Hydrotalcite-like materials as precursors of catalysts for the production of hydrogen from methanol

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At present, 80% of global energy demand is satisfied by non-renewable resources and mainly from fossil fuel. The increasing interest toward alternative energy sources, in order to reduce the environmental pollution and greenhouse effect, makes hydrogen as one of best promising fuel for the future, for many reasons. It is largely available in nature, it posses the highest energy density (120700 kJ/kg) and its combustion is really clean, because it produces mainly water, either when used as fuel in internal combustion apparatus, or employed to feed electrochemical cells.

The use of gaseous hydrogen on a large scale involves the solution of big problems, in order to represent a valid alternative in next future [1]. These problems are connected with its production, storage and distribution. At present, UE Commission in some of its programs, such the “Hydrogen platform”, points out that the use of hydrogen in a large scale must involve its not polluting production and its conversion in electric energy in fuel cells operating either on intermittent charge application, as in electric cars, residential and civil buildings, portable devices, or continuous charge applications, as in stationary systems, or in energy-heat combined cycle systems.

Among the first type systems we can mention:
Proton Exchange Membrane Fuel Cells (PEMFCs):
the electrolyte is a polymeric membrane which allows the proton transport. They work with a hydrogen stream essentially free from CO, which is a poison for Pt catalyst at the anode. They work at relatively low temperatures (60-80°C). Their high energy density and remarkable flexibility make them especially suitable for on-board applications in electric cars.

Direct Methanol Fuel Cells (DMFCs):
they are polymeric electrolyte cells with proton transport, fed by methanol and air. The methanol anodic oxidation produces CO₂ and protons, which pass across the membrane and produce water with cathode reduced oxygen. Anodic catalysts are of Pt/Ru-type, and the cell works at temperatures below 150°C. Their development problems are connected with methanol diffusion towards the cathode through the polymeric membrane, and the high cost of the catalysts. In the second class, we can mention phosphoric acid cells, molten carbonate cells and the solid oxides cells which do not need a highly pure hydrogen. In this context, FC technology can become strategic only if the production hydrogen with a low cost and a low environmental impact will be possible.

At present, 97% of hydrogen is obtained from fossil fuels, and for the remaining 3% by water electrolysis. Hydrogen production from hydrocarbons or alcohols reforming seems to be the most profitable method. Methanol reforming is mainly interesting for the PEMFCs applied to vehicles, since it can be reformed at relatively low temperature, with high H₂ yields, it is low cost and easy to store and to transport. Several companies, such as General Motors, Ford, Daimler-Chrysler,
Volkswagen, Mazda, Honda, Nissan, Toyota, and others, are engaged in the development of a PEMFC technology based on methanol reforming.

In the following, some considerations on the reforming processes will be reported. Hydrogen can be obtained by partial oxidation of methanol (POM, reaction 1) or steam reforming (SRM, reaction 2).

\[
\text{CH}_3\text{OH} + \frac{1}{2} \text{O}_2 = 2\text{H}_2 + \text{CO}_2 \quad \Delta H = -192.2 \text{ kJ/mole (1)}
\]

\[
\text{CH}_3\text{OH} + \text{H}_2\text{O} = 3\text{H}_2 + \text{CO}_2 \quad \Delta H = +49.4 \text{ kJ/mol (2)}
\]

Combining the two reactions, one exothermic and the other endothermic, it is possible to obtain the oxidative steam reforming of methanol (OSRM) [2] that allows to work with an autothermal reactor (ATR), which does not need any external heat supply. Furthermore, this process produces gas streams with high H\textsubscript{2} concentration (up to 67% v/v), as it is required for having a high yield from PEMFCs. Unfortunately, the catalysts up to now proposed for OSRM produce relevant amounts of CO, and further purification treatments are necessary. The modern technology [3] suggests CO elimination in two catalytic stages, involving the water gas shift (WGS, reaction 3) and the selective oxidation (PROX, reaction 4) processes.

\[
\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2 \quad (3)
\]

\[
\text{CO} + \frac{1}{2} \text{O}_2 = \text{CO}_2 \quad (4)
\]

The reaction (3) reduces CO concentration to 0.5-1%, while the (4) lowers it to less than 10 ppm [3]. Best results are obtained with systems based on metallic copper, often in the presence of ZnO and eventually other metal oxides such as Al\textsubscript{2}O\textsubscript{3}, ZrO\textsubscript{2}, CeO\textsubscript{2} [2,4,5-11]. In this type of catalysts, ZnO acts as a promoter, but it may be also directly involved in the catalysis. Other oxides, such as Al\textsubscript{2}O\textsubscript{3}, probably improve the activity by favouring Cu dispersion. Different preparation procedures are studied for the synthesis of Cu-based catalysts to obtain highly dispersed metal phases. Besides the conventional impregnation method [12], leaching of alloys [13], sol-gel precipitation [12], eventually in the presence of templating agents [14], precipitation from microemulsions [6] are reported. Systems derived from Cu-Zn-Al hydroxy carbonate precursors with a hydrotalcite-type structure are specially interesting as OSRM catalysts [15-19]. The decomposition of these precursors leads to a mixture of oxides that, after H\textsubscript{2} reduction, produces catalysts with highly dispersed metallic Cu [19].

Hydrotalcite-like compounds, also known as Layered Double Hydroxides or anionic clays, are the only example of layered solids with positively charged layers balanced by exchangeable anions. They are presently used as catalysts, supports for catalysts, anionic exchangers, additives, flame retardants [20-22]. The structure of the layers arises from the connection by edges of M(OH)\textsubscript{6} octahedra, where M is a bivalent metal. After a partial isomorphous substitution of bivalent cations with trivalent ones, the layers gain positive charges that are balanced by anions intercalated in the interlayer region [20].

Their general formula is: [M(II)\textsubscript{1-x}M(III)\textsubscript{x}(OH)\textsubscript{2}]\textsubscript{(A\textsubscript{x/n})}mH\textsubscript{2}O, where M(II) can be Mg, Zn, Ni, Cu, Fe, Co, Mn and M(III)=Al, Cr, Fe, A(=n) is the layer-charge compensating organic or inorganic anion, m is the mol/mol of the co-intercalated solvent (generally water), x ranges between 0.2 and 0.4. Hydrotalcites can be loaded with small amounts of noble metals such as Pd(II) and Rh(III) [23], or can intercalate these ions as anionic complexes in order to active other processes like PROX.

An original synthesis method for the preparation of these compounds is the urea method based on the precipitation from “homogeneous solution” of bivalent and trivalent metal hydroxy carbonates by hydrolysis of urea [24]. This method can be also used to prepare hydrotalcite-like compounds.
containing more than two metals in the layer structure. This is important to obtain the compositional flexibility required for such catalytic systems. Furthermore this method is specially useful to prepare pure hydrotalcite containing Cu(II), since the Cu(II), that in octahedral coordination shows the Jahn-Teller distortion, cannot be easily accommodated in the brucitic structure of layers. This allowed progressive improvements of catalytic performances that resulted in a lowering of the threshold temperature and reducing of CO formation. At present, these catalysts give complete methanol conversion at 200-300 °C with CO concentrations lower than 100 ppm. Significant results were obtained in the characterization of surface chemical properties and in understanding the influence of these properties on the catalytic behaviour, investigating the role of the different Cu species and of acid properties of the metal oxides matrix. The kinetic study led to identify the reaction network and to relate the activity of different surface functional groups with the different reactions, thus giving useful suggestions for optimizing the catalytic systems [16-19,25].

The urea method allows the preparation of hydrotalcite-like compounds having a high crystallinity degree and a narrow particle size distribution. However, the presence of Cu(II) ions makes the synthetic procedure more complex, at least for two reasons. First Cu(II) ions show the Jahn-Teller effect that favours the formation of distorted octahedral structures, secondarily Cu(II) ions can depleted by ammonia originated from urea hydrolysis. The optimization of the synthesis conditions allowed to obtain materials having high Cu content without segregation of undesired phases (paratacamite in chloride solution or hydroxynitrate in nitrate solutions). Pure hydrotalctic phases, with a maximum value of Cu content in the range of 22-25% (of metal molar ratio) and a high specific surface area (130-250 m²/g at 450°C) were obtained.

TG curves of these samples showed two broad weight losses, the first occurring between room temperature and 200 °C is mainly associated to the loss of co-intercalated water, the second one, between 200 and 450 °C, is attributed to the loss of constitutional water and carbon dioxide that leads to the formation of metal oxides and aluminates.

FT-IR studies showed the presence of Cu$^{2+}$ and Cu$^{+}$ species together with the metallic Cu. Similar results were obtained from Temperature Programmed Oxidation (TPO) measurements, in which it was observed that Cu(0), Cu(I) and Cu(II) can be present in the reaction conditions. Temperature Programmed Reduction (TPR) measurements show that the reduction of Cu(II) species occurs in two steps and in the case of biphasic materials the reduction temperature range is shifted towards higher temperature.

Temperature Programmed Desorption (TPD) of NH$_3$ measurements showed different acidic sites related to Al$_2$O$_3$, ZnO and CuO.

Combined TPR and N$_2$O passivation allowed the calculation of the Cu amount on the surface of the catalysts, that was in the range of 15-23 % of the total Cu amount.

Catalytic activity tests indicated that the catalysts derived from the hydrotalctic precursors had a good activity and selectivity, giving almost complete conversion of CH$_3$OH in the temperature range of 300-350°C. The H$_2$ yield increased with the Cu content and reached the theoretical maximum value of 2.76 in the temperature range of 300-350°C. A decrease of the threshold temperature with the increase of the Cu content in the catalyst was also observed. The activation of the catalysts starts at low temperature (about 220-230°C with a Cu content of 10-15 metal molar ratio %). CO$_2$ is the main product, while the CO production is very low and appears only in the temperature range of 350-400°C. Secondary products (CH$_2$O, C$_2$H$_5$O) are detected with mass spectrometry suggesting a very complex reaction mechanism.

In conclusion hydrotalcite-like materials are good precursors of OSRM catalysts. After calcination and subsequent reduction materials containing Cu dispersed at atomic level in the oxide matrix were obtained. Increasing the Cu content over 22-25% other phases appeared and the derived catalysts loss their activity probably because sintering of the oxides occurs. IR study suggested that the reaction mechanism involved CH$_3$OH adsorption forming methoxy groups bonded both to active Cu species and to the alumina matrix. These groups evolved to formate species that, at increasing temperature, were oxidized to CO$_2$ before desorption.
These systems don’t allow a direct use in the PEMFCs of the gaseous flux obtained from the reforming of methanol yet, anyway the optimization of the synthesis led to a considerable lowering of CO formed in the catalytic act. The amount of CO is much lower than those reported in literature for these kinds of materials.

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References


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SUPPLEMENTARY MATERIAL

The hydrotalcitic precursors were obtained with urea method [24]. Solid urea, up to urea/Al molar ratio 6, was added to an aqueous solution, obtained by mixing 0.5 M solutions of Al(NO$_3$)$_3$, Zn(NO$_3$)$_2$ and Cu(NO$_3$)$_2$ in the proper volume ratio. The solution was kept at 90 °C for three days under vigorous stirring. The precipitate obtained was separated from the mother solution, washed with deionised water and then suspended in a 0.05 M solution of Na$_2$CO$_3$, in order to exchange nitrate ions eventually present.

The catalysts were obtained by heating the precursors in dry airflow at a 2 or 10 °C/min rate up to 450 °C. Then the samples were reduced in situ with 2% H$_2$/He mixture.

XRPD patterns of the samples were recorded with a computer controlled Philips XPert APD diffractometer using Cu–Ka radiation (40 kV, 30 mA). XRPD patterns at programmed temperatures have been taken in a HT A. Parr diffraction camera. TG analyses were performed in air by a Netzsch STA449C Thermal Analyser at a heating rate of 5 °C min$^{-1}$. N$_2$ adsorption–desorption isotherms were obtained at -196 °C, on samples previously degassed at 100 °C, using a computer controlled Micromeritics 2010 apparatus. The IR spectra were recorded with a Nicolet Protegé 460 Fourier Transform instrument. A Micromeritics 2900 apparatus equipped with a Thermal Conductivity Detector (TCD) was employed for TPR and TPO measurements. TPR measurements were carried out on calcined samples at a rate of 10 °C min$^{-1}$ using a 5% H$_2$/Ar mixture. Catalytic activity measurements were carried out in a laboratory flow apparatus with a fixed bed reactor. A gas-chromatograph HP 5890, equipped with a Porapak–molecular sieve double-packed column and a TCD detector, was employed for the analysis of H$_2$, CO, CO$_2$, O$_2$, CH$_4$, CH$_3$OH, H$_2$O. From concentrations and volume of effluent stream, total and partial conversions were calculated. The tests were carried out at T =200–400 °C, feeding with H$_2$O/CH$_3$OH/O$_2$ mixtures at 1.1:1:0.12 molar ratio and space velocity GHSV=0.6×10$^6$ or 1.2×10$^6$ h$^{-1}$. 

Table 1

<table>
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<tr>
<th>Sample</th>
<th>Composition of solid</th>
<th>HTlc phase (%)</th>
<th>Other phases (%)</th>
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<td>% metal molar ratio</td>
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<tr>
<td></td>
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<td>Zn</td>
<td>Al</td>
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<td>52</td>
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<td>100</td>
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<tr>
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<td>100</td>
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Fig. 1