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Power-to-Gas: Storing surplus electrical energy. Study of catalyst synthesis and operating conditions

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ABSTRACT

Energy storage is needed in order to sustain the energy system on renewable energies like wind and solar power. Power-to-Gas (PtG) is a technology that enables the storage of the renewable electricity in a chemical carrier such as hydrogen, via water electrolysis, or methane, via carbon dioxide methanation. In this work a series of catalysts based on nickel and alumina, the catalyst commonly employed for carbon dioxide methanation, have been synthesised employing different calcination temperatures to study the influence of this parameter in the activity of the catalysts. As a result of this study 673 K was determined as the most suitable Moreover, the catalysts have also been tested at different pressures to determine the most suitable operating pressure. Although due to Le Chatelier's Principle a higher pressure results in an increasing yield, the study carried out proved that 10 bar is the most suitable pressure as the difference in the yield when increasing the pressure it is not high enough taking into account the costs and risks associated with higher pressures.

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Introduction

World's energy system is based on fossil fuels, both for transportation and electricity generation. In the first case, oil accounts for more than 95% of the use while most of the electricity generated worldwide (>60%) is produced from coal and natural gas [1]. An energy system based on fossil fuels has several disadvantages like i) pollution due to the burning of fossil fuels, which can result in natural disasters and health diseases [2], ii) reliability, as it has been already demonstrated that fossil fuels will not be available in the long-term [3] and iii) energetic dependence, due to the highly localised availability of the fossil fuels [4].

Among the different alternatives to the fossil fuels, like hydropower, nuclear energy or renewable energies, the latter seems to be the most promising one as it is able to cope with the three main drawbacks associated to the fossil fuels. The use of renewable energy sources does not generate pollution, they are infinite and even if in a different degree, they are available everywhere. However, they do have different disadvantages. The main renewable energy sources like solar and wind power are dependent on conditions that cannot be controlled like sun and wind so they are variable and intermittent. One way of improving the flexibility of the renewable energy sources is to store the excess of electricity, produced when the demand is low, in a chemical carrier like hydrogen or methane to be stored for being used later, employed for energy generation in situ or as a fuel for transportation.

The technology that makes possible the transformation of this excess of electricity in chemical carriers is called Powerto-Gas (PtG). This process can take place in one or two steps

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[5], depending on the chemical carrier chosen as the way to store electricity. First of all, hydrogen is produced by water electrolysis. The second step is performed if methane is produced as the chemical carrier; the methanation reaction is carried out with carbon dioxide from different sources reacting with the hydrogen produced in the first step of the PtG process. A scheme of the PtG process is presented in Fig. 1.

Even if producing only hydrogen instead of methane would result in a higher yield of the overall process, the production of methane has several advantages. Methane storage is cheaper and easier than hydrogen storage [6]; it can be directly injected into the wide and well established natural gas network [7], or easily burn to generate energy. PtG has proved to be a suitable technology to produce synthetic natural gas (SNG) and has already been demonstrated at industrial scale [8].

The main objective of this research is to improve the second step of the PtG technology, the carbon dioxide methanation process. In order to attain this objective it is necessary to understand the main reactions that are part of the carbon dioxide methanation, being the main one the carbon dioxide hydrogenation reaction (Eq. (1)). This reaction is part of a mechanism comprised by two reactions: reverse water-gas shift (Eq. (2)) and carbon monoxide hydrogenation reaction (Eq. (3)). Finally, the Boudouard reaction (Eq. (4)) could also happen as a side reaction [9–11].

$$\mathrm{CO}_{2}(g) + 4\mathrm{H}_{2}(g) \leftrightarrow \mathrm{CH}_{4}(g) + 2\mathrm{H}_{2}\mathrm{O}(g) \quad \Delta\mathrm{H}_{r}^{0} = -165.1 \frac{\mathrm{kJ}}{\mathrm{mol}} \tag{1}$$

$$\mathrm{CO}_2(g) + \mathrm{H}_2(g) \leftrightarrow \mathrm{CO}(g) + \mathrm{H}_2\mathrm{O}(g) \quad \Delta\mathrm{H}_r^0 = +41.2 \frac{\mathrm{kJ}}{\mathrm{mol}}$$
 (2)

$$CO(g) + 3H_2(g) \leftrightarrow CH_4(g) + H_2O(g) \quad \Delta H_r^0 = -206.3 \frac{kJ}{mol}$$
 (3)

$$2CO(g) \leftrightarrow C(s) + CO_2(g) \quad \Delta H_r^0 = -172.5 \frac{kJ}{mol}$$
⁽⁴⁾

As it can be seen, all the reactions but the reverse watergas shift (Eq. (2)) are highly exothermic reactions making an efficient heat removal essential to ensure that thermodynamics do not limit carbon dioxide conversion and to avoid the catalytic deactivation due to sintering. Also, an inefficient heat removal would enhance the rate of the reverse water-gas shift (Eq. (2)) due to its endothermic nature and increase the production of carbon monoxide, while selectivity to methane would be hindered.

The main reaction, carbon dioxide hydrogenation (Eq. (1)), it is widely known since the early 1900s as Sabatier reaction [12]. Even though it is a thermodynamically favourable reaction, a catalyst is needed to improve the kinetics of the reaction and make it feasible. The process has been investigated using several catalysts based on group VIIIB metals like cobalt, iron, nickel, palladium, platinum, rhodium or ruthenium synthesised over different oxides as catalytic supports; like Al_2O_3 , CeO_2 , SiO_2 , TiO_2 or ZrO_2 [13–17]. Among all the active metals that can be employed for carbon dioxide hydrogenation nickel is the most studied one as it presents a high activity and it is a relatively cheap material [18]. However, nickel based catalysts also present a main drawback: catalytic deactivation due to sintering [14].

In this research a series of nickel based catalysts were synthesised over gamma alumina (γ -Al₂O₃). These catalysts were calcined at three different temperatures to analyse the influence of this synthesis condition in the performance of the catalyst.

Although the effect of the calcination temperature has already been studied, it has been proved that an increase in the calcination temperature decreased the CO_2 conversion and the CH_4 selectivity due to the decrease of the nickel

Natural gas grid

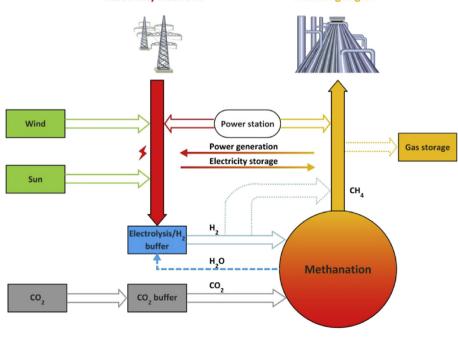


Fig. 1 – Scheme of the PtG process.

Electricity network

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