*Catalysis Letters Vol. 82, No. 1–2, September 2002 (©2002)*

# Oxidative reforming of bio-ethanol over CuNiZnAl mixed oxide catalysts for hydrogen production *

S.Velu [a,†], N. Satoh [a], Chinnakonda S. Gopinath [b], and K. Suzuki [a,‡]

[a] *Ceramics Research Institute, National Institute of Advanced Industrial Science and Technology (AIST)*
*2266-98 Anagahora, Simoshidami, Moriyama-ku, Nagoya 463-8560, Japan*
[b] *Catalysis Division, National Chemical Laboratory, Pune 411 008, India*

Received 30 January 2002; accepted 8 May 2002

Hydrogen ($H_2$) is expected to become an important fuel for the future to be used as an energy carrier in automobiles and electric power plants. A promising route for $H_2$ production involves catalytic reforming of a suitable primary fuel such as methanol or ethanol. Since ethanol is a renewable raw material and can be cheaply produced by the fermentation of biomass, the ethanol reforming for $H_2$ production is beneficial to the environment. In the present study, the steam reforming of ethanol in the presence of added $O_2$, which in the present study is referred to as oxidative steam reforming of ethanol (OSRE), was performed for the first time over a series of CuNiZnAl mixed oxide catalysts derived from layered double hydroxide (LDH) precursors. The effects of Cu/Ni ratio, temperature, $O_2$/ethanol ratio, contact time, CO co-feed and substitution of Cu/Ni by Co were investigated systematically in order to understand the influence of these parameters on the catalytic performance. An ethanol conversion close to 100% was noticed at 300 °C over all the catalysts. The Cu-rich catalysts favor the dehydrogenation of ethanol to acetaldehyde. The addition of Ni was found to favor the C–C bond rupture, producing CO, $CO_2$ and $CH_4$. Depending upon the reaction condition, a $H_2$ yield between 2.5 and 3.5 moles per mole of ethanol converted was obtained. A CoNi-based catalyst exhibited better catalytic performance with lower selectivity of undesirable byproducts, namely $CH_3CHO$, $CH_4$ and CO.

**KEY WORDS:** $H_2$ production; ethanol reforming; autothermal reforming; oxidative reforming; CuNi-based catalysts; layered double hydroxides.

## 1. Introduction

In recent years, fuel cells have been considered to be the most efficient, convenient and zero-emission power generation system for both mobile and stationary applications [1]. Proton-exchange membrane fuel cells (PEMFCs), which operate at low temperature, are suitable candidates for power generation in automobiles. The PEMFC, however, uses pure hydrogen ($H_2$) or $H_2$-rich gas as a fuel. Catalytic onboard generation of $H_2$ from a suitable primary fuel coupled with PEMFC is, therefore, the key option for the 21st century to respond creatively to the global climate and environmental changes and to make our way toward a sustainable future [1–3].

Among the various liquid fuels, currently methanol appears to be the preferred primary fuel for PEMFCs. Thus, catalytic methodologies for the decomposition, steam reforming, partial oxidation and oxidative steam reforming of methanol (OSRM) have been developed recently for onboard $H_2$ production from methanol [4–11]. Bio-ethanol, which is a mixture of water and ethanol, produced by the fermentation of biomass, is a renewable raw material and could be used as an alternative primary fuel for $H_2$ production for automobiles and stationary power plants. Unlike reforming of methanol and gasoline, which are fossil-fuel based systems, the reforming of biomass-derived ethanol to produce $H_2$ for fuel cells has the additional significant advantage of being $CO_2$ neutral as the $CO_2$ produced in the reforming reaction is consumed for the biomass growth. It has been known that for each billion gallons of ethanol consumed for fuel cells, about 6.5 million tonnes of $CO_2$ emission can be avoided [12]. Furthermore, EtOH is a preferred fuel due to large production in warm countries and can be utilized for power generation in small scale at remote areas too.

Unlike methanol reforming, the catalytic methodology for ethanol reforming to produce $H_2$ for fuel cells is not well developed. Marino *et al.* [13,14] reported the steam reforming of ethanol (SRE) as a method for $H_2$ production over Cu and Ni supported on $Al_2O_3$ catalysts. The effluent of the reactor contained a wide range of liquid and gaseous products such as $H_2$, CO, $CO_2$, $CH_4$, $CH_3CHO$, $CH_3COOH$, $C_2H_5OC_2H_5$, etc. The product distribution was found to depend on the catalyst composition. Addition of nickel to the $Cu/Al_2O_3$ system enhanced the ethanol gasification and reduced the selectivity of acetaldehyde and acetic acid. Haga *et al.*

---

* Based on the oral presentation in the 4th World Congress on Oxidation Catalysis, Berlin, Germany, 16–21 September, 2001.

[†] Present address: The Energy Institute, and Department of Energy and Geo-Environmental Engineering, The Pennsylvania State University, 209 Academic Projects Building, University Park, PA 16802, USA.

[‡] To whom correspondence should be addressed.

1011-372X/02/0900-0145

[15] reported the SRE reaction over Co supported on $Al_2O_3$, $SiO_2$, MgO, $ZrO_2$ and activated carbon. The effluent of the reactor contained liquid and gaseous products such as those observed over Cu-Ni/$Al_2O_3$ catalysts. The catalytic performance was found to depend strongly on the nature of the support. Accordingly, a Co/$Al_2O_3$ catalyst was found to exhibit a high selectivity for steam reforming of ethanol. Apart from the above few experimental results, there exist some reports on the thermodynamic analysis of the SRE reaction [16,17].

Stoichiometrically, the SRE reaction for $H_2$ production can be represented by

$$CH_3CH_2OH(l) + 3H_2O(l) \Leftrightarrow 6H_2(g) + 2CO_2(g); \quad \Delta H^{o}_{298} = +347.4\,\mathrm{kJ\,mol^{-1}} \quad (1)$$

The reaction under standard conditions is highly endothermic. According to Brown [2], the SRE reaction would require an energy equal to 60 kJ/mol of usable $H_2$. Thus, the SRE process is energy demanding and highly inconvenient for the onboard production of $H_2$ for fuel cells. On the other hand, the partial oxidation of ethanol is exothermic. Depending on the ethanol/oxygen ratio, various products could be obtained as shown in equations (2)–(5) [18]. However, it has been hypothesized that, as described recently for the reforming of methanol (OSRM reaction), the addition of a small amount of oxygen to the SRE reaction would lead to a combined steam reforming and partial oxidation reaction, which in the present study is referred to as oxidative steam reforming of ethanol (OSRE). In this reaction, the exothermic partial oxidation of ethanol would supply heat energy necessary for the endothermic steam reforming. The $O_2$/ethanol molar ratio should be adjusted in such a way that the overall reaction is close to thermal neutral producing predominantly $H_2$ and $CO_2$ (equation (6)).

$$CH_3CH_2OH(l) + 1.5O_2(g) \Leftrightarrow 3H_2(g) + 2CO_2(g); \quad \Delta H^{o}_{298} = -510.0\,\mathrm{kJ\,mol^{-1}} \quad (2)$$

$$CH_3CH_2OH(l) + 1.5O_2(g) \Leftrightarrow 2H_2(g) + H_2O(l) + CO(g) + CO_2(g); \quad \Delta H^{o}_{298} = -227.0\,\mathrm{kJ\,mol^{-1}} \quad (3)$$

$$CH_3CH_2OH(l) + O_2(g) \Leftrightarrow CH_4(g) + 2CO_2(g) + H_2O(l); \quad \Delta H^{o}_{298} = -433.2\,\mathrm{kJ\,mol^{-1}} \quad (4)$$

$$CH_3CH_2OH(l) + 0.5O_2(g) \Leftrightarrow CH_3CHO(g) + H_2O(l); \quad \Delta H^{o}_{298} = -174.8\,\mathrm{kJ\,mol^{-1}} \quad (5)$$

$$CH_3CH_2OH(l) + 3\text{-}(2\delta)H_2O(l) + \delta O_2 \Leftrightarrow 6\text{-}(2\delta)H_2(g) + 2CO_2(g); \quad \text{if } \delta = 0.6, \quad \Delta H^{o}_{298} = +4.4\,\mathrm{kJ\,mol^{-1}} \quad (6)$$

In the present study, a new series of CuNiZnAl–mixed oxides with various Cu : Ni atomic ratios have been prepared by the thermal decomposition of CuNiZnAl hydrotalcite (HT)-like layered double hydroxides (LDHs) as precursors. The reason for using LDHs as catalyst precursors is, because after calcination, they lead to mixed oxides with high surface area, high thermal stability, and the formation of well-dispersed metallic particles on reduction treatment, which are essential for an effective catalyst [19]. Similar CuNiAl and NiZnAl mixed oxide catalysts derived from LDH precursors have been employed recently for the oxidation of phenol in aqueous solution and hydrogenation of acetylene, respectively [20, 21].

The catalytic performance of CuNiZnAl mixed oxides has been evaluated systematically in the OSRE reaction for the first time. The data obtained have also been compared with those of the SRE reaction performed in the absence of air under similar experimental conditions.

## 2. Experimental

### 2.1. Synthesis and characterization of CuNiZnAl mixed oxide catalysts

CuNiZnAl LDHs with different Cu : Ni atomic ratios were synthesized by coprecipitation at a constant pH (∼10) using respective metal nitrates as precursors and a mixture of NaOH and $Na_2CO_3$ as precipitants [22]. These LDH precursors were then calcined at 450 °C for 5 h to obtain corresponding mixed oxide catalysts. The structural, textural and redox properties of the as-synthesized and/or calcined samples were characterized by means of X-ray fluorescence (XRF) spectroscopy, X-ray diffraction (XRD), $N_2$ adsorption–desorption, and temperature-programmed reduction (TPR) methods as described earlier [22, 23].

### 2.2. Catalytic activity measurements

The SRE and OSRE reactions were performed in a conventional fixed-bed flow reactor (4 mm i.d.) using 100 mg of the catalyst (grain size 0.30–0.355 mm) in the temperature range between 200 and 300 °C at atmospheric pressure [7–9]. The catalyst was first reduced in a stream of $H_2$ (20–30 $cm^3$/min) from room temperature to 300 °C (the Ni-rich CuNiC-4 sample without Cu was reduced at 500 °C) with a heating rate 5 °C/min and dwelling at this temperature for 3 h before cooling down to the reaction temperature. Subsequently, a premixed water and ethanol with an $H_2O$/ethanol molar ratio of 3.0 was fed into the pre-heater by means of a micro-feeder (ethanol space velocity, WHSV = 107 mole $h^{-1}$ kg(catalyst)$^{-1}$). The flow rate of synthetic air (20.2 vol% of $O_2$ in $N_2$) was adjusted by means of a mass flow controller by varying the $O_2$/ethanol molar ratio from 0 to 0.80. However, the

Table 1
Physicochemical properties of CuNiZnAl mixed oxide catalysts

| Catalyst | Chemical composition (atomic ratio) [a] | | | | Textural properties [b] | |
|---|---|---|---|---|---|---|
| | Cu | Ni | Zn | Al | BET SA ($m^2\,g^{-1}$) | PV ($cm^3\,g^{-1}$) |
| CuC-1 | 2.53 | 0.00 | 0.77 | 1 | 42 | 0.23 |
| CuNiC-2 | 1.79 | 2.39 | 0.78 | 1 | 59 | 0.25 |
| CuNiC-3 | 0.93 | 2.99 | 0.81 | 1 | 70 | 0.23 |
| NiC-4 | 0.00 | 4.26 | 0.79 | 1 | 103 | 0.63 |

[a] Determined by X-ray fluorescence spectroscopy.
[b] Calculated from $N_2$ adsorption–desorption isotherms.

data collected with an $O_2$/ethanol molar ratio of 0.4 were used for comparison. The reaction products were analyzed on-line using two gas chromatographs (Shimadzu GC-14B and GL Sciences, Japan, GC-320). The Shimadzu GC-14B equipped with a Porapak-T column and flame ionization detector (FID) was able to detect the liquid products (ethanol, acetaldehyde, etc.), while the GC-320 equipped with an activated carbon column and thermal conductivity detector (TCD) was able to detect the gaseous products ($H_2$, CO, air, $CH_4$ and $CO_2$). In order to estimate the contents of CO, $CO_2$ and $CH_4$ more accurately, the effluent of the GC-320 was also passed through a methanizer and a third GC (GL Sciences, Japan) equipped with a FID [7,8].

## 3. Results and discussion

### 3.1. Bulk characterization (chemical analysis, XRD and TPR)

The chemical compositions and textural properties (BET surface area and pore volume) of CuNiZnAl mixed oxide catalysts prepared in the present study are summarized in table 1. The Cu : Ni atomic ratio in the synthesis gel was varied by keeping the nominal Zn : Al atomic ratios as constant. XRD patterns of the as-synthesized materials (not shown) corresponded to the typical layered rhombohedral structure of HT-like layered double hydroxides (LDHs; JCPDS file No. 37-629). The Cu-rich samples are accompanied by the malachite (MT) phase, [$Cu_2CO_3(OH)_2$; JCPDS file No. 41-1390] [22].

Figure 1 shows the XRD patterns of all the calcined materials. The Cu-rich CuC-1 exhibits diffraction patterns attributed to a mixture of CuO and ZnO phases. Substitution of Ni for Cu decreases the crystallinity of CuO and ZnO phases with a concomitant increase in the crystallinity of the NiO phase. The Ni-rich NiC-4 exhibits a relatively well-crystallized NiO. No ZnO phase could be detected in the Ni-containing catalysts. The catalysts derived from intermediate compositions contain a mixture of CuO and NiO phases.

The TPR profiles of all samples calcined at 450 °C are shown in figure 2. The specimens CuC-1 through CuNiC-3 containing Cu exhibit a sharp $H_2$ consumption peak around 200 °C due to the reduction of CuO phase [22]. The onset temperature of the peak is almost similar for all the samples although the broadness of the peak decreases and becomes sharp with increasing Ni content. The Ni-rich NiC-4, on the other hand, exhibits a strong $H_2$ consumption band centering on 500 °C, and this is attributed to the reduction of the NiO phase [23]. $H_2$ consumption corresponding to the reduction of $Ni^{2+}$ can also be noticed as weak shoulders in the CuNiC-2 and CuNiC-3 samples around 400 °C.

### 3.2. Catalytic oxidative reforming of bio-ethanol

Steam reforming of ethanol in the presence and absence of air over CuNiZnAl mixed oxide catalysts after reduction (*in situ*) produced a mixture of $H_2$, CO,

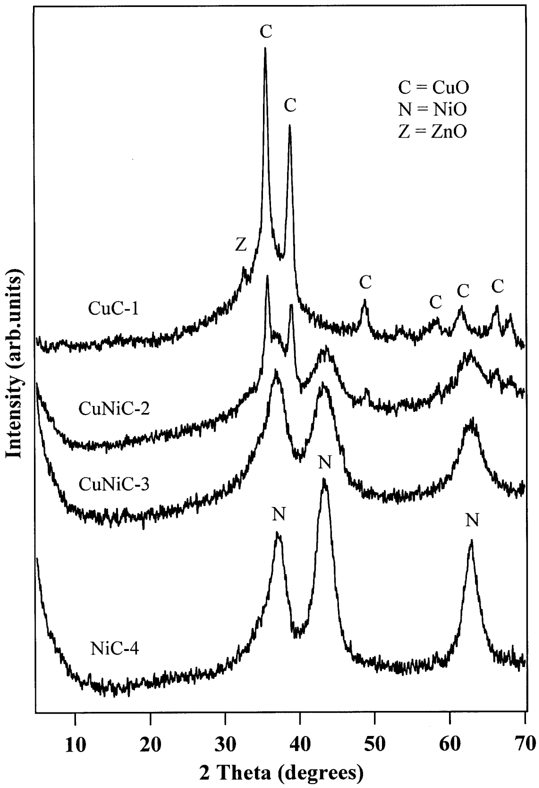

Figure 1. XRD patterns of CuNiZnAl mixed oxide catalysts.

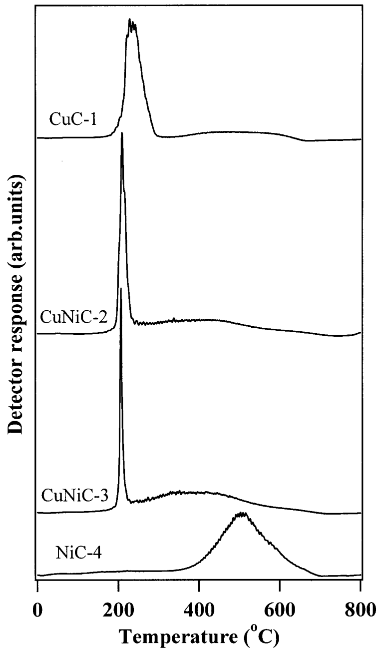

Figure 2. TPR profiles of CuNiZnAl mixed oxide catalysts.

$CO_2$, $CH_4$ and $CH_3CHO$ as major products. Traces of $CH_3COOH$ have also been detected under certain reaction conditions. The effect of bulk (Cu + Zn)/(Ni + Al) atomic ratio on the ethanol conversion and product selectivity in the OSRE reaction is shown in figure 3. It can be seen that both the Ni-free CuZnAl oxide catalyst (CuC-1) and the Cu-free NiZnAl oxide catalyst (NiC-4) are equally active in terms of ethanol conversion. This is in contrast to the report by Marino *et al.* [13,14] wherein a similar $Ni/K/Al_2O_3$ catalyst has been found to be inactive for the gasification of ethanol.

The addition of Ni to the CuZnAl system or Cu to the NiZnAl system does not influence the ethanol conversion significantly and it remains close to 90% over all the catalysts. On the other hand, the added Ni strongly influences the product selectivity. Since the Zn and Al contents are almost similar for all samples, the (Cu + Zn)/(Ni + Al) ratio can be considered as the Cu/Ni ratio. The Cu-rich CuC-1 catalyst is highly selective for $CH_3CHO$ formation and the selectivity decreases with concomitant increase in the selectivity of CO, $CO_2$ and $CH_4$ with increasing Ni content. The $H_2$ yield, which is defined as the moles of $H_2$ produced per mole of ethanol injected, varies between 2.6 and 3.0. The higher selectivity of $CH_3CHO$ and lower selectivity of CO, $CO_2$ and $CH_4$ over CuC-1 catalyst clearly indicates that under the present experimental conditions the catalyst favors the dehydrogenation of ethanol to $CH_3CHO$ (equation (5)). Similar results were also observed in the reactions of ethanol over copper supported on $Al_2O_3$, $SiO_2$, MgO, $ZrO_2$ and ZnO [24]. The decrease in the selectivity of $CH_3CHO$, with consequent increase in the selectivity of $CH_4$, CO and $CO_2$ over Ni-containing catalysts, could be attributed to the involvement of the reforming activity (C—C bond rupture) of Ni.

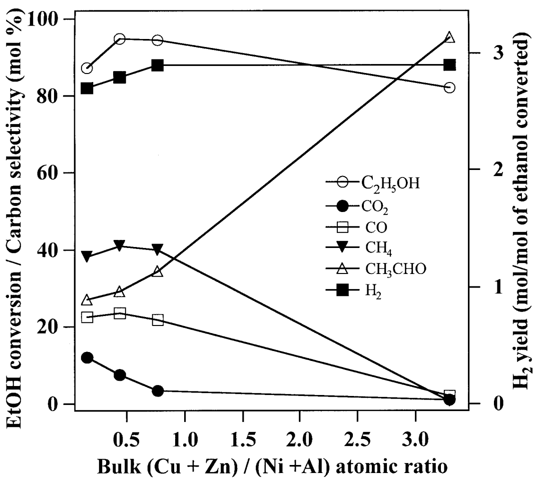

Figure 3. Effect of (Cu + Zn)/(Ni + Al) atomic ratio on the catalytic performance in the oxidative reforming of bio-ethanol over CuNiZnAl mixed oxide catalysts. Temperature 300 °C. Carbon selectivity indicates the selectivity of CO, $CO_2$, $CH_4$ and $CH_3CHO$.

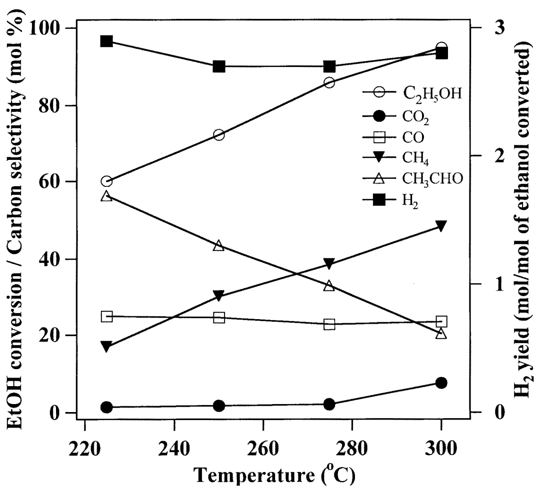

Figure 4. Effect of temperature on the catalytic performance in the oxidative reforming of bio-ethanol over CuNiC-3 catalyst. Ethanol space velocity: 107 mole $h^{-1}$ kg(cat.)$^{-1}$; $H_2O$/ethanol = 3; $O_2$/ethanol = 0.4. Carbon selectivity indicates the selectivity of CO, $CO_2$, $CH_4$ and $CH_3CHO$.

The effect of temperature on catalytic performance over CuNiC-3 in the OSRE reaction is shown in figure 4. Ethanol conversion increases with increasing reaction temperature. The selectivity of $CH_3CHO$ decreases while that of $CH_4$ increases parallel to the ethanol conversion. This indicates that $CH_4$ formation is favored with increasing reaction temperature. However, the selectivity of CO remains almost unchanged while the selectivity of $CO_2$ increases marginally up to around 270 °C and then to a large extent above this temperature.

Figure 5 depicts the effect of $O_2$/ethanol molar ratio on catalytic performance in the OSRE reaction over CuNiC-3 performed at 300 °C. The ethanol conversion

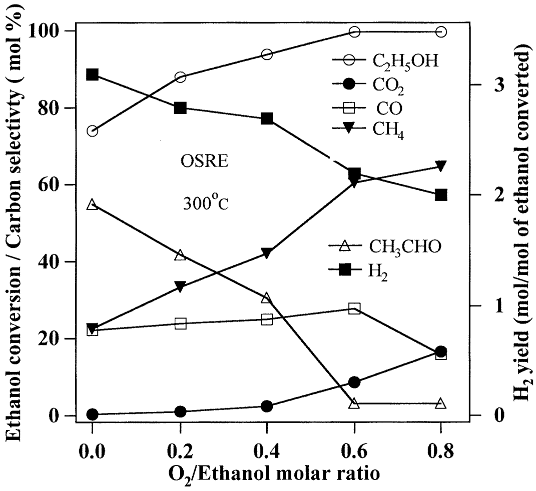

Figure 5. Effect of $O_2$/ethanol molar ratio on the catalytic performance in the reforming of bio-ethanol over CuNiC-3 catalyst. Ethanol space velocity: 107 mole h$^{-1}$ kg(cat.)$^{-1}$; $H_2O$/ethanol = 3; temperature = 300 °C. Carbon selectivity indicates the selectivity of CO, $CO_2$, $CH_4$ and $CH_3CHO$.

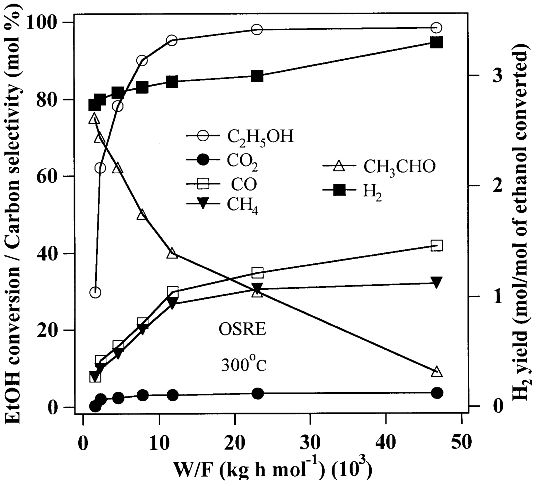

Figure 6. Effect of space velocity on the catalytic performance in the oxidative reforming of bio-ethanol over CuNiC-3 catalyst. $H_2O$/ethanol = 3; $O_2$/ethanol = 0.4; temperature = 300 °C. Carbon selectivity indicates the selectivity of CO, $CO_2$, $CH_4$ and $CH_3CHO$.

increases with increasing $O_2$/ethanol ratio and it attains about 100% at the $O_2$/ethanol ratio of 0.6. The selectivity of $CH_4$ also increases parallel to the methanol conversion while the selectivity of $CH_3CHO$ shows the reverse trend. The selectivity of both CO and $CO_2$ increases to some extent until an $O_2$/ethanol ratio of 0.4. Above this ratio, there is an abrupt increase in the selectivity of $CO_2$. The CO selectivity, on the other hand, drops down at the higher $O_2$/ethanol ratio of 0.6. The $H_2$ yield decreases from about 3 moles/mole of ethanol converted in the SRE reaction in the absence of oxygen to about 2 moles/mole of ethanol at the high $O_2$/ethanol ratio of 0.8. It can be inferred from these results that the addition of oxygen improves the ethanol conversion and also oxidation of $CH_3CHO$ to $CH_4$ and $CO_2$ probably *via* acetic acid intermediate. In order to obtain a relatively higher $H_2$ yield and lower selectivity of $CH_4$ and $CH_3CHO$, an $O_2$/ethanol ratio of 0.4 has been considered in the present study.

In an effort to understand the reaction path in which the OSRE reaction proceeds over the present catalyst system, the effect of weight hourly space velocity (WHSV) of ethanol was performed over CuNiC-3 catalyst at 300 °C. In figure 6, the inverse of WHSV (W/F) or pseudo contact time (or for the sake of simplicity contact time) is plotted against ethanol conversion and product selectivity. It can be seen that the ethanol conversion increases monotonously with increasing contact time up to around 0.01 kg h mol$^{-1}$ and then levels off. The selectivity of $CH_3CHO$ is highest at low contact times and it decreases at the expense of the selectivity of CO, $CO_2$ and $CH_4$ with increasing contact times. The $H_2$ yield increases from about 3 moles per mole of ethanol converted at low contact times to about 3.5 moles at higher contact times.

The effect of contact time on the catalytic performance in the SRE reaction in the absence of air has also been performed for the sake of comparison. The reaction was performed under the same experimental conditions as those employed in the OSRE reaction except that Ar (15 cm$^3$/min) was used as carrier gas without co-feeding air. On comparing the data presented in figure 6 and figure 7, it appears that the dependence of ethanol conversion and selectivities of acetaldehyde, CO, $CO_2$ and $CH_4$ on contact time in the SRE reaction is similar to those observed in the OSRE reaction. However, the selectivity of CO and $CH_4$ are close to each other in the OSRE reaction while the CO selectivity is less than that of $CH_4$ in the SRE reaction. Also, the rate of $CO_2$ formation is faster in the SRE reaction

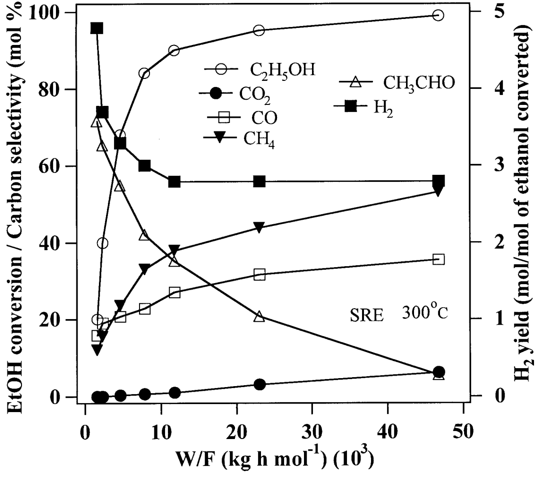

Figure 7. Effect of space velocity on the catalytic performance in the reforming of bio-ethanol over CuNiC-3 catalyst in the absence of air. $H_2O$/ethanol = 3; temperature = 300 °C. Carbon selectivity indicates the selectivity of CO, $CO_2$, $CH_4$ and $CH_3CHO$.

than that of the OSRE reaction. More interestingly, a high $H_2$ yield close to 5 moles/mole of ethanol converted is observed at low contact times and the yield decreases rapidly to about 3 moles with increasing contact time up to around 0.01 kg h mol$^{-1}$ and then levels off. Based on the results shown in figures 6 and 7 it can be concluded that dehydrogenation of ethanol to acetaldehyde is the major reaction in the ethanol reforming as long as copper is present in the catalyst formulation. The acetaldehyde subsequently decomposes into CO, $CO_2$ and $CH_4$ in the SRE reaction or it decomposes *via* acetic acid in the OSRE reaction. Marino *et al.* [14] also suggested a similar pathway for the ethanol reforming reaction over Cu/Ni/K/$\gamma$-$Al_2O_3$ catalysts.

The formation of a large amount of $CH_4$ in the ethanol reforming is undesirable because it competes with the $H_2$ yield. It is known from the literature [15] that ethanol decomposes to form $CH_4$ on Ni and Pt catalysts. It is also known very well [15,25,26] that transition metals (Cu, Ni and Co) are active in the hydrogenation of CO and $CO_2$ to $CH_4$ (methanation reactions). Hence, it is possible that a part of the $CH_4$ observed in the ethanol reforming would have been formed by the hydrogenation of carbon oxides produced by the ethanol reforming reaction. In order to verify this, a known amount of CO or $CO_2$ was added to the OSRE reaction mixture (ethanol, water and air). The experiment was performed in such a way that the OSRE reaction mixture was diluted with about 8 cm$^3$/min Ar gas. After 2 h of the reaction, the Ar gas was replaced by the same quantity of CO or $CO_2$ gas and the data were collected for about 90 min. The CO or $CO_2$ was then replaced by Ar gas and the data were collected for another 2 h. Figure 8 shows the effect of CO addition on the product distribution in the OSRE reaction over CuNiC-3 performed at 300 °C. It can be seen from the figure that the addition of CO to the reaction mixture does not affect the $CH_4$ yield and it remains unchanged throughout the experiment. On the other hand, the yields of $CO_2$ and $H_2$ increased upon CO addition. When the CO addition was stopped the outlet concentrations of $CO_2$ and $H_2$ reverted to the original value. Note also that the ethanol conversion remains close to 100% throughout the experiment and hence the difference in the outlet concentrations of CO, $CO_2$ and $H_2$ during this experiment is not due to any change in the ethanol conversion but is due to the influence of added CO. The increase in the outlet concentrations of $CO_2$ and $H_2$ upon CO addition clearly indicates the involvement of a water–gas shift (WGS) reaction (equation (7)). The addition of $CO_2$, on the other hand, did not affect the outlet concentrations of any of the products, including $H_2$ and $CH_4$. These results indicate that under the reaction conditions the hydrogenation of CO and/or $CO_2$ to $CH_4$ is insignificant over the present catalyst system and $CH_4$ is formed solely by the decomposition of acetaldehyde and/or acetic acid (equation (8)).

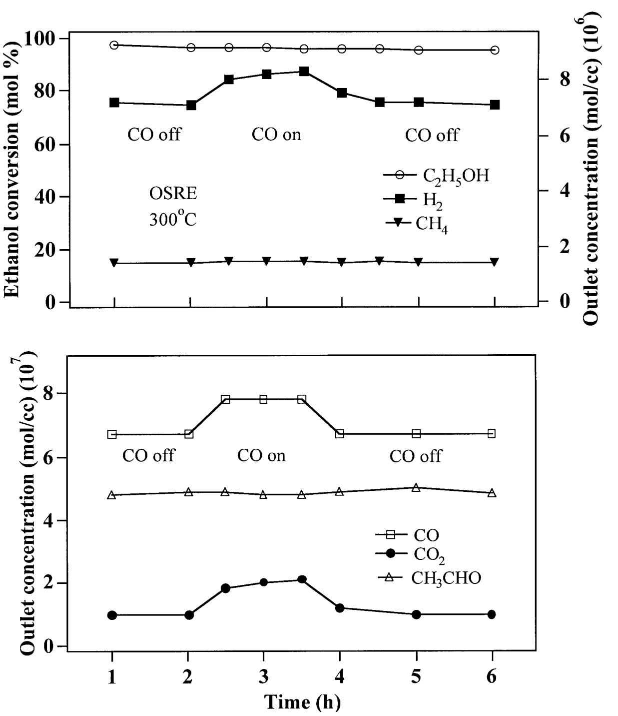

Figure 8. Effect of CO co-feed on the catalytic performance in the oxidative reforming of bio-ethanol over CuNiC-3 catalyst. Carbon selectivity indicates the selectivity of CO, $CO_2$, $CH_4$ and $CH_3CHO$. Ethanol space velocity: 107 mole h$^{-1}$ kg(cat.)$^{-1}$; $H_2O$/ethanol = 3; $O_2$/ethanol = 0.4; temperature = 300 °C.

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \tag{7}$$

$$CH_3CHO \Leftrightarrow CH_4 + CO \tag{8}$$

In order to understand the role of each element (Cu, Ni, Zn and Al) in the SRE and OSRE reactions, a wide range of new catalysts similar to that of CuNiC-3 with various compositions were prepared *via* LDH precursors using the same synthesis procedure. The data collected for the same catalyst under different experimental conditions and different catalysts under the same experimental conditions are compared in table 2. As can be seen, there is no significant improvement in the catalytic performance of CuNiC-3 with respect to reduction temperature. In fact, the selectivity of $CH_3CHO$ is higher than that obtained over catalyst reduced at 300 °C. It is likely that at higher reduction temperature the particle size of Cu increases and this suppresses the gasification of $CH_3CHO$ in the subsequent step. The result suggests that the reduction temperature should be limited to 300 °C as long as Cu is present in the catalyst. The ethanol conversion is less and the $CH_3CHO$ selectivity is higher in the SRE reaction compared with the same in the OSRE reaction. Substitution of Zn completely by Al in the CuNiC-3 catalyst (CuNiC-3 (WOZn)) increases the $CH_4$ selectivity, probably due to the involvement of the CO/$CO_2$ hydrogenation reaction. On the other hand, the selectivity of $CH_3CHO$ increases and the ethanol

Table 2
Effect of catalyst compositions and reaction conditions on the catalytic performance in the reforming of bio-ethanol

| Catalyst | EtOH conversion (mol%) | $H_2$ yield[a] | Carbon selectivity (mol%) | | | | Carbon balance[b] (%) |
|---|---|---|---|---|---|---|---|
| | | | $CO_2$ | CO | $CH_4$ | $CH_3CHO$ | |
| CuNiC-3 | 94.9 | 2.8 | 7.8 | 23.5 | 48.1 | 20.5 | 98 |
| CuNiC-3 (450)[c] | 93.4 | 2.9 | 2.6 | 22.5 | 42.1 | 32.8 | 98 |
| CuNiC-3 (SRE)[d] | 82.3 | 3.1 | 1.5 | 20.4 | 26.1 | 42.0 | 96 |
| CuNiC-3 (WOZn)[e] | 99.2 | 2.3 | 1.8 | 22.8 | 60.0 | 15.4 | 96 |
| CuNiC-3 (WOAl)[f] | 88.0 | 2.3 | 3.4 | 21.8 | 40.3 | 34.4 | 104 |
| CuCoC-3[g] | 65.5 | 3.7 | 1.8 | 6.4 | 2.8 | 89.0 | 99 |
| CuNiCoC-3[h] | 99.1 | 2.2 | 2.8 | 22.6 | 70.2 | 4.3 | 95 |
| NiC-4[i] | 87.3 | 2.9 | 12.1 | 22.4 | 38.3 | 27.2 | 99 |
| CoNiC-3[j] | 90.8 | 2.5 | 25.9 | 20.6 | 35.6 | 17.9 | 93 |
| CoNiC-3 (SRE)[d] | 82.7 | 3.0 | 3.7 | 24.9 | 40.9 | 30.4 | 87 |
| $Ni/La_2O_3$ (SRE)[k] | ≈12 | – | 9.0 | 20.0 | 11.0 | 60.0 | – |

Reaction conditions: reaction temperature = 300 °C, $H_2O$/ethanol = 3, ethanol space velocity (WHSV) = 107 mole $h^{-1}$ kg(cat.)$^{-1}$, $O_2$/ethanol = 0.4, data collected after 3 h of the reaction.

[a] Moles of $H_2$ produced per mole of ethanol converted.

[b] Carbon balance = (moles of carbon products ($CO_2 + CO + CH_4 + CH_3CHO$) formed/moles of ethanol converted) × 100.

[c] Catalyst reduced at 450 °C over 3 h.

[d] Steam reforming of ethanol in the absence of oxygen.

[e] CuNiAl mixed oxide catalyst without zinc.

[f] CuNiZn mixed oxide catalyst without aluminum.

[g] CuCoZnAl mixed oxide catalyst having the same composition as that of CuNiC-3.

[h] CuNiCoC-3 catalyst was prepared by substituting Co for Zn in CuNiC-3 catalyst.

[i] NiZnAl oxide catalyst without Cu and reduced at 500 °C.

[j] CoNiZnAl oxide catalyst with the same composition as CuNiC-3 catalyst, but Cu replaced by Co. Catalyst reduced at 500 °C.

[k] Data at 400 °C reported in ref. [27].

conversion decreases upon complete substitution of Al by Zn in the same catalyst (CuNiC-3 (WOAl)).

The effect of substitution of Cu or Ni by Co on the catalytic performance in the OSRE reaction has also been investigated. As can be seen from the data in table 2, the ethanol conversion drops dramatically (to 65.5%) and the selectivity of $CH_3CHO$ is very high (~90%) when Ni is completely substituted by Co. This means that Co is less active towards C–C bond rupture compared with Ni under the present experimental conditions. The catalyst CuNiCoC-3 containing all three active elements, namely Cu, Ni and Co, is very active for ethanol conversion as well as C–C bond rupture (selectivity of acetaldehyde is only around 4%). However, the catalyst produces a large amount of $CH_4$ ($CH_4$ selectivity is about 70%). It is interesting to note that a complete substitution of Cu by Co (CoNiC-3 catalyst) decreases the selectivity of $CH_4$ and acetaldehyde and increases the selectivity of $CO_2$. This suggests that a CoNi-based catalyst would be better for the reforming of ethanol in the presence of air.

It is also interesting to note from table 2 that the performance of catalysts reported in the present study is several times more active and selective for $H_2$ at a lower temperature of around 300 °C, either in the SRE or OSRE reaction, compared with the $Ni/La_2O_3$ catalyst reported recently for the SRE reaction [27]. Thus, it appears that the CoNi-based mixed oxide catalysts are promising candidates and the OSRE is a convenient method for the onboard reforming of bio-ethanol to produce $H_2$ for fuel cells for automobile applications.

## 4. Conclusions

The oxidative steam reforming of ethanol (OSRE) reaction performed over CuZnAl oxide catalyst without Ni and NiZnAl oxide without Cu are equally active, exhibiting an ethanol conversion close to 100% at 300 °C. The CuZnAl oxide catalyst produces $CH_3CHO$ and $H_2$ as major products, while the NiZnAl oxide catalyst produces a mixture of $H_2$, CO, $CO_2$ and $CH_4$. The addition of Ni to the CuZnAl oxide system favors the C–C bond rupture and improves the gasification of ethanol. The reaction over CuNiZnAl mixed oxide catalyst proceeds through the formation of $CH_3CHO$ intermediate, which subsequently decomposes to CO, $CO_2$ and $CH_4$. Depending upon the reaction conditions, a $H_2$ yield between 2.5 and 3.5 moles per mole of ethanol converted could be obtained over these catalysts.

The CoNi-based catalysts exhibit better catalytic performance with lower selectivity of undesirable by-products, namely $CH_3CHO$, $CH_4$ and CO. Further work on the optimization of catalyst formulations and reaction operating conditions in order to improve the $H_2$ selectivity and reduce the selectivity of $CH_3CHO$, $CH_4$ and CO to the accepted level is currently underway.

## Acknowledgments

One of the authors (S.V.) would like to express his sincere gratitude to the Japan Science and Technology Corporation (JST) for financial assistance through the Cooperative System for Supporting Priority Research.

## References

[1] C. Song, Am. Chem. Soc. Fuel Chem. Division Preprint 46 (2001) 8.
[2] L.F. Brown, Int. J. Hydrogen Energy 26 (2001) 381.
[3] J. Rostrup-Nielson, Phys. Chem. Chem. Phys. 3 (2001) 283.
[4] W.-H. Cheng, Acc. Chem. Res. 32 (1999) 685.
[5] J.P. Breen and J.R.H. Ross, Catal. Today 51 (1999) 521.
[6] L. Alejo, R. Lago, M.A. Peña and J.L.G. Fierro, Appl. Catal. A: General 162 (1997) 281.
[7] S. Velu, K. Suzuki, M. Okazaki, M.P. Kapoor, T. Osaki and F. Ohashi, J. Catal. 194 (2000).
[8] S. Velu, K. Suzuki, M.P. Kapoor, F. Ohashi and T. Osaki, Appl. Catal. A: General 213 (2001) 47.
[9] S. Velu, K. Suzuki and T. Osaki, Catal. Lett. 69 (2000) 43.
[10] T.L. Reitz, P.L. Lee, K.F. Czaplewski, J.C. Lang, K.E. Popp and H.H. Kung, J. Catal. 199 (2001) 193.
[11] S. Murcia-Mascaros, R.M. Navarro, L. Gomez-Sainero, U. Costantino, M. Nocchetti and J.L.G. Fierro, J. Catal. 198 (2001) 338.
[12] Biofuels, DOE/GO 10099, 736 (1999).
[13] F. Marino, M. Jobbagy, G. Baronetti and M. Loborde, Stud. Surf. Sci. Catal. 130 (2000) 2147.
[14] F. Marino, M. Boveri, G. Baronetti and M. Loborde, Int. J. Hydrogen Energy 26 (2001) 665.
[15] F. Haga, T. Nakajima, H. Miya and S. Mishima, Catal. Lett. 48 (1997) 223.
[16] K. Vasudeva, N. Mitra, P. Umasanker and S.C. Dhingra, Int. J. Hydrogen Energy 21 (1996) 13.
[17] I. Fishtik, A. Alexander, R. Datta and D. Geana, Int. J. Hydrogen Energy 25 (2000) 31.
[18] A. Yee, S.J. Morrison and H. Idriss, J. Catal. 186 (1999) 279.
[19] F. Cavani, F. Trifiro and A. Vaccari, Catal. Today 11 (1991) 173.
[20] A. Alejandre, F. Medina, X. Rodriguez, P. Salagre and J.E. Sueiras, Stud. Surf. Sci. Catal. 130 (2000) 1763.
[21] A. Monzon, E. Romeo, C. Roya, R. Trujillano, F.M. Labajos and V. Rives, Appl. Catal. A: General 185 (1999) 53.
[22] S. Velu, K. Suzuki, S. Hashimoto, N. Satoh and S. Tomura, J. Mater. Chem. 11 (2001) 2049.
[23] S. Velu, K. Suzuki, M.P. Kapoor, S. Tomura, F. Ohashi and T. Osaki, Chem. Mater. 12 (2000) 719.
[24] N. Iwasa and Takezawa, Bull. Chem. Soc. Jpn. 64 (1991) 2619.
[25] Y. Liu and D. Liu, Int. J. Hydrogen Energy 24 (1999) 351.
[26] M. Agnelli and C. Mirodatos, J. Catal. 192 (2000) 204.
[27] A.N. Fatsikostas, D.I. Kondarides and X.E. Verykios, Chem. Commun. (2001), 851.