engineering proceedings

Proceeding Paper

Cobalt Nanocomposites as Catalysts for Carbon Dioxide Conversion to Methanol †

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† Presented at the 1st International Electronic Conference on Processes: Processes System Innovation, 17–31 May 2022; Available online: https://sciforum.net/event/ECP2022.

Abstract: Carbon capture and utilisation (CCU), has arisen as an alternative to the reduction of CO_2 concentration in the 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 compared to noble metals. Cobalt and its oxides exhibit interesting electronic and magnetic properties and are being used as catalysts in a wide range of reactions. In this work, we present a systematic comparison of 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. For this purpose, a fixed bed reactor operating with continuous flow is used, under mild temperature (160–260 °C) and pressure (10–15 bar) conditions. Several parameters are measured 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 reaction time, and methanol selectivity, which evaluates the production of reaction side products such as carbon monoxide. How the adsorption capacity provided by the porous supports can enhance the catalytic capacity of cobalt and cobalt oxide is confirmed, as well as how porous supports such as zeolite and graphene clearly improve this capacity compared with a non-porous support such as silicon dioxide.

Keywords: methanol; nanocomposites; heterogeneous catalysis; cobalt

Citation: Moral-Vico, J.; García, A.C.; Sánchez, A. Cobalt Nanocomposites as Catalysts for Carbon Dioxide Conversion to Methanol. *Eng. Proc.* **2022**, *19*, 32. https://doi.org/10.3390/ECP2022-12614

Academic Editor: Antoni Sánchez

Published: 17 May 2022

1. Introduction

In 2018, 33 gigatons of CO_2 were released into the atmosphere. This was enough to provoke an increase in the concentration of this gas in the atmosphere, from 280 ppm to 410 ppm [1]. CO_2 is one of the main causes of global warming, which stands as one of the main concerns that humanity is facing at present. For this reason, research on reducing the presence of CO_2 is important. Part of this research focuses on capturing gas to store it and then inject it underground. These are the so-called carbon capture and storage (CCS) methods. These processes, while not entirely environmentally sustainable because they require the use of fossil fuels as an energy source, are such efficient methods that they could result in an almost 20% reduction in carbon dioxide concentration in the atmosphere. However, CCS methods have a very high cost when building facilities at the industrial level, and 75% of the total costs are dedicated to the CO_2 capture method [2]. Due to the high costs of the CCS methods, carbon capture and utilization (CCU) methods are arising as more economically viable processes to address the excess of atmospheric CO_2 concentrations. These methods are based on the use of CO_2 to obtain other valuable products, such as chemical precursors and renewable fuels. Methanol stands out 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 from CO_2 to methanol has been demonstrated to be efficiently achieved in heterogeneous catalytic systems.

Many different catalysts exist for the completion of the CO_2 hydrogenation-to-methanol reaction. However, many of them have high costs, as in the case of palladium and gold [4]. Other metals and metallic oxides that entail lower costs are under study; copper stands out due to its abundance on earth. Many copper catalysts have been synthesized to optimize the interfaces between copper and metal oxide supports, due to copper's low effectiveness in activating CO_2 when used alone. The clearest example is the $Cu/ZnO/Al_2O_3$ catalyst, which is used industrially for the hydrogenation of CO and CO_2 [5]. However, copper compounds deactivate under CO_2's conversion to methanol conditions [6], leading to increased interest in studying other earth-abundant metals that are already used for another type of catalysis [7]. Cobalt meets these conditions, which makes it an interesting material for study in its elemental state and as an oxide, and both materials have been studied with 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 conversion of CO_2 to methanol. Catalytic tests were performed at a mild operating pressure (10 bar) and 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 methanol production per gram of catalyst and hour of experiment, with results shown in Figure 1. As expected, the results of elemental cobalt show the lowest amount of methanol that was obtained, as single metals are normally less active than oxides or bimetallic systems [8].

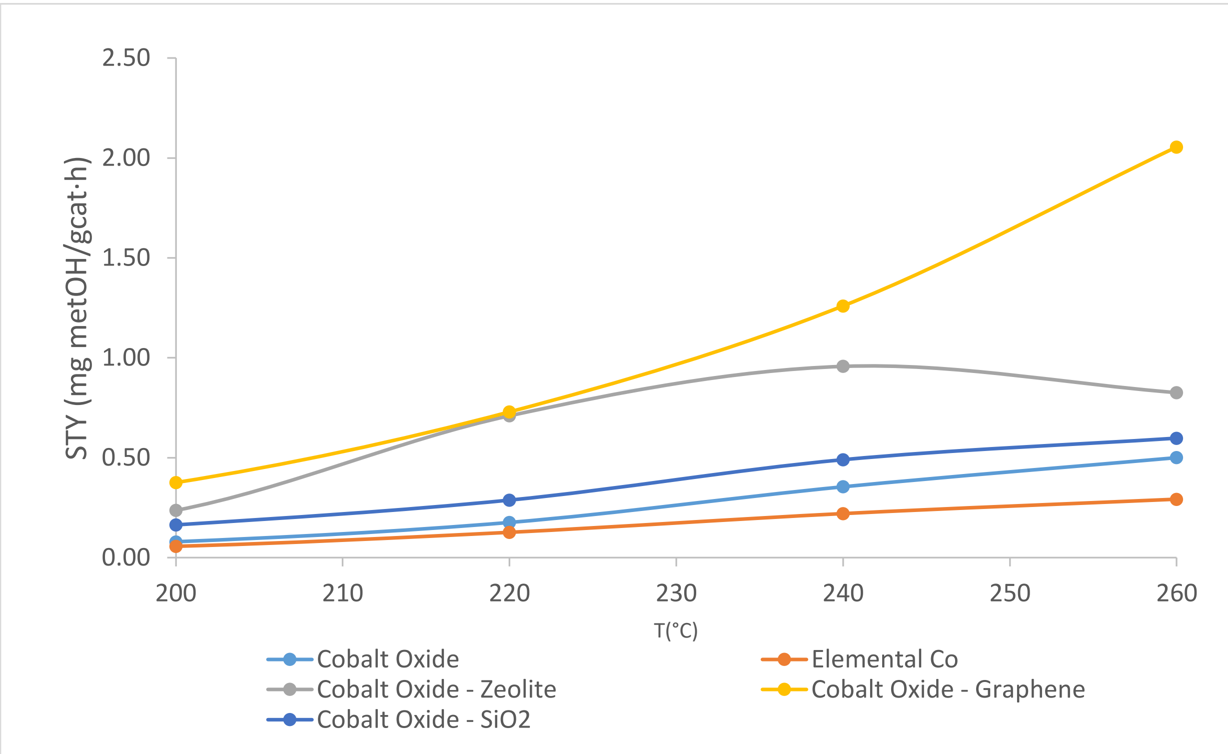

Figure 1. STY results of different cobalt compounds. Tests were performed at 10 bar.

The use of a support enhances methanol production, since STY is increased for all materials with a support. However, the use of porous supports is beneficial for the methanol synthesis. This is in agreement with the literature, where it has been demonstrated that the presence of porous materials improves CO_2 adsorption and the distribution of the active sites [9].

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

3. Conclusions

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

Author Contributions: Conceptualisation, A.S. and J.M.-V.; methodology, A.C.G.; validation, J.M.-V. and A.C.G.; formal analysis, A.C.G. and J.M.-V.; investigation, A.C.G. and J.M.-V.; resources, A.S. and J.M.-V.; data curation, A.C.G.; writing—original draft preparation, J.M.-V.; writing—review and editing, A.C.G., J.M.-V. and A.S.; visualisation, A.C.G.; supervision, J.M.-V. and A.S.; project administration, A.S.; funding acquisition, A.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Fundación Ramón Areces in the hallmark of the META2NOL project granted in the XIX National Contest of Life and Matter Sciences Projects, grant number CIVP19A5952.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Acknowledgments: Anna Carrasco García thanks UAB for the PIF scholarship granted for the completion of her PhD thesis.

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

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