Ph.D. COURSE IN INDUSTRIAL ENGINEERING – XXXIII CYCLE

Student: **Ruocco Concetta**

Tutor: **Palma Vincenzo**

Catalysts for sustainable hydrogen production via bioethanol reforming in a fluidized bed membrane reactor

Abstract

Hydrogen, widely regarded as the next generation fuel for transportation as well as stationary applications, can be produced from renewable sources. Bioethanol is a prosperous sustainable energy carrier mainly obtained via biomass fermentation and bioethanol reforming provides a promising method for hydrogen generation from renewables. Bioethanol (i.e. ethanol produced from biomass) mainly contains water and ethanol; however, different types of organic as well as inorganic impurities are present, which may have a significant effect on the reforming reaction and play a crucial rule on catalyst deactivation. In this regard, as impurities removal is a highly energetic demanding process, the use of crude bioethanol is of major importance for a cost effective industrial application of bioethanol reforming.

Ethanol steam reforming (ESR) is and endothermic reaction which, according to the thermodynamics, allows producing six hydrogen moles for every mole of converted ethanol. However, the reaction mechanism is very complex and the formation of various by-products (including coke) can reduce hydrogen selectivity. Under a thermal point of view, oxygen addition to the reacting system, due to contribution of oxidation reactions, can provide the heat necessary to carry out the reaction allowing, at the same time, an easier removal of carbonaceous species eventually deposited on catalyst surface. The role of the reactor configuration on the process efficiency is also crucial: fluidised bed reactors, due to the enhanced contact between gas and solid phases, can improve coke gasification; moreover, the excellent catalyst mixing helps avoiding hot or cold-spots phenomena, thus enhancing catalyst lifetime. In addition, the choice of fluidized bed membrane reactors can lead to a high degree of process intensification, assuring the selective separation of a reaction product (i.e. hydrogen) with a consequent increase of fuel conversion beyond the thermodynamic limitations as well as the direct product separation.

Several catalytic formulations have been investigated for ethanol reforming; however, the issue of catalyst durability (hundreds of hours of operation), especially in the case of raw bioethanol, was poorly investigated in the recent literature.

The main objective of this work is to develop highly active and stable catalytic formulations for the oxidative steam reforming of biomass-derived ethanol in a fluidized bed membrane reactor. A previously developed Pt-Ni/CeO_2-SiO_2 catalyst, tested in a fixed bed mode, was the starting point of this research activity. The bimetallic catalyst was tested in a fluidized bed reactor at 500°C and a preliminary screening was performed in the presence of a simulated bioethanol stream (i.e. pure water and ethanol). Its performance were compared with several catalytic formulations, developed in the attempt of improving the stability and reducing the carbon formation rate of the first generation catalyst. In this regard, alkali metals were added and Ni was substituted by Co obtaining, however, a worse activity and stability compared to the Pt-Ni/CeO_2-SiO_2 catalyst. Thus, for the latter sample, the influence of cerium salt precursor (nitrate, ammonium nitrate and acetylacetonate) on catalyst durability was investigated, finding that the organic salt can assure a better active species dispersion and a consequent improvement of sample stability.

The influence of the water/ethanol ratio, oxygen/ethanol ratio and temperature on the activity and stability of the 3Pt-10Ni/CeO_2-SiO_2 catalyst prepared from acetylacetonate was studied in order to select the operative conditions minimising carbon formation rate (i.e. 4, 0.5 and 500°C, respectively), which were fixed for the further tests.

In view of mitigating the costs of the final catalyst, the chance of reducing Pt loading as well as substituting platinum by cheaper metals (i.e. silver or ruthenium) was also investigated. Silver substitution was detrimental in terms of catalyst activity while ruthenium appeared a promising metal for oxidative steam reforming of ethanol. The highest activity was recorded over the 0.5Pt-10Ni/CeO_2-SiO_2 and 0.5Ru-10Ni/CeO_2-SiO_2 catalysts which, together with the monometallic Ni/CeO_2-SiO_2 sample, were selected for the development of a kinetic model able to predict the products gas distribution as a function of reaction temperature. The model involves four reactions (ethanol decomposition, methane oxidation, methane steam reforming, water gas shift) and assures a fairly good agreement with experimental data.

However, looking at the stability performance of the catalysts prepared at different loadings of the noble metals, it was clear that a content of 2 wt% was required to minimize the carbon formation rate for both the Pt

and Ru series; in addition, the highest durability was recorded over the 2Pt-10Ni/CeO_2-SiO_2, which was selected for the tests under fuel grade bioethanol, provided by Eldor corporation S.p.a.

The sample was tested for several hours at 500°C, H_2O/C_2H_5OH ratio of 4 and O_2/C_2H_5OH ratio of 0.5; the contact time was fixed to 250 ms and two kinds of experiments were performed: catalyst alone and catalyst mixed with the bare CeO_2-SiO_2 in a volumetric ratio of 1 to 4. The results demonstrated that the presence of the filler is detrimental in terms of stability, due to its higher acidity compared to the final catalyst. On the contrary, the 2Pt-10Ni catalyst assured complete conversion and a stable hydrogen yield (around 45%) for more than 200 hours; thereafter, a gradual deactivation was observed. However, after 450 hours, a new stationary condition was reached, with no more activity loss observed for further 50 hours. The carbon formation rate measured at the end of the test is considerably lower than the values reported over other catalysts; anyway, to the best of our knowledge, no tests performed under raw bioethanol in a fluidized bed reactor for more than 200 hours are available in the literature, which helps to conclude that the 2Pt-10Ni/CeO_2-SiO_2 catalyst is a very promising candidate for oxidative reforming of commercial Fuel grade bioethanol.

Finally, the formulation developed in this work was preliminary tested in a fluidized bed catalytic integrated membrane reactor (in collaboration with TUe University of Eindhoven), working in the Oxidative ESR reaction, finding an hydrogen recovery factor of 35% at 500°C and 4 bar, which is similar or higher than the values reported by other authors applying the same pressure difference (almost 400 kPa).