# Hydrogen Production from Ethanol for Fuel Cell Applications

D.Kunzru
Department of Chemical Engineering, I.I.T.Kanpur, Kanpur-208016
Email: dkunzru@iitk.ac.in

Ethanol is a renewable resource as it can be produced from biomass without contributing to the greenhouse gas emissions. Reforming of ethanol to produce hydrogen is a potentially attractive process. The reactions involved include steam reforming followed by water-gas shift and selective oxidation of CO. The development of suitable catalysts for these reactions is crucial for the viability of the process. Recent studies suggest that the promising catalysts are supported Rh and Rh/Ni catalysts for steam reforming, Pt-ceria based catalysts for water-gas shift reaction and Pt-Rh or Cu-ceria catalysts for selective oxidation of CO. Microreactors are well-suited for fabricating microfuel processors for portable power applications. Further research on catalyst development and heat integration schemes is required to commercialize this process.

## 1. Introduction

Most of the energy we use today is obtained from non-renewable fossil fuels. This has not only depleted the reserves of fossil fuels, especially crude oil, but has also caused severe environmental pollution. Intense research efforts are being made to develop alternative renewable energy sources .In recent years , considerable effort has been expended in developing fuel cells. Hydrogen can be used in fuel cells to produce electricity very efficiently and cleanly, since the only by-product is water. It is expected that in the near future, hydrogen will be used, to a large extent, as a secondary energy carrier for the production of electricity for mobile and small-to-medium scale stationary applications. Barreto et al.(2003) have discussed the scenario for a sustainable hydrogen economy in the 21st century and concluded that fuel cells will play a major role in meeting the energy demands of the future. In order to support sustainable hydrogen economy, it is crucial to produce hydrogen cleanly from renewable resources.

The conventional methods of hydrogen production are based on reforming of natural gas or naphtha. Among the different feedstocks available, alcohols are very promising candidates because these are easily decomposed in the presence of water and generate hydrogen-rich mixture at a relatively lower temperature. Steam reforming of methanol has been extensively studied in recent years ( Iwasa et al.,2003;Zhang and Shi,2003). The main drawback is its relatively high toxicity. Among the various processes proposed, steam reforming of ethanol for the production of hydrogen is very attractive because ethanol can be produced by fermentation of renewable resources like biomass, is easy to transport and is nontoxic. More importantly, ethanol is $CO_2$ neutral since the amount of $CO_2$ produced by steam reforming is consumed by the biomass growth, and this offers a nearly closed carbon loop and does not contribute to greenhouse gas emissions.

The reactions involved for producing hydrogen from ethanol include (i) steam reforming (ii) high temperature water-gas shift reaction (iii) low temperature water gas shift reaction and (iv) selective carbon monoxide oxidation.
The overall reactions are as follows:

Steam reforming $C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2$ , $\Delta H^0_{298K} = 174 kJ/mol$ (1)

Water-gas shift $CO + H_2O \Leftrightarrow CO_2 + H_2$ , $\Delta H^0_{298K} = -41 kJ/mol$ (2)

Selective CO oxidation $CO + \frac{1}{2}O_2 \rightarrow CO_2$ , $\Delta H^0_{298K} = -283 kJ/mol$ (3)

In the steam reforming reaction, in addition to $H_2$ and $CO_2$, significant amounts of CO and $CH_4$ are also formed due to side reactions. For use in fuel cells, the CO content has to be reduced to less than 10 ppm. Water-gas shift reactors are therefore used to reduce the CO concentration and produce additional $H_2$. Even after the low temperature shift reactor, the CO concentration is around 1% and is further reduced by selective oxidation. The major challenge is to develop highly active, selective and durable catalysts for the reactions involved.

This paper reviews the latest catalyst developments for the steam reforming of ethanol, water-gas shift reaction and selective ( or preferential) oxidation of CO. Moreover, the possibility of using microreactors for producing hydrogen from ethanol is discussed.

## 2. Ethanol Steam Reforming

### 2.1 Reforming reactions

Haryanto et al. (2005) have summarized the reaction pathways that can occur during ethanol steam reforming over metal catalysts. The important reactions include:

$$C_2H_5OH \rightarrow CH_3CHO + H_2 \quad (4)$$
$$C_2H_5OH \rightarrow C_2H_4 + H_2O \quad (5)$$
$$CH_3CHO \rightarrow CH_4 + CO \quad (6)$$
$$CH_3CHO + H_2O \rightarrow 2CO + 3H_2 \quad (7)$$
$$CH_4 + H_2O \Leftrightarrow CO + 3H_2 \quad (8)$$
$$CO + H_2O \Leftrightarrow CO_2 + H_2 \quad (9)$$
$$2CH_3CHO \rightarrow CH_3COCH_3 + CO + H_2 \quad (10)$$

In addition, coke formation can occur by the Boudouard reaction and from ethylene

$$2CO \rightarrow CO_2 + C \quad (11)$$
$$C_2H_4 \rightarrow coke \quad (12)$$

A thermodynamic analysis shows that an increase in temperature and high water-to ethanol ratios favour the formation of $H_2$. Different metals can catalyze different reactions in the above reaction scheme and therefore selection of a proper catalyst is essential for obtaining high conversion and high $H_2$ selectivity.

### 2.2 Noble metal catalysts

The catalytic performance of supported noble metal catalysts (Rh, Ru, Pt, Pd) for steam reforming of ethanol has been investigated by Liguras et al. (2003) in the temperature range of 600-850°C. They studied the effect of the nature of the support ($Al_2O_3$, MgO, $TiO_2$) and the metal loading ( 0-5%). For low loaded catalysts, Rh was found to be significantly more active and selective towards hydrogen. The catalytic performance of Rh and, particularly Ru, improved significantly at higher loadings, resulting in higher activity and higher hydrogen selectivity. At high loadings, the catalytic activity and selectivity of Ru catalysts was comparable to that of Rh. At $800^0$C and a water/ethanol ratio of 3:1, the 5% $Ru/Al_2O_3$ catalyst was able to completely convert ethanol with a hydrogen selectivity above 95%.

The nature of the support affects the performance of the catalyst, especially the coke formation.Acidic supports, such as $\gamma$ - alumina favour ethanol dehydration resulting in the formation of ethylene, which is a coke precursor, eqn. (12). The dehydration can be reduced by using basic supports such as MgO. Frusteri et al. (2004a) investigated the performance of MgO-supported metal catalysts and reported the activity to be in the order of Rh> Co>Ni>Pd. The most selective catalyst was Ni/MgO whereas Rh supported on MgO was the most resistant to coke formation. Pd, Ni and Co were affected by metal sintering.

A wide range of catalysts were tested by Aupretre et al. (2002) by changing both the active phase (Rh, Pt, Pd, Ru, Ni, Cu, Zn, Fe) and the oxide support ($Al_2O_3$, 12% $CeO_2$-$Al_2O_3$, $CeO_2$, $CeO_2$-$ZrO_2$, $ZrO_2$). At $700^0$C and atmospheric pressure, $\gamma$-$Al_2O_3$ supported Rh and Ni gave the best performance compared to Pt, Cu, Zn or Fe. For Rh catalysts, 1% Rh/ $\gamma$-$Al_2O_3$ showed the highest selectivity (88 %) while 1% Rh/$CeO_2$-$ZrO_2$ exhibited the highest yield of hydrogen. Similar results were obtained for Ni catalysts. They reported that activity in the steam reforming reaction directly varies as degree of mobility of surface OH groups, and selectivity towards $CO_2$ is controlled by the activity in the water-gas shift reaction. The ceria based supports were highly active for the water-gas shift reaction. Aupretre et al. ( 2005) studied SR of ethanol over Rh supported on $Mg_xNi_{1-x}Al_2O_3$ spinel oxide.The spinel layer was introduced to control the acidic and basic properties of the catalyst, and thereby the formation of ethylene and acetaldehyde.Rh was the most active metal in the presence of nonacidic and moderately basic supports. Fierro et al. (2003) also reported high activity and selectivity to $H_2$ on $Rh/Al_2O_3$ catalysts. In addition, the catalyst was highly stable. Breen et al.(2002) studied various oxide-supported metal catalysts for steam reforming of ethanol. They found that $Al_2O_3$-supported catalysts promote dehydration of ethanol to ethylene and the order of activity of metals for such catalysts is Rh>Pd>Ni = Pt. However, with $CeO_2/ZrO_2$ supported catalysts, ethylene was not formed. Kugai et al. (2006) studied the effect of nano-crystalline $CeO_2$ supports on the performance of Ni-Rh bi-metallic catalyst. They found that addition of Ni improved the dispersion of Rh /$CeO_2$. These studies suggest that of all the noble metals, Rh catalysts supported on MgO or $CeO_2$ are the most promising. Due to its relatively lower cost, Ru should also be investigated further. More work is also required on bi-metallic catalysts containing both noble and non-noble metals.

## 2.3 Non-noble metal catalysts

The most commonly used non-noble metal for steam reforming of ethanol is nickel. Nickel based catalysts supported on $Al_2O_3$, MgO, $La_2O_3$, $SiO_2$ and $Y_2O_3$ with additions of Cu, Cr, Zn, Na or K have been investigated for ethanol reforming reactions (Klouz et al., 2002; Comas et al., 2004; Fatsikostas et al., 2002). It is generally accepted that Ni promotes C-C bond scission whereas additives like Cr, Cu are the active agents for subsequent oxidation to produce CO and $H_2$. Freni et al. (2003) found that Ni/MgO exhibited high activity and selectivity to $H_2$ due to the lower tendency of Ni to oxidize during reaction.

The addition of Li and K enhanced the catalyst stability of Ni/MgO catalysts mainly by depressing Ni sintering (Frusteri et al., 2004b). Fatsikostas and Verykios (2004) studied ethanol reforming over Ni catalysts supported on $\gamma$-$Al_2O_3$, $La_2O_3$ and $La_2O_3$/$\gamma$-$Al_2O_3$. The impregnation of $Al_2O_3$ with $La_2O_3$ reduced carbon deposition which was attributed to the formation of lanthanum oxycarbonate species. Biswas and Kunzru (2007) studied the effect of support and metal loading over Ni/$CeO_2$-$ZrO_2$ catalysts.

Among the catalysts examined, $Ni/Ce_{0.74}Zr_{0.26}O_2$ with 30 wt% Ni loading exhibited high catalyst activity and hydrogen selectivity at $600^oC$. The effect of $Al_2O_3$, $La_2O_3$, and $Y_2O_3$ as support was examined by Sun et al. (2005).The catalyst activity and hydrogen selectivity were highest with $La_2O_3$ and lowest for $Al_2O_3$.

Marino et al. (2004) tested Cu-Ni-K/$\gamma$-$Al_2O_3$ catalyst for ethanol steam reforming reaction. Copper-nickel catalysts on $\gamma$-$Al_2O_3$ and doped with potassium hydroxide, were suitable for hydrogen production at a relatively low temperature of $300^0C$. Cu was active agent for steam reforming, Ni favored the C-C bond rupture and potassium neutralized the acidic sites of the support**.** Youn et al. (2006) studied the effect of second metal (Ce, Co, Cu, Mg and Zn) addition on Ni/ $\gamma$-$Al_2O_3$ catalysts in the auto-thermal reforming of ethanol. Among the dopants tested, Cu was found to be most efficient promoter and it was active for WGS. In addition to that, Cu also served as a barrier to prevent the growth of Ni particles and decreased the interaction between Ni-species and $\gamma$-$Al_2O_3$ which facilitated the reduction of Ni-Cu/ $\gamma$-$Al_2O_3$ catalyst. A series of CuNiZnAl multi component mixed metal oxide catalysts with various Cu/Ni ratio was tested for OSR of bio-ethanol by Velu et al. (2005). Nickel significantly reduced the carbon products. Dehydrogenation of ethanol to acetaldehyde reaction was favored over Cu based catalyst whereas introduction of Ni favored the C-C bond rupture. The effect of different dopants (Cr, Fe, Zn or Cu) on $Ni/Al_2O_3$ catalysts for OSR of ethanol was investigated by Fierro et al. (2005). Nickel promoted the SR and WGS reactions while $Al_2O_3$ promoted the dehydration reaction. Moreover, Cu was more active for methane steam reforming compared to Cr, Zn and Fe. These studies show that of all the non-noble metal catalysts investigated, Ni (doped or undoped) supported on $La_2O_3/Al_2O_3$ or $CeO_2/ZrO_2$ is the most promising catalyst.

## 3. Water-gas Shift Reaction

In the steam reforming reaction, in addition to $H_2$ and $CO_2$, significant amounts of CO and $CH_4$ are also formed due to side reactions. Water-gas shift reaction is therefore used to reduce the CO concentration and produce additional $H_2$. This is a mildly exothermic, reversible reaction ($\Delta H_{298} = -41.2kJ/mol$) and requires low temperature for high equilibrium conversion. Conventionally, WGS reaction for synthesis gas manufacture has been used industrially for the last several decades. To limit the reactor size and improve the equilibrium conversion, it is conducted in two stages. In the first or high temperature stage (HTS), ~90% of the CO is converted to $H_2$ at 350-$400^oC$ on $Fe_2O_3/Cr_2O_3$ catalysts. This is followed by a low temperature stage (LTS) where 90% of the remaining CO is converted on CuO/ZnO operated at 200-$300^oC$. Current WGS catalysts are not suitable for use in small scale portable power applications, mainly because of the high residence time requirement and also due to the pyrophoricity of the catalysts used (Panagiotopoulou and Kondarides, 2006). The development of microdevices offers the possibility of producing $H_2$ from renewable feedstocks in compact devices. However, the significantly lower residence time requirement of microreactors warrants development of more active WGS catalysts. The application of integrated microstructured reactors/heat exchangers also allows adjustment of the temperature profile in a single WGS reactor, which can cover the whole range from HTS to LTS.

Several catalysts have been tested for the combined HTS/LTS reaction. Most of these are based on noble metals such as Pt, Rh, Ru, Pd or Au. Wheeler et al. (2004) studied WGS over noble metals, with and without ceria, supported on alumina foam monoliths for contact times between 0.8 and 50 ms. The activity of the metals was in the order Ni > Ru > Rh > Pt >Pd. The maximum CO conversion with Ni was 80% and 45% with Pt. Addition of 5.0 wt% ceria, increased the rate of reaction over all the metals; the most pronounced effect was observed on Pt. However, the activity order was nearly the same (Ni ≈ Ru >Pt >Rh > Pd).These metals also promoted the undesirable methanation reaction in the order Ru > Rh > Ni >Pt > Pd. The most promising catalyst in terms of selectivity, activity and stability was Pt/ ceria. Two mechanism have been proposed for WGS ,*viz*., adsorptive mechanism and redox mechanism (Kolb et al., 2005). Panagiotopoulou and Kondarides (2006) examined the effect of different supports on the catalytic performance of noble metal catalysts. For all metal support combinations, Pt was significantly more active than Ru, Rh or Pd. The catalytic activity of Pt and Ru catalysts was 1-2 orders of magnitude higher on reducible supports ( TiO2, CeO2, La2 O3 and YSZ) than on nonreducible supports ( Al2O3, SiO2 and MgO ).In the redox mechanism, the reducibility of the support has a direct effect on the activity whereas in the adsorptive mechanism, it can enhance the decomposition of the surface intermediates, that has been proposed as the rate-limiting step( Choi and Stenger,2003). Kolb et al.(2005) tested Pt/$CeO_2$-$Al_2O_3$, Pt-Rh/$CeO_2$-$Al_2O_3$; Pt-Pd/$CeO_2$-$Al_2O_3$ and Pt-Ru/$Al_2O_3$ catalyst both at HTS and LTS reaction conditions. Pt/$CeO_2$-$Al_2O_3$ was identified as the most promising catalyst. The optimum platinum content was found to range between 3 and 5 wt.%, whereas the optimum ceria content ranged between 12 and 24 wt.%.Au/$CeO_2$ was shown to be a very active and stable catalyst for WGS but only if the gold particles are nanosized. Larger particles are ineffective in catalyzing the reaction (Tabakova *et al.*, 2004). Goerke et al.(2004) applied Au/$CeO_2$ and Ru/$ZrO_2$ on microstructured metal foils. At a residence time of <30 ms and 250-350$^0$C, use of Rh/$ZrO_2$ catalyst resulted in CO conversion of more than 95%.At these low residence times, Au/$CeO_2$ was not an effective catalyst. These studies suggest that Pt-ceria based catalysts are the most effective. Efforts should be made to reduce the loading of the noble metal and reduce the catalyst deactivation.

## 4. Preferential Oxidation of CO

Even after the HTS and LTS, the CO concentration is around 1% and needs to be further reduced to less than 20 ppm in order to avoid rapid deactivation of the platinum electro-catalyst in the fuel cell. This is achieved by preferential oxidation of CO (PROX). Trimm(2005) has reviewed the techniques for minimization of CO. Several studies have been conducted on gold based catalysts and have been summarized by Trimm. Although gold-based catalysts are effective, they have the disadvantage that hydrogen oxidation becomes significant above 80$^0$C. Platinum is a catalyst which is active for CO oxidation. Several investigators have studied the use of Pt-group metals supported on oxides (Oh and Sinkevitch, 1993; Kahlich *et al.*, 1997; Manasilp and Gulari, 2002). Delsmen *et al.*, (2004) used a selective Pt-Ru/$\alpha$-$Al_2O_3$ catalyst to promote the oxidation of CO over the oxidation of hydrogen. The stability of these catalysts in a fuel gas mixture containing 1% CO – 0.5% $O_2$-50% $H_2$-10% $H_2O$-15%$CO_2$-He was excellent. Cominos *et al.* (2005) investigated nine different noble metal catalysts for the selective oxidation of CO. The most active were Pt-Ru/$\gamma$-$Al_2O_3$, Rh/$\gamma$-$Al_2O_3$ and Pt-Rh/$\gamma$-$Al_2O_3$, whereas the most stable was Pt-Rh/$\gamma$-$Al_2O_3$. The catalyst exhibited steady performance in a micro-structured reactor for 50h while reducing 1.12% CO to 10 ppm with inlet $O_2$ to CO ratio of 4.Cheaper Cu-based catalysts have also been investigated as a substitute for the noble metal catalysts. Most studies have incorporated ceria as this promotes the formation of oxygen vacancies in the copper–ceria and improves the reducibility of copper. In a recent review, Lopez et al. (2008) have compared the performance of different Cu-based catalysts and concluded that ‘addition of modifiers (e.g. Zr, Sn, Co, etc.) to the copper–ceria catalysts does not produce any improvement in the catalytic activity of these catalysts and that chelating methods are the most appropriate procedures for the preparation of CO-PROX catalysts’. More work is required on the deactivation characteristics of Cu-based catalysts.

## 5. Microreactors for Ethanol Steam Reforming

Microreactors (MR) are devices in which the fluid (reactant) flows through multiple parallel channels. The dimensions of the channels are typically in the range of 10-500 µm. For catalytic reactions, the catalyst can be deposited on these channels by various techniques (Mielle, 2006). The main feature of MR is their high surface to volume ratio in the range of 10,000-50,000 $m^2/m^3$, whereas typical laboratory and production vessels usually do not exceed 1000 $m^2/m^3$ and 100 $m^2/m^3$, respectively (Ehrfeld et al., 2000). The heat transfer coefficient in microdevices exceed those of conventional heat exchangers by at least one order of magnitude.

Conventional packed bed reactors have too high a reactor volume to be applied to small fuel cells. Moreover, these reactors show limitations in heat and mass transfer and are not able to fulfill the dynamic demands of fuel cell systems. Microreactors, with their low reactor volumes and high heat and mass transfer rates, are ideally suited for such applications. To have high thermal efficiency, micro-reactors need to be designed such that the heat from the exothermic reactions is utilized for heating and evaporation of the fuel as well as for providing heat to the endothermic reactions. Moreover, the catalysts for steam reforming, water-gas shift reaction, and selective oxidation need to be active, selective and stable. Another problem is that the optimum temperature for each of the above reactions is different, thus heat exchangers need to be incorporated in the microfuel processor. Although no published literature is available on steam reforming of ethanol in microreactors, several investigators have studied the reforming of methanol in microreactors , including techniques for heat integration(Park *et al.,*2005; Shah et al.,2005). Reuse et al. (2004) reported on the autothermal reforming of methanol by coupling the steam reforming and total oxidation.

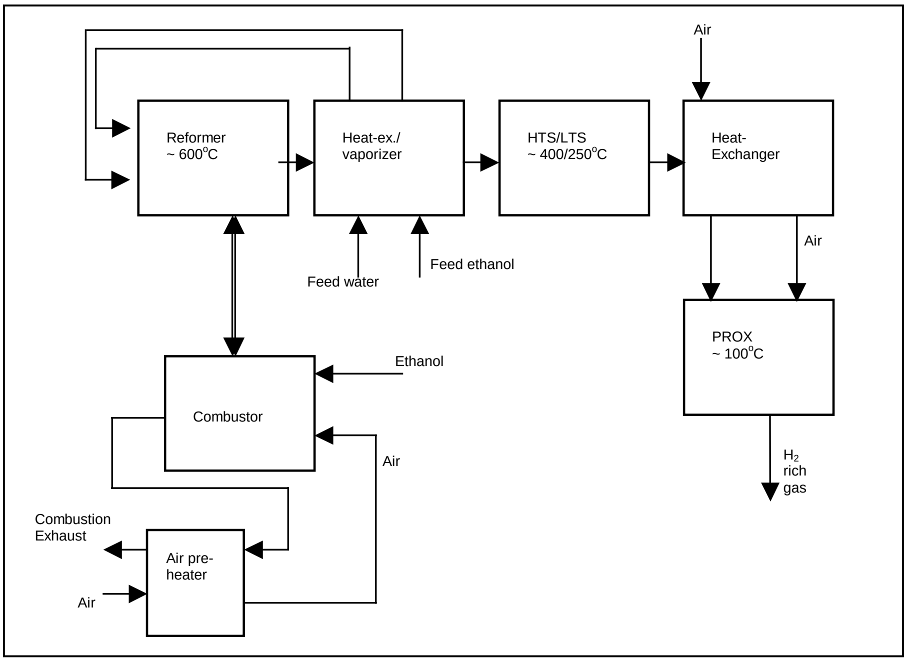

Figure 1: Schematic diagram for an integrated reactor for steam reforming of ethanol

In comparison to methanol, an ethanol microfuel processor poses more challenges due to the higher temperature requirement during steam reforming (~ $600^0C$) and the necessity of the WGS reactor which is not required with methanol because the CO concentration in the reformer exit stream is usually < 1% (Cominos et al., 2005). A possible scheme for heat integration, shown in Fig. 1, is to catalytically combust part of the fuel to provide the endothermic heat of the steam reforming reaction and use the reformer exit gases for heating and vaporizing the fuel and water. Another possibility is to reform ethanol autothermally by adding small amount of oxygen or air with the reformer feed. This has the disadvantage of reducing the hydrogen yield (Biswas and Kunzru, 2008) but in this arrangement the combustor is not required. The process can also be improved by using a two-stage PROX reactor to limit the hydrogen oxidation (Trimm, 2005).

## 6. Conclusions

From this survey, it can be concluded that the most active and selective catalysts for steam reforming of ethanol are Rh and/or Ni based. The main limitation is catalyst deactivation due to coking and sintering. Further work on bimetallic catalysts is required. The present day WGS catalysts ar not suitable for use in microreactors and more active catalysts need to be developed. It would be advantageous if the same catalyst can be used for both HTS and LTS. Till date, Pt-ceria catalysts have been found to be the most effective. The major challenge in selective oxidation of CO is to prevent the simultaneous oxidation of hydrogen. Pt-Rh supported on alumina and copper-ceria based catalysts hold promise.

Microreactors are well-suited for generating hydrogen from ethanol for portable power applications but further R&D is required in catalyst development, reactor design and heat integration schemes.

## 7. References

Aupretre, F., C. Descorme and D. Duprez, 2002, Catal. Commun., 3, 263.

Aupretre, F., C. Descorme, D. Duprez, D. Casanave and D. Uzio, 2005, J. Catal. 233, 464.

Baretto, L.,A. Makihira and K. Riahi, 2003, Int. J. Hydrogen Energy, 28, 267.

Biswas, P. and D. Kunzru, 2007, Int. J. Hydrogen Energy, 32, 969.

Biswas, P. and D. Kunzru, 2008, Chem. Eng. J., 136, 41.

Breen, J.P., R. Burch and H.M. Coleman, 2002, Appl. Catal. B: Environ. 39, 65.

Choi, Y. and H.G. Stenger, 2003, J. Power Sources, 124, 432.

Comas, J., F. Marino, M. Laborde and N. Amadeo, 2004, Chem. Eng. J., 98, 61.

Cominos, V., V. Hessel, C. Hofmann, G. Kolb, R. Zapf, A. Ziogas, E.R. Delsmen and J.C .Schouten, 2005, Catal. Today, 110, 140.

Delsmen, E.R., M.H.J.M. De Croon, A. Pierik, G.J. Kramer, P.D. Cobden, C. Hofmann, V. Cominon and J.C. Schouten, 2004, Chem. Eng. Sci., 59, 4795.

Ehrfeld, W., V. Hessel and H. Lowe, 2000, Microreactors. Wiley-VCH, Germany.

Fastikostas, A.N. and X.E. Verykios, 2004, J. Catal., 225, 439.

Fastikostas, A.N., D.I. Kondarides and X.E. Verykios, 2002, Catal. Today, 75, 145.

Fierro, V., O. Akadim, H. Provendier and C. Mirodatos, 2005, J. Power Sources, 145, 659.

Fierro, V., O. Akdim and C. Mirodatos, 2003, Green Chem., 5, 20.

Frusteri, F., S. Freni, V. Chiodo, L. Spadaro, O. Di Blasi, G. Bonura and S. Cavallaro, 2004a, Appl. Catal. A: Gen., 270, 1.

Frusteri, F., S. Freni, L. Spadaro, V. Chiodo, G. Bonura, S. Donato and S.Cavallaro, 2004b, Catal. Commun., 5, 611.

Goerke, O., P. Pfeifer and K. Schubert, 2004, Appl. Catal. A: Gen., 263, 11.

Haryanto, A., S. Fernando, N. Murali and S. Adhikari, 2005, Energy & Fuels, 19, 2098.

Iwasa, N., T. Mayanagi, W. Nomura, M. Arai and N. Takezawa, 2003, Appl. Catal. A: Gen., 248, 153.

Kahlich, M.J., H.A. Gasteiger and R.J. Behm, 1997, J. Catal., 171, 93.

Klouz,V., V.Fierro, P. Denton, H. Katz, J.P. Lisse, S.B. Mauduit and C. Mirodatos, 2004, J. Power Sources, 105, 26.

Kolb, G., H. Pennemann and R. Zapf, 2005, Catal. Today, 110, 121.

Kugai J., V. Subramani, C. Song, M.H. Englehard and Y. Chin, 2006, J. Catal., 238, 426.

Liguras,D.K., D.I. Kondarides and X.E. Verykios, 2003, Appl. Catal. B: Environ. 43, 345.

Lopez, I., T. Valdés- Solís and G. Marban, 2008, Int. J. Hydrogen Energy, 33, 197.

Manasilp, A. and E. Gulari, 2002, Appl. Catal. B: Environ., 37, 17.

Marino, F., M. Boveri, G. Baronetti and M. Laborde, 2004, Int. J. Hydrogen Energy., 29, 67.

Mielle, V., 2006, Appl. Catal. A: Gen. 315, 1.

Oh, S.H and R.M. Sinkevitch, 1993, J. Catal., 142, 254.

Panagiotopoulou, P. and D.I. Kondarides, 2006, Catal. Today, 112, 49.

Park, G.G.,S.D. Yim, Y.G. Yoon, C.S. Kim, D.J. Seo and K. Eguchi, 2005, Catal. Today, 110, 108.

Reuse, P., A. Renken, K. Haas-Santo, O. Gorke and K. Schubert, 2004, Chem. Eng. J., 101, 133.

Shah, K. X. Ouyang and R.S. Besser, 2005, Chem. Eng. & Technol, 28, 303.

Sun, J., X.P. Qiu, F. Wu and W.T. Zhu, 2005, Int. J. Hydrogen Energy, 30, 437.

Tabakova, T., F. Boccuzzi, M. Manzoli, J.W. Sobczak, V. Idakiev andD. Andreeva, 2004, Appl.Catal. B: Environm., 49, 73.

Trimm, D.L., 2005, Appl. Catal. A: Gen. 296, 1.

Velu, S., K. Suzuki, M. Vijayaraj, S. Barman and C.S. Gopinath, 2005, Appl. Catal. B: Environ., 55, 287.

Wheeler, C., A. Jhalani, E.J. Klein, S. Tummala and L.D. Schmidt, 2004,J. Catal., 223, 191.

Youn, M.H., J.G. Seo, P. Kim, J.J. Kim, H.I. Lee and I.K. Song, 2006, J. Power Sources, 162, 1270.

Zhang, X. and P. Shi, 2003, J. Mol. Catal A: Chem 194, 99.