

Review

# Reforming catalysts for hydrogen generation in fuel cell applications

Praveen K. Cheekatamarla\*, C.M. Finnerty

*ND Energy, NanoDynamics Inc., 901 Fuhrmann Blvd, Buffalo, NY 14203, USA*

Received 1 January 2006; received in revised form 2 April 2006; accepted 3 April 2006

Available online 23 May 2006

## Abstract

The objective of this review paper is to present a summary of the specific contributions in the field of fuel processing, particularly, outlines various developments involving catalytic reforming of a range of fuels for the development of an efficient fuel-processing unit for syngas production in fuel cell applications. Two major topics are discussed (i) the basic reactions involved in each of the processes and (ii) various catalyst systems that have been tested. A final short section offers some new possible routes for future research.

© 2006 Elsevier B.V. All rights reserved.

*Keywords:* Fuel processing; Catalyst; Reforming; Hydrogen; Fuel cell

## Contents

1. Introduction .....	490
2. Basic reactions involved .....	491
2.1. Steam reforming .....	491
2.2. Partial oxidation reforming .....	491
2.3. Autothermal reforming .....	491
2.4. Hydrogen source .....	491
3. Reforming of light hydrocarbons .....	492
3.1. Methane .....	492
3.2. Ethane, propane and butane .....	493
4. Reforming of higher hydrocarbons .....	493
5. Reforming of oxygenated hydrocarbons .....	495
5.1. Methanol .....	495
5.2. Ethanol .....	496
5.3. Dimethyl ether .....	496
6. Conclusions .....	497
References .....	497

## 1. Introduction

The use of fuel cells for electric power generation has immense potential since they offer efficiency and the environmental and operational benefits better than those obtained from

conventional technologies [1]. Hydrogen, the fuel for fuel cells can be stored in suitable storage devices or produced on-board by the catalytic reforming process. Hence, there is great interest in converting hydrocarbons and oxygenated hydrocarbons into hydrogen. Frieghtliner Inc. has successfully demonstrated on-board steam reforming of methanol for auxiliary power applications in trucks in 2003 [2]. Ballard makes fuel cells which have been used experimentally by several car makers, and were most convincingly demonstrated recently by Daimler's

\* Corresponding author. Tel.: +1 303 949 1629; fax: +1 716 853 8996.  
E-mail address: [praveen\\_chemi@yahoo.com](mailto:praveen_chemi@yahoo.com) (P.K. Cheekatamarla).

NECAR II, based on a Mercedes V-class MPV. Now Daimler has NEBUS, a fuel-celled powered bus, in regular service around Stuttgart, Germany [3].

The process of converting petroleum fuels to hydrogen-rich gas products that have been developed in the past generally fall into one of these classes – steam reforming (SR), partial oxidation (POX), autothermal reforming (ATR), dry reforming (DR) or a combination of two or more. Despite their advantages, each of these processes has barriers such as design, fuel, and operating temperature. A range of fuel cell systems and common fuel reforming methods have been reviewed by Larminie and Dicks [4], Hirschenhofer et al. [5]. The choice of reforming processes for producing fuel-cell feeds of the necessary quality has been thermodynamically analyzed using different fuels [6]. Similarly, the challenges and opportunities of various fuel reforming technologies for application in low and high-temperature fuel cells have been thoroughly reviewed [7].

The design of a fuel reforming catalyst is a difficult undertaking. Weight, size, activity, cost, transient operations, versatility to reform different fuels/compositions, catalyst durability and fuel processor efficiency are critical considerations for both stationary and automotive fuel cell applications. A desirable catalyst is one which catalyzes the reaction at low temperatures, is resistant to coke formation, and is tolerant of different concentrations of poison (e.g. sulfur, halogens, heavy metals, etc.) for extended periods of time. The trends in fuel processor development with respect to the catalyst development for various steps involved in the generation of fuel cell grade hydrogen has been extensively discussed in a previous paper published in the year 2002 [8]. The goal of the present paper is to review and discuss some of the latest achievements in the catalyst development (after year 2002), particularly, reforming catalysts to generate hydrogen from different fuel sources. The type of substrate used to support the washcoat and catalyst is known to significantly impact catalyst performance, however, the present article discusses only about the reforming chemistry on different metals and supports and the interaction between the gases and the catalyst interface and the influence of promoters.

## 2. Basic reactions involved

The process of converting different fuels to hydrogen-rich gas products have been widely examined analyzed and implemented in fuel reforming.

### 2.1. Steam reforming

Steam reforming (SR) has the highest efficiency for hydrogen production. However, SR is an endothermic reaction and so an external source of heat is needed.

### 2.2. Partial oxidation reforming

Catalytic partial oxidation (exothermic, POX) and CO<sub>2</sub> reforming (endothermic, dry reforming (DR)) have also been investigated.

Table 1  
Heats of reaction corresponding to the dry reforming (DR) of different fuels

Feed	Products	$\Delta H_{298}^{\circ}$ (kJ/mol)
CH <sub>4</sub>	C, 2H <sub>2</sub>	74.8
CH <sub>4</sub> , CO <sub>2</sub>	2CO, 2H <sub>2</sub>	247.3
11CH <sub>4</sub> , 5O <sub>2</sub> , CO <sub>2</sub>	22H <sub>2</sub> , 12CO	-9.92
C <sub>3</sub> H <sub>8</sub> , 3CO <sub>2</sub>	6CO, 4H <sub>2</sub>	150.567

### 2.3. Autothermal reforming

The ideal fuel processor should combine the advantages of CPOX and SR/DR to avoid complicated heat exchange. Hydrogen production using autothermal reforming (ATR), which is a combination of SR and POX reactions, has recently attracted considerable attention due to its higher energy efficiency than other processes and also as a low investment process using a simple system design [9]. The ATR is a stand-alone process in which the entire hydrocarbon conversion is carried out in one reactor with out the necessity of having to implement an efficient heat transfer method between the endothermic and exothermic reactions.

### 2.4. Hydrogen source

Various fuels have been investigated for H<sub>2</sub> generation by reforming technologies for fuel cell systems. Suitable fuels include gaseous hydrocarbons (HC) such as methane, propane, LPG, butane [10] and liquid HCs such as alcohols [11], gasoline [12,13], diesel [14,15], and JP8 [15,16]. The selection of hydrogen source (fuel) for a particular application depends on technical and/or economic, political factors.

The basic reactions involved in each of the processes mentioned above are separately presented here. The first two columns listed in Tables 1–4 represent the feed stream and product stream components respectively and the last column lists the heat of reaction for each of the reactions mentioned. DR, POX, SR, and ATR reactions involving a range of fuels are represented in Tables 1–4, respectively. It has to be noted that the product set mentioned in Table 4 only represents the equilibrium composition for  $x$  and  $n$  values presented.

The following sections discuss various catalyst systems that have been developed for reforming different types of fuels over

Table 2  
Heats of reaction corresponding to the partial oxidation (POX) of different fuels

Feed	Products	$\Delta H_{298}^{\circ}$ (kJ/mol)
CH <sub>4</sub>	C, 2H <sub>2</sub>	74.8
CH <sub>4</sub> , (1/2)O <sub>2</sub>	CO, 2H <sub>2</sub>	-35.7
CH <sub>4</sub> , 2O <sub>2</sub>	CO <sub>2</sub> , 2H <sub>2</sub> O	-802
CH <sub>4</sub> , (3/2)O <sub>2</sub>	CO, 2H <sub>2</sub> O	-519
CH <sub>3</sub> OH	CO, 2H <sub>2</sub>	89.2
CH <sub>3</sub> OH, (1/2)O <sub>2</sub>	CO <sub>2</sub> , 2H <sub>2</sub>	-152
CH <sub>3</sub> OH, (3/2)O <sub>2</sub>	CO <sub>2</sub> , 2H <sub>2</sub> O	-677
C <sub>8</sub> H <sub>18</sub> (gasoline), 4O <sub>2</sub>	8CO, 9H <sub>2</sub>	-659.9
C <sub>8</sub> H <sub>18</sub> , 12.5O <sub>2</sub>	8CO <sub>2</sub> , 9H <sub>2</sub> O	-5100.2

Table 3  
Heats of reaction corresponding to the steam reforming (SR) of different fuels

Feed	Products	$\Delta H_{298}^{\circ}$ (kJ/mol)
CH <sub>4</sub> , H <sub>2</sub> O	CO, 3H <sub>2</sub>	206.2
CH <sub>4</sub> , 2H <sub>2</sub> O	CO <sub>2</sub> , 4H <sub>2</sub>	165.1
CH <sub>4</sub> , CO <sub>2</sub>	2CO, 2H <sub>2</sub>	274
CH <sub>3</sub> OH, H <sub>2</sub> O	CO <sub>2</sub> , 3H <sub>2</sub>	49.6
C <sub>2</sub> H <sub>6</sub> , 2H <sub>2</sub> O	2CO, 5H <sub>2</sub>	347.3
C <sub>2</sub> H <sub>5</sub> OH, H <sub>2</sub> O	2CO, 4H <sub>2</sub>	255.8
C <sub>2</sub> H <sub>5</sub> OH, 3H <sub>2</sub> O	2CO <sub>2</sub> , 6H <sub>2</sub>	173.4
C <sub>2</sub> H <sub>5</sub> OH, CO <sub>2</sub>	3CO, 3H <sub>2</sub>	297
C <sub>3</sub> H <sub>8</sub> , 3H <sub>2</sub> O	3CO, 7H <sub>2</sub>	497.7
C <sub>8</sub> H <sub>18</sub> , 8H <sub>2</sub> O	8CO, 17H <sub>2</sub>	1247.8
C <sub>8</sub> H <sub>18</sub> , 8CO <sub>2</sub>	16CO, 9H <sub>2</sub>	1604

the past few years, classified in to gaseous hydrocarbons, liquid hydrocarbons and oxygenated hydrocarbons.

### 3. Reforming of light hydrocarbons

Syngas (CO + H<sub>2</sub>) production via the reforming of lighter hydrocarbons such as natural gas, methane, ethane, propane, etc. is well studied and there have been a number of studies involving catalytic improvements such as the effect of additives, catalyst modifiers and promoters are discussed below. A review based on theoretical and experimental studies was discussed in the past [8,17,18].

#### 3.1. Methane

Carbon dioxide reforming of gaseous hydrocarbons has been a popular method for syngas production and a number of catalytic systems involving both precious and non-noble metals have been investigated. The reaction behavior and carbon deposition during the CO<sub>2</sub> reforming of methane was investigated over Al<sub>2</sub>O<sub>3</sub>-supported Co catalysts as a function of metal loading (6–9 wt.%) and calcination temperature (500–1000 °C). It was found that the stability of these catalysts was strongly dependent on the Co loading and calcination temperature [19]. Stable activities were found when a balance between carbon formation and its oxidation could be achieved.

Modification of cobalt catalysts supported on different metal oxides by additives such as alkaline-earth metal oxides and noble metals such as Pt, Ni and Ru showed a major improvement on the catalytic stability by decreasing both the metal oxidation and coke deposition [20–22] during dry reforming of methane.

Table 4  
Heats of reaction corresponding to the autothermal reforming (ATR) of different fuels

Feed	Products	$\Delta H_{298}^{\circ}$ (kJ/mol)
CH <sub>4</sub> , $x/2O_2$ , $(1-x)H_2O$	CO, $(3-x)H_2$	$206.2 - 241.8 \times x$
C <sub>8</sub> H <sub>18</sub> , $xO_2$ , $(16-2x)H_2O$	8CO <sub>2</sub> , $(25-2x)H_2$	$165.8 - 572 \times x$
CH <sub>3</sub> OH, $xO_2$ , $(1-2x)H_2O$	CO <sub>2</sub> , $(3-2x)H_2$	$131 - 572 \times x$
C <sub>2</sub> H <sub>5</sub> OH, 0.61O <sub>2</sub> , 1.8H <sub>2</sub> O	2CO <sub>2</sub> , 4.784H <sub>2</sub>	0
C <sub>n</sub> H <sub>m</sub> O <sub>o</sub> , $xO_2$ , $(2n-2x-o)H_2O$	$nCO_2$ , $(2n-2x-o+m/2)H_2$	$n\Delta H_{f,CO_2} - (2n-2x-o), \Delta H_{f,H_2O} - \Delta H_{f,fuel}$

Unsupported and supported molybdenum carbide catalysts (5–40 wt.% Mo<sub>2</sub>C) were also utilized in the dry and steam methane reforming reactions that showed similar performance as that of precious group metal catalysts [23]. A strong electronic interaction between molybdenum carbide and zirconia support was attributed to the improved activity and stability of these catalysts [23–25]. Over supported catalysts, CO<sub>2</sub> activation would take place at the vicinity of Mo<sub>2</sub>C and ZrO<sub>2</sub>, and the chance for oxidation of carbide may decrease. Also the rate determining step would be the dissociation of methane, the chance of polymerization of inactive carbon may also decrease. These are the reasons that the supported catalysts are more stable and durable for dry reforming reaction [23]. Most of these reactions were reported at relatively higher temperatures (>900 °C) and lower space-velocities (5000–10000 h<sup>-1</sup>) compared to other catalytic systems.

Effect of promoters such as Cu, La, Mo, Ca, Ce, Y, K, Cr, Mg, Mn, Sn, V, Rh, Pd and their combinations was investigated for improving the stability of Ni catalysts supported on alumina for methane reforming using a combination of CO<sub>2</sub> and/or steam and/or O<sub>2</sub>. All these promoters were reported to show a positive effect on the activity and stability of nickel catalysts either by decreasing the metal sintering and/or coke deposition or by increasing the metal dispersion resulting in an intimate contact between the reacting gases and metal/support of the catalyst [26–44].

Platinum and rhodium based catalysts supported on alumina promoted by an oxygen ion conducting promoter such as ceria or zirconia was also reported to improve the catalytic activity and stability for dry reforming of methane in the temperature range of 500–850 °C. The activity enhancement was ascribed to the high dispersion of zero-valent metal resulting in an increased metal–support interface area and increased oxygen mobility [45–50].

The catalytic activity of Ni supported on clinoptilolite with varying Ni loadings was studied and the results showed that at 700 °C, 8 wt.% Ni/clinoptilolite gave the highest activity during dry reforming of methane with remarkable stability of >100 h [44].

Steam reforming of methane on supported nickel catalysts with different promoters has been studied by many workers [51–54]. Some additives such as ceria have been reported as effective in suppressing carbon deposition during methane, ethane and propane steam reforming [55,56]. For example, alkaline earth oxides were added to reduce carbon deposition [57]. Effects of supports such as silica, alumina, and zirconia for nickel

catalysts have been studied in steam reforming of methane at low temperatures, 500 °C compared to the usual conditions of above 700 °C. Decomposition of methane on nickel surface is believed as a first step of the steam reforming of methane; then the carbon species formed on the surface react subsequently with steam or surface oxygen species. It was shown that zirconium oxide, which can absorb water at 500 °C, is an effective support and surface hydroxyl groups contribute significantly to the steam reforming at 500 °C [58].

Oha et al. have proposed a highly active Ni/Ce–ZrO<sub>2</sub>/θ-Al<sub>2</sub>O<sub>3</sub>, catalyst for on-site H<sub>2</sub> generation by steam methane reforming to address the catalyst deactivation at higher temperatures. This catalyst showed stable activity for more than 250 h and the study on the effect of operating conditions during the reactor start up revealed that higher alumina content in the catalyst in presence of excess steam can lead to the formation of inactive NiAl<sub>2</sub>O<sub>4</sub> phase [59].

### 3.2. Ethane, propane and butane

PGM catalysts for steam reforming of methane, propane and butane were reported by a number of researchers and the main components in the catalyst involved Pt, Ni, Pd, Rh and several combinations in a bimetallic (e.g. Pt–Ni) and trimetallic phase (e.g. Pt–Pd–Rh). These catalysts were supported on an alumina phase promoted by an oxygen ion conductor like ceria and coke suppressants such as magnesium, calcium or potassium. The main factor for improved performance in all the cases was the presence of a synergistic interaction between metallic sites [60–62].

The addition of oxygen in the steam reforming reaction of gaseous hydrocarbons (methane, ethane, propane, LPG, butane) was also explored in several investigative studies. The amount of oxygen was controlled in order to make the reaction self sustaining as in the case of autothermal reaction. Other methods involved combining steam, oxygen and carbon dioxide in various proportions for reforming the lighter hydrocarbons (tri-reforming). The main component in the oxidative reforming reactions was nickel promoted by small quantities of noble metals such as Pt, Pd, Ir, Rh, and Ru. Similar to the other catalytic systems discussed above, solid solutions of ZrO<sub>2</sub> or alumina with alkaline earth oxide and/or rare earth oxide were utilized in the autothermal reaction to enhance the overall stability and activity [63–68]. Most of the proposed catalysts showed the highest selectivity to hydrogen relative to the fuel converted at temperatures above 700 °C.

Jing et al. have reported the usage of SrO (10 wt.%) promoted Ni/SiO<sub>2</sub> catalyst for combined partial oxidation and dry reforming of methane and ethane for enhanced activity and stability against sintering and coking attributed to a metal–support interaction (SMSI) [69]. Similar catalytic studies were also reported on a Rh catalyst supported on a Mg–Al mixed metal oxide. Based on this study, a novel and sufficiently general concept for fabricating mono- and multi-component heterogeneous catalysts for various reactions catalyzed by metals and/or metal oxides supported on Mg–Al mixed oxide was proposed. Also, it was shown that amount of metal could be lowered from 2.0 to 0.1% of the

weight of support which was resistant to coke formation at stoichiometric steam/carbon ratio of 1 for over 14 h time-on-stream with no sign of deactivation or decrease in catalytic activity or in selectivity to syngas product [70].

Attention has been increasingly paid to the partial oxidation (POX) of lower alkanes to synthesis gas, due to its intrinsic energy saving process. The partial oxidation of ethane (POE) on Co loaded on various supports was recently reported and the performance varied as follows: Y<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, ZrO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub> ≥ SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> > MgO. CeO<sub>2</sub> was the most preferable support and the mechanism included combustion of ethane to H<sub>2</sub>O and CO<sub>2</sub> and subsequent reforming of ethane with H<sub>2</sub>O and CO<sub>2</sub> to synthesis gas [71].

## 4. Reforming of higher hydrocarbons

Krumplet et al. have reviewed the development of new reforming catalysts. Accordingly, they have developed many reforming catalysts supported on an oxide-ion-conducting substrate (Ce, Zr, La) doped with non-reducible element (Gd, Sm, etc.). Also reported was the activity of different transition metals (Fe, Cu, Co, Ag, Ru, Ni, Pt, Pd, Rh) [72] for converting *iso*-octane in to hydrogen rich products. All metals exhibited 100% conversion above 700 °C at conditions of O/C = 0.46 (oxygen-to-*iso*-octane molar ratio of 3.7), H<sub>2</sub>O/C = 1.14, and GHSV = 3000 h<sup>-1</sup>. Below 600 °C, conversion drops more swiftly for first-row transition metals (particularly Ni and Co) than for second-row (Ru) and third-row (Pt, Pd). The second and third-row transition metals exhibit a higher H<sub>2</sub> selectivity (>60%) than the first-row transition metals at temperatures above 650 °C.

The contribution of lattice oxide ion has been reported for the oxidation reactions over metal oxide catalysts. Migration of oxide ion is recognized through diffusion depending on the defect structure of metal oxide catalyst. The theory of oxygen bank function including migration of oxide ion through bulk diffusion has been shown to improve the catalytic activity and stability [73].

Hydrogen supply to a PEFC by reforming kerosene fuel has been investigated and reported by Fukunaga et al. [74]. They have developed a kerosene fuel processing system involving a Ni-based sulfur adsorbent (lifetime > 4000 h) and a proprietary reforming catalyst with a catalyst life of about 12,000 h at the conditions of outlet temperature: 730 °C; S/C molar ratio: 3; LHSV: 0.5 h<sup>-1</sup>.

The application of ceria based catalysts for steam reforming a range of hydrocarbons (C<sub>1</sub>, C<sub>2</sub>, *n*-C<sub>4</sub>, *n*-C<sub>6</sub>, *n*-C<sub>8</sub>, dimethyl hexane, cyclohexane, benzene, and toluene) has been reported by Wang and Gorte [75], accordingly, ceria supported precious metals showed superior performance for steam reforming of liquid fuels, compared to the ones supported on alumina. Similar results have been reported for Pt based catalysts loaded on ceria and alumina [16]. The transfer of oxygen from the ceria support to metal has been shown to catalyze oxidation, steam reforming and improve the water–gas shift (WGS) activities of the supported catalyst. It was also proposed that a ceria–zirconia mixed oxide may offer much higher activity compared to

ceria alone, possibly due to a higher reducibility of the mixed oxide [76].

A catalyst deactivation model has been developed and reported based on a nickel catalyst for steam reforming of higher hydrocarbons in a circulating fluidized bed membrane reformer with and without hydrogen selective membranes. An engineered control approach with in-site control for carbon deposition free region with a minimum/critical steam-to-carbon (S/C) ratio during heptane steam reforming has been proposed. The overall mathematical model included random carbon deposition and catalyst deactivation models [77]. Simulations showed that heptane tends to form carbon (deposition) at S/C ratios below 1.4 at operating temperatures above 700 K agreeing well with the experimental data [78] and the proposed model shows promise for designing other reformers.

Wang et al. have recently developed and reported novel catalysts for liquid hydrocarbon (heptane) steam reforming which showed much higher activities, resistance against coking and sulfur poisoning compared to the traditional Ni/Al<sub>2</sub>O<sub>3</sub> catalysts. The use of zeolites, particularly cerium doped ZSM-5 as the catalyst support instead of alumina showed great improvement in the activity and sulfur tolerance of nickel catalyst. Addition of a second metal (Co, Mo, Re, Pd) to the Ni–alumina catalyst also resulted in better activity and stability at much lower operating temperatures [79–81]. Similarly, Ming et al. of Innovatek have also proposed a novel catalyst for steam reforming various hydrocarbons such as natural gas, *iso*-octane, retail gasoline, and hexadecane. Their proprietary catalyst showed great stability in presence of significant amounts of sulfur and also no carbon deposition or coking. A variant of this catalyst also resulted in total CO concentrations less than 1% during the tests for water–gas shift reaction [82].

The performance of bimetallic catalysts based on noble metals for autothermal reforming of synthetic diesel and JP8 fuel has been presented. Accordingly, it was deduced that the addition of a second metal such as Pd, Ni not only improves the activity of Pt–ceria catalysts, but also provides high resistance to deactivation due to sulfur poisoning at the conditions of H<sub>2</sub>O/O<sub>2</sub>/C molar ratio of 2.5/0.5/1, reactor temperature of 400 °C, and GHSV of 17000 h<sup>-1</sup>. Characterization of these formulations showed that the enhanced stability is due to a strong metal–metal and metal–support interaction in the catalyst. The improved performance of these bimetallic catalysts was attributed to structural and electronic effects rather than the degree of metal dispersion [16].

The partial oxidation reforming of *iso*-octane was performed over a Ni-based catalyst supported on MgO/Al<sub>2</sub>O<sub>3</sub>. It was reported that a Ni/M/MgO/Al<sub>2</sub>O<sub>3</sub> catalyst was more active than the other catalyst formulations in the POX-reforming of *iso*-octane, particularly, Ni/Fe/MgO/Al<sub>2</sub>O<sub>3</sub> catalyst showed enhanced sulfur tolerance over the commercial ICI catalyst [83] at a reaction temperature of 700 °C, space velocity = 8776 h<sup>-1</sup>, feed molar ratios of H<sub>2</sub>O/C = 3 and O/C = 1. It was also recommended that the modified Ni/(Co,Fe)/MgO/Al<sub>2</sub>O<sub>3</sub> system may be used as a substitute to the commercial reforming catalyst for fuel cell-powered vehicles. XRD characterization showed the crystal structures of NiO, MgAl<sub>2</sub>O<sub>4</sub> and FeAl<sub>2</sub>O<sub>4</sub> in their cata-

lyst; however, no reasons were suggested for the improvement in the activity of these catalysts.

Other bimetallic catalysts that were tested for *iso*-octane reforming included Ni–W, Ni–Mn and Rh–Ce supported on alumina mesh for generation of hydrogen-rich gas [84]. This study utilized a novel spray-pulse reactor with hybrid plasma-catalytic systems [85]. The Rh–Ce catalyst exhibited the highest activity, as compared to Ni–Mn and Ni–W. The alternate wet and dry conditions created on the catalyst using pulse spray feed of *iso*-octane at 600 °C yielded twice the amount of hydrogen compared to the continuous liquid feed condition. This improvement is very important considering the fact that the steam to carbon ratio used in their study was close to stoichiometry.

Steam reforming of gasoline to produce hydrogen was studied by employing nickel based catalysts to inhibit the catalyst deactivation while controlling the selectivity to form CO<sub>2</sub> as opposed to CO. The alumina based Ni catalyst was modified by a second metal (Mo, Re) and the CO<sub>2</sub> selectivity improved vastly on Ni–Re/Al<sub>2</sub>O<sub>3</sub> by coupling the WGS reaction with SR. The multifunctional Ni–Re catalyst also showed good tolerance to sulfur poison compared to Ni–Mo catalyst, this unique role was attributed to the formation of Ni–Re alloy during the synthesis and the sulfur tolerance due to the formation of S–Re binds. It was also reported that the addition of ZSM-5 also enhanced the performance of these catalysts [86]. Autothermal reforming of gasoline to produce hydrogen was extensively studied using different metals and supports utilizing perovskites [87].

Reforming of diesel oil in supercritical water using commercial Ni-based catalysts for fuel cell applications has been studied and reported. This process was showed to generate hydrogen at temperatures lower than the conventional industrial reforming processes [88]. Steam reforming [89] and autothermal reforming [90,91] of diesel fuel on precious group metal based catalysts was reported by a number of researchers and it was shown that oxygen–ion conducting support shows superior performance compared to alumina. JP8 and synthetic diesel reforming for applications in both SOFC and PEFC was reported more recently [92–95].

The activity, durability and hydrogen selectivity of alumina-supported nickel or platinum catalysts doped with a thermal stabilizer and activity promoter, such as lanthanum and cerium oxide, respectively, were studied [94]. The participation of lanthanum in the reaction was attributed to the improved performance of Pt-based catalysts. Conversely, in the case of Ni-based catalysts, a lower carbon deposition and a higher thermal stability of metallic Ni particles under reaction conditions were observed for catalyst using Ce–La-modified alumina as support [94].

The investigation on the application of non-precious group metal based catalysts for hydrocarbon reforming has gained some momentum in the past few years because of obvious reasons. Along these lines, the usage of group VI metal carbides in reforming a range of hydrocarbons was successfully demonstrated [96–99]. Bulk molybdenum carbide catalysts were used for steam and/or oxygen reforming of higher hydrocarbons such as gasoline and diesel for hydrogen generation in fuel cell applications, without the necessity of employing a pre-reforming step.

In contrast with noble metal and Ni based catalysts, much lower steam/carbon ratios were used and the catalyst showed a stable performance over the time period tested [98–101].

## 5. Reforming of oxygenated hydrocarbons

### 5.1. Methanol

Methanol as a hydrogen carrier has received attention due to its advantages over hydrocarbons and ethanol, such as high hydrogen-to-carbon ratio, molecular simplicity (no C–C bond), relatively low reforming temperatures (250–350 °C) due to its low energy chemical bond, and low sulfur content (<0.5 ppm).

Hydrogen production by steam reforming of methanol has been successfully demonstrated and a large variety of catalysts have been reported to be active for methanol steam reforming. The majority of these have been copper-based [102–105]. The use of CeO<sub>2</sub>-based catalysts has shown a rapid increase in the past few years. CeO<sub>2</sub> has the cubic fluorite structure and foreign cations, such as Si<sup>4+</sup>, Th<sup>4+</sup>, Zr<sup>4+</sup>, Y<sup>3+</sup>, La<sup>3+</sup>, Sc<sup>3+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup> and Cu<sup>2+</sup> can be introduced into the CeO<sub>2</sub> lattice and can improve the physical properties of the CeO<sub>2</sub> [106]. A high oxygen mobility [107], strong interaction with the supported metal (SMSI) [108] render the CeO<sub>2</sub>-based materials very interesting for catalysis and as a support.

Commercial copper-containing water–gas shift and methanol synthesis catalysts [109,110] have also been found to be active for methanol reforming. Shishido et al. have proposed a homogeneous precipitation method by urea hydrolysis for the preparation of active Cu/ZnO and Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts. The high activity of these catalysts was attributed to highly dispersed Cu metal particles with high accessibility to methanol and steam [111]. Similarly, a Cu/ZrO<sub>2</sub> catalyst prepared by an oxalate gel-coprecipitation method was claimed to be highly active and stable in the methanol steam reforming reaction as compared to the catalysts prepared by conventional aqueous-coprecipitation and impregnation methods [112].

The effect of promoters on the activity of alumina and/or ZnO catalysts was thoroughly investigated for applications in low temperature fuel cells. Of all the promoters tested (Cr, Zr, Zn, Fe) the addition of Zr, Zn was able to enhance the overall activity and stability of copper based catalysts. It was shown that the ZrO<sub>2</sub>-promoter can lower Al content on the surface of catalyst in effect, and weaken the interaction between CuO and Al<sub>2</sub>O<sub>3</sub> so as to avoid the generation of CuAl<sub>2</sub>O<sub>4</sub> spinel-type compound [113–115].

A new form of copper crystals were synthesized and reported for methanol steam reforming reactions. Accordingly, alloy catalysts were prepared by leaching various structures of Al–Cu–Fe alloys (quasi-crystal, beta- or theta-phase) in NaOH and Na<sub>2</sub>CO<sub>3</sub> aqueous solutions. At high temperatures (e.g., 360 °C), the catalytic activity of the quasi-crystal catalyst for the methanol steam reforming was much higher than that of other phase catalysts. It was proposed that the high catalytic activity and the excellent thermal stability of copper particles on quasi-crystal catalyst were due to the immiscibility of Fe with Cu and the interaction with quasi-crystal surface [116].

A laser based method for photo-catalytic reforming/transformation of methanol at ambient temperature using n-type WO<sub>3</sub> semiconductor catalyst and a p-type NiO catalyst has been investigated and reported [117]. A non-explosive mixture of gases containing hydrogen, carbon monoxide and methane with high concentration of hydrogen was produced. This method proved to be an efficient process for generation of hydrogen [117,118].

Supported Pt and Pd based catalysts promoted by zinc, Ru, and TiO<sub>2</sub> were also reported for steam reforming of methanol [119–122]. The improved activity and selectivity were attributed to the occurrence of SMSI and/or an alloy formation, respectively.

Oxygen assisted steam reforming of methanol was also conducted on different supported catalysts. The promoting effect of ceria on a copper oxide catalyst prepared via different methods was reported. The formation of a solid solution in the Ce<sub>0.9</sub>Cu<sub>0.1</sub>O<sub>Y</sub> prepared by complexation–combustion (cc) method resulted in a better performance compared to others. The incorporation of Cu atoms into CeO<sub>2</sub> lattice lead to an increase of oxygen vacancy and the analytical results indicated that the Cu<sup>+</sup> is the main Cu species for the Ce<sub>0.9</sub>Cu<sub>0.1</sub>O<sub>Y</sub>-cc sample and the synergistic function between Cu<sup>2+</sup>/Cu<sup>+</sup> and Ce<sup>4+</sup>/Ce<sup>3+</sup> occurred in the red-ox cycle [123].

Catalytic performances of Pd/ZnO in oxidative methanol reforming reaction were studied as a function of Pd loading and dopant effect. It was confirmed that the formation of Pd–Zn alloy is essential to the selective production of hydrogen. Cr, Fe or Cu addition into Pd/ZnO was shown to increase the selectivity to hydrogen production by decreasing CO formation [124,125].

The steam reforming of methanol has been thoroughly studied in the past decade as discussed above, but the main drawback is its relatively high toxicity. In contrast, ethanol is less toxic and could be considered a renewable fuel capable of being produced from biomass. Besides this, it does not contribute to the increase of the greenhouse effect since the steam reforming of ethanol releases the same amount of CO<sub>2</sub> as that absorbed by the biomass. Haga et al. [126] had studied the catalytic properties of Ti, Zr, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Sb, Ru, Pt or Rh, supported on Al<sub>2</sub>O<sub>3</sub> for ethanol steam reforming at 400 °C, and concluded that Co/Al<sub>2</sub>O<sub>3</sub> catalyst showed more selectivity for the overall reaction. Supported cobalt catalysts for ethanol steam reforming have been reported by a number of researchers. Cobalt-loaded (1%) catalysts were prepared by impregnation on MgO,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>, ZnO, La<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, and Sm<sub>2</sub>O<sub>3</sub>. Ethanol steam reforming occurred to a large degree over ZnO, La<sub>2</sub>O<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub>, and CeO<sub>2</sub>-supported catalysts; depending on the support, different cobalt-based phases were identified: metallic cobalt particles, Co<sub>2</sub>C, CoO, and La<sub>2</sub>CoO<sub>4</sub>. ZnO-supported samples showed the best catalytic performance with a hydrogen selectivity up to 73.8% [127]. The addition of sodium to the ZnO supported Co catalyst showed a positive effect resulting in higher hydrogen yield and stabilization of the catalysts toward deactivation by lowering the carbon deposition [128]. Higher cobalt loading (8 and 18%) on Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> also yielded very high conversions and H<sub>2</sub> selectivities during ethanol steam reforming at relatively lower temperatures (400 °C) [129,130].

## 5.2. Ethanol

Reforming of ethanol in presence of steam and/or oxygen has been a general practice for hydrogen production. Nickel based catalysts supported on  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{La}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{Y}_2\text{O}_3$  and YSZ with additions of Cu, Cr, Zn, Na or K have been investigated for ethanol reforming reactions [131–133]. It is generally accepted that Ni promotes C–C bond scission whereas the additives like Cr, Cu are the active agents for subsequent methanol oxidation to produce CO and  $\text{H}_2$ . It was shown that the catalysts  $\text{Ni}/\text{Y}_2\text{O}_3$  and  $\text{Ni}/\text{La}_2\text{O}_3$  exhibit relative high activity for ethanol steam reforming at  $250^\circ\text{C}$  with a conversion of ethanol of 81.9 and 80.7%, and a selectivity of hydrogen of 43.1 and 49.5%, respectively. When temperature reached  $320^\circ\text{C}$ , the conversion of ethanol increased to 93.1 and 99.5% and the selectivity of hydrogen was 53.2 and 48.5%, respectively. This was attributed to the scavenging of coke deposition on the Ni surface by lanthanum oxycarbonate species existing on top of the Ni particles [134,135]. The effect of alkali addition (Li, Na, K) on nickel catalysts supported on basic carriers such as  $\text{MgO}$  as opposed to acidic carriers was also investigated. In a more recent study, it was found that Li and Na promote the NiO reduction but negatively affect the dispersion of the Ni/ $\text{MgO}$  catalyst, whereas K does not significantly affect either morphology or dispersion. Li and K enhance the stability of Ni/ $\text{MgO}$  mainly by depressing Ni sintering. Coke formation on bare and doped catalysts occurs but with orders of magnitude lower than those claimed for Ni supported on an acidic carrier. Coke formation is strongly suppressed due to the benefits induced by the use of basic carrier which positively modify the electronic properties of supported Ni [136–138].

The catalytic performance of supported noble metal catalysts for the steam reforming (SR) and oxidative steam reforming (OSR) of ethanol has been investigated in the temperature range of  $600\text{--}850^\circ\text{C}$  with respect to the nature of the active metallic phase (Rh, Ru, Pt, Pd, Ni), the nature of the support ( $\text{Al}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{MgO}$ ,  $\text{TiO}_2$ ) and the metal loading (0–5 wt.%) [139–141]. It was shown that the alumina-supported catalysts are very active at lower temperature for the dehydration of ethanol to ethene which, at higher temperatures, is converted in to  $\text{H}_2$ , CO, and  $\text{CO}_2$  as the major products and  $\text{CH}_4$  as a minor product. The order of activity of the metals was  $\text{Rh} \geq \text{Ru} > \text{Pd} > \text{Ni} = \text{Pt}$ , and for low-loaded catalysts, Rh is significantly more active and selective toward hydrogen formation compared to Ru, Pt and Pd, which show a similar behavior [142,143]. The catalytic performance of Rh and, particularly, Ru is significantly improved with increasing metal loading, leading to higher ethanol conversions and hydrogen selectivities at given reaction temperatures. With ceria/zirconia-supported catalysts, the formation of ethene is not observed and the order of activity at higher temperatures is  $\text{Pt} \geq \text{Rh} > \text{Pd}$ . By using combinations of a ceria/zirconia-supported metal catalyst with the alumina support it was shown that the formation of ethene does not inhibit the steam reforming reaction at higher temperatures [144,145]. It was concluded that the support plays a significant role in the steam reforming of ethanol and that the metal-ceria interaction affects the adsorption–decomposition of ethanol to  $\text{CH}_4$

and CO products and their subsequent reforming reactions with steam.

## 5.3. Dimethyl ether

Dimethyl ether (DME) is a liquid fuel similar to LNG and LPG and has high H/C ratio comparable to methanol and non-corrosive and innocuous nature unlike methanol [146] and can be reformed at lower temperatures than hydrocarbons. Synthesis of DME from syngas has been reported by many researchers, particularly, DME derived from regenerable resources, e.g. biomass, will impact on emission of  $\text{CO}_2$  and contribute to realization of a sustainable society [146–151]. Cu-based spinel-type oxides have been reported for steam reforming of DME. Addition of  $\text{Al}_2\text{O}_3$  to Cu catalysts improved DME conversion since hydrolysis of DME was promoted over acid-sites on  $\text{Al}_2\text{O}_3$ . Higher catalytic activity was shown over the composite of  $\text{Al}_2\text{O}_3$  and Cu–Mn, or Cu–Fe, or Cu–Cr oxide than that of  $\text{Al}_2\text{O}_3$  and Cu/ZnO/ $\text{Al}_2\text{O}_3$ . Cu–Fe and Cu–Mn catalysts demonstrated high activity for methanol steam reforming, which was ascribed to high performance for DME steam reforming. It was shown that the selectivity towards hydrogen and  $\text{CO}_2$  could be easily controlled by optimizing the ratio of Cu/Fe/Mn and that of  $\text{Al}_2\text{O}_3$  [152,153].

The effects of various supports on the catalytic activity of  $\text{Ga}_2\text{O}_3$  for the steam reforming of DME have been reported. Among the various supported catalysts tested,  $\text{Ga}_2\text{O}_3/\text{TiO}_2$  was reported as having the highest DME steam reforming activity in terms of conversion and  $\text{H}_2$  yield ascribed to an electronic interaction between  $\text{Ga}_2\text{O}_3$  and  $\text{TiO}_2$  [154].

A research group at university of wisconsin has recently demonstrated a novel process for generating hydrogen from biomass-derived oxygenated compounds such as methanol, ethylene glycol, glycerol, sugars and sugar–alcohols [155]. Unlike reforming for producing hydrogen from non-renewable petroleum feedstocks, the aqueous-phase carbohydrate reforming (ACR) of renewable biomass resources does not increase the levels of atmospheric carbon dioxide. In addition, ACR reactions take place at substantially lower temperatures (e.g. 500 K) than conventional alkane reforming processes (e.g. 900 K), which minimizes undesirable decomposition reactions typically encountered at elevated temperatures. According to their study, it was observed that the overall catalytic activity (based on  $\text{CO}_2$  rate) for ethylene glycol reforming decreases in the following order for silica-supported metals:  $\text{Pt} \sim \text{Ni} > \text{Ru} > \text{Rh} \sim \text{Pd} > \text{Ir}$ . Silica supported Rh, Ru and Ni showed a low selectivity for production of  $\text{H}_2$  compared to alkane production at 498 K, whereas, Pt and Pd catalysts exhibited relatively high selectivities for  $\text{H}_2$ . They have later proposed a Pt/ $\text{Al}_2\text{O}_3$  and Sn modified Ni catalyst for the same reaction [156,157], which showed similar reactivity for APR of methanol and ethylene glycol at consistent C/ $\text{H}_2\text{O}$  feed ratios, indicating that C–C bond cleavage is not rate limiting for ethylene glycol reforming.

As part of the development of biomass based hydrogen economy, some researchers have focused on reforming phenol type compounds for hydrogen production in fuel cell applications. Some of the promising candidates include  $\text{MgO}$  and/or Ce–Zr–O

Table 5  
Components of a preferable catalytic system depending on reforming process and hydrogen source

1st metal	2nd metal	Support/carrier/substrate	Promoter	Reforming reaction	H <sub>2</sub> source
Co, Ru, Pt, Pd, Rh	–	Al <sub>2</sub> O <sub>3</sub>	Rare earth oxide, ZrO <sub>2</sub> , IIA oxides	Dry, SR, OSR	Gaseous hydrocarbons: C <sub>1</sub> –C <sub>4</sub>
Ni, Pt, Ru, Pd, Rh	Co, Mo, Re	CeO <sub>2</sub> , La <sub>2</sub> O <sub>3</sub> , ZrO <sub>2</sub> , Ce doped ZSM5, Ce/Zr/La doped Al <sub>2</sub> O <sub>3</sub>	Gd, Sm	All reforming reactions	C <sub>8</sub> –C <sub>18</sub>
Cu	Co	CeO <sub>2</sub> , ZrO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub>	ZnO, ZrO <sub>2</sub>	SR	Methanol
Pt, Pd, Ni	Ru, Cr, Cu, Fe	TiO <sub>2</sub> , ZnO, La <sub>2</sub> O <sub>3</sub> , MgO	Li, Na, K	SR, OSR	Ethanol

sol–gel supported Rh and Fe catalysts. It was shown that the steam reforming of phenol reaction is favored over small Rh particles and depends on support chemical composition, steam concentration and reaction temperature. However, more than one kind of carbonaceous species was found to accumulate on the Rh/Ce–Zr–O (sol–gel) catalyst, which was later modified by adding MgO that altered the surface acidity and basicity, thus influencing the hydrogen activity and selectivity of the reaction [158–160].

## 6. Conclusions

Based on the observations from the advances in the reforming catalyst research over the past few years, the authors would like to propose most preferable components for a catalytic system. The first four columns of Table 5 represent the components of a catalyst depending up on the source of hydrogen. The role of a second metal and a promoter is to improve the overall performance of the catalyst by inhibiting the metal oxidation, coke deposition, metal sintering or to improve the dispersion for an improved gas–solid reaction.

Development and utilization of more efficient energy conversion devices are necessary for sustainable and environmentally friendly development in the 21st century. While the novel fuel reforming catalysts discussed in this paper incorporates several improvements over conventional ones, there are additional enhancements, which could increase performance.

There is still a demand to create energy-efficient and stable reforming catalyst and processing scheme, especially for sulfur bearing liquid hydrocarbons. Issues regarding catalyst coking and sulfur poisoning in true long-term studies (>2000 h of operation) need to be addressed.

Also, the development of cost-effective alternatives (group VI metal carbides, perovskites, hexaaluminates, etc.) to noble metal based catalysts needs to be investigated.

The application of semi-conductor processing technology in the catalyst development is relatively new and the synthesis of nano-metal catalysts by chemical vapor deposition combined with plasma/wet/dry etching or ion-implantation of impurities to modify the metal sites and bond energies of active sites could be a promising route. Similarly, the application of plasma enhanced reforming reactions in the fuel processor development needs to be further explored. At atmospheric gas pressure, catalytic processes may be induced by different plasma activation mech-

anisms. First of all the plasma may simply cause gas heating, vibrational excitation and dissociation of molecules. Due to electronic and ionic collision processes, dissociation of molecules and heating proceed much faster than in any conventional reactor/heat exchanger. Thus in a compact reactor near thermal degrees of dissociation may be achieved if a plasma with high specific input energy density is applied to the flowing gas. The plasma may generate intermediate species having a sufficiently long lifetime to induce reactions on a catalyst placed down the plasma reactor.

## References

- [1] B.D. McNutt, L.R. Johnson, Competing against entrenched technology: implications for U.S. government policies and fuel cell development, in: Presented at the Pre-Symposium Workshop of the Sixth Grove Fuel Cell Symposium, London, UK, 1999.
- [2] Freightlinertrucks Inc., News release, August 2003: [http://www.freightlinertrucks.com/about\\_us/press\\_room/press\\_release.asp?id=315](http://www.freightlinertrucks.com/about_us/press_room/press_release.asp?id=315).
- [3] Interconnection.biz, News release, January 2004: <http://www.interconnection.biz/carnews6136.asp>.
- [4] J. Larminie, A.L. Dicks, Fuel Cell Systems Explained, Wiley, New York, 2000, p. 308.
- [5] J.H. Hirschenhofer, D.B. Stauffer, R.R. Engleman, M.G. Klett, Fuel Cell Handbook, 4th ed., DOE/FETC-99/1076, US Department of Energy, Federal Energy Technology Center, Morgantown, WV, November 1998.
- [6] T.A. Semelsberger, L.F. Brown, R.L. Borup, M.A. Inbody, Int. J. Hydrogen Energ. 29 (2004) 1047–1064.
- [7] C. Song, Catal. Today 77 (2002) 17–49.
- [8] A.F. Ghenciu, Curr. Opin. Solid State Mater. Sci. 6 (2002) 389.
- [9] S. Wieland, F. Baumann, K.A. Startz, Proceedings of the Fuel Cell Seminar on New Catalysts for Autothermal Reforming of Gasoline and Water–Gas Shift Reaction, Portland, Oregon, 2000.
- [10] S. Ayabe, H. Omoto, T. Utaka, R. Kikuchi, K. Eguchi, Appl. Catal. A: Gen. 63 (2002) 1–9.
- [11] S. Ahmed, M. Krumplet, R. Kumar, S.H.D. Lee, J.D. Carter, R. Wilkenhoener, C. Marshall, Catalytic partial oxidation reforming of hydrocarbon fuels, in: Presented at the Fuel Cell Seminar, Palm Springs, CA, 1998.
- [12] D.J. Moon, K. Sreekumar, S.D. Lee, H.S. Kim, Appl. Catal. A: Gen. 215 (2001) 1.
- [13] P.K. Cheekatamarla, W.J. Thomson, Appl. Catal. A: Gen. 287 (2005) 176.
- [14] C. Pereira, J.M. Bae, S. Ahmed, M. Krumplet, Liquid Fuel reformer development: ATR of diesel fuel, in: Presented at the US Department of Energy, 2000 Hydrogen Program technical review, San Ramon, CA, 2000.
- [15] P.K. Cheekatamarla, A.M. Lane, J. Power Sources 152 (2005) 256.
- [16] P.K. Cheekatamarla, A.M. Lane, Int. J. Hydrogen Energ. 30 (2005) 1277.
- [17] M. Andersen, O. Lytken, J. Engbek, G. Nielsen, N. Schumacher, M. Johansson, I. Chorkendorff, Catal. Today 100 (2005) 191.
- [18] M. Krumplet, T.R. Krause, J.D. Carter, J.P. Kopasz, S. Ahmed, Catal. Today 77 (2002) 3.



- [19] E. Ruckenstein I, H.Y. Wang, J. Catal. 205 (2002) 289.
- [20] K. Nagaoka, K. Takanabe, K. Aika, Appl. Catal. A: Gen. 268 (2004) 151.
- [21] R. Bouarab, O. Akdim, A. Auroux, O. Cherifi, C. Mirodatos, Appl. Catal. A: Gen. 264 (2004) 161.
- [22] K. Nagaoka, K. Takanabe, K. Aika, Appl. Catal. A: Gen. 255 (2003) 13.
- [23] S. Naito, M. Tsuji, T. Miyao, Catal. Today 77 (2002) 161.
- [24] M.L. Pritchard, R.L. McCauley, B.N. Gallaher, W.J. Thomson, Appl. Catal. A: Gen. 275 (2004) 213.
- [25] A.R.S. Darujati, D.C. LaMont, W.J. Thomson, Appl. Catal. A: Gen. 253 (2003) 397.
- [26] J. Lee, E. Lee, O. Joo, K. Jung, Appl. Catal. A: Gen. 269 (2004) 1.
- [27] R. Martinez, E. Romero, C. Guimon, R. Bilbao, Appl. Catal. A: Gen. 274 (2004) 139.
- [28] T. Xiao, T. Suhartanto, A.P.E. York, J. Sloan, M.L.H. Green, Appl. Catal. A: Gen. 253 (2003) 225.
- [29] Z. Hou, O. Yokota, T. Tanaka, T. Yashima, Appl. Catal. A: Gen. 253 (2003) 381.
- [30] J.A.C. Dias, J.M. Assaf, Catal. Today 85 (2003) 59.
- [31] H. Roh, H.S. Potdara, K. Juna, J. Kim, Y. Oh, Appl. Catal. A: Gen. 276 (2004) 231.
- [32] J.B. Wang, L. Kuo, T. Huang, Appl. Catal. A: Gen. 249 (2003) 93.
- [33] H. Chen, C. Wang, C. Yu, L. Tseng, P. Liao, Catal. Today 97 (2004) 173.
- [34] J. Juan, M.C. Martinez, M.J. Gómez, Appl. Catal. A: Gen. 264 (2004) 169.
- [35] X.E. Verykios, Int. J. Hydrogen Energ. 28 (2003) 1045.
- [36] A. Shamsi, Appl. Catal. A: Gen. 277 (2004) 23.
- [37] J. Guo, H. Lou, H. Zhao, D. Chai, X. Zheng, Appl. Catal. A: Gen. 273 (2004) 75.
- [38] S. Seok, S. Choi, E. Park, S. Han, J. Lee, J. Catal. 209 (2002) 6.
- [39] C.E. Quincozes, S.P. Vargas, P. Grange, M. Gonzalez, Mater. Lett. 56 (2002) 698.
- [40] Z. Houa, O. Yokota, T. Tanakab, T. Yashima, Appl. Surf. Sci. 233 (2004) 58.
- [41] A. Valentini, V. Carreño, L. Fernando, P. Widor, E. Leite, E. Longo, Appl. Catal. A: Gen. 255 (2003) 211.
- [42] J.B. Wang, Y. Wu, T. Huang, Appl. Catal. A: Gen. 272 (2004) 289.
- [43] C. Resini, L. Arrighi, M. Delgado, Int. J. Hydrogen Energ. 31 (2006) 13.
- [44] W. Nimwattanukul, A. Luengnaruemitchai, S. Jitkarnka, Int. J. Hydrogen Energ. 31 (2006) 93.
- [45] S. Damyanova, J.M.C. Bueno, Appl. Catal. A: Gen. 253 (2003) 135.
- [46] L. Mo, J. Fei, C. Huang, X. Zheng, J. Mol. Catal. A: Chem. 193 (2003) 177.
- [47] M.M. Souza, M. Schmal, Appl. Catal. A: Gen. 255 (2003) 83.
- [48] Y. Chena, B. Liawb, W. Lai, Appl. Catal. A: Gen. 230 (2002) 73.
- [49] X.E. Verykios, Appl. Catal. A: Gen. 255 (2003) 101.
- [50] U.L. Portugal, A.C.S.F. Santos, S. Damyanova, C.M.P. Marques, J.M.C. Bueno, J. Mol. Catal. A: Chem. 184 (2002) 311.
- [51] Q. Zhang, Y. Li, B. Xu, Catal. Today 98 (2004) 601.
- [52] A. Effendi, Z. Zhang, K. Hellgardt, Catal. Today 77 (2002) 181.
- [53] T. Borowiecki, G. Giecko, M. Panczyk, Appl. Catal. A: Gen. 230 (2002) 85.
- [54] N. Laosiripojana, W. Sangtongkitcharoen, S. Assabumrungrat, Fuel 85 (2006) 323.
- [55] N. Laosiripojana, S. Assabumrungrat, J. Power Sources, in press (corrected proof, available online 28 November 2005).
- [56] R. Takahashi, S. Sato, T. Sodesawa, Appl. Catal. A: Gen. 273 (2004) 211.
- [57] T. Takeguchi, Y. Kani, T. Yano, J. Power Sources 112 (2002) 588.
- [58] Y. Matsumura, T. Nakamori, Appl. Catal. A: Gen. 258 (2004) 107.
- [59] Y. Oha, H. Roh, K. Jun, Int. J. Hydrogen Energ. 28 (2003) 1387.
- [60] Y. Wanga, Y.H. China, R.T. Rozmiarek, Catal. Today 98 (2004) 575.
- [61] G. Kolb, R. Zapf, V. Hessel, H. Lowe, Appl. Catal. A: Gen. 277 (2004) 155.
- [62] A.K. Avc, D.L. Trimm, A. Aksoylu, Z. Önsan, Appl. Catal. A: Gen. 258 (2004) 235.
- [63] T. Takeguchi, S. Furukawa, M. Inoue, K. Eguchi, Appl. Catal. A: Gen. 240 (2003) 223.
- [64] J.A.C. Dias, J.M. Assaf, J. Power Sources 130 (2004) 106.
- [65] B. Silberova, H.J. Venvik, J.C. Walmsley, A. Holmen, Catal. Today 100 (2005) 457.
- [66] M. Nurunnabi, Y. Mukainakano, S. Kado, Appl. Catal. A: Gen. 299 (2006) 145.
- [67] S. Cho, J. Park, W. Yoon, Catal. Commun. 7 (2006) 42.
- [68] V. Recupero, L. Pino, A. Vita, F. Cipiti, M. Cordaro, M. Laganà, Int. J. Hydrogen Energ. 30 (2005) 963.
- [69] Q. Jing, H. Lou, J. Fei, Z. Hou, X. Zheng, Int. J. Hydrogen Energ. 29 (2004) 1245.
- [70] N. Iwasaki, T. Miyake, E. Yagasaki, Catal. Today 111 (2006) 391.
- [71] A.I. Tsyganoka, M. Inaba, T. Tsunoda, K. Suzuki, K. Takehira, T. Hayakawa, Appl. Catal. A: Gen. 275 (2004) 149.
- [72] M. Krumplet, T.R. Krause, J.D. Carter, J.P. Kopasz, S. Ahmed, Catal. Today 77 (2002) 3.
- [73] Y. Moro-Ok, W. Ueda, K. Lee, J. Mol. Catal. A: Chem. 199 (2003) 139.
- [74] T. Fukunaga, H. Katsuno, H. Matsumoto, O. Takahashi, Y. Akai, Catal. Today 84 (2003) 197.
- [75] X. Wang, R.J. Gorte, Appl. Catal. A: Gen. 224 (2002) 209.
- [76] P. Fornasiero, G. Balducci, R. Di Monte, J. Kašpar, V. Sergo, G. Gubitosa, A. Ferrero, M. Graziani, J. Catal. 164 (1996) 173.
- [77] Z. Chen, Y. Yan, S. Elnashaie, Chem. Eng. Sci. 59 (2004) 1965.
- [78] R. Nielsen, J. Catal. 33 (1974) 184.
- [79] L. Wang, K. Murata1, M. Inaba, Appl. Catal. A: Gen. 257 (2004) 43.
- [80] J. Zhang, Y. Wang, R. Maa, D. Wu, Appl. Catal. A: Gen. 243 (2003) 251.
- [81] D.L. Trimm, A.A. Adesina, N.W. Cant, Catal. Today 93–95 (2004) 17.
- [82] Q. Ming, T. Healey, L. Allen, P. Irving, Catal. Today 77 (2002) 51.
- [83] D. Moon, J. Woo, S.D. Lee, B. Lee, B. Ahn, Appl. Catal. A: Gen. 272 (2004) 53.
- [84] R. Biniwalea, A. Mizunob, M. Ichikawa, Appl. Catal. A: Gen. 276 (2004) 169.
- [85] M.G. Sobacchi, A.V. Saveliev, A.A. Fridman, L.A. Kennedy, S. Ahmed, T. Krause, Int. J. Hydrogen Energ. 27 (2002) 635.
- [86] L. Wang, K. Murata, M. Inaba, Appl. Catal. B: Environ. 48 (2004) 243.
- [87] A. Qia, S. Wang, G. Fu, C. Ni, D. Wu, Appl. Catal. A: Gen. 281 (2005) 233.
- [88] K. Pinkwart, T. Bayh, W. Lutter, M. Krausa, J. Power Sources 136 (2004) 211.
- [89] J. Hu, Y. Wang, D. VanderWiel, Chem. Eng. J. 93 (2003) 55.
- [90] D. Liu, T.D. Kaun, H. Liao, S. Ahmed, Int. J. Hydrogen Energ. 29 (2004) 1035.
- [91] P.K. Cheekatamarla, A.M. Lane, J. Power Sources 152 (2005) 256.
- [92] GTI-led team to develop diesel/JP8 SOFC for Army, Fuel Cells Bulletin Volume 2004, issue 5, 2004, p. 6.
- [93] J. Hu, Y. Wang, D. VanderWiel, C. Chin, D. Palo, R. Rozmiarek, R. Dagle, J. Cao, J. Holladay, E. Baker, Chem. Eng. J. 93 (2003) 55.
- [94] R.M. Navarro, M.C. Álvarez-Galván, F. Rosa, J.L.G. Fierro, Appl. Catal. A: Gen. 297 (2006) 60.
- [95] P.K. Cheekatamarla, A.M. Lane, J. Power Sources 154 (2006) 223.
- [96] A.P.E. York, Chem. Commun. 1 (1997) 39.
- [97] S. Bej, C. Bennett, A. Christopher, L.T. Thompson, Appl. Catal. A: Gen. 250 (2003) 197.
- [98] J. Patt, D.J. Moon, C. Phillips, L.T. Thompson, Catal. Lett. 65 (2000) 193.
- [99] P.K. Cheekatamarla, W.J. Thomson, Appl. Catal. A: Gen. 287 (2005) 176.
- [100] P.K. Cheekatamarla, W.J. Thomson, Hydrogen generation from 2,2,4-trimethyl pentane reforming over molybdenum carbide at low steam-to-carbon ratios, J. Power Sources, in press.
- [101] P.K. Cheekatamarla, W.J. Thomson, J. Power Sources, in press (available online 18 October 2005).
- [102] Y. Liu, T. Hayakawa, K. Suzuki, S. Hamakawa, T. Tsunoda, Appl. Catal. A: Gen. 223 (2002) 137.
- [103] Y. Mena, H. Gnaser, R. Zapf, V. Hessel, C. Ziegler, G. Kolb, Appl. Catal. A: Gen. 277 (2004) 83.
- [104] H. Oguchi, T. Nishiguchi, T. Matsumoto, Appl. Catal. A: Gen. 281 (2005) 69.
- [105] C. Fukuhara, H. Ohkura, Y. Kamat, Appl. Catal.: A: Gen. 273 (2004) 125.
- [106] M. Pijolat, M. Prin, M. Soustelle, J. Chem. Soc.: Faraday Trans. 91 (1995) 3941.

- [107] P. Fornasiero, G. Balducci, R.D. Monte, J. Kaspar, V. Sergo, G. Gubitosa, A. Ferrero, M. Graziani, *J. Catal.* 164 (1996) 173.
- [108] L. Fan, K. Fujimoto, *J. Catal.* 172 (1997) 238.
- [109] D. Loffler, S.D. McDermott, C.N. Renn, *J. Power Sources* 114 (2003) 15.
- [110] C. Yao, L. Wang, Y. Liu, *Appl. Catal. A: Gen.* 297 (2006) 151.
- [111] T. Shishido, Y. Yamamoto, H. Moriok, *Appl. Catal. A: Gen.* 263 (2004) 249.
- [112] L. Fenga, D. Fa, L. Ming, *Int. J. Hydrogen Energ.* 29 (2004) 1617.
- [113] B. Lindström, L.J. Pettersson, P. Menon, *Appl. Catal. A: Gen.* 234 (2002) 111.
- [114] P.H. Matter, D.J. Braden, U.S. Ozkan, *J. Catal.* 223 (2004) 340.
- [115] B. Lindström, J. Agrell, L.J. Pettersson, *Chem. Eng. J.* 93 (2003) 91.
- [116] S. Kameoka, T. Tanabe, A. Tsai, *Catal. Today* 93 (2004) 23.
- [117] M.A. Gondal, A. Hameed, Z.H. Yamani, *J. Mol. Catal. A: Chem.* 222 (2004) 259.
- [118] A. Hameed, M.A. Gondal, *J. Mol. Catal. A: Chem.* 233 (2005) 35.
- [119] N. Iwasa, T. Mayanagi, W. Nomura, M. Arai, N. Takezawa, *Appl. Catal. A: Gen.* 248 (2003) 153.
- [120] T. Miyao, M. Yamauchi, S. Naito, *Catal. Today* 87 (2003) 227.
- [121] T. Miyao, M. Yamauchi, S. Naito, *Appl. Catal. A: Gen.* 299 (2006) 285.
- [122] M. Bowker, D. James, P. Stone, *J. Catal.* 217 (2003) 427.
- [123] W. Shan, Z. Feng, Z. Li, J. Zhang, *J. Catal.* 228 (2004) 206.
- [124] S. Liu, K. Takahashi, M. Aya, *Catal. Today* 87 (2003) 247.
- [125] S. Liu, K. Takahashi, K. Uematsu, M. Ayabe, *Appl. Catal. A: Gen.* 277 (2004) 265.
- [126] F. Haga, T. Nakajima, K. Yamashita, S. Mishima, S. Suzuki, S. Suzuki, *Nippon Kagaku Kaishi Catal. Today* 1 (1997) 33.
- [127] J. Llorca, N. Homs, J. Sales, *J. Catal.* 209 (2002) 306.
- [128] J. Llorca, N. Homs, J. Sales, J.G. Fierro, *J. Catal.* 222 (2004) 470.
- [129] M.S. Batista, R.K.S. Santos, E.M. Assaf, *J. Power Sources* 134 (2004) 27.
- [130] M.S. Batista, R.K.S. Santos, E.M. Assaf, J.M. Assaf, *J. Power Sources* 124 (2003) 99.
- [131] V. Klouz, V. Fierro, P. Denton, *J. Power Sources* 105 (2002) 26.
- [132] J. Comas, F. Mariño, M. Laborde, *Chem. Eng. J.* 98 (2004) 61.
- [133] A.N. Fatsikostas, D.I. Kondarides, X.E. Verykios, *Catal. Today* 75 (2002) 145.
- [134] J. Suna, X. Ping, Q. FengWuc, *Int. J. Hydrogen Energ.* 30 (2005) 437.
- [135] J. Suna, X. Qiu, F. Wua, W. Zhu, *Int. J. Hydrogen Energ.* 29 (2004) 1075.
- [136] F. Frusteri a, S. Freni, V. Chiodo, L. Spadaro, *J. Power Sources* 132 (2004) 139.
- [137] S. Frenia, S. Cavallaro, N. Mondello, L. Spadaro, *J. Power Sources* 108 (2002) 53.
- [138] F. Frusteri a, S. Freni, V. Chiodo, L. Spadaro, *Appl. Catal. A: Gen.* 270 (2004) 1.
- [139] J.P. Breen, R. Burch, H.M. Coleman, *Appl. Catal. B: Environ.* 39 (2002) 65.
- [140] D.K. Liguras, D.I. Kondarides, X.E. Verykios, *Appl. Catal. B: Environ.* 43 (2003) 345.
- [141] M.A. Goula, S.K. Kontou, P.E. Tsiakaras, *Appl. Catal. B: Environ.* 49 (2004) 135.
- [142] E.C. Wanat, K. Venkataraman, L.D. Schmidt, *Appl. Catal. A: Gen.* 276 (2004) 155.
- [143] S. Cavallaro, V. Chiodo, S. Freni, N. Mondello, *Appl. Catal. A: Gen.* 249 (2003) 119.
- [144] R.M. Navarro, M.C. Alvarez, M. Cruz, *Appl. Catal. B: Environ.* 55 (2005) 229.
- [145] C. Diagne, H. Idriss, K. Pearson, *Chimie* 7 (2004) 617.
- [146] R.L. Borup, M.A. Inbody, T.A. Semelsberger, J.I. Tafoya, D.R. Guidry, *Catal. Today* 99 (2005) 263.
- [147] Y. Fu, T. Hong, J. Chen, *Thermochim. Acta* 434 (2005) 22.
- [148] T.A. Semelsberger, R.L. Borup, *J. Power Sources* 152 (2005) 87.
- [149] R.L. Semelsberger, R.L. Borup, *Int. J. Hydrogen Energ.* 30 (2005) 425.
- [150] T.A. Semelsberger, K.C. Ott, R.L. Borup, H.L. Greene, *Appl. Catal. B: Environ.* 61 (2005) 281.
- [151] F. Yaripour, F. Baghaei, I. Schmidt, J. Perregaard, *Catal. Commun.* 6 (2005) 147.
- [152] T.H. Fleisch, A. Basu, M.J. Gradassi, J.G. Masin, *Stud. Surf. Sci. Catal.* 107 (1997) 117.
- [153] Y. Tanaka, R. Kikuchi, T. Takeguchi, *Appl. Catal. B: Environ.* 57 (2004) 211.
- [154] T. Mathew, Y. Yamada, A. Ueda, H. Shioyama, T. Kobayashi, *Appl. Catal. A: Gen.* 300 (2006) 58.
- [155] G.W. Huber, J.A. Dumesic, *Catal. Today* 111 (2006) 119.
- [156] J.W. Shabaker, D.A. Simonetti, R.D. Cortright, J.A. Dumesic, *J. Catal.* 231 (2005) 67.
- [157] J.W. Shabaker, R.R. Davda, G.W. Huber, R.D. Cortright, J.A. Dumesic, *J. Catal.* 215 (2003) 344.
- [158] K. Polychronopoulou, C.N. Costa, A.M. Efstathiou, *Appl. Catal. A: Gen.* 272 (2004) 37–52.
- [159] K. Polychronopoulou, J.L.G. Fierro, A.M. Efstathiou, *J. Catal.* 228 (2004) 417.
- [160] K. Polychronopoulou, C.N. Costa, A.M. Efstathiou, *Catal. Today*, in press (corrected proof, available online 28 December 2005).