, when Rh is present along with Ni.

The above results further supports that Rh is more effective for C–C bond cleavage than Ni. However, the beneficial effect of adding Ni, especially about 5 wt% Ni, can be clearly seen from an increased selectivity of H_2 and CO_2 and decreased selectivity of CO, which are highly desirable for the production of H_2 for fuel cell applications. The H_2 selectivity decreases and the CH_4 selectivity increases for the catalyst containing 10 wt% of Ni, probably due to the hydrogenation of CO/CO_2 to CH_4 under the reaction conditions. Based on this study, a Ni-Rh/CeO_2 catalyst containing about 5 wt% Ni and 1 wt% Rh exhibits better catalytic performance in the OSRE reaction.

3.2.3. Effect of H_2O/EtOH and O_2/EtOH molar ratio

The effect of H_2O/EtOH and O_2/EtOH ratios on the catalytic performance in the OSRE reaction was also investigated under low ethanol conversion levels, below 60% in order to understand the role of these oxidants in ethanol conversion and product selectivity. The H_2O/EtOH and O_2/EtOH ratios were adjusted in such a way that the net inlet gas flow rate was kept constant by adjusting the flow rate of the carrier gas, Ar. The results shown in figure 6 indicate that decreasing the H_2O/EtOH ratio by 50% while keeping the same O_2/EtOH ratio has no significant impact on the H_2 selectivity. However, the ethanol conversion drops by about 15%. The selectivity of CO and acetaldehyde increases, probably due to the lack of secondary reactions of acetaldehydes and CO to CO_2 and H_2. On the other hand, the ethanol conversion was decreased by 50% with decreasing O_2/EtOH ratio to half while keeping the same H_2O/EtOH ratio (compare the results of H_2O/EtOH ratio; O_2/EtOH ratio = 4; 0.4 versus 4; 0.2). The selectivity of acetaldehyde goes up while that of CO_2 drops down. These results indicate that the O_2/EtOH

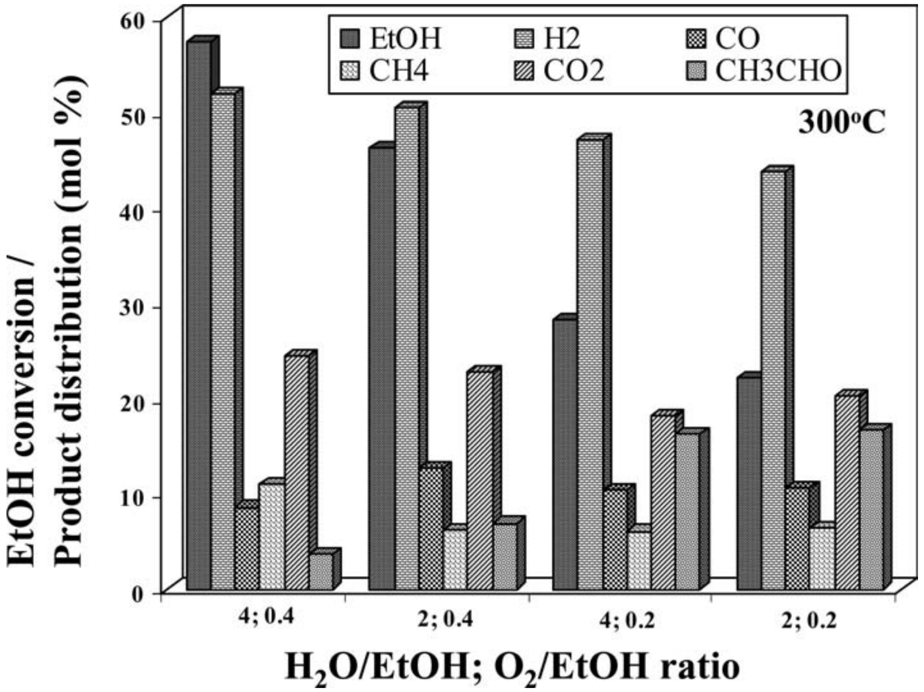


Figure 6. Effect of H_2O/EtOH and O_2/EtOH ratios on the catalytic performance in the oxidative steam reforming of ethanol over Ni(5)Rh(1)/CeO_2 catalyst. GHSV = 244,000 h^{-1}.

ratio has a stronger impact than that of H_2O/EtOH ratio on the catalytic performance in the OSRE reaction (within the ranges studied). This suggests that oxygen promotes ethanol reforming more effectively than water.

In order to further understand the effect of oxidants on the catalytic performance, various reactions of ethanol were conducted over Ni(5)Rh(1)/CeO_2 catalyst, including decomposition of ethanol (DCE)/dehydrogenation of ethanol (DHE) when using ethanol as a sole reactant, POE, SRE and OSRE reactions. The results are summarized in table 2. Since the ethanol conversions in all the reactions, except OSRE, was very low, reactions were compared at the same temperature of around 350 °C. As can be seen, the reaction of ethanol as a sole reagent produces H_2 and acetaldehyde without any C_1 products. This indicates that ethanol undergoes mainly dehydrogenation over this catalyst. Addition of water and/or oxygen produces C_1 products. This suggests that both oxidants (oxygen and water) enhance the C–C bond cleavage although the effect of oxygen is larger.

Comparison between the POE and the other reactions gives some hints on the effect of water. The POE shows a high CO_2 selectivity, however, the selectivity of H_2 in the POE is much less compared with that in the

Table 2
Various reactions of ethanol over Ni(5)Rh(1)/CeO_2 catalyst under comparable reaction conditions

Reaction	EtOH Conversion (mol%)	Product distribution (mol%)					
		H_2	CO	CO_2	CH_4	CH_3CHO	Acetone
SRE	12.7	57.8	10.8	5.6	5.9	18.8	1.1
OSRE	94.4	51.8	5.0	27.7	15.0	0.3	0.2
POE	44.1	36.8	12.2	25.3	6.6	17.0	2.1
DCE/DHE	2.9	60.0	0.0	0.0	0.0	38	2.0

SRE = Steam reforming of ethanol.
OSRE = Oxidative steam reforming of ethanol.
POE = Partial oxidation of ethanol.
DCE = Decomposition of ethanol.
DHE = Dehydration of ethanol.
Reaction temperature = 350 °C, GHSV = 24,379 h^{-1}.
In SRE, H_2O/EtOH = 4.
In OSRE, H_2O/EtOH = 4 and O_2/EtOH = 0.4.
In POE, O_2/EtOH = 0.4.
Ethanol was the sole reactant in the DCE/DHE.

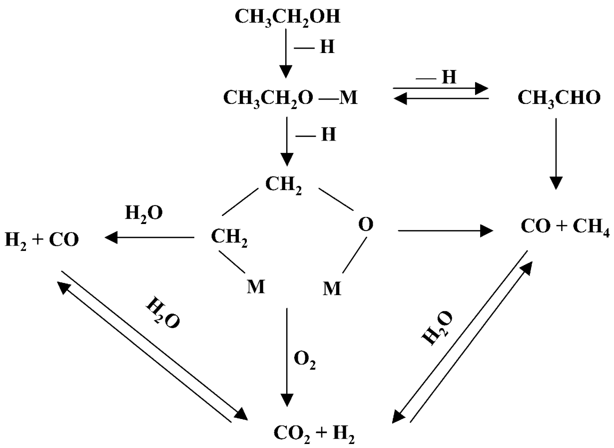
other reactions, probably due to the oxidation of H_2 to H_2O under the present experimental conditions. In addition, a large quantity of acetaldehyde formation is observed in the POE as is observed in the SRE. These results indicate that the added oxygen in the POE reaction is mainly involved in dehydrogenation to acetaldehyde rather than C–C bond rupture.

4. Discussion

4.1. Reaction pathway

The present study clearly indicates that the OSRE reaction is more efficient than other reaction systems in terms of low operating temperature, high H_2 selectivity and low selectivity of undesirable CO and acetaldehyde. The reaction under different contact times revealed that acetaldehyde selectivity decreases and the selectivity of CH_4 increases with increasing contact time, which implies that the reaction over the present catalyst systems proceeds through the formation of acetaldehyde intermediate either by dehydrogenation or oxidative dehydrogenation. Recent studies by Cavallaro *et al.* [9,26] on the steam reforming and OSRE over Rh/Al_2O_3 catalyst at 650 °C also indicated that the reaction proceeds through the formation of acetaldehyde, which further decomposes to CO and CH_4, or reforming into carbon oxides and H_2 in the presence of O_2 in the feed gas. The authors have also demonstrated that the beneficial effect of OSRE reaction over the SRE reaction in terms of catalyst stability and coke deposition.

Studies on the reactions of ethanol over various metal surfaces indicated that ethanol is adsorbed as an ethoxide species [18,27]. On Rh and Ni metals, the adsorbed ethoxide species forms a five-membered oxametallacycle intermediate, which favors the C–C bond cleavage effectively. Once the oxametallacycle intermediate is formed, it can either decompose to CH_4 and CO, oxidize to CO_2 and H_2 or react with H_2O to produce H_2 and CO. The CO formed in the steam reforming and decomposition of oxametallacycle intermediate can also undergo WGS and/or CO oxidation to produce CO_2.



Scheme 1. Plausible mechanism for the oxidative steam reforming of ethanol over $NiRh/CeO_2$ catalyst.

Based on the results observed in the present study and information available in the literature, a plausible reaction mechanism is proposed for the reforming of ethanol in the presence of H_2O and O_2 as shown in scheme 1. The scheme shows the formation of oxametallacycle intermediate, which is subsequently reformed into H_2, CO_2 in the presence of H_2O and O_2 and decomposed into a mixture of CO and CH_4. Diagne *et al.* [28] in a recent study on the SRE over Rh/CeO_2–ZrO_2 catalyst also proposed that ethanol reforming occurs via oxametallacycle intermediate.

The formation of acetaldehyde, however, indicates that the reaction proceeds not only through the oxametallacycle intermediate, but also acetaldehyde intermediate. As can be seen from table 3, oxidative steam reforming of acetaldehyde is highly efficient, converting acetaldehyde into H_2 and CO_2 with only traces of CO. On the other hand, steam reforming of acetaldehyde under the same experimental conditions produces H_2 and CO as major products and the conversion of acetaldehyde is about nine times less efficient compared to that observed in the oxidative steam reforming reaction. These results indicate that acetaldehyde intermediate can also undergo C–C bond

Table 3
Steam reforming and oxidative steam reforming of acetaldehyde over $Ni(5)Rh(1)/CeO_2$ catalyst under identical reaction conditions

Reaction	CH_3CHO Conversion (mol%)	Product distribution (mol%)					
		H_2	CO	CO_2	CH_4	EtOH	Acetone
SR	10.6	52.0	20.7	12.6	9.5	1.8	3.4
OSR	94.6	52.0	3.3	35.0	9.6	0.0	0.1

SR = Steam reforming of acetaldehyde.
OSR = Oxidative steam reforming of acetaldehyde.
Reaction temperature = 350 °C, GHSV = 24,379 h^{-1}.
In SR, H_2O/CH_3CHO = 4.
In OSR, H_2O/CH_3CHO = 4 and O_2/CH_3CHO = 0.4.

rupture to produce H_2, carbon oxides, and CH_4 as shown in scheme 1.

4.2. Role of Ni and Rh

Among the catalysts tested in the present study, the catalyst, $Ni(5)Rh(1)/CeO_2$ exhibits a higher ethanol conversion, higher selectivity for H_2 and CO_2 and lower selectivity for undesirable CO and acetaldehyde. Fundamental studies on the adsorption of ethanol over various transition metals surfaces indicated that Rh is unique forming a stable five-membered oxametallacycle intermediate, which undergoes C–C bond cleavage more efficiently than η^1(O)-aldehyde species formed on the surfaces of Cu and Ag or η^2(C,O)-aldehyde species formed on the Ru, Pd and Pt surfaces [18,27]. In fact, a comparison of steam reforming and OSRE over catalysts containing Ni, Pt, Ru, Pd, Rh, etc, by different researchers revealed that the catalyst containing Rh performs better [10,12,14]. The effect of Ni and Rh loadings on the catalytic performance in the present study also shows (figures 4 and 5) that catalyst containing Rh alone [$Ni(0)Rh(1)/CeO_2$] is more effective for C–C bond cleavage, producing less acetaldehyde than the catalyst containing only Ni without Rh [$Ni(10)Rh(0)/CeO_2$]. Rh metal is known to activate the carbon–hydrogen bonds as well [18]. Thus, the role of Rh is to efficiently break the C–C and C–H bonds to produce a mixture of H_2 and carbon oxides.

The role of Ni in the present study is probably to convert CO into CO_2 and H_2 by WGS as the selectivity for H_2 and CO_2 increased while the selectivity for CO decreased upon addition of 5 wt% of Ni in the Rh/CeO_2 catalyst (figures 4 and 5). Decrease in CO selectivity with concomitant increase in CO_2 selectivity observed with increasing contact time also supported this conclusion. In addition, Ni/CeO_2 catalysts are known in the literature to favor the WGS reaction [19]. A recent study on the OSRE over NiZn-based catalysts demonstrated that co-feeding of CO in the OSRE reaction produced more H_2 and CO_2, thereby confirming the occurrence of CO WGS reaction over Ni-based catalysts under the OSRE conditions [11].

A detailed FTIR study by Sheng *et al.* on the reactions of ethanol over $Rh\text{-}Pt/CeO_2$ catalyst showed that Rh forms adsorbed H_2 and carbon oxides [18]. The second metal Pt is necessary to combine adsorbed H atoms to form molecular H_2. Based on these results the authors have suggested that a metal such as Pt possessing hydrogenation activity is necessary along with Rh in the reforming of ethanol to produce H_2. The second metal Ni in the present study is also very well-known for hydrogenation reactions. Thus, as suggested by Sheng *et al.* [18], the added Ni would also help combining adsorbed H atoms on the catalyst surface to form molecular H_2 in addition to its role in WGS reaction. However, because the difference in H_2 selectivity is small between Ni-free Rh/CeO_2 catalyst and that containing 5 wt% Ni, and also because of the observation that the CO selectivity decreases with consequent increase in CO_2 selectivity with increasing Ni content (figures 4 and 5), it appears that the role of Ni is mainly to participate in the WGS reaction, at least under the present experimental conditions.

Since Rh is an expensive metal, the 1 wt% loading used in the present study may be too high although recent studies used up to 5 wt% of Rh on Al_2O_3 supports [9,10,14] for the reforming of ethanol. Further work is in progress to reduce the Rh content as low as possible by adding an another metal that is relatively cheaper than Rh, but further improving the catalytic performance for the selective production of H_2 from bio-ethanol.

5. Conclusions

1. A new Ni-Rh bimetallic catalyst supported on a high-surface-area CeO_2 has been developed for the reforming of bio-ethanol to produce H_2-rich gas at relatively lower temperature.
2. OSRE reaction is more efficient for producing mainly a mixture of H_2 and CO_2 with low selectivity towards undesirable CO and acetaldehyde with about 100% ethanol conversion at relatively lower temperature, below 400 °C. Steam reforming of ethanol in the absence of O_2 over the same catalyst requires high temperature to achieve about 100% ethanol conversion. However, high temperature reforming favors the formation of large amount of CO, which would require more complicated CO clean-up before feeding the reformed gas into the PEMFC.
3. The catalyst containing 5 wt% Ni and 1 wt% Rh exhibits better performance. Further increase in Ni content decreases the H_2 selectivity and increases the selectivity of acetaldehyde and CH_4.
4. Under similar experimental conditions, 1 wt% Rh/CeO_2 catalyst without Ni is twice as active as 10 wt% Ni/CeO_2 catalyst without Rh and this indicates that Rh is more effective in breaking C–C bond.
5. The role of Rh is to break the C–C and C–H bonds of ethanol to produce a mixture of H_2 and CO_x. Ni helps converting CO into CO_2 and H_2 through WGS reactions.

Acknowledgments

The authors gratefully acknowledge Nippon Shokubai Co., Ltd, Japan and the Pennsylvania State University for supporting this work and the Rhodia Chemicals Company for generous gift of high-surface-area CeO_2 samples.

References

[1] C.S. Song, Catal. Today 77 (2002) 17.

[2] L.F. Brown, Int. J. Hydrogen Energy 26 (2001) 381.

[3] J.R. Rostrup-Nielsen, Phys. Chem. Chem. Phys. 3 (2001) 283.

[4] S. Velu and K. Suzuki, Topics Catal. 22 (2003) 235.

[5] J. Agrell, B. Lindstrom, L.J. Pettersson and S.G. Jaras, in: *Catalysis*, J.J. Spivey (ed.), Vol. 16 (The Royal Society of Chemistry, London, 2002) ch. 3, p. 67..

[6] A.F. Ghenciu, Curr. Opin. Solid State Materials Sci. 6 (2002) 389.

[7] G.A. Deluga, J.R. Salge, L.D. Schmidt and X.E. Verykios, Science 303 (2004) 993.

[8] J. Llorca, P.R. Piscina de la, J.A. Dalmon, J. Sales and N. Homs, Appl. Catal. B 43 (2003) 355.

[9] S. Cavallaro, V. Chiodo, A. Vita and S. Freni, J. Power Sources 123 (2003) 10.

[10] V. Fierro, O. Akdim and C. Mirodatos, Green Chem. 5 (2003) 20.

[11] S. Velu, N. Satoh, C.S. Gopinath and K. Suzuki, Catal. Lett. 82 (2002) 145.

[12] J.P. Breen, R. Burch and H.M. Coleman, Appl. Catal. B 39 (2002) 65.

[13] A.N. Fatsikostas, D.I. Kondarides and X.E. Verykios, Catal. Today 75 (2002) 145.

[14] D.K. Liguras, D.I. Kondarides and X.E. Verykios, Appl. Catal. B 43 (2003) 345.

[15] D. Srinivas, C.V.V. Satyanarayana, H.S. Potdar and P. Ratnasamy, Appl. Catal. A 246 (2003) 323.

[16] S. Cavallaro, N. Mondello and S. Freni, J. Power Sources 102 (2001) 198.

[17] W. Wang, Z. Wang, Y. Ding, J. Xi and G. Lu, Catal. Lett. 81 (2002) 63.

[18] P.-Y. Sheng, A. Yee, G.A. Bowmaker and H. Idriss, J. Catal. 208 (2002) 393.

[19] Y. Li, Q. Fu and F.-S. M., Appl. Catal. B 27 (2000) 179.

[20] F. Sadi, D. Duprez, F. Gerard and A. Miloudi, J. Catal. 213 (2003) 226.

[21] J. Kugai, S. Velu and C.S. Song, Prepr. Pap. Am. Chem. Soc., Div. Fuel Chem. 226 (2003) U563.

[22] P. Fornasiero, J. Kaspar, V. Sergo and M. Graziani, J. Catal. 182 (1999) 56.

[23] E. Rogemond, R. Frety, V. Perrichon, M. Primet, S. Salasc, M. Chevrier, C. Gauthier and F. Mathis, J. Catal. 169 (1997) 120.

[24] W. Shan, M. Luo, P. Ying, W. Shen and C. Li, Appl. Catal. A 246 (2003) 1.

[25] S. Tang, J. Lin and K.L. Tan, Catal. Lett. 51 (1998) 169.

[26] S. Cavallaro, V. Chiodo, S. Freni, N. Mondello and F. Frusteri, Appl. Catal. A 249 (2003) 119.

[27] M. Mavrikakis and M.A. Barteau, J. Mol. Catal. A 131 (1998) 135.

[28] C. Diagne, H. Idriss and A. Kiennemann, Catal. Commun. 3 (2002) 565.