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Methanol as an Energy Source and/or Energy Carrier in Membrane Processes

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Abstract: Methanol is commonly considered a hydrogen source and/or hydrogen carrier. In fact, methanol can be produced by partial oxidation of biomass and in this case it is considered a source for hydrogen and therefore for energy. It can also be produced from carbon dioxide and hydrogen; in this case, it can be seen as a hydrogen carrier because it is easier to transport and store than hydrogen. This work gives an overview of methanol production and use both for hydrogen production and as a feed to fuel cells. Different processes for the production and reactions of methanol are reported, with particular regard to the membrane processes that produce methanol and simplify methanol reactions with respect to traditional systems.

Keywords: Methanol, traditional reactors, membrane reactors, hydrogen production, fuel cells

INTRODUCTION—A BRIEF HISTORY OF METHANOL

Methanol, also known as methyl alcohol or wood alcohol, is a chemical compound having the formula CH_3OH. It is the lowest molecular weight

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alcohol, and at low temperature is a light, volatile, colorless, flammable, poisonous liquid. Methanol is produced naturally in the anaerobic metabolism by many varieties of bacteria. As a result, there is a small amount of methanol vapor in the atmosphere. After several days, atmospheric methanol is oxidized by oxygen (with sunlight energy) into water and carbon dioxide.

Methanol was probably discovered by R. Boyle in 1661 during the distillation of raw vinegar on cedar. He called the new compound *adiaphorus spiritus lignorum.* Anyway, there are no written reports about the use of this compound before the 19th century.

The chemical and molecular nature of methanol was discovered, independently, by J.B.A. Dumas and J. Von Liebig in 1834. The term "methyl" was used for the first time in chemistry in late 1835 owing to their research.

During that time, several efforts were made by many researchers to synthesize methanol. The first was by M. Berthelot in 1857 using dry wood distillation. Referring to this research methanol was commonly called "wood alcohol."

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METHANOL PRODUCTION

Traditional Systems

Several techniques have been developed to produce methanol. A promising route uses biomass wood or garbage (via partial oxidation reaction) (1). The feasibility of achieving this conversion was demonstrated in a large-scale system in which a product gas is initially produced by pyrolysis of the waste material. The product yield for the conversion process is estimated to be 185 kg of methanol per metric ton of solid waste (2, 3). However, this method was also used before the discovery of a catalytic process. In fact, today, catalysis plays a key role in methanol production. The first synthetic methanol was produced in 1923 by BASF chemists in Leuna (Germany) (4). This process, known as the "high-pressure" process, which operated at up to 250–350 bar and 320–450°C, remained the dominant technology for over 45 years. In the 1960s, ICI (now Synetix) made improvements on the use of copper catalysts. The new process, called the "low-pressure" process, which operates at 35–55 bar and 200–300°C, today is the only one used in a market of 35 million metric tons production and 28 demand capacity (5).

Methanol is mainly produced as chemical grade. The market for this type of methanol is found in chemical and solvent applications. Using the type of raw methanol quality produced through its liquid phase technology, Air Products and Chemicals Inc. currently has an extensive fuel grade methanol test program. The catalysts used for methanol synthesis are copper-based. Several techniques have been developed to stabilize the catalysts in terms of catalyst lifetime. The highest active and high selective catalysts for methanol production are today $Cu/ZnO/Al_2O_3$ catalysts (6). These catalysts are already active at 200°C and selective towards the formation of H_2 and CO_2.

All the catalysts actually used in the low-pressure methanol synthesis contain copper oxide, zinc oxide and one or more stabilizer compounds. A typical composition of the catalysts used for the synthesis is reported in Table 1.

Recent studies focus on methods of producing methanol differently from traditional fixed bed reactors. For example, Wang et al. (7) introduced the study of a trickle bed reactor (TBR) to overcome the problem of heat dissipation occurring in traditional reactors. A TBR is a fixed bed of catalyst with a co-current gas-liquid downflow over the catalyst bed. Similar to slurry reactors, heat removal in this type of reactor is much more efficient than the traditional fixed bed ones. Slamet et al. (8) studied the photocatalytic reduction of CO_2 on copper-doped titania, showing that the photoreduction of CO_2 with water at the solid/liquid interface of copper-doped titania photocatalysts occurs at temperatures up to 100°C with methanol as the main product.

The methanol synthesis reaction system is an equilibrium system. The main reactions for the methanol production are the following:

$$CO + 2H_2 = CH_3OH \qquad \Delta H_{298K} = -90.70\,\text{kJ/mol} \qquad (1)$$

$$CO_2 + H_2 = CO + H_2O \qquad \Delta H_{298K} = +41.19\,\text{kJ/mol} \qquad (2)$$

$$CO_2 + 3H_2 = CH_3OH + H_2O \qquad \Delta H_{298K} = -49.51\,\text{kJ/mol} \qquad (3)$$

From a theoretical point of view, in order to improve methanol production in traditional reactors, two other routes, different from the catalyst improvements, can also be followed (9–13):

a. recycling of the unconverted synthesis gas after products separation by condensation;

b. in situ product removal of the products of the reaction.

For example, an attempt at in situ product removal was made by Westerterp et al. (10), who proposed the selective adsorption of water and methanol on a solid, in a trickle bed reactor. On the other hand, water produced during methanol synthesis via CO_2 hydrogenation (reaction 2) greatly reduces the methanol synthesis rate by suppressing reaction 3. Moreover, water produced during methanol synthesis from CO_2 conversion accelerates the

Table 1. Methanol synthesis catalyst composition

Producer	Cu [%]	Zn [%]	Al [%]
BASF	65–75	20–30	5–10
Süd Chemie	65–75	18–23	5–10
ICI	61	30	9
Du Pont	50	19	31
Haldor Topsøe	50–60	21–25	15–28

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crystallization of Cu and ZnO contained in a Cu/ZnO-based catalyst, resulting in the catalyst's deactivation (11, 12).

The last important issue in the industrial methanol process is that synthesis gas composition from the steam reforming reactor is essentially low in H_2, so that the additional H_2 could enhance methanol production (13). A continuous product removal from the reaction zone making use of membranes improves both the reactants conversion and methanol yield (9). This aspect will be explained in depth in the next section. Some other developments of the catalyst system and reactor improvements for methanol synthesis are presented in the review of Tijm et al. (5).

Membrane Processes in Methanol Production

Membrane reactors (MRs) can be used in order to address all the key issues of the methanol production reported here. According to the IUPAC definition, an MR (Figure 1) is a device that combines the separation properties of membranes with the typical characteristics of catalytic reaction steps in only one unit. In particular, the membrane does not only play the role of a separator but also as part of the reactor itself. In other words, a membrane reactor is an engineering device that selectively removes one or more products from the reaction system, giving the possibility of achieving a higher conversion than a traditional process at a fixed temperature (or, for endothermic reactions, the same conversion but at a lower temperature).

Basically, the MR can be used in methanol production in different ways. The first way is to supply the reactants on the catalytic zone in a controlled manner. In this case, it is useful to introduce hydrogen through a dense membrane, in order to always have the best reactants molar ratio on the catalytic surface. With this objective, Rahimpour et al. (13) used a Pd-Ag membrane reactor to increase CO conversion in methanol synthesis. They found that CO conversion can be promoted beyond thermodynamic

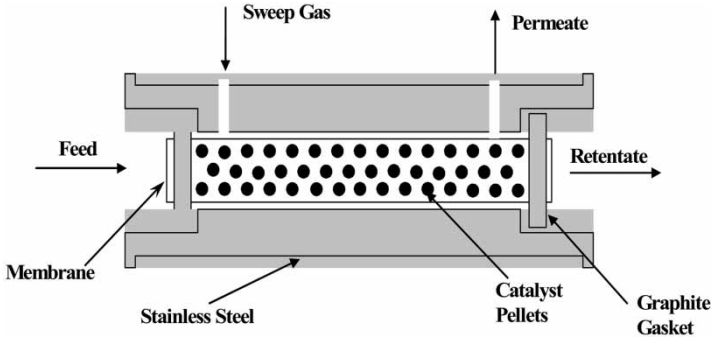

Figure 1. Scheme of a membrane reactor.

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equilibrium by adding the hydrogen reactant to the reactor space through the palladium-based membrane.

The second method is to use the membrane reactor to remove the products continuously from the reaction zone. This way is clearly based on the well-known Le Chatelier principle. This application of an MR for improving conversion in methanol synthesis was first suggested by Struis et al. (9): reaction experiments were performed in a lithiated Nafion membrane reactor at 200°C and 0.43 MPa. They demonstrated the feasibility of in situ product separation from a catalytic methanol synthesis reactor. The same key parameters to be studied in order to achieve improvements were claimed in their work: high-pressure operation, membrane structure, and module configuration. Recently, the same authors have published another paper regarding both an experimental study (using the same lithiated Nafion membrane reactor) and a modelling study (14). The previous experimental results were verified and the approach was also studied from a theoretical viewpoint. The results indicated that the membrane reactor has a higher conversion than the traditional fixed bed reactor under the same experimental conditions. However, their application is limited since the allowable working temperature of a Nafion membrane is lower than 200°C (It is actually closer to 150°C).

In their paper Chen and Yuan (15) reported a theoretical analysis of membrane reactor behaviour in a systematic manner based on a one-dimensional isothermal pseudo-homogeneous parallel flow model with a non-uniform distribution of membrane permeation rate. In particular, they simulated methanol synthesis from CO_2 in a silicone rubber/ceramic composite membrane reactor. The theoretical results, in part tested and verified by experiment, showed that the conversion of the main reaction in the membrane reactor increased by 22% against the traditional fixed bed reactor.

Also from a theoretical point of view Barbieri et al. (16) studied methanol synthesis in ceramic membrane reactors, dealing with the improvements in term of methanol production and selectivity. They proposed the use of zeolite membranes for methanol synthesis owing to their selectivities and satisfactory permeabilities. Zeolite membranes with different methanol and water permeance values were considered in the membrane reactor modeling. Their thermodynamic analysis shows that MR can operate at higher temperature and lower pressure than a traditional system, achieving higher conversions and higher selectivity. Moreover, lower residence time and lower reaction volume can be used in a membrane reactor with respect to a traditional system. The reactor simulations were performed by using the data of both organophilic and hydrophilic membranes. Both membrane reactor simulations showed better results than a traditional reactor (TR). In particular, the organophilic membrane reactor showed a higher yield than the hydrophilic membrane reactor.

From an experimental point of view, Gallucci et al. (17) performed experiments on methanol production in a zeolite membrane reactor to overcome the lack of experimental data on CO_2 conversion into methanol using a zeolite MR. The results showed a good performance of the MR with respect to the

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TR: at the same experimental conditions, CO_2 conversion for the MR was higher than that related to the TR. This improvement can also be seen in the sense that the same CO_2 conversions of TR can be reached by working with MR in less drastic conditions, for instance working at lower temperatures and pressures. This aspect should notably reduce the energy demand. In fact, for instance, with the membrane reactor at $H_2/CO_2 = 3$ and $T = 225°C$ it is possible to obtain the same conversion of a TR working at 265°C.

It should be stressed that, when zeolite membrane reactors are used, particular attention should be paid to the operating temperature: to avoid methanol yield loss, the critical temperature of methanol must not be exceeded. In fact, the methanol (and water) selective removal is obtained by the capillary condensation of methanol (and/or water) inside the zeolite pores. This separation is only effective if methanol can condense into the membrane pore, and this can be obtained only at temperatures as low as the methanol critical temperature (238°C).

It should be said that, by coupling the good results obtained in the catalyst developments with a new membrane reactor concept (using polymeric or inorganic membranes), it could be possible to obtain very high reactants conversion and high methanol yield at low temperatures and pressures. In other words, the performances of the traditional reactors are improved by using highly selective and active catalysts, while the performances of membrane reactors are improved by tuning other variables such as the membrane thickness, the membrane selectivity to a fixed product, the sweep gas flow rate, etc.

Table 2 summarizes the improvements that can be achieved by using a membrane reactor with respect to a traditional one. In particular, the most promising results are obtained when methanol and/or water are selectively removed from the reaction zone.

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USE OF METHANOL IN REACTIONS

C1 chemistry refers to the utilization of single carbon-bearing molecules, such as carbon monoxide, syngas (a mixture of CO and hydrogen),

Table 2. Improvements obtained using MRs for methanol production

Membrane used	Results respect to the TR	Reference
Lithiated Nafion	40% Methanol yield improvement	(9)
Pd-Ag	9% Respect to the thermodynamic equilibrium	(13)
Lithiated Nafion	40% Methanol yield improvement	(14)
Silicone rubber/ceramic	22% Conversion improvement	(15)
Zeolite	60% Conversion improvement	(16)
Zeolite	132% Conversion improvement	(17)

carbon dioxide, methane and methanol, for the production of valuable chemicals, petrochemical intermediates, and ultra-clean transportation fuels. C1 chemistry could also be used to produce high-purity hydrogen or premium chemicals from synthesis gas or from methanol. C1 chemistry has become a major area of research interest for the production of pure chemicals and transportation fuels (18).

Methanol has some advantages as a fuel and source of chemical products, such as being more easily transportable than methane or other gas fuels, having high energy density, desulphurization being unnecessary and reaction proceeding at a moderate temperature (200–400°C) (19).

Recent global energy shortage and more stringent emission regulations have stimulated research and development in the field of fuel cells. If the fuel cell is fed by a humid hydrogen stream, the highest energy efficiency is reached. The main problem is that hydrogen is not available in nature and so a fuel processor is critical technology for the development, for example, of a polymer-electrolyte membrane fuel cell (PEMFC) for on-board and stationary applications (20). Methanol and gasoline are both considered as the two most promising energy carriers for fuel cells (21). In particular, methanol can also be used in direct methanol fuel cells (DMFC) as fuel.

There are four main alternatives for the conversion of methanol into hydrogen:

Steam reforming:

$$CH_3OH + H_2O \Longleftrightarrow CO_2 + 3H_2 \qquad \Delta H_{298K} = 49.51\,\mathrm{kJ/mol}$$

Partial oxidation:

$$CH_3OH + 0.5O_2 \Longleftrightarrow CO_2 + 2H_2 \qquad \Delta H_{298K} = -192.2\,\mathrm{kJ/mol}$$

Oxidative steam reforming:

$$CH_3OH + H_2O \Longleftrightarrow CO_2 + 3H_2 \qquad \Delta H_{298K} = 90.7\,\mathrm{kJ/mol}$$
$$CH_3OH + 0.5O_2 \Longleftrightarrow CO_2 + 2H_2 \qquad \Delta H_{298K} = -192.2\,\mathrm{kJ/mol}$$

Methanol decomposition:

$$CH_3OH \Longleftrightarrow CO + 2H_2 \qquad \Delta H_{298K} = 90.70\,\mathrm{kJ/mol}$$

In the following each of them is considered in detail.

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Methanol Steam Reforming

Traditional Systems

The first studies about methanol steam reforming considered this reaction as the reverse of methanol production from CO and H_2:

$$CO + 2H_2 \Longleftrightarrow CH_3OH \qquad \Delta H_{298K} = -90.70\,\text{kJ/mol} \tag{1}$$

The main hypotheses were: (1) methanol steam reforming proceeded towards carbon monoxide and hydrogen production, and afterwards (2) the water gas shift reaction takes place (22–25):

$$CH_3OH \Longleftrightarrow CO + 2H_2 \qquad \Delta H_{298K} = +90.70\,\text{kJ/mol} \tag{2}$$

$$CO + H_2O \Longleftrightarrow CO_2 + H_2 \qquad \Delta H_{298K} = -41.19\,\text{kJ/mol} \tag{3}$$

Later, it was proposed that methanol was synthesized by carbon dioxide direct hydrogenation, and so the supposed reaction path for the methanol steam reforming reaction system was also changed. Carbon dioxide formation by the reaction between methanol and water was proposed in several articles and different opinions about the importance of the water gas shift reaction were also proposed, while the direct methanol decomposition reaction was declared to be unimportant by different researchers (26, 27).

Nowadays, according to the literature, the chemical reactions considered are the following:

$$CH_3OH \Longleftrightarrow CO + 2H_2 \qquad \Delta H_{298K} = +90.70\,\text{kJ/mol} \tag{2}$$

$$CO + H_2O \Longleftrightarrow CO_2 + H_2 \qquad \Delta H_{298K} = -41.19\,\text{kJ/mol} \tag{3}$$

$$CH_3OH + H_2O \Longleftrightarrow CO_2 + 3H_2 \qquad \Delta H_{298K} = +49.51\,\text{kJ/mol} \tag{4}$$

Reactions (2) and (4) are both reversible and endothermic reactions and proceed under volume increase, so the highest methanol conversions are obtained at high temperature and low pressures. The exothermic reaction (3) is the well-known water gas-shift reaction, which takes place simultaneously with methanol steam reforming and proceeds without volume change. However, when this reaction system is carried out in TRs it leads to a hydrogen-containing mixture, so hydrogen needs purification before being fed to a polymer electrolyte membrane fuel cell (28). This separation is mainly devoted to removing CO, which poisons the anodic catalyst of the PEMFC.

Transition metals (Pd, Pt, Rh) exhibit high methanol decomposition activity to CO and H_2. Reactions such as methanol steam reforming, oxidative steam reforming, methanol synthesis and water gas shift reactions proceed at high rates on Cu-based catalysts but not on precious metal catalysts (20, 29).

Iwasa et al. (30) first discovered that, when supporting Pd and other precious metal on ZnO, the catalytic function of metals can be greatly modified, resulting in a high active and selective catalyst for methanol

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steam reforming, which was not found previously on precious metals. In particular, these authors found that at 493 K the selectivities obtained over ZnO supported catalysts always exceed those over SiO_2 supported ones. No reaction occurred over ZnO or Zn alone.

Chin et al. (20) studied a series of Pd/ZnO catalysts with a nominal Pd concentration of 4.8, 9.0 and 16.7 wt%. They found that, increasing Pd loading from 4.8 to 16.7%, results in the shift of the conversion profile to lower temperatures. Among the three catalysts examined, the 16.7 wt% Pd/ZnO catalyst exhibits the lowest CO selectivity.

Segal et al. (31) studied methanol steam reforming over layered double hydroxide-derived (LDHs) catalysts. They found that the Ni/Al and Co/Al LDHs catalysts were active in the methanol steam reforming reaction, but the activation temperature (315–320°C) was significantly higher than that of Cu/Al catalysts. Furthermore, no catalytic activity was observed for the Mg/Al LDH catalyst.

Following Agrell et al. (32) it is possible to operate the Cu/Al catalyst under conditions where CO concentrations are much lower than those predicted by thermodynamics, as long as the temperature is low enough and the contact time is short enough to prevent the complete conversion of methanol. Thus, there is a trade-off between high methanol conversion and low CO-levels.

Lindström et al. (33) and Pettersson et al. (34) studied the activity of copper-based catalysts containing 10 wt% active materials on γ-alumina pellets. Catalysts are binary and ternary promoted copper catalysts. The promoters used were chromium, zinc and zirconium. In general, high copper contents yield increased hydrogen concentrations in the product gas, except for Cu/Zn where the activity is virtually unchanged. An explanation can be that zinc cannot influence the dispersion of copper in a positive way at high copper concentrations. On the other hand, chromium promotes catalyst activity, especially at high temperature. These authors found that ternary Cu/Cr/Zn and Cu/Cr/Zr mixtures give lower CO concentrations than binary Cu/Cr, Cu/Zn and Cu/Zr mixtures.

Shen and Song (35) studied the influence of the preparation method on the performance of Cu/Zn catalysts for methanol steam reforming reaction. Several methods including impregnation, co-precipitation and hydrothermal synthesis were employed for the preparation of catalyst for methanol steam reforming, and the catalytic results show that the preparation method plays an important role in methanol steam reforming. In particular, the catalyst with lower copper-reduction temperature shows higher activity in producing hydrogen from methanol steam reforming. Another important result is that the catalyst prepared by a proper co-precipitation method in their laboratory showed high performance with high methanol conversion and low CO formation in the products at a lower reaction temperature, when compared to the commercial catalyst and laboratory catalysts prepared by other methods.

Takahashi et al. (36) studied catalysts prepared from amorphous alloys. In particular, they studied the methanol steam reforming over Cu-Zr-Au

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amorphous alloys and over Cu-Zr-Pd amorphous alloys. For $(Cu_{50}Zr_{50})_{90}Au_{10}$ alloy, the initial activity is quite low and the activity increased with the number of regenerations. Methanol conversion decreased with process time due to the coke deposition on the alloy surface. These authors also demonstrated that the gold content positively affects the initial conversion. For Cu-Zr-Pd catalysts, the conversion is not affected by the palladium content. Furthermore, the conversion does not change with the number of regeneration cycles.

Liu et al. (37) studied the effect of ceria on Cu/CeO_2 catalysts activity. They prepared 3.9 wt% Cu/CeO_2 catalysts by both a co-precipitation method and an impregnation method. The 3.9 wt% Cu/CeO_2 (co-p.) shows a conversion of methanol higher than those over 3.9 wt% Cu/CeO_2 (impr.), Cu/ZnO, Cu/Zn(Al)O and Cu/Al_2O_3 with the same Cu loading under the same reaction experimental conditions. This fact indicates that the synthesis method influences the catalytic activity of the catalysts. Furthermore, it has been reported that Cu^+ species are important for both the activation of the steam reforming of methanol and its reverse reaction. Since CeO_2 strongly interacts with the supported metal, the following electron transfer can occur between the CeO_2 (support) and Cu (particles):

$$Ce^{4+} + Cu \Longleftrightarrow Ce^{3+} + Cu^{+}$$

In this reaction Cu^+ species are produced and the Cu/CeO_2 catalysts are active and stable (38).

Zhang and Shi (39) reported the effect of CeO_2 concentration in CeO_2 promoted Cu/Al_2O_3 catalysts prepared by a co-precipitation method. An increase in methanol conversion with increasing CeO_2 concentration was found. In particular, beyond 20 wt% of CeO_2, methanol conversion begins to decrease. The promoted catalysts show high selectivity for hydrogen and low selectivity for CO. Their results also show: (a) the promoted Cu/Al_2O_3 catalysts exhibit a better catalytic performance as compared to the unpromoted ones; (b) CeO_2 has an important influence on improving catalytic activity and decreasing the outlet CO concentration.

Tsai and Yoshimura (40) carried out the steam reforming reaction over quasi-crystalline Al-Cu-Fe catalyst. Icosahedral quasi-crystals were discovered in 1984, and their promising application is catalysis. In their work, a nominal alloy of stable quasi-crystal $Al_{63}Cu_{25}Fe_{12}$ was prepared. The size of copper and copper oxide particles is estimated to be around 15 nm. The sample used in methanol steam reforming shows that the quasi-crystalline phase still persists in the sample even after the catalytic reaction. For understanding the origin of high activity on the quasicrystalline alloy, the concentration of metallic ions in the leaching solution was analyzed. The analysis identified a very thin film with Cu^{2+} species at the surface of the leaching samples, before and after the catalytic reaction. The authors concluded that the excellent activities of the reactions are due to the existence of copper or copper oxide particles at the surface of the quasi-crystal.

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Membrane Processes for the Methanol Steam Reforming

In the methanol steam reforming reaction carried out in a traditional reactor, the reformate gas contains approximately 75% by volume of hydrogen, the rest being carbon dioxide and carbon monoxide. Thus, the hydrogen produced is further purified to a level of 95% for industrial application or even higher (less than 10 ppm) for fuel cells applications. Actually, different purification processes such as gas separation membranes or the widely used pressure swing adsorption (PSA) process are industrially available. By considering the need for an extra purification facility, the whole pure hydrogen production process becomes very complicated and expensive. Another factor to be considered is that the efficiency of the PSA process is not higher than 85% and this would limit the overall recovery yield of hydrogen (41, 42).

Although their advantages in equilibrium limited reactions such as dehydrogenation reactions are well-documented in the literature (43), membrane reactors are rarely considered in comparison to the additional cost of integrating the reactor and the membrane unit. Methanol steam reforming units for the fuel cell systems, in particular for automotive applications, may succeed in breaking this tendency. In fact, for fuel cells, both hydrogen yield and high-hydrogen purity are key factors (44). Moreover, membrane reactors are more compact and lighter than the traditional ones and also the thermal mass is reduced; thus they are simpler to operate. Therefore, the total absence of impurities in the fuel cell feed coming from the dense membrane reactor, allows maximum power output at low specific weight and high efficiency. Considering all these advantages, we can state that a worthwhile process for methanol steam reforming is the membrane process in which a dense selective membrane is used for selectively removing hydrogen from the reaction side which shifts the thermodynamic equilibrium towards the reaction products.

Although high methanol conversion values can be achieved in dense membrane reactors, in the work of Rei et al. (45) it is shown how a palladium membrane reactor can give also an increase in the forward reaction rate. In fact, they found that the hydrogen spillover from the Pd-membrane makes the active site on the catalyst surface more efficient and free for the new reactant molecules. As shown in Figure 2, a dense and thin Pd-based membrane can be used to remove only hydrogen from the reaction side and obtain high methanol conversion and high CO-free hydrogen production (28, 46). In the same figure, both methanol conversion and hydrogen recovery versus temperature are reported. It is possible to see that the membrane reactor gives better results in terms of methanol conversion compared to a traditional reactor operating at the same experimental conditions. It can also be seen that up to 90% of the total hydrogen produced in the membrane reactor can be recovered as a CO-free hydrogen stream. Methanol conversion, as well as hydrogen recovery, in this system also

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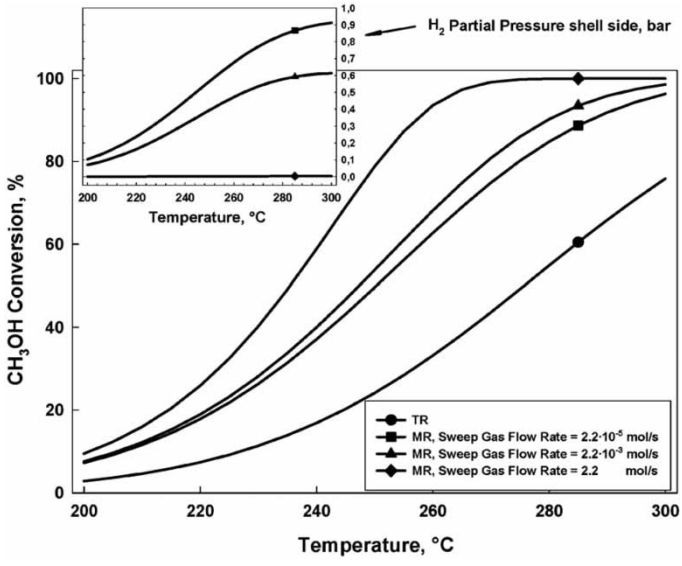

Figure 2. CH_3OH conversion vs temperature for the traditional reactor and membrane reactor. Reprinted from (46) with permission from ACS.

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depends on the sweep gas flow rate. In fact, by increasing the sweep gas flow rate both the methanol conversion and the hydrogen recovery increase too.

Concerning the sweep gas, it should be pointed out that in a dense palladium membrane reactor, water can also be used in the shell side of the reactor. In this case, the shell outlet stream is an H_2-water mixture which can easily be separated by a flash stage and the CO-free wet H_2 stream can directly be fed into a fuel cell, resulting in high fuel cell efficiency.

Finally, for methanol steam reforming, different membrane types showed high hydrogen selectivity; among these membranes the Pd-based (47, 48), Pd/V/Pd, $Pd_{75}Ag_{25}$, $Pd_{60}Cu_{40}$ (44), or the Pd-supported membranes (49, 50) are worth noting for their stability.

Partial Oxidation and Oxidative Methanol Steam Reforming

Traditional Systems

Normally, methanol partial oxidation is also carried out in the presence of water. The combination of methanol steam reforming and partial oxidation is called *oxidative methanol steam reforming*:

$$CH_3OH + H_2O \Longleftrightarrow 3H_2 + CO_2 \qquad \Delta H_{298K} = 49.51\,\text{kJ/mol} \tag{5}$$

$$CH_3OH + 0.5O_2 \Longleftrightarrow 2H_2 + CO_2 \qquad \Delta H_{298K} = -192.2\,\text{kJ/mol} \tag{6}$$

The large amount of energy produced by reaction (6) suggests the use of this energy to promote the reaction (5). By tuning the quantities of oxygen and water in the feed mixture, it is possible to make the whole process isothermal and, in this case, it is called *autothermal reforming* (47):

$$\begin{aligned} &CH_3OH + 0.8H_2O + 0.1O_2 \Longleftrightarrow 2.8H_2 + CO_2 \\ &\Delta H_{298K} = 0\,kJ/mol \end{aligned} \tag{7}$$

The reaction (7) is promoted by Cu/ZnO-based catalysts (51), the same catalyst used in the methanol steam reforming reaction, while only reaction (6) is promoted by Pt/Al_2O_3 catalysts (52).

By finely tuning the reaction temperature (270°C) it is possible to obtain a high reaction rate with low carbon monoxide and methane selectivities (53). To avoid total methanol oxidation the reaction (6) is carried out with a low amount of oxygen.

In the oxidative methanol steam reforming process, Velu et al. (54) used different CuZnAl(Zr) catalysts, obtaining a methanol conversion around 90% at 230°C. They showed that methanol conversion and hydrogen production is strongly affected by the catalyst composition, the feed flow ratios O_2/CH_3OH and H_2O/CH_3OH (Figure 3). In this figure it can also be seen that both methanol conversion and hydrogen production have a maximum at $H_2O/CH_3OH = 1$, and the hydrogen production is 3 times the carbon dioxide production and 300 times the carbon monoxide production. In the same figure, the ratio "hydrogen production/methanol conversion" is reported: it is almost constant (around 3) for the whole range of H_2O/CH_3OH investigated.

The oxidative methanol steam reforming reaction was studied in traditional and membrane reactors. For example, Ma et al. (52) used different adiabatic traditional catalytic reactors ($433\ K < T < 573\ K$), with spherical and/or cylindrical doubled bed geometry, to promote the internal thermal exchange between the steam reforming and the partial oxidation zones. Their analysis showed that the cylindrical coaxial reactor and the double-bedded single reactor normally requires an optimal H_2O/CH_3OH feed flow ratio 3–4 times the feed flow ratio required by a spherical reactor. In their study, the best configuration is the spherical one with the oxidation catalyst placed in the central part and the reforming catalyst in the external part.

Membrane Processes for the Partial Oxidation and Oxidative Methanol Steam Reforming

Lin et al. (50) used a double-shell palladium membrane reactor for the methanol partial oxidation reaction system. In the first shell the methanol steam reforming reaction takes place on a Cu-based catalyst, while in the second shell the oxidation reaction proceeds on a Pd/Al_2O_3 catalyst. The hydrogen is continually removed by means of a highly selective palladium

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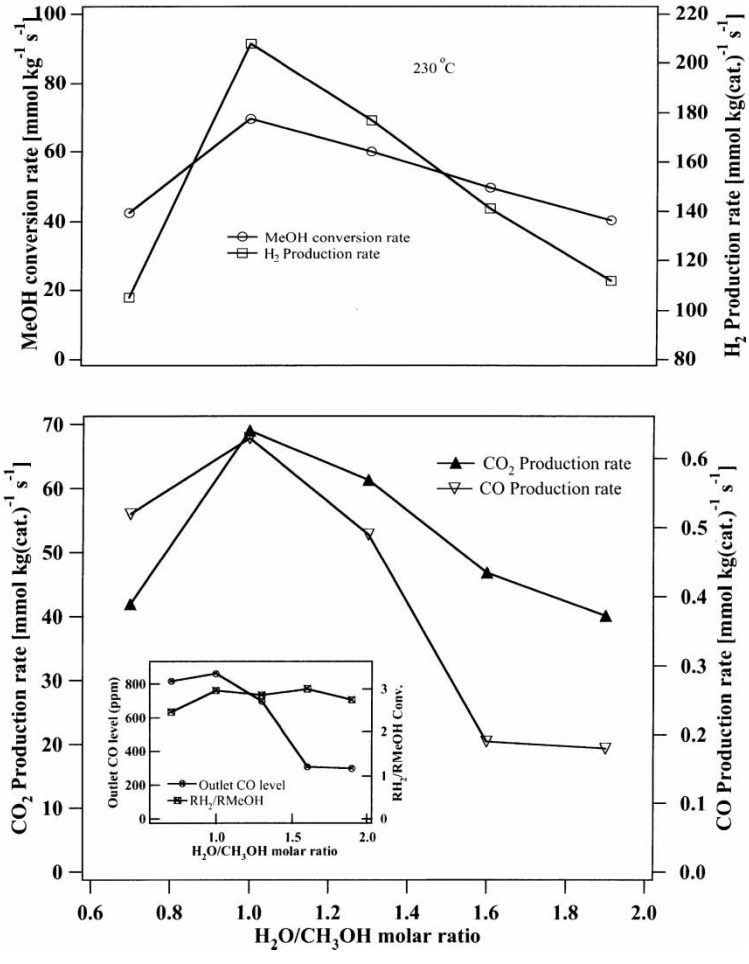

Figure 3. Effect of H_2O/CH_3OH molar ratio on the catalytic performances in the oxidative steam reforming reaction. Reprinted from (54) with permission from Elsevier.

membrane. They studied the pressure effect on the reaction. In particular, by increasing the pressure from 6 to 15 bar, the hydrogen removed increases from 28% to 73%. Moreover, high hydrogen removal results in a lower CO and CO_2 selectivity than the traditional system.

Basile et al. (55) used a Pd-Ag dense membrane in which the oxidative methanol steam reforming takes place on a Cu-based catalyst. The O_2/CH_3OH feed flow ratio was changed from 0 to 0.25 (mol/mol). The best results in terms of methanol conversion, hydrogen production and catalyst selectivity are obtained at a feed flow ratio 0.17. Too much oxygen (O_2/

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$CH_3OH = 0.25$) can give a fast catalyst deactivation and hydrogen consumption by means of the un-reacted oxygen can occur (Figure 4).

Compared with methanol steam reforming, oxidative steam reforming has a higher reaction rate, which results in a higher hydrogen production and a higher hydrogen partial pressure in the reaction side. For this reason the advantages of the MR in the oxidative steam reforming of methanol are more evident with respect to methanol steam reforming. A higher value of hydrogen recovery can be reached at the low temperature in which the reaction takes place.

Methanol Decomposition Reaction

Traditional Systems

The methanol decomposition reaction to a mixture of carbon monoxide and hydrogen mixture (syngas)

$$CH_3OH \Longleftrightarrow 2H_2 + CO \qquad \Delta H_{298K} = 90.7\,\mathrm{kJ/mol}$$

is a hydrogen source for fuel cells (after carbon monoxide separation). It represents a source in chemical and/or materials processes, but it can also be used as additional fuel in gas turbines (in particular at peak hours) (56).

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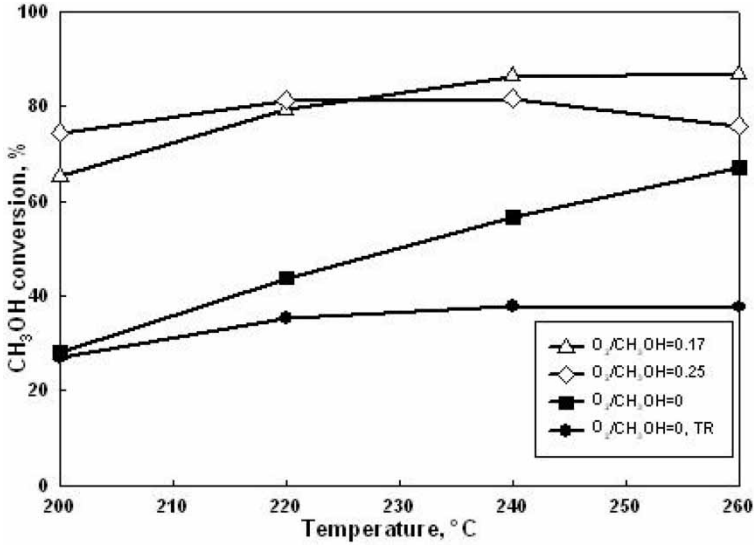

Figure 4. Methanol conversion vs. temperature at various O_2/CH_3OH feed ratios.

The equilibrium conversion is around 100% at 473 K, and atmospheric pressure.

Different catalysts were studied for this reaction. The Ni-based catalysts are not selective towards the syngas production due to the methane formation (57). The Pt-based and the Pd-based catalysts show a high selectivity at low temperature, but this selectivity is strongly affected by the catalyst support. A CeO_2 support is commonly used (57, 58); Cr can also improve the stability of such a catalyst (59).

Other researchers used Cu-based, Zn/Cr-based, and VIII group metal-based catalysts for this reaction. It was found that Cu-based catalysts activity can be improved by adding a small quantity of alkali in the catalysts (60), as reported in Table 3. In particular, the best results in terms of methanol conversion as well as hydrogen selectivity can be achieved with a Cu/Cr/Mn/K catalyst, which gives a 63% methanol conversion and a 91.6% hydrogen selectivity, while with a Cu/Cr/Mn catalyst these values are 42% and 67.8%, respectively. Following Cheng et al. (59), the only problem is that carbon monoxide and carbon dioxide selectivity also increase, whereas dimethyl ether and methyl formate decrease. Cu/Cr-based catalysts with a little quantity of Mn, Ba or Si oxides show high activity at low temperature also.

Cr-oxide acidity promote the production of dimethylether from methanol dehydrogenation. Anyway, the use of potassium as a promoter can reduce dimethylether formation and promote CO formation. It was also demonstrated that Cu-based catalysts deactivation, by carbon deposits at high temperature, can be drastically reduced by using CO_2 in the reactor feed (60). In each case, removing the carbon deposits, the catalyst can be reactivated by means of an oxidation step, followed by a reduction step for getting the Cu in the metallic form (59).

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Table 3. Methanol decomposition over alkali-promoted and unpromoted Cu/Cr/Mn catalysts (after (59))

Reaction temperature (°C)	Catalyst	MeOH conversion (%)	CO Selectivity (%)	H_2 Selectivity (%)
225	Cu/Cr/Mn	42.4	35.7	67.8
	Cu/Cr/Mn/Na (2%)	44.4	46.1	73.9
	Cu/Cr/Mn/K (2%)	43.3	54.3	78.1
250	Cu/Cr/Mn	49.6	55.1	78.8
	Cu/Cr/Mn/Na (2%)	53.4	59.5	79.5
	Cu/Cr/Mn/K (2%)	53.1	72.3	86.7
275	Cu/Cr/Mn	59.8	66.5	82.1
	Cu/Cr/Mn/Na (2%)	62.7	71.9	86.1
	Cu/Cr/Mn/K (2%)	63.2	81.6	91.6

Membrane Processes for the Methanol Decomposition Reaction

The methanol decomposition reaction was also studied in a Pd-based membrane reactor (61). Pure methanol was fed, at 200–250°C and at 0.12–0.2 MPa in the membrane reactor, by using a dense, tubular $Pd_{91}Ru_6In_3$ membrane 0.2 mm thick and a Pd/SiO_2 catalyst. It was observed that selective hydrogen removal promotes the formation of by-products like CO_2 with small amounts of H_2O, CH_4, acetone and acetic acid. Considering the reactant conversion, at 0.2 MPa the TR gives a conversion of about 42% while the MR gives a conversion of about 55%. The difference between the TR and the MR increases by increasing the reaction pressure. This is because the higher the reaction pressure the higher the hydrogen partial pressure in the reaction zone and so the higher the hydrogen removal from the reaction zone, with a greater effect in shifting the equilibrium.

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Methanol Oxidation

Traditional Systems

The catalytic methanol oxidation reaction

$$CH_3OH + 0.5O_2 \Longleftrightarrow 2H_2 + CO_2 \qquad \Delta H_{298K} = -192.2\,\text{kJ/mol}$$

is an exothermic reaction positively affected by low temperatures.

The low catalytic activity at such a low temperature makes the process kinetically feasible at moderate temperatures. However, these temperatures are affected by: the catalyst type and composition, the reaction time, the feed flow ratio, the catalyst preparation technique, etc.

Recently, for example, Alejo et al. (62) demonstrated that $Cu_{40}Zn_{55}Al_5$ catalysts show a good activity for more than 110 hrs at 230°C while $Cu_{40}Zn_{60}$ catalysts already lose their activity after 20 hrs.

Other researchers demonstrated that $Cu_{40}Zn_{60}$ catalysts with a feed flow ratio $O_2/CH_3OH = 1$ can produce hydrogen at 185°C if the catalyst is produced by micro-emulsion, while the temperature is 215°C if the catalyst is produced by the co-precipitation technique. When the O_2/CH_3OH feed flow ratio is 0.5, the methanol conversion is 75% at 325°C ($Cu_{40}Zn_{60}$ catalysts produced by micro-emulsion). The oxygen partial pressure influences both the catalytic activity and the product distribution (63).

Membrane Processes for the Methanol Oxidation

Membrane reactors were also used to carry out methanol oxidation reaction. For example, Brinkmann et al. (64) used a tubular multilayer ceramic membrane (α-Al_2O_3 and γ-Al_2O_3) and carried out the reaction using a

Pt-based catalyst. At 350°C and 1 bar, by using a stoichiometric O_2/CH_3OH feed flow ratio, the methanol conversion was 100%. Other studies (65) used catalytic Pd membrane (25 μm thick) at 0.2 bar and 350°C. It was observed that the oxygen in the reactive mixture avoids the carbon deposit formation on the catalytic surface owing to the carbon dioxide reaction formation that takes place.

γ-Al_2O_3 ceramic membranes supported on α-Al_2O_3 were used by Ren et al. (66) in the temperature range 200–450°C and at 4 kPa giving dimethylether formation (maximum at 450°C). Above this temperature, the main products are CO and H_2.

Figure 5 shows a scheme of the hydrogen production from methanol and its use. In the following the use of methanol in fuel cell applications is considered in detail. Before concluding this section, it is worth highlighting that the Pd membranes suffer of some limitations. Two of them, in particular, are:

- The hydrogen embrittlement that is caused by the large distortion in the lattice structure due to the α-β phase transformation. When the cyclic stress is present by adsorption and desorption of hydrogen, the palladium becomes very brittle. This mechanical instability is somewhat decreased by making alloys with other metals such as Ag, Ru, Rh or other rare earths.
- The sensitivity to poisoning in the presence of CO, H_2S, SO_2, sulphur, arsenic, chlorine, mercury, zinc, unsaturated hydrocarbons, and so on.

Other specific problems related to composite palladium-based membranes are due to the instability of thin Pd films on a ceramic support. Other problems regard the ceramic-metallic adherence and interface. All of these aspects are reported in the specialised literature.

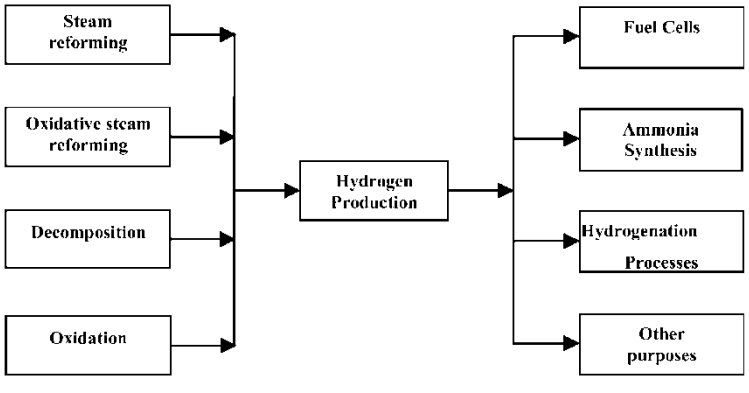

Figure 5. Scheme of hydrogen production methods from methanol and its uses.

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METHANOL IN FUEL CELLS

Today, an important application of methanol is its use as an energy carrier in the so-called direct methanol fuel cells (DMFCs). In the following the main important aspects of this application are considered.

Concept

In the case of DMFC, the fuel cell is directly fed with methanol. The DMFCs have potential uses in portable devices like mobile telephones or laptop computers, because the methanol can be directly fed as liquid to the fuel cell and so the whole system is much easier than one using hydrogen (that requires a hydrogen storage system or fuel processor) (67).

In a DMFC, methanol is oxidized at the anode and oxygen is reduced at the cathode, in the following cell reactions (68):

$$\text{Anode: } CH_3OH_{(l)} + H_2O_{(l)} \longrightarrow CO_{2(g)} + 6H^+_{(l)} + 6e^-$$

$$\text{Cathode: } 3/2\ O_2(g) + 6H^+_{(l)} + 6e^- \longrightarrow 3H_2O_{(l)}$$

A scheme of a DMFC is reported in the following Figure 6, where the transport of the species through the membrane, are indicated (69).

DMFCs have been widely studied in the last few years from both a theoretical and an experimental point of view. A research in the literature databases gives more than 300 papers in the last 3 years dealing with DMFCs. All the theoretical aspects of DMFCs are reported by Sousa et al. (70) in their review.

Actually, compared with the Li ions batteries (used for portable devices), DMFCs have a very low energy density (71). To create a portable DMFC with high power density, a high methanol concentration in aqueous solution has to be used. Because of the methanol crossover through the membrane, usually in a DMFC a methanol concentration of 2 M is used. The transported methanol can react directly in the cathode reducing the DMFC voltage and poisoning the cathode catalyst (72). The suggested topics to increase the DMFC performances are the ion exchange membranes and the catalysts (73).

Concerning the catalysts, most of the papers focused on the active metals in binary, ternary and quaternary metal alloyed catalysts. The typical candidates for active metals are Pt, Pd, Rh, Ru supported alloys. In addition to the various kind of alloys used (and their compositions), the choice of adequate support, typically a carbon one, is a key factor that can affect the performance of the fuel cell. In the past, carbon blacks were mainly used as supporting materials for fuel cell applications. In the recent past, nanostructured carbon material, graphite carbon nanofiber and carbon nanotubes (CNTs) were utilized as the support materials of catalysts (74–76). Recently, Han et al. (75)

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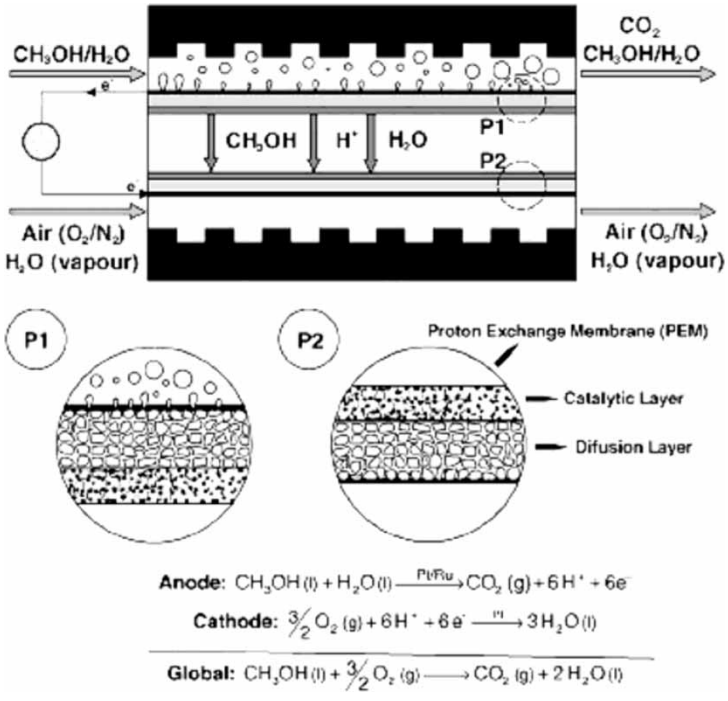

Figure 6. Sketch of a Direct Methanol Fuel Cell (DMFC). Reprinted from (69) with permission from Elsevier.

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reported a method to produce the carbon nanotube catalyst in two steps. In the first step they refluxed CNT with nitric acid at different concentrations and, afterwards, the metal precursor was attached to the fuctionalized surface with reducing agents. They found that the nitric acid concentration is important to control catalyst morphology. Guo et al. (76) produced PtRu catalysts with high metal loading and uniform dispersion on nanotubes and made a comparison with a commercial catalyst with the same amount of metal, finding out that, in the whole range of discharging current density, the performances of the DMFC with their catalyst is superior to the performance achievable with the commercial catalyst.

Membrane for DMFC Fuel Cells

The membrane used in the fuel cells has to show the following characteristics (72):

1. high proton conductivity and low membrane resistance (membrane should be thin);

2. high mechanical stiffness and negligible changes in the membrane area between the dry and the swollen state;
3. reduction of the methanol crossover;
4. high chemical stability during DMFC operation;
5. low manufacture cost.

Unfortunately, the membranes developed until now do not satisfy simultaneously all the above criteria.

Different authors proposed experimental solutions for reducing methanol crossover and producing low cost membranes. For example, Yamaguchi et al. (72) proposed a pore-filling electrolyte membrane composed of two materials: a porous substrate (with pore size of 1 micron or less) and a polymer able to fill the pores of the substrate (Figure 7). With this membrane type, methanol crossover is successfully reduced and a high methanol concentration (10 M) can be used, resulting in high power density DMFCs. Among the low-cost membranes for fuel cell applications, the sulfonated (poly-ether-ether ketone with cargo) PEEK-WC membranes seem to be really interesting (77, 78). Drioli et al. (77) and Paturzo et al. (78) showed the ease in preparing these membranes. In particular, the membranes of Drioli et al. present a methanol permeability lower than Nafion membranes.

In order to reduce methanol crossover, other authors proposed organic/inorganic composite membranes (79, 80). In particular, Zhang and Zhou (80), proposed a composite membrane made of sulfonated poly(ether ether ketone) and layered silicate organic-montmorillonite. The membranes

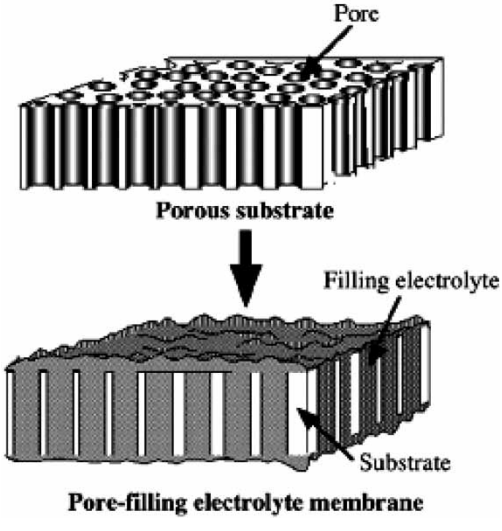

Figure 7. The concept of the pore-filling membranes. Reprinted from (72) with permission from Elsevier.

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produced exhibit a high conductivity at high temperature and low methanol permeability. Moreover, this kind of membrane is easy to produce and cheaper than the commercial perfluorinated membranes.

Although more effort still needs to be made in the fields of electrode catalysts and membranes for DMFC, a very important step to be optimized is the membrane electrode assembly (MEA) production. In fact, the fabrication of MEAs is mostly still done by hand and so affected by poor reproducibility, small size and long fabrication times. A continuous production of electrodes and MEAs is desirable for reaching more reproducible characteristics and lower costs (81).

Different processes for electrode layers generation are generally presented in the literature. In the first process the catalytic active materials are applied to commercial (or self-made) diffusion backings. Afterwards the electrodes are attached to an electrolyte membrane (generally Nafion) by hot-pressing. The production of the MEA could also be done by spraying the catalyst directly on the membrane surface and, afterwards, rolling the MEA in order to have a good fixation.

Lindermeir et al. (81), for example, reported different methods for producing MEA which can have different shapes (i.e., the catalyst is attached to the membrane or to the diffusers), depending on the preparation method (Figure 8).

Other papers explain the performance of passive DMFCs (meaning a DMFC in which external pumps or other devices for fuel and oxidant

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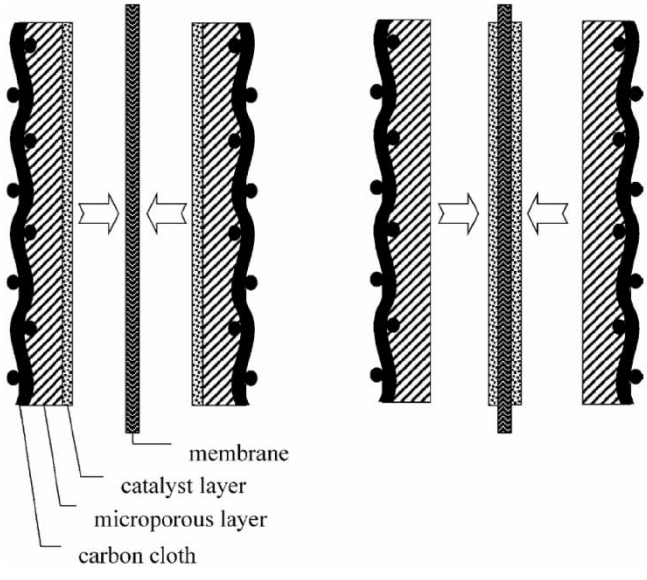

Figure 8. Different configurations of catalyst/diffusion backing and membrane for MEAs. Reprinted from (81) with permission from Elsevier.

supply are removed) (82, 83), of micro DMFC (in which the active area is in the order of 1–2 cm^2) for high power applications (84) and of DMFCs stack for high power systems (85).

Significant efforts are still necessary in order to commercialize a stable and functional direct methanol fuel cell system.

CONCLUSIONS

In this work an overview on methanol production and use both in reactions and in direct methanol fuel cells is presented, with particular attention to the membrane processes that can be used in these reaction systems for improving their performances. Concerning methanol production, the two most promising methods are the partial oxidation of biomass and the reaction between carbon dioxide and hydrogen. In the first case, methanol can be seen as a hydrogen (and power) source, while in the second case it can be seen as a hydrogen (and power) carrier. Although the catalysts for methanol production are available and well-studied, much effort is needed for process improvement. From this perspective, membrane reactors can be used for increasing methanol yield and process performances. Concerning methanol reactions to produce hydrogen, both the catalysts and reactor configurations have to be optimized. In particular, the catalysts have to be improved in stability and selectivity, while the reactor configurations can be improved by using palladium-based membrane reactors. In this way, it is possible to increase the hydrogen production and purification level. In more detail, the holy grail for this research area could be the optimization of the catalyst stability in the temperature range where the membranes (Pd-based) give the optimum in terms of hydrogen permeation rate and mechanical stability. In our opinion, future research should be focused on the optimization of a catalyst different from the Cu-based ones, in order to combine catalyst stability and the high hydrogen permeation rate requested by the processes.

Finally, concerning the use of methanol in fuel cells, much effort has to be made to improve mainly the quality of the membranes used in the cells. The main problem is still methanol crossover, which is responsible for power cell loss and catalyst deactivation. Also in this case, the membrane development is a key aspect to be considered for the success of the whole process.

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REFERENCES

1. Güllü, D. and Demirbaş, A. (2001) Biomass to methanol via pyrolysis process. *Ener. Convers. Manag.*, 42: 1349–1356.
2. Brown, H.P. (1952) *Textbook of Wood Technology*; McGraw-Hill: New York; Vol. II.
3. Sorensen, H.A. (1983) *Energy Conversion System*; Wiley: New York.
4. Farbenindustrie Akt.-Ges, I.G. (1932) Verfahren Zur Darstellung von Methanol und Seinen Homologen. German Patent 565,309, Issued November 30.
5. Tijm, P.J.A., Waller, F.J., and Brown, D.M. (2001) Methanol technology developments for the new millennium. *Appl. Cat. A: Gen.*, 221: 275–282.
6. Parris, G.E. and Klier, K. (1986) The specific copper surface areas in Cu/ZnO methanol synthesis catalysts by oxygen and carbon monoxide chemisorption: evidence for irreversible CO chemisorption induced by the interaction of the catalyst components. *J. Catal.*, 97: 374–384.
7. Wang, J., Anthony, R.G., and Akgerman, A. (2005) Mathematical simulations of the performance of trickle bed and slurry reactors for methanol synthesis. *Comp. Chem. Eng.*, 29 (11–12): 2474–2484.
8. Slamet, Nasution, H.W., Purnama, E., Kosela, S., and Gunlazuardi, J. (2005) Photocatalytic reduction of CO_2 on copper-doped titania catalysts prepared by improved-impregnation method. *Cat. Comm.*, 6: 313–319.
9. Struis, R.P.W.J., Stucki, S., and Wiedorn, M. (1996) A membrane reactor for methanol synthesis. *J. Membrane Sci.*, 113: 93–100.
10. Westerterp, K.R., Kczynski, M., Bodewes, T.N., and Vrijland, M.S.A. (1989) Neue Konvertersysteme für die Methanol-Synthese. *Chem. Ing. Technol.*, 61: 193–199.
11. Wu, J., Saito, M., Takeuchi, M., and Watanabe, T. (2001) The stability of Cu/ZnO-based catalysts in methanol synthesis from a CO_2-rich feed and from a CO-rich feed. *Appl. Catal. A: Gen.*, 218: 235–240.
12. Rahimpour, M.R., Fathikalajahi, J., and Jahanmiri, A. (1998) Selective kinetic deactivation model for methanol synthesis from simultaneous reaction of CO_2 and CO with H_2 on a commercial copper/zinc oxide catalyst. *Can. J. Chem. Eng.*, 76: 753–760.
13. Rahimpour, M.R. and Ghader, S. (2004) Enhancement of CO conversion in a novel Pd-Ag membrane reactor for methanol synthesis. *Chem. Eng. Proc.*, 43 (9): 1181–1188.
14. Struis, R.P.W.J. and Stucki, S. (2001) Verification of the membrane reactor for methanol synthesis. *Appl. Catal. A: Gen.*, 216: 117–129.
15. Chen, G. and Yuan, Q. (2004) Methanol synthesis from CO_2 using a silicone rubber/ceramic composite membrane reactor. *Separ. Purif. Technol.*, 34: 227–237.
16. Barbieri, G., Marigliano, G., Golemme, G., and Drioli, E. (2002) Simulation of CO_2 hydrogenation with CH_3OH removal in zeolite membrane reactor. *Chem. Eng. J.*, 85 (1): 53–59.
17. Gallucci, F., Paturzo, L., and Basile, A. (2004) An experimental study of CO_2 hydrogenation into methanol involving a zeolite membrane reactor. *Chem. Eng. Proc.*, 43: 1029–1033.
18. Roberts, C.B. and Elbashir, N.O. (2003) An overview to "Advances in C1 chemistry in the year 2002". *Fuel Process. Technol.*, 83: 1–9.
19. Sekizawa, K., Yano, S., Educhi, K., and Arai, H. (1998) Selective removal of CO in methanol reformed gas over Cu-supported mixed metal oxide. *Appl. Cat. A: Gen.*, 169: 291–297.

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20. Chin, Y.H., Dagle, R., Hu, J., Dohnalkova, A.C., and Wang, Y. (2002) Steam reforming of methanol over highly active Pd/ZnO catalyst. *Cat. Today*, 77: 79–88.
21. Han, J., Kim, I., and Choi, K.S. (2000) Purifier-integrated methanol reformer for fuel cell vehicles. *J. Power Sources*, 86: 223–227.
22. Meyer, A.P., Bett, J.A.S., Vartanian, G., and Sederquist, V. (1978) U.S. Army Technical Report DAAK70-77-C-0195.
23. Santacesaria, E. and Carrà, S. (1978) Kinetics of steam reforming of methanol. *Riv. Combust.*, 32 (7–8): 227–232.
24. Amphlett, J.C., Evans, M.J., Mann, R.F., and Weir, R.D. (1985) Hydrogen-production by the catalytic steam reforming of methanol. 2. Kinetics of methanol decomposition using girdler G66b catalyst. *Can. J. Chem. Eng.*, 63: 605–611.
25. Amphlett, J.C., Mann, R.F., and Weir, R.D. (1988) Hydrogen-production by the catalytic steam reforming of methanol. 3. Kinetics of methanol decomposition using C18HC catalyst. *Can. J. Chem. Eng.*, 66 (6): 950–956.
26. Dümpelmann, R. (1992) Kinetische Untersuchungen des Methanolreforming und der Wassergaskonvertierungsreaktion in einem konzentrationsgeregelten Kreislaufreaktor. Ph.D. Dissertation, Eidgenössischen Technischen Hochschule: Zürich.
27. Jiang, C.J., Trimm, D.L., Wainwright, M.S., and Cant, N.W. (1993) Kinetic study of steam reforming of methanol over copper-based catalyst. *App. Cat. A*, 93 (2): 245–255.
28. Basile, A., Gallucci, F., and Paturzo, L. (2005) A dense Pd/Ag membrane reactor for methanol steam reforming: experimental study. *Cat. Today*, 104: 244–250.
29. Takezawa, N. and Iwasa, N. (1997) Steam reforming and dehydrogenation of methanol: Difference in the catalytic functions of copper and group VIII metals. *Cat. Today*, 36: 46–56.
30. Iwasa, N., Masuda, S., and Takezawa, N. (1995) Steam reforming of methanol over Ni, Co, Pd a nd Pt supported on ZnO. *React. Kinet. Cat. Lett.*, 55 (2): 349–353.
31. Segal, S.R., Anderson, K.B., Carrado, K.A., and Marshall, C.L. (2002) Low temperature steam reforming of methanol over layered double hydroxide-derived catalysts. *Appl. Cat. A*, 231: 215–226.
32. Agrell, J., Birgersson, H., and Boutonnet, M. (2002) Steam reforming of methanol over a $Cu/ZnO/Al_2O_3$ catalyst: a kinetic analysis and strategies for suppression of CO formation. *J. Power Sources*, 106: 249–257.
33. Lindström, B. and Pettersson, L.J. (2001) Hydrogen generation by steam reforming of methanol over copper-based catalysts for fuel cell applications. *Int. J. Hydrogen Ener.*, 26: 923–933.
34. Lindström, B. and Pettersson, L.J. (2002) Steam reforming of methanol over copper-based monoliths: the effects of zirconia doping. *J. Power Sources*, 106: 264–273.
35. Shen, J.P. and Song, C. (2002) Influence of preparation method on performance of Cu/Zn-based catalysts for low-temperature steam reforming and oxidative steam reforming of methanol for H_2 production for fuel cells. *Cat. Today*, 77: 89–98.
36. Takahashi, T., Inoue, M., and Kai, T. (2001) Effect of metal composition on hydrogen selectivity in steam reforming of methanol over catalysts prepared from amorphous alloys. *Appl. Cat. A: Gen.*, 218: 189–195.
37. Liu, Y., Hayakawa, T., Suzuki, K., and Hamakawa, S. (2001) Production of hydrogen by steam reforming of methanol over Cu/CeO_2 catalysts derived from $Ce_{1-x}Cu_xO_{2-x}$ precursors. *Cat. Comm.*, 2: 195–200.

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38. Fan, L. and Fujimoto, K. (1997) Reaction mechanism of methanol synthesis from carbon dioxide and hydrogen on ceria-supported palladium catalysts with SMSI effect. *J. Cat.*, 172: 238–242.
39. Zhang, X. and Shi, P. (2003) Production of hydrogen by steam reforming of methanol on CeO_2 promoted Cu/Al_2O_3 catalysts. *J. Mol. Cat. A: Chemical*, 194: 99–105.
40. Tsai, A.P. and Yoshimura, M. (2001) Highly active quasicrystalline Al-Cu-Fe catalysts for steam reforming of methanol. *Appl. Cat. A: Gen.*, 214: 237–241.
41. Chauvel, A. and Lefebvre, G. (1989) *Petrochemical Processes: Technical and Economic Characteristics*; Gulf Publishing Co.: Houston, 1.
42. Gallucci, F., Comite, A., Capannelli, G., and Basile, A. (2006) Steam reforming of methane in membrane reactor an industrial case study. *Ind. Eng. Chem. Res.*, 45 (9): 2994–3000.
43. Paturzo, L., Basile, A., and Drioli, E. (2002) High temperature membrane reactors and integrated membrane operations. *Rev. Chem. Eng.*, 18 (6): 511–551.
44. Wieland, S., Melin, T., and Lamm, A. (2002) Membrane reactors for hydrogen production. *Chem. Eng. Sci.*, 57 (9): 1571–1576.
45. Rei, B.M.H., Yeh, G.T., and Pan, C.W. (2004) Catalysis-spillover-membrane-2 [1] The rate enhancement of methanol steam reforming reaction in a membrane catalytic reactor. *Cat. Today*, 97: 167–172.
46. Gallucci, F., Paturzo, L., and Basile, A. (2004) Hydrogen recovery from methanol steam reforming in a dense membrane reactor: simulation study. *Ind. Eng. Chem. Res.*, 43: 2420–2432.
47. Emonts, B., Hansen, J.B., Schmidt, H., Grube, T., Höhlein, B., Peters, R., and Tschauder, A. (2000) Fuel cell drive system with hydrogen generation in test. *J. Power Sour.*, 86: 228–236.
48. Buxbaum, R. ⟨http://www.Rebresearch.com/Mressay.html (oct. 2006)⟩.
49. Lin, Y.-M. and Rei, M.-H. (2001) Study on the hydrogen production from methanol steam reforming in supported palladium membrane reactor. *Cat. Today*, 67: 77–84.
50. Lin, Y.-M. and Rei, M.-H. (2000) Process development for generating high purity hydrogen by using supported palladium membrane reactor as steam reformer. *Int. J. Hydrogen Ener.*, 25 (3): 211–219.
51. Amphlett, J.C., Evans, M.J., Jones, R.A., Mann, R.F., and Weir, R.D. (1981) Hydrogen-production by the catalytic steam reforming of methanol. 1. The thermodynamics. *Can. J. Chem. Eng.*, 59: 720–727.
52. Ma, L., Jiang, C., Adesina, A.A., Trimm, D.L., and Wainwright, M.S. (1996) Simulation studies of atothermal reactor system for H-2 production from methanol steam reforming. *Chem. Eng. J. Biochem. Eng. J.*, 62 (2): 103–111.
53. Schuessler, M., Lamla, O., Stefanovski, T., Klein, C., and zur Megede, D. (2001) Autothermal reforming of methanol in an isothermal reactor—Concept and realisation. *Chem. Eng. Technol.*, 24 (11): 1141–1145.
54. Velu, S., Suzuki, K., Kapoor, M.P., Ohashi, F., and Osaki, T. (2001) Selective production of hydrogen for fuel cells via oxidative steam reforming of methanol over CuZnAl(Zr)-oxide catalysts. *Appl. Cat. A*, 213 (2): 47–63.
55. Basile, A., Gallucci, F., and Paturzo, L. (2005) Hydrogen production from methanol by oxidative steam reforming carried out in a membrane reactor. *Cat. Today*, 104: 251–259.
56. Cheng, W.-H., Shiau, C.-Y., Liu, T.H., Tung, H.L., Chen, H.H., Lu, J.-F., and Hsu, C.C. (1998) Stability of copper based catalyst enhanced by carbon dioxide in methanol decomposition. *Appl. Cat. B*, 18: 63–70.

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57. Liu, Y., Hayakawa, T., Ishii, T., Kumagai, M., Yasuda, H., Suzuki, K., Hamakawa, S., and Murata, K. (2001) Methanol decomposition to synthesis gas at low temperature over palladium supported on ceria-zirconia solid solution. *Appl. Cat. A*, 210: 301–314.
58. Imamura, S., Higashihara, T., Saito, Y., Aritani, H., Kanai, H., Matsumura, Y., and Tsuda, N. (1999) Decomposition of methanol on Pt-loaded ceria. *Cat. Today*, 50 (2): 369–380.
59. Cheng, W.-H. (1995) Deactivation and regeneration of Cu/Cr based methanol decomposition catalysts. *Appl. Cat. B*, 7: 127–136.
60. Cheng, W.-H., Shiau, C.-Y., Liu, T.H., Tung, H.L., Lu, J.-F., and Hsu, C.C. (1998) Promotion of Cu/Cr/Mn catalyst by alkali additives in methanol decomposition. *Appl. Cat. A*, 170 (2): 215–224.
61. Hara, S., Xu, W.-C., Sakaki, K., and Itoh, N. (1999) Kinetics and hydrogen removal effect for methanol decomposition. *Ind. Eng. Chem. Res.*, 38 (2): 488–492.
62. Alejo, L., Lago, R., Peña, M.A., and Fierro, J.L.G. (1997) Partial oxidation of methanol to produce hydrogen over Cu-Zn-based catalysts. *Appl. Cat. A*, 162: 281–297.
63. Agrell, J., Hasselbo, K., Jansson, K., Järås, S.G., and Boutonnet, M. (2001) Production of hydrogen by partial oxidation of methanol over Cu/ZnO catalysts prepared by microemulsion technique. *Appl. Cat. A*, 239–250.
64. Brinkmann, T., Perera, S.P., and Thomas, W.J. (2001) An experimental and theoretical investigation of a catalytic membrane reactor for the oxidative dehydrogenation of methanol. *Chem. Eng. Sci.*, 56 (6): 2047–2061.
65. Amandusson, H., Ekedahl, L.-G., and Dannetun, H. (1999) Methanol induced hydrogen permeation through a palladium membrane. *Surface Sci.*, 442 (2): 199–205.
66. Zaspalis, V.T., Vanpraag, W., Keizer, K., Vanommen, J.C., Ross, J.R.H., and Burggraaf, A.J. (1991) Reactions of methanol over catalytically active alumina membranes. *Appl. Cat.*, 74 (2): 205–222.
67. Ren, X.M., Zelenay, P., Thomas, S., Davey, J., and Gottesfeld, S. (2000) Recent advances in direct methanol fuel cells at Los Alamos National Laboratory. *J. Power Sourc.*, 86: 111–116.
68. Sandhu, S.S., Crowther, R.O., and Fellner, J.P. (2005) Prediction of methanol and water fluxes through a direct methanol fuel cell polymer electrolyte membrane. *Electrochim. Acta*, 50: 3985–3991.
69. Silva, V.S., Weisshaar, S., Reissner, R., Ruffmann, B., Vetter, S., Mendes, A., Madeira, L.M., and Nunes, S. (2005) Performance and efficiency of a DMFC using non-fluorinated composite membranes operating at low/medium temperatures. *J. Power Sourc.*, 145: 485–494.
70. Sousa, R., Jr. and Gonzalez, E.R. (2005) Mathematical model of polymer electrolyte fuel cells. *J. Power Sourc.*, 147: 32–45.
71. McGrath, K.M., Prakash, G.K.S., and Olah, G.A. (2004) Direct methanol fuel cells. *J. Ind. Eng. Chem.*, 10: 1063–1080.
72. Yamaguchi, T., Kuroki, H., and Miyata, F. (2005) DMFC performances using a pore-filling polymer electrolyte membrane for portable usages. *Elect. Comm.*, 7: 730–734.
73. Park, G.G., Yang, T.H., Yoon, Y.G., Lee, W.Y., and Kim, C.S. (2003) Pores size effect on the DMFC catalyst supported on porous materials. *Int. J. Hydrogen Ener.*, 28: 645–650.

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74. Liu, Y.C., Qiu, X.P., Huang, Y.Q., and Zhu, W.T. (2002) Mesocarbon microbeads supported Pt-Ru catalysts for electrochemical oxidation of methanol. *J. Power Sourc.*, 111: 160–164.
75. Han, K.I., Lee, J.S., Park, S.O., Lee, S.W., Park, Y.W., and Kim, H. (2004) Studies on the anode catalysts of carbon nanotubes for DMFC. *Electrochim. Acta*, 50: 791–794.
76. Guo, J., Sun, G., Wang, Q., Wang, G., Zhou, Z., Tang, S., Jiang, L., Zhou, B., and Xin, Q. (2006) Carbon nanofibers supported Pt-Ru electrocatalysts for direct methanol fuel cells. *Carbon*, 44 (1): 152–157.
77. Drioli, E., Regina, A., Casciola, M., Oliveti, A., Trotta, F., and Massari, T. (2004) Sulfonated PEEK-WC membranes for possible fuel cell applications. *J. Membrane Sci.*, 228: 139–148.
78. Paturzo, L., Basile, A., Iulianelli, A., Jansen, J.C., Gatto, I., and Passalacqua, E. (2005) E. High temperature proton exchange membrane fuel cell using a sulfonated membrane obtained via H_2SO_4 treatment of PEEK-WC. *Cat. Today*, 104: 213–218.
79. Silva, V.S., Ruffmann, B., Vetter, S., Mendes, A., Madeira, L.M., and Nunes, S. (2005) Characterization and application of composite membranes in DMFC. *Cat. Today*, 104: 205–212.
80. Gaowen, Z. and Zhentao, Z. (2005) Organic/inorganic composite membranes for application in DMFC. *J. Membrane Sci.*, 261: 107–113.
81. Lindermeir, A., Rosenthal, G., Kunz, U., and Hoffmann, U. (2004) On the question of MEA preparation for DMFCs. *J. Power Sources*, 129: 180–187.
82. Liu, J.G., Zhao, T.S., Chen, R., and Wong, C.W. (2005) The effect of methanol concentration on the performance of a passive DMFC. *Elect. Comm.*, 7: 288–294.
83. Ye, Q. and Zhao, T.S. (2005) A natural-circulation fuel delivery system for direct methanol fuel cells. *J. Power Sources*, 147: 196–202.
84. Lu, G.Q. and Wang, C.Y. (2005) Development of micro direct methanol fuel cells for high power applications. *J. Power Sources*, 144: 141–145.
85. Kim, D., Lee, J., Lim, T.H., Oh, I.H., and Ha, H.Y. (2006) Operational characteristics of a 50 W DMFC stack. *J. Power Sources*, 155 (1–2): 203–212.

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