A ruthenium catalyst for the efficient production of hydrogen from methanol.

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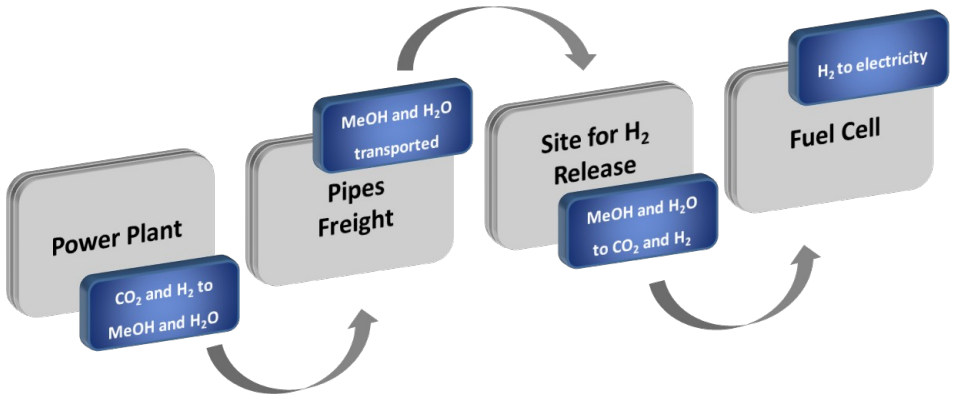
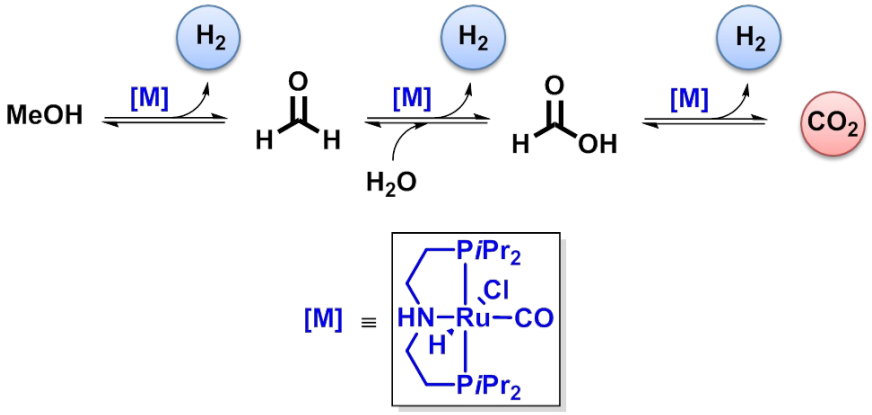
Hydrogen is an ideal fuel as its combustion releases energy and water as the sole by-product. Its widespread use would allow to successfully tackle several issues, the increasing demand for energy, the pollution and green-house gases arising from the use of fossil fuels.

However, mainly because of its physical and chemical properties, hydrogen is not an ideal energy vector: it is a flammable gas with a limited volumetric energy density which, for fuel applications, especially in the field of mobile applications, has to be either compressed at very high pressure (350-700 bars) or liquefied at very low temperature (-253 °C). Methanol, on the other hand, is liquid at room temperature and contains 12.6 % w/w hydrogen, which could be released on demand through its aqueous reforming. In order to render this process efficient, a catalytic system needs to be devised which can promote such reaction at a reasonable temperature. The carbon dioxide released in the process might be hydrogenated back to methanol using hydrogen obtained again from renewable sources, ideally from water electrolysis powered by solar energy.



Researchers from the Institute of Biomolecular Chemistry – CNR, the University of Sassari and the Leibniz Institute for Catalysis at the University of Rostock have recently devised a catalytic system based on a ruthenium complex which promotes hydrogen evolution from methanol and water below 100 °C.



M. Nielsen, E. Alberico, W. Baumann, H.-J. Drexler, H. Junge, S. Gladiali, M. Beller
Efficient Low Temperature Aqueous-Phase Methanol Dehydrogenation to H_2 and CO_2
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The ruthenium catalyst ensures that, for each molecule of methanol and water consumed, three molecules of hydrogen are generated, along with one molecule of carbon dioxide. The reaction proceeds better in the presence of a high concentration of base which sequestrates CO_2 as carbonate or formate. In order to optimize reaction conditions, the influence of several experimental parameters such as type of catalyst, catalyst concentration, MeOH/water ratio, base concentration and temperature have been investigated.

Under optimized conditions, an “homeopathic” amount of catalyst, 1.8 parts per million, is able to generate hydrogen at 91 °C from a 9:1 MeOH : water solution having an 8M KOH content. Under these conditions, 2700 equivalents of hydrogen per equivalent of catalyst are evolved in one hour. The efficiency per hour rises to 4700 if no water is used. By lowering the methanol / water ratio to 4:1 and the base concentration (1M NaOH) while increasing the catalyst amount to 21 ppm, the initial efficiency per hour drops to 800. During the first four hours, the solution pH decreases from 13 to 10 and the CO_2 / H_2 ratio falls from 9:1 to 3:1 over the same time interval. However the gas phase composition remains stable over almost three weeks and the system achieves an overall turnover number of 350000.

The catalyst has not been tested in methanol fuel cells but the results of the research collaboration shed light on the possibility of improving their efficiency, with foreseeable applications in portable devices. For application in the automobile sector, the efficiency of the system will have to be improved substantially.