Effect of reaction conditions on the product yield in the CO2 hydrogenation reaction over a K-Co-Cu-Al catalyst

Vitor Duarte Lage1\*, Anthony Le Valant2, Nicolas Bion2, Fabio Souza Toniolo1\*

1Programa de Engenharia Química – PEQ/COPPE – Universidade Federal do Rio de Janeiro, Cidade Universitária, Rio de Janeiro CEP 21941-972, RJ, Brasil.

2Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP)/Université de Poitiers - CNRS, Poitiers, França.

Resumo/Abstract

RESUMO - Converter CO2 em produtos químicos de valor agregado é uma alternativa promissora para as recentes questões energéticas e ambientais, mas projetar um catalisador de metal não nobre capaz de converter CO2 de forma ativa e seletiva em produtos desejáveis ainda é um desafio. Neste trabalho, relatamos o efeito das condições de reação na atividade e seletividade de um catalisador K-Co-Cu-Al preparado por coprecipitação para a hidrogenação de CO2 a álcoois superiores (HAs). Investigamos diferentes temperaturas de redução, temperaturas de reação, velocidades espaciais e razões H2/CO2 para maximizar o rendimento de HAs. Observamos aumento no rendimento dos produtos de alto valor agregado (hidrocarbonetos C2+ e HAs) ao encontrar a temperatura ótima de redução, e ao reduzir a velocidade espacial e a razão H2/CO2. K­‑Co‑Cu‑Al reduzido a 400 ºC apresenta elevada seletividade a HAs de 45% e rendimento de 5,6 mmol.h‑1.gcat‑1, sob condições amenas (250 °C, 30 bar, H2/CO2 de 1,5 e 14200 mL.h‑1.gcat‑1), o que representa um dos maiores desempenhos entre os estudos relacionados, especialmente em meio aos catalisadores à base de Co.

*Palavras-chave: Hidrogenação de CO2, produção de álcoois superiores, catalisadores de cobalto, catalisadores de cobre, catalisadores bimetálicos.*

ABSTRACT - Converting CO2 into value-added chemicals is a promising alternative to recent energetic and environmental issues, but designing a non-noble metal catalyst capable of actively and selectively converting CO2 into desirable products is yet a challenge. Herein, we report on the effect of the reaction conditions on the activity and selectivity of a K-Co-Cu-Al catalyst prepared by a coprecipitation method for the CO2 hydrogenation to higher alcohols (HAs). We investigated different reduction temperatures, reaction temperatures, space velocities, and H2/CO2 ratios to optimize its HAs yield. We observed gains in the yield of desired products (C2+ hydrocarbons and HAs) when finding the optimum reduction temperature and reducing space velocity and H2/CO2 ratio. K-Co-Cu-Al reduced at 400 ºC exhibits a high HAs selectivity of 45% (21% for ethanol) and space-time yield of 5.6 mmol.h‑1.gcat‑1, under mild conditions (250 °C, 30 bar, H2/CO2 ratio of 1.5, and 14200 mL.h‑1.gcat‑1), which represents one of the best performances among related studies, especially amidst Co-based catalysts.

*Keywords:* *CO2 hydrogenation, higher alcohol production, Co-based catalyst, Cu-based catalyst, Bimetallic catalyst.*

## Introduction

The CO2 hydrogenation reaction has become a promising alternative for the current environmental and energetic challenges, as it can transform CO2, resulting from industrial activities, to produce value-added products and feedstock (1,2). This reaction leads to several different products, such as CO, CH4 —both undesired in most cases—, C2+ hydrocarbons (HCs), methanol, and C2+ alcohols, also known as higher alcohols (HAs), among others (3–6). Each product has its pros, cons, and academic challenges. HAs, for example, are desirable when applicability, energy density, safety, and sustainability are accounted (7,8). Furthermore, an ongoing academic endeavor is to tune the catalyst nature and the reaction conditions to best select the reaction pathway that leads to the desired products (4,5).

Aiming HAs, Co-based catalysts stand out as earth-abundant metal catalysts (9), with the advantage of higher CO2 conversion (5,6,10). However, it is necessary to form Co-alloys or to interact Co with oxide supports, to promote HAs selectivity over CH4 (5,10). These modified Co-based catalysts (CoAlOx, Na-Co/SiO2, LaCoGaO3, CoNiAlOx) have been studied in both continuous and batch reactions for HAs synthesis and their CO2 conversion ranges from 5-67%, their selectivity to HAs from 0.05-92%, and their space-time yield (STY) from 0.01-2.16 mmol.h-1.gcat-1 (10).

In that sense, we proposed to investigate the effect of the reaction conditions on the HAs selectivity and yield of a K‑Co‑Cu‑Al catalyst on CO2 hydrogenation. Cu can be used to form Co-based alloys (11,12), as it can promote CO-insertion (13) and inhibit C-O bond cleavage (10,14). Alkali metals, especially K, in turn, can donate electrons to Co sites and are widely used as basicity promoters (9,15,16).

Regarding reaction conditions, finding the best temperature, H2/CO2 ratio, and space velocity (SV), among other parameters, is crucial to improving HAs selectivity and yield. Increasing the temperature favors CO2 conversion but hinders HAs formation (5,17). Similarly, increasing the H2/CO2 ratio can favor conversion, usually favoring CH4 and HCs, due to excess H2, as the lack of it can favor methanol (5,18). Increasing the space velocity can result in low conversion, on the other hand, decreasing it can favor some reaction pathways over others, leading to undesired products (5,19,20). Hence, the need to tune such conditions to balance conversion and product selectivity, increasing the yield of the desired product (5). Most of the Co-based catalysts have optimum performance around 140-250 ºC with space velocity between 3000-6000 mL.h-1.gcat-1 (6). The effect of H2/CO2 ratio has not been widely explored.

## Experimental

*Catalyst Preparation*

The K-Co-Cu-Al catalyst was prepared via a modified coprecipitation method (21,22). The alkaline solution was formed by NaOH (2 M) and Na2CO3 (0.5 M). The precursor solution (1 M) was prepared by dissolving Co(NO3)2.6H2O, Cu(NO3)2.5H2O, and Al(NO3)3.9H2O in deionized water with Co:Cu:Al molar ratio of 2:1:1. Both solutions were added drop-wise to a recipient under agitation to maintain pH 10. The resulting solution was aged overnight, filtered, and washed 3 times in deionized water (21,22). The filtered cake was suspended in a K2CO3 solution (0.1 M) and immersed in an ultrasonic bath to remove excess Na and add approximately 1 wt.% K to the catalyst (23–25). The sample was again filtered and washed 3 times with deionized water and then calcined in a muffle in static air at 500 ºC for 3 h (23,26).

*Characterization*

The metal content was determined by ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) carried out on a Perkin Elmer Optima 2000DV spectrometer. The textural properties of calcined catalysts were determined by N2 physisorption using a Micromeritics Tristar instrument. The reduction profile was analyzed in temperature-programmed reduction (TPR) experiments employing a Micromeritics Autochem II 2920 apparatus equipped with a thermal conductivity detector (TCD), with 10% H2 flow (30 mL.min-1) from 30 to 1000 ºC (5 ºC.min-1). The surface morphology of the sample before and after reduction was investigated by a scanning electron microscope (SEM), FEI/Thermo Fischer MEV Inspect, with STEM (scanning transmission electron microscopy) mode attack to it.

For phase identification, X-ray diffraction (XRD) experiments were carried out on a Brucker D8-Advance diffractometer using the Co-Kα radiation (1.79 Å). The in situ XRD analysis was performed by heating the sample from room temperature (RT) to 500 °C (10 °C.min-1) under 3% H2 flow. The sample was placed over a Kanthal holder, and the XRD patterns were recorded at RT, 250, 300, 400, and 500 °C.

The basicity profile was analyzed in CO2 temperature-programmed desorption (CO2-TPD) experiments in a multipurpose testing unit equipped with an online quadrupole mass detector QUADSTAR 422 (QMS 200, BALZERS). For that, CO2 adsorption was conducted by passing pure CO2 (30 mL.min-1) for 30 min and then flushing the reaction with He (60 mL.min-1) for 60 min. The TPD was performed by heating (20 °C.min-1) the sample to 800 °C. The effluent gases were monitored by the online mass detector (m/z = 2, 4, 28, 30, 32, 44, and 46).

*Catalytic Tests*

The CO2 hydrogenation catalytic tests were executed in a continuous fixed-bed stainless steel reactor. The sample (0.3 g, 0.160‑0.100 mm sieved fraction) was packed between two layers of SiC (0.125 mm). Prior to the reaction, the samples were reduced *in situ* at 4 different temperatures (250, 300, 400, and 500 ºC) for 30 min under pure H2 flow (30 ml.min-1). The initial tests were carried out at 250 °C and 30 bar in an H2/CO2/N2 flow (ratio: 3/1/0.25) with gas-hourly space velocity (GHSV) set to 14200 mL.gcat-1.h-1 for 24 h. After determining the optimum reduction temperature, we investigated different reaction temperatures (200 and 300 °C), H2/CO2 ratio (H2/CO2 ratio: 1.5), and GHSV (10625 mL.gcat-1.h-1). It is worth mentioning that, for each reaction parameter investigated, the others were fixed according to the previously described initial test conditions. The catalytic performance was expressed by CO2 conversion (XCO2), C-based product selectivity (Si), and the product space-time yield (STYi).

## Results and Discussion

*Characterization*

The metallic content (wt.%) of K-Co-Cu-Al was determined by ICP-OES as 0.8%, 34.9%, 18.7%, and 9.0% for the respective elements. The Co:Cu:Al molar ratio was 1.8:0.9:1, close to the intended during the synthesis. The samples did not present any detectable amounts of Na, confirming the treatment with K2CO3 solution was efficient in removing the excess Na. As for the N2 physisorption, K-Co-Cu-Al displayed surface area of 69 m2.g-1, pore volume of 0.37 cm3.g-1, and pore diameter of 18 nm. The values are in good agreement with the expected area (50-150 m2.g-1) for mixed oxides prepared by the modified coprecipitation method (21,26).

The reduction and basicity profiles of K-Co-Cu-Al are displayed in **Figure 1**. On the TPR (Figure 1a), we observed two distinct regions: one from 200 to 400 ºC, ascribed to the reduction of Cu2+ to Cu0, along with Co3+ to Co2+ (22,27,28); and a second broad region above 400 ºC related to a two-step reduction of bulk Co3+ to Co0, the reduction of Co2+ to Co0, and the reduction of spinel-like structures (22,28). On the CO2-TPD (Figure 1b), we observed a sharp peak (~110 °C), a sinusoidal pattern (150-350 °C) due to the re-adsorption of CO2 (29–32), and a broader peak (250-300 °C). The broad peak increased intensity when the sample was reduced at 400 ºC but disappeared when the K‑Co‑Cu‑Al was reduced at 500 ºC. In terms of types of basicity, the region below 200 °C can be attributed to weak basicity sites (Bronsted basicity, i.e., surface OH) (33–36); the second region, to moderate basicity sites (Lewis basicity, metal-oxygen pairs) (35–37); and desorption above 500 ºC, could be assigned to strong basicity cites (Lewis basicity, low coordination oxygen atoms) (11,37). In that sense, our catalyst displays predominantly moderate basicity, especially when reduced at 400 °C. These sites are reported as crucial to HAs formation (18,36).

Chart, histogram

Description automatically generated

**Figure 1.** TPR (a) and CO2-TPD (b) of K-Co-Cu-Al.

The in situ XRD experiments for K-Co-Cu-Al are presented in **Figure 2**. Before reduction, we observe the presence of a mix of CuO and Co3O4 diffraction patterns. It is also likely that peaks related to Co-Al spinel-like structures and Co-Cu alloy oxides are present with the same diffraction pattern as Co3O4 (27,38). Recent works reported similar materials containing a mixture of different phases and spinel structures (22,27,28). After reduction at 250 °C, Cu0 becomes the predominant Cu-related phase. At 400 °C, it is possible to identify both CoO and Co0 phases. The CoO diffraction peaks become weaker after reduction at 500 ºC, indicating an increase in Co0 content. This decrease in Coẟ+ content could be associated with the decrease in moderate basicity sites observed in the CO2-TPD experiments, as M‑O pairs are associated with this type of basicity. Moreover, the increase in Co0 content can lead to strong basicity, promoting CO2 methanation (11), interestingly, this is not observed in K-Co-Cu-Al. The effect of reduction temperature on K-Co-Cu-Al activity was further discussed in the next section. Moreover, the morphology of the catalyst is observed in **Figure 3**, which after reduction at 400 ºC, displayed nanoparticles. It is theorized that these nanoparticles are formed, initially by Cu0, early reduced. These nanoparticles favor hydrogen spillover, allowing Co to be reduced at lower temperatures as it is usually reduced (22,27,28), as confirmed by H2-TPR and *in situ* XRD.

Diagram

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**Figure 2.** *In situ* XRD of K-Co-Cu-Al.

A picture containing text, tree, sky, outdoor

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**Figure 3.** STEM images of K-Co-Cu-Al calcined (a), and after reduction ate 400 °C (b).

*Effect of Pretreatment*

We initially tested K-Co-Cu-Al in the CO2 hydrogenation reaction at 30 bar, 250 ºC, H2/CO2 ratio of 3, and gas-hourly space velocity (GHSV) of 14200 mL.gcat-1.h-1. Henceforth, the products are coded as CH4 (methane), CO (carbon monoxide), HCs (C2-5 alkanes and alkenes), methanol, ethanol, and C3+OH (propanol, isopropanol, and other C3+ oxygenates). We evaluated CO2 conversion, product selectivity (HCs and oxygenates, CO, and CH4), and HCs and oxygenates (methanol, ethanol, and C3+OH) space-time yield (STY).

The effect of the reduction pretreatment is shown in **Figure 4**. Increasing the reduction temperature to 400 ºC leads to an increase in CO2 conversion and the selectivity towards products of interest. Contrastingly, after reduction at 500 ºC, we observed a decrease in CO2 conversion and selectivity towards HCs and oxygenates. It is likely that above 400 ºC, the reduction increases the Co0/Coδ+ ratio, hindering the catalyst activity (17,39,40), as indicated by in situ XRD. As reported, an optimum Co0/Coδ+ ratio is necessary to tune a cobalt-based catalyst activity and selectivity in the CO2 hydrogenation reaction (10,17,37,41). Furthermore, these catalytic test results reflect the CO2-TPD profile. Reducing at 500 ºC, reduced the CO2 uptake and led to the disappearance of the peak attributed to moderate basicity, and associated with ethanol selectivity (18) and CO2 hydrogenation activity (36).

Gráfico, Gráfico de barras

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**Figure 4.** Effect of reduction temperature (pretreatment).

*Effect of Reaction Temperature*

We also evaluated two different reaction temperatures, 50 ºC above and below the previously used temperature, on the catalytic performance of K-Co-Cu-Al, which is displayed in **Figure 5**. In general, increasing the reaction temperature leads to an increase in CO2 conversion, from 7% at 200 ºC to 30% at 300 ºC. The increase in temperature to 300 ºC led to CO formation, and, amidst the products of interest (HCs and oxygenates), favored HCs and methanol formation. Decreasing to 200 ºC seems to cause an increase in ethanol selectivity and a decrease in HCs selectivity but with a low CO2 conversion. Hence, the highest HAs STY was observed at 250 °C.

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**Figure 5.** Effect of reaction temperature.

*Effect of Space-Velocity*

We tested the effect of changing the flow GHSV of the reaction system from 14200 (300 mg of catalyst) to 10625 mL.h-1.gcat‑1 (400 mg of catalyst), by changing the catalyst mass loaded to the reactor, the results are shown in **Figure 6**.

Gráfico

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**Figure 6.** Effect of space-velocity.

A decrease in SV leads to an increase in CO2 conversion from 17% to 24% –an increase of roughly 40%, meanwhile, the change in mass represented an increase of 33%­–, inhibits the production of CH4, and promotes the formation of HAs. Increasing SV hinders CO insertion, which has slow reaction rate than the C-C coupling and hydrogenation reactions, thus HAs formation can be increased by decreasing SV. On the other hand, lowering too much the space velocity could lead to a decrease in STY (20).

*Effect of H2/CO2 Ratio*

Finally, we evaluated the effect of changing the H2/CO2 ratio from 3 (3:1), as commonly used in most of the recently reported literature (6,9,12,20,36,42–45), which can be seen in **Figure 7**. We observed a decrease in the nominal value of CO2 conversion from 17% to 12% by reducing the H2/CO2 ratio from 3 (3:1) to 1.5 (3:2). Nonetheless, decreasing the H2/CO2 ratio equals reducing H2 intake and incrementing CO2 intake, that is, at H2/CO2 ratio of 1.5, 60% more CO2 is feed to the reactor than at H2/CO2 ratio of 3. Therefore, we can infer that, in fact, reducing the H2/CO2 ratio leads to an increase in the amount of CO2 converted (moles of CO2 converted at the same space velocity). Furthermore, with that decrease, CH4 selectivity also decreased from 39% to 22%, and the STY of the products of interest was increased namely, the STY of ethanol and C3+OH increased 2 times, and the STY of HCs increased by roughly 1.2 times. It is reported that the increase in H2/CO2 ratio leads to a decrease in HAs selectivity (18).

Gráfico, Gráfico de barras

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**Figure 7.** Effect of H2/CO2 ratio.

*Final Remarks*

Tuning the reduction temperature from 250 to 400 °C increases the selectivity towards products of interest (HCs and oxygenates) from 47% to 61%. Furthermore, decreasing the space velocity (SV) from 14200 to 10625 mL.h‑1.gcat‑1 leads to HCs and oxygenates selectivity of 72%; meanwhile, changing the H2/CO2 ratio from 3 to 1.5 increases selectivity to 78%. It is worth mentioning that very few published papers have explored space velocity above 6000 mL.h‑1.gcat‑1 (20,43), as it can favor the yield of undesired products, such as CH4 and CO. Contrastingly, we achieved selectivity towards these undesired products below 30%, working above 10000 mL.h‑1.gcat‑1. Moreover, the H2/CO2 ratio was not much explored in the revised literature (9,12,18,20,36,42–44).

In terms of space-time yield (STY), changing SV from 14200 to 10625 mL.h‑1.gcat‑1 leads to a STY of desired products of 7.8 mmol.h‑1.gcat‑1 (STYEthanol: 2.4; STYHCs: 3.2; STYC3+OH: 2.2); whereas decreasing the H2/CO2 ratio from 3 to 1.5 leads to STY of 9.1 mmol.h‑1.gcat‑1 (STYEthanol: 3.1; STYHCs: 3.5; STYC3+OH: 2.5). The STY for methanol was below 0.2 mmol.h‑1.gcat‑1 for both cases, hence not accounted. Noteworthy, to the best of our knowledge, K‑Co‑Cu‑Al, in both cases (SV: 10625 mL.h‑1.gcat‑1 or H2/CO2 ratio: 1.5), displays one of the lowest selectivity towards undesired products and highest higher alcohols STY in the current literature (9,12,18,20,36,42–44).

## Conclusions

We investigated a K-Co-Cu-Al catalyst for the CO2 hydrogenation to higher alcohols (HAs), and the effect of the reaction conditions on the activity and selectivity of this catalyst. Overall, finding the optimum reduction temperature (400 °C) helps decrease the yield towards undesired products, as well as, increasing CO2 conversion. Finally, optimizing the reaction conditions plays an important role on increase the yield of products of interest. For instance, K‑Co‑Cu‑Al, after changes in space-velocity and H2/CO2 ratio displays HAs STY of 4.6 and 5.6 mmol.h‑1.gcat‑1, respectively. To the best of our knowledge, the HAs STY is one the highest among related studies, that is, for continuous reactors, especially for Co-based catalysts.

## Acknowledgment

The authors would like to acknowledge CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil) – Finance Code 001 and COFECUB (Comitê Francês de Avaliação da Cooperação Universitária com o Brasil – Ph-C 912/18), European Union (ERDF) and Région Nouvelle Aquitaine for the financial support, as well as UFRJ (Universidade Federal do Rio de Janeiro), the Université de Poitiers and CNRS (Centre National de la Recherche Scientifique) for letting this research to be developed in their facilities and with the aid. The authors also would like to thank Dr. Carla R. Moreira and INT (Instituto Nacional de Tecnologia) for the STEM images.

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