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Cobalt Nanocomposites as Catalysts for Carbon Dioxide Conversion to Methanol †

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Abstract: Carbon capture and utilisation (CCU), has arised as one of the alternatives for the reduction of CO_2 concentration in atmosphere by converting it into value added products. CO_2 conversion to methanol presents certain drawbacks such as high pressure and temperature conditions, and to solve these issues new materials are being investigated. Among them, cobalt stands out due to its abundance and low price when compared to noble metals. Cobalt and its oxides exhibit interesting electronic and magnetic properties and are used as catalysts in a wide range of reactions. In this work we present a systematic comparison among different cobalt and cobalt oxide nanocomposites in terms of their efficiency as catalysts for CO_2 hydrogenation to methanol, and how porous and non porous supports can enhance their catalytic capacity. With this purpose a fixed bed reactor operating with continuous flow is used, under mild conditions of temperature (160–260 °C) and pressure (10–15 bar). Several parameters are measured in order to evaluate the efficiency of the catalysis: CO_2 conversion; space time yield (STY), which indicates the methanol production yield per mass unit of catalyst and time of reaction, and methanol selectivity, which evaluates the production of side products of the reaction such as carbon monoxide. It is confirmed how the adsorption capacity provided by the porous supports can enhance the catalytic capacity of cobalt and cobalt oxide, and how porous supports such as zeolite and graphene clearly improve this capacity if compared with a non porous support such as silicon dioxide.

Keywords: methanol; nanocomposites; heterogeneous catalysis; cobalt

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1. Introduction

Only in 2018, 33 gigatons of CO_2 were released into the atmosphere. This amount was enough to provoke an increase in the concentration of this gas in the atmosphere from 280 ppm to 410 ppm [1]. As widely known CO_2 is one of the main causes of global warming, which stands as one of the main concerns that humanity is facing nowadays. For this reason, the research in this area is important in order to reduce the presence of CO_2. Part of this research focuses on gas capture to store it and then inject it underground. These are the so-called CCS (carbon capture and storage) methods. These processes, while not entirely environmentally sustainable because they require fossil fuels as an energy source, are such an efficient method that they could result in almost 20% of the reduction of carbon dioxide in the atmosphere. However, CCS methods have a very high cost for building facilities at the industrial level, and 75% of the total cost are dedicated to the CO_2 capture method [2]. Due to the high costs of CCS methods, CCU (carbon capture and utilization) methods arise as more economically viable processes to address the excess of CO_2 atmospheric concentrations. These methods are based in the use of CO_2 to obtain other valuable products such as chemical precursors and renewable fuels. Methanol stands out among these due to its utility as a feedstock for obtaining other chemical products and its use as

a renewable energy source [3]. In this framework, the conversion of CO_2 to methanol has been demonstrated to be efficiently achieved in heterogeneous catalytic systems.

Many different catalysts exist for the completion of the reaction of CO_2 hydrogenation towards methanol. However, many of them imply high costs, such as in the case of palladium and gold [4]. In this sense, other metals and metallic oxides which entail lower costs are under study, among them copper stands out due to its abundance on earth. Many copper catalysts have been synthesized to optimize interfaces between copper and metal oxide supports, due to the copper low effectiveness to activate CO_2 when used alone. The clearest example is $Cu/ZnO/Al_2O_3$ catalyst, which is used industrially for hydrogenation of CO and CO_2 [5]. However, copper compounds deactivate under the CO_2 conversion to methanol conditions [6], which causes an increasing interest in studying other earth abundant metals which are already used for other type of catalysis [7]. In particular cobalt accomplishes these conditions, which makes of it an interesting material to be studied in its elemental state, as an oxide and studying both materials in different supports such as graphene, zeolite, and silicon dioxide.

2. Results and Discussion

The catalytic activity of the different cobalt compounds was investigated for the catalytic reaction of CO_2 hydrogenation to methanol. Catalytic tests were performed at a mild operating pressure (10 bar) and at a flow rate of 10 mL/min, with temperature varying between 180 and 260 °C. Five different cobalt compounds were tested: elemental cobalt, cobalt oxide (Co_3O_4), cobalt oxide supported on zeolite (Co_3O_4—zeolite), cobalt oxide supported on graphene (Co_3O_4—graphene), and cobalt oxide supported on silicon dioxide (Co_3O_4—SiO_2). Their catalytic results were expressed in terms of space time yield (STY), which expresses the production of methanol per gram of catalyst and hour of experiment, and whose results are shown in Figure 1. As expected, the results of elemental cobalt show the lowest amount of methanol obtained, as single metals are normally less active than oxides or bimetallic systems [8].

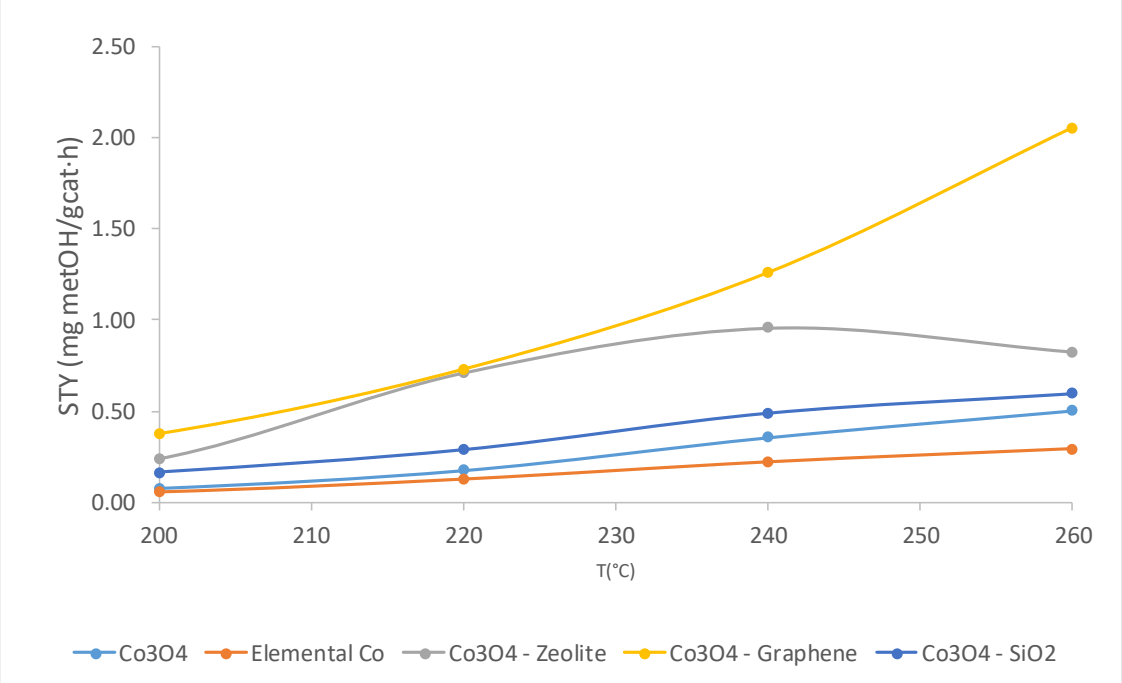

Figure 1. STY results of different cobalt compounds. Tests were performed at 10 bar.

It can also be appreciated how the use of a support enhances the production of methanol, since STY is increased for all the materials with a support. However, it is clearly

observed how the use of porous supports is beneficial for the methanol synthesis. This is in agreement with literature, where it has been demonstrated how the presence of porous materials improves CO_2 adsorption and the distribution of the active sites [9].

In terms of conversion and selectivity, cobalt compounds do not show much better results than those observed in literature for zinc or copper oxides, and no significant differences have been found between the different studied cobalt materials.

3. Conclusions

Cobalt has shown to be a good catalyst for the conversion of CO_2 to methanol, and in particular, cobalt oxide has shown a better performance than the elemental cobalt material. The use of a support has been studied, confirming the enhancement of cobalt oxide performance in terms of catalysis when supports are used. This effect is much improved when the used supports are porous materials such as zeolite and graphene.

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Conflicts of Interest: The authors declare no conflict of interest.

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