

# Transformation of Carbon Dioxide into Linear Carbonates and Methane over Cu-Ni and Ru-Fe Supported on Pellets Activated Carbon

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Carbon dioxide (an abundant, inexpensive, and renewable carbon resource) is one of the most significant greenhouse gases that cause global warming and climate changes. Carbon dioxide can be used to synthesize useful chemical products such as linear carbonates like dimethyl and diethyl carbonate and methane. Carbon dioxide valorisation (from biomass or industrial flue gases, for instance) using catalytic processes is an excellent alternative to reduce greenhouse gas emissions. As the use of catalyst as a powder imply the need for a large amount of catalyst in the catalytic bed and the consequent problems with pressure drop, the use of carbon powders processed into pellets (cylindrically-shaped pieces) is mandatory to reduce the total catalyst volume, the pressure drop in the catalytic bed, and the formation of hotspots.

In this work, Cu, Ni, Cu-Ni, Ru, Fe, and Ru-Fe monometallic and bimetallic catalysts were synthesized by the wetness impregnation over pellets of activated carbon and evaluated in the production of dimethyl carbonate and diethyl carbonate (Cu, Ni, Cu-Ni) and methane (Ru, Fe, Ru-Fe). The highest catalytic activity (in terms of turnover frequency) was obtained over bimetallic catalysts with Cu: Ni, 2:1, 3:1 molar ratio in dimethyl and diethyl carbonate, respectively and Ru in methane formation. The increased activity was attributed to the synergetic interaction between metals in the alloy formed on the surface of the catalyst. Results suggest that the synthesized catalysts could potentially be used for carbon dioxide fixation processes.

## 1. Introduction

Carbon dioxide transformation and storage is an important technology to reduce the amount of greenhouse gas emissions and mitigate climate change in the future (Darton and Yang, 2018). Carbon dioxide is an abundant, cheap, recyclable, renewable and non-toxic carbon resource, it can be used to synthesize useful chemical products such as syngas (from CO<sub>2</sub> and CH<sub>4</sub>), methane (from CO<sub>2</sub> and H<sub>2</sub>), urea (from ammonia and CO<sub>2</sub>), methanol (from hydrogen and CO<sub>2</sub>), ethanol (from hydrogen and CO<sub>2</sub>), dimethyl carbonate (from methanol and CO<sub>2</sub>), diethyl carbonate (from ethanol and CO<sub>2</sub>) (Olajire, 2013) or higher alcohols (Figure 1). These compounds have attracted much attention, both from an economical and an environmental point of view (Soodsuansi et al., 2018). Dimethyl carbonate (DMC) and diethyl carbonate (DEC) are used as an electrolyte for lithium-ion batteries, fuel additives, organic solvents and, alkylating agents (Zhang et al., 2014). Synthetic route from carbon dioxide avoids the problems caused by the use of toxic, flammable, and corrosive gases in the traditional synthesis routes, i.e., phosgene and hydrogen chloride (alcoholysis of phosgene), carbon monoxide oxidative carbonylation or ethyl nitrite route. Methane, the main component of natural gas, is an abundant reserve and environmentally friendly feature as a fuel. It is highly attractive since it generally generates fewer pollutants such as NO<sub>x</sub> and releases fewer greenhouse emissions per energy produced. The transformation of carbon dioxide and hydrogen (Sabatier reaction) to form methane, is a promising technique to use CO<sub>2</sub> as feedstock to produce substitute natural gas (Zheng et al., 2016).

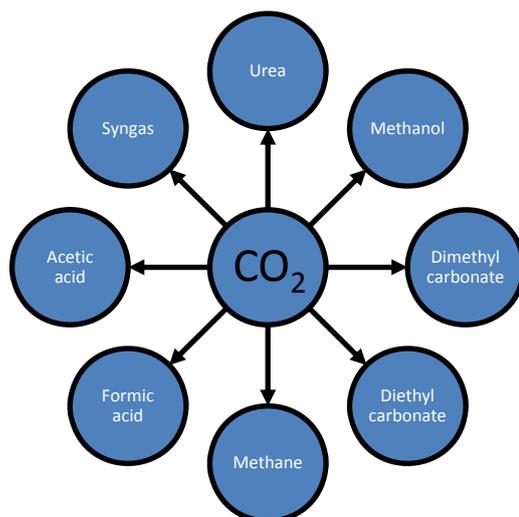


Figure 1. Reaction routes for carbon dioxide transformation

It is a challenge to activate and utilize carbon dioxide effectively because of its highly thermodynamically stable and kinetically inert by nature, in which the implementation of this synthesis route requires extreme pressure conditions or the use of the catalysts. Both, linear carbonates formation and Sabatier reaction have been developed with the use of catalyst as a powder imply the need for a large amount of catalyst in the catalytic bed and the consequent problems with pressure drop, therefore, despite their excellent performance scaling-up of these processes is not yet feasible because of the large amount of catalyst that would be required. The use of carbon powders processed into pellets (cylindrically shaped pieces) or monoliths; on the other hand, it can reduce the ratio of catalyst mass to reactor volume, as well as the pressure drop in the bed (Orrego-Romero et al., 2016). Besides, the formation of hotspots could be prevented. Thence, a pelletized or monolith-based catalytic system would greatly facilitate scaling-up the reactions. However, although monolithic structured AC-based catalysts or adsorbents have been widely used for abatement of pollutant emissions, is scarce literature on the use of AC-based pelletized catalysts. In this work, the synthesis and evaluation of catalyzed catalysts in the linear carbonate and methane formation are presented.

## 2. Materials and methods

### 2.1 Catalysts Preparation

Activated carbon (AC) from Merck 90% particle size  $< 100 \mu\text{m}$  was pretreated in order to remove impurities as follows. Commercial AC was treated with 2 M HCl solution for 12 h under reflux. The solid was then filtered, washed and dried in an oven at  $110 \text{ }^\circ\text{C}$  for 12 h. Finally, the AC was oxidized with aqueous 4 M  $\text{H}_2\text{SO}_4$  for 4 h, then filtered, washed and dried at  $100 \text{ }^\circ\text{C}$ ; the resulting material was kept in a desiccator before its use as a support (Figure 2). The monometallic and the bimetallic samples were prepared by conventional wetness impregnation on the pretreated AC.  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Fe}(\text{NO}_3)_3$ , and ruthenium solution were used as metal precursors to obtain a loading nominal metal oxide of 20% weight total with Cu-Ni molar ratio of .3-1, 2-1, 1-1, 1-2 and 1-3 and a total loading metal oxide of 5% in Ru and Fe samples. The aqueous solution containing the metallic precursor(s) was mixed with the activated carbon for 24 h at room temperature and afterward roto-evaporated at reduced pressure for 3 h. The resulting materials were then dried at  $90 \text{ }^\circ\text{C}$  for 12 h and heated in flowing  $\text{N}_2$  ( $25 \text{ mL min}^{-1}$ ) at  $0.5 \text{ }^\circ\text{C min}^{-1}$  up to  $500 \text{ }^\circ\text{C}$ , held at that temperature for 3 h, and then reduced in 5%  $\text{H}_2/\text{Ar}$  while heating at  $0.5 \text{ }^\circ\text{C min}^{-1}$  until  $600 \text{ }^\circ\text{C}$ .

### 2.2 Catalyst evaluation

Catalytic tests were performed in continuous stainless steel (SS) tubular fixed-bed reactor (ID 7 mm), Figure 3, packed with 1.0 g of catalyst. After loading the catalyst, the reactor was sealed and purged using Ar or  $\text{N}_2$ . By linear carbonate synthesis, methanol or ethanol were introduced into the reactor by saturating a stream of  $\text{CO}_2$  flowing through an SS bubbler containing the liquid alcohol at room temperature. The reaction temperature was controlled by a hotbox system that included an electric forced-convection heater to keep both the reactor and the bypass at the same temperature, avoiding possible condensation. For linear carbonates, reactions were carried out for 3 h at  $90 \text{ }^\circ\text{C}$ , 13 bar, and total gas flow was about  $50 \text{ mL/min}$  (actual flowrate at

reaction conditions). For linear carbonates, the main signal 22 amu, 75 amu, and 91 amu were analyzed on-line with a mass spectrometer (QMS ThermoStar 200 (Pfeiffer)); they correspond to carbon dioxide dimethyl carbonate, and diethyl carbonate, respectively.

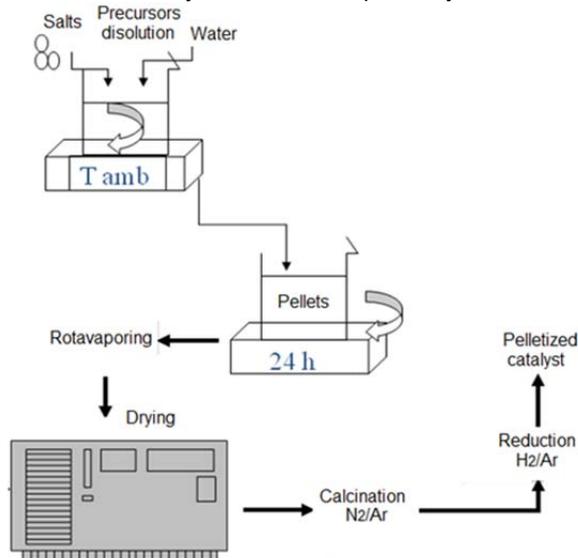


Figure 2. Catalysts preparation over Pellets of Activated carbon

For methanation reaction, the products were analyzed using on-line gas chromatography in a Micro GC Varian equipped with Molecular Sieve and Porapak columns. The catalytic activity was analyzed in terms of turnover frequency TOF number (Eq 1) and carbon dioxide conversion (Eq 2)

$$TOF(h^{-1}) = \frac{mol \text{ linear carbonate}}{h \cdot active \text{ sites} \cdot (mol)} \quad (1)$$

$$CO_2 \text{ conversion} = \frac{CO_2 \text{ inlet} - CO_2 \text{ outlet}}{CO_2 \text{ inlet}} * 100 \quad (2)$$

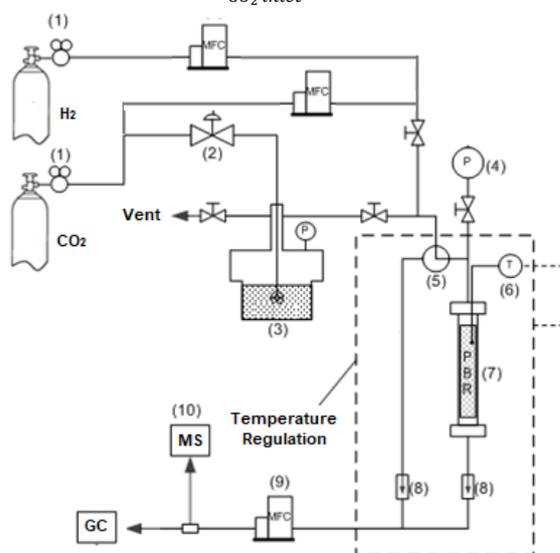


Figure 3. Reaction system setup for DMC, DEC, and methane. (1) Pressure reducer valve, (2) control valve, (3) bubbler containing ethanol, (4) pressure gauge, (5) three-way valve, (6) type-K thermocouple, (7) tubular fixed-bed reactor of 7 mm I.D, (8) check valve, (9) mass flow controller, (10) mass spectrometer. (Arbelaez-Perez et al., 2018).

### 3. Results and Discussion

According to experimental data, in linear carbonate formation (dimethyl and diethyl carbonate) and methanation, there was no formation of carbonates or CO<sub>2</sub> conversion during blank runs, no tests with the support. Figure 4 shows the catalytic activity of monometallic and bimetallic samples (in terms of turnover frequency) in linear carbonate formation.

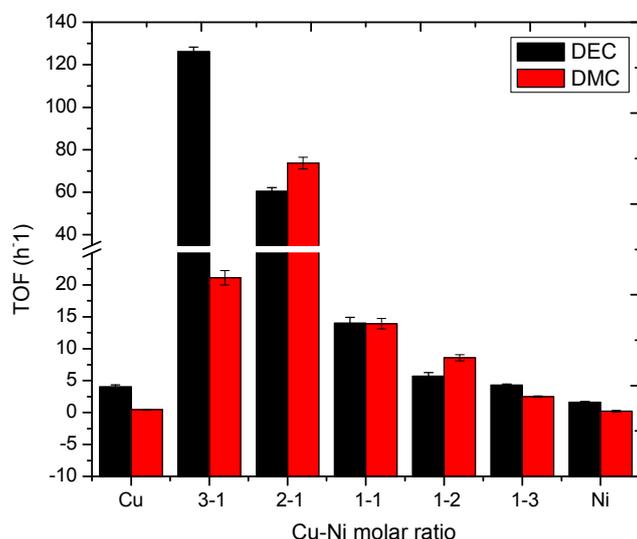


Figure 4. Turnover Frequency for linear carbonate formation. Reaction conditions: 110°C, 13 bars, alcohol: CO<sub>2</sub> feed molar ratio of 2:1, the mass of the catalyst 1 g.

Experimental results show that Cu-Ni bimetallic samples display a higher turnover frequency than the Cu and Ni monometallic ones. The monometallic Cu catalyst exhibited higher catalytic activity than Ni monometallic catalyst in agreement with data reported by Bian et al., (2009), who reported the ability of Cu to activate CO<sub>2</sub> to form negatively charged CO<sub>2</sub><sup>δ-</sup> species, which can further convert to carbonate. When Cu-Ni bimetallic catalysts were tested in the reaction, the reaction rate increased significantly, owing to Cu-Ni interaction; in fact, the presence of the second metal is needed to achieve the significant activity. Moreover, TOF follows similar trends in dimethyl and diethyl carbonate formation. In fact, the increase of the reaction rate as a function of the Cu molar ratio agrees with data reported by Bian et al., (2009) in dimethyl and Arbelaez et al. (2012) carbonate synthesis in this composition range. The best catalytic activity is achieved for the content of Cu for the Cu-Ni 2-1 (73.6 h<sup>-1</sup>) and 3-1 (126. h<sup>-1</sup>) molar ratio in DMC and DEC formation, respectively. According to Figure 4 results, TOF values are much more abundant in bimetallic catalysts, implying that the synergistic effect of Cu and Ni likely plays a significant role in agreement with Cu-Ni alloy formation evidenced by XRD. In fact, in bimetallic samples were evidenced signals well-defined diffraction peaks that can be associated to a cubic phase Cu-Ni alloy ( $2\theta = 43.7^\circ$  and  $2\theta = 50.9^\circ$ , JCPDS file No-47-1406), which are intermediate peaks to Cu<sup>0</sup> ( $2\theta = 43.3^\circ$ ,  $50.4^\circ$ , JCPDS file No. 4-0836) and Ni<sup>0</sup> ( $2\theta = 44.5^\circ$ ,  $51.8^\circ$ , JCPDS file No. 4-0850). The improvement in the catalytic properties of Cu-Ni bimetallic materials previously reported for the linear diethyl and dimethyl carbonate formation appears to be caused by the electronic interactions between the completely filled d-band of Cu and the partially filled d-band of Ni, although geometric interactions may be at play (Bian et al., 2009).

Additional Nitrogen adsorption/desorption isotherms for Cu and Ni monometallic and Cu-Ni:3-1 and Cu-Ni:2-1 bimetallic catalysts (not shown) showed no significant changes on activated carbon morphology. On the other hand, the Cu-Ni:3-1 (670 m<sup>2</sup>/g) and Cu-Ni:2-1 (692 m<sup>2</sup>/g) bimetallic catalyst samples show better adsorption capacity in agreement with the higher surface area compared to Cu (532 m<sup>2</sup>/g) and Ni (627 m<sup>2</sup>/g) monometallic catalysts. All samples displayed type IV isotherms with hysteresis loop type H4, according to IUPAC classification. These isotherms are usually found on mesoporous solids consisting of aggregated particles or agglomerates forming slit-shaped pores, with non-uniform size and shape

Based on the results of catalysts characterization and catalytic activity presented above, it can be inferred that the activity of the catalyst is promoted not only due to a synergistic effect between copper and nickel (all bimetallic catalysts are more active than monometallic samples), but also to the formation of Cu-Ni alloy as the most active species in the reaction. The formation of the alloy, which seems to play a decisive role in the activity of the catalyst, likely occurs via the mingling of copper and nickel at the atomic scale, resulting in one crystalline phase.

Both Cu and Ni have been reported as active metals surfaces for carbon dioxide activation (Lapidus et al., 2007). Besides, Ni reveals a higher oxygen affinity compared to Cu. Therefore, it can be argued that the addition of Ni into Cu structure (where Cu-Ni alloy is formed), generates active sites that are more stable and reactive for catalyzing the direct synthesis of dimethyl carbonate from methanol and CO<sub>2</sub> and diethyl carbonate from ethanol and CO<sub>2</sub>. Moreover, Yang et al. (Yang et al., 2012) showed that the presence of Ni sites on Ni-Cu stabilizes the O-containing intermediates and therefore lowers the energetic barriers for most of the subsequent steps during the alcohol synthesis from CO<sub>2</sub> hydrogenation.

Monometallic and bimetallic Ru and Fe catalysts on the methanation of carbon dioxide are shown in Figure 5. According to experimental results, Fe monometallic catalyst exhibited lower catalytic activity than Ru monometallic catalysts. Fe monometallic sample exhibited a carbon dioxide of around 27%. Additionally, it was revealed that the catalytic performance of Ru-Fe catalysts was strongly influenced by ruthenium addition. In bimetallic catalysts, the interaction between two metals affected electronic and geometric structures of the catalyst, changing the physicochemical properties of the catalysts, having a contributory effect on achieving more active and stable catalysts. The metal loading does not affect carbon dioxide conversion significantly. The enhanced carbon dioxide conversion was the result of the introduction of Ru to the structure of the Fe as a result of new active sites by Ru-Fe alloy evidenced by X-Ray diffraction (not shown in this work).

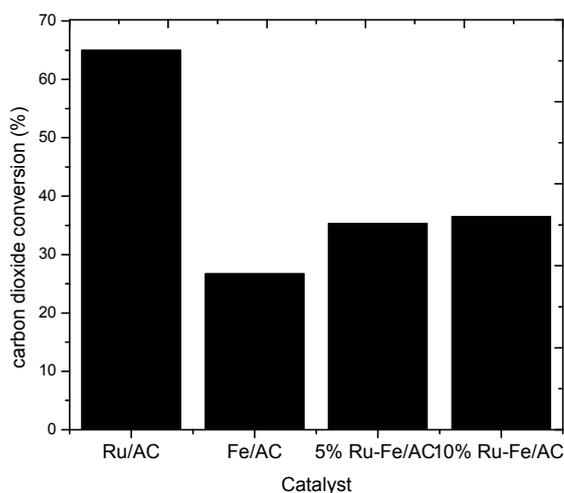


Figure 5. Carbon dioxide conversion over monometallic and bimetallic Ru and Fe catalysts. Reaction conditions: 375°C, 1 bar, the mass of the catalyst 0.25 g.

#### 4. Conclusions

Monometallic Cu and Ni and bimetallic catalysts supported on activated carbon were synthesized and evaluated for the transformation of carbon dioxide with methanol and ethanol in dimethyl and diethyl carbonate, respectively. It was found that the catalytic activity of the bimetallic samples (in terms of alcohol conversion) increases with the Cu content. The most active catalysts were the Cu-Ni:2-1 and Cu-Ni:3-1 molar ratio sample for DMC and DEC formation, in linear carbonate formation, the increased activity was attributed to the synergistic interaction between metals evidenced by X-Ray diffraction. In methanation experiments, monometallic Ru supported in pelletized catalysts exhibited the highest catalytic activity than Fe samples. Additionally, it was observed that the addition of ruthenium into an iron pelletized catalyst was favorable for carbon dioxide methanation reaction. The experimental results exhibited that the prepared catalyst can potentially be used in applications for the CO<sub>2</sub> fixation.

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