

## Article

# Study of the Direct CO<sub>2</sub> Carboxylation Reaction on Supported Metal Nanoparticles

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**Abstract:** 2,5-furandicarboxylic acid (2,5-FDCA) is a biomass derivate of high importance that is used as a building block in the synthesis of green polymers such as poly(ethylene furandicarboxylate) (PEF). PEF is presumed to be an ideal substitute for the predominant polymer in industry, the poly(ethylene terephthalate) (PET). Current routes for 2,5-FDCA synthesis require 5-hydroxymethylfurfural (HMF) as a reactant, which generates undesirable co-products due to the complicated oxidation step. Therefore, direct CO<sub>2</sub> carboxylation of furoic acid salts (FA, produced from furfural, derivate of inedible lignocellulosic biomass) to 2,5-FDCA is potentially a good alternative. Herein, we present the primary results obtained on the carboxylation reaction of potassium 2-furoate (K2F) to synthesize 2,5-FDCA, using heterogeneous catalysts. An experimental setup was firstly validated, and then several operation conditions were optimized, using heterogeneous catalysts instead of the semi-heterogeneous counterparts (molten salts). Ag/SiO<sub>2</sub> catalyst showed interesting results regarding the K2F conversion and space–time yield of 2,5-FDCA.

**Keywords:** carboxylation; metal nanoparticles; heterogeneous catalysis; FDCA; furoic acid



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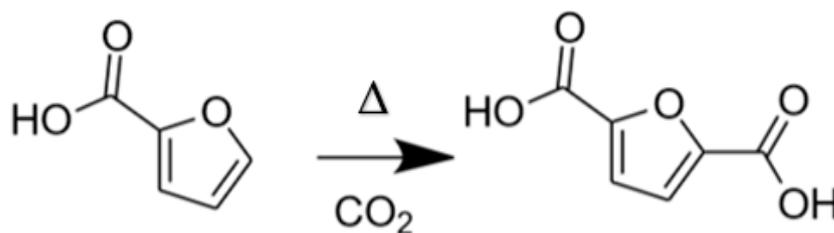
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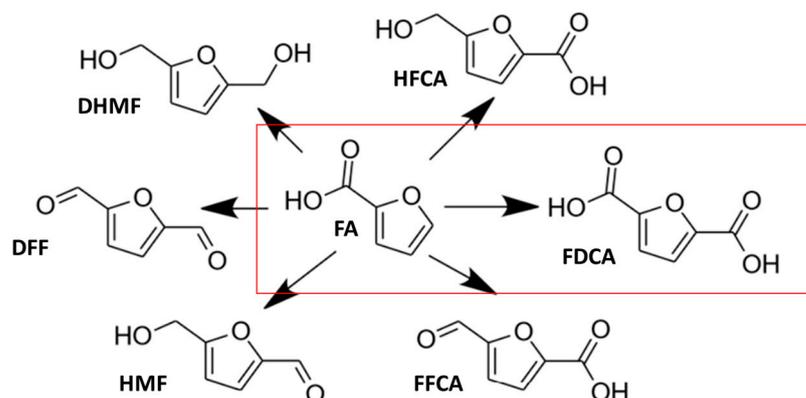
## 1. Introduction

Recently, the production of 2,5-furandicarboxylic acid (2,5-FDCA) from biomass has awakened interest [1–9]. 2,5-FDCA is one of the most important building blocks for the production of polymers, such as the poly(ethylene furandicarboxylate) (PEF), which can replace poly(ethylene terephthalate) (PET), derived from terephthalic acid (TA), a non-sustainable molecule. Two main routes have been studied in the literature for the 2,5-FDCA synthesis from C<sub>6</sub> or C<sub>5</sub> compounds transformation. Moreover, 5-hydroxymethylfurfural (HMF) oxidation to 2,5-FDCA has been widely studied, and although it has shown to have the best catalytic results, some problems regarding 2,5-FDCA selectivity are found due to the formation of unstable intermediate products [4–6,10–14]. Moreover, HMF is quite unstable and provokes serious problems during the oxidation process. In addition, HMF generally obtained from fructose need to be of very high purity. On the other hand, 2,5-FDCA synthesis from hemicellulose-derived chemicals is of great importance. Indeed, furfural could substitute HMF, as its industrial production from non-edible resources is a mature process. Production of furoic acid synthesis from furfural oxidation, using heterogeneous catalysts in a alkaline [15–17] or base free media [6,18], has been studied. Then, the C–H carboxylation of furoic acid with CO<sub>2</sub> can form 2,5-FDCA (Figure 1). This reaction has shown to be more selective than that from HMF [19–21].



**Figure 1.** Reactional scheme of CO<sub>2</sub> carboxylation of furoic acid to 2,5-furandicarboxylic acid (2,5-FDCA).

However, the main problem in the 2,5-FDCA synthesis from furoic acid is the carboxylate group insertion on hydrocarbon C-H bonds [22,23]. As C1 feedstock, CO<sub>2</sub> presents thermodynamic and kinetic limitations [24]. Indeed, in the esterification of aromatic hydrocarbons with CO<sub>2</sub>, a low equilibrium conversion at every temperature is obtained [24]. Consequently, several solutions have been studied to perform the direct C-H carboxylation, by using a base as a reagent, as previously developed by Kolbe and Schmitt [25–27], a Lewis acid [28], transition metal catalysts [29] and enzymes [19,30]. In terms of mechanism, those reagents could influence the mode of C-H cleavage that could be an electrophilic aromatic substitution, a C-H deprotonation by base or a C-H oxidation and subsequent CO<sub>2</sub> insertion. This reaction can take place both in basic or acidic conditions. In basic media, the use of a strong base deprotonates the C-H group with the most acidic proton, which is at position 5 in furoic acid (FA) [31], to form a strong nucleophilic carbon atom, being able to react with weakly electrophilic carbon dioxide. In acidic media, CO<sub>2</sub> is activated via coordination with a Lewis acid, leading to a reaction between the reactant and the activated CO<sub>2</sub> [32]. This reaction can occur at relatively low temperatures but requires high CO<sub>2</sub> pressure, and poor yield of the target product is reached due to the different parallel reactions that could occur. A general schematization of this process is illustrated in Figure 2.



**Figure 2.** Possible carboxylation reaction routes from furoic acid (FA) to 2,5-furandicarboxylic acid (FDCA), 5-hydroxymethylfurfural (HMF), 2,5-dihydroxymethylfuran (DHMF), 5-hydroxymethyl-2-furancarboxylic acid (HFCA), 2,5-diformylfuran (DFF) and 5-formyl-2-furancarboxylic acid (FFCA).

In this context, the Henkel reaction of alkaline salts of aromatic acids to synthesize symmetrical diacids has been reported in the literature [33,34]. This reaction involves the thermal rearrangement or disproportionation of alkaline salts derived from aromatic acids to both the unsubstituted and the symmetrical aromatic diacids. This process is carried out under carbon dioxide or inert atmosphere, at high pressure, between 350 and 550 °C, producing potassium terephthalate and benzene from potassium benzoate in the presence of a metallic salt (e.g., cadmium, zinc . . . ) [35–39]. Furthermore, the HCl acidification of potassium terephthalate produces TA, which is used to synthesize PET.

Alkaline salts of furoic acid disproportionate to produce 2,5-FDCA in a similar way to that observed in the Henkel reaction for TA synthesis [40–44]. However, formation of

furan is also observed during the reaction. The latter could be hydrogenated to produce 1,4-butanediol [45]. Polycondensation of 1,4-butanediol and 2,5-FDCA can be performed in order to produce poly(1,4-butylene 2,5-furandicarboxylate) (PBF), which is a renewable alternative to PET [46].

For instance, Pan et al. [44] performed a reaction involving potassium furoate as reactant and  $ZnCl_2$  as catalyst, under 38 Bar of  $CO_2$ , at 250 °C, for 3 h. They reported high selectivity of 86% to 2,5-FDCA, with a conversion of 61%. However, purity of 2,5-FDCA was not completely detailed.

Regarding the selectivity of the reaction, Thiyagarajan et al. [40,43] recently demonstrated the formation of asymmetrical diacids, as 2,4-FDCA in addition to the 2,5-FDCA. A series of catalytic tests using potassium 2-furoate as reactant in a Kugelrohr glass oven were performed, giving rise to FDCAs' formation. A yield of up to 91%, using  $CdI_2$  as catalyst, at 260 °C, for 5.5 h, under a low flow of  $N_2$  [40], was obtained. After esterification of the crude reaction mixture, they demonstrated the presence of both the 2,5-FDCA and the 2,4-FDCA asymmetrical diacids with a 70:30 molar ratio [40].

Several homogeneous or semi-heterogeneous catalysts (as  $CdI_2$  and  $ZnCl_2$  or  $Cs_2CO_3$  and  $K_2CO_3$ , respectively) have shown their efficiency in the FDCA synthesis from furoic acid. However, the use of those types of catalysts complicates the purification/separation step of the desired product. The development of heterogeneous catalysts to overcome the homogeneous catalyst problematic could be a solution.

The main objective of this work is to study the possibility of using heterogeneous catalysts for the 2,5-FDCA synthesis from furoic acid derivatives. Experimental conditions were set based on those reported in the literature, for the Henkel reaction (devices, operation conditions and reactant/catalyst ratio). Additionally, we discuss herein which operation parameters could be optimized and which kind of heterogeneous catalyst could promote the 2,5-FDCA synthesis.

## 2. Results

### 2.1. Validation of the Reaction Setup

Regarding the 2,5-FDCA synthesis, one of the main objectives was using a Kugelrohr apparatus, under conditions similar to those reported in the literature [40]. Thiyagarajan et al. [40] performed the production of the 2,5-furan and 2,4-furandicarboxylic acid through Henkel reaction [33,36]. Typically, 10 g of potassium 2-furoate and 22 mol% of  $CdI_2$  were mechanically mixed and loaded in a round flask, which was introduced in the Kugelrohr oven. The optimum operating conditions were 260 °C during 5.5 h, under a continuous flow of  $N_2$  and a slow rotation of the reactor. A similar experiment using 10-times-less reactant and catalyst was performed in our laboratory. A comparison of our results from the NMR analysis with those obtained in the literature is shown in Table 1. Furthermore, in order to determine the chemical shift (in ppm) of FA and 2,5-FDCA peaks in DMSO using NMR, pure compounds were analyzed separately (Supplementary Materials Figures S1 and S2, respectively).

**Table 1.** Validation of the experimental setup for the Henkel reaction, using the Kugelrohr apparatus.

Experiment	$X_{K2F}$ (%)	FDCAs Formation (%)	$S_{2,5-FDCA}$ (%)	$S_{2,4-FDCA}$ (%)
Literature [40]	92	91	70	30
This work	73	69	69	31

Conditions: 530 mg of  $CdI_2$ , 1 g of K2F,  $F_{N_2} = 45 \text{ mL min}^{-1}$ , 20 rpm,  $T = 260 \text{ °C}$ ,  $t = 5.5 \text{ h}$ .

Results calculated from NMR analysis (Supplementary Materials Figure S3) showed a K2F conversion and a 2,5-FDCA formation slightly lower than that obtained by Thiyagarajan et al. [40]. However, the individual selectivity of furandicarboxylic acids remains of the same order. Regarding the results, it was concluded that the Kugelrohr glass oven is suitable for the Henkel reaction tests.

## 2.2. Dual Catalytic System (Ag/SiO<sub>2</sub> + CdI<sub>2</sub>)

The Henkel reaction to produce 2,5-FDCA from K2F has shown good results using CdI<sub>2</sub> as catalyst [40]. However, the reaction temperature must reach at least 260 °C to achieve good conversions. At this temperature, CdI<sub>2</sub> starts to decompose (melting point is 387 °C), thus leading to a better interaction between the solid K2F and the semi-melted catalyst. In order to decrease the working temperature, one of the proposed solutions was to use a heterogeneous catalyst in addition to the CdI<sub>2</sub> catalyst, in CO<sub>2</sub> atmosphere. The temperature was decreased from 260 to 200 °C, to observe the evolution of the results compared to those in the literature [40]. Results are shown in Table 2.

**Table 2.** Influence of temperature for the 2,5-FDCA synthesis using Ag/SiO<sub>2</sub> and CdI<sub>2</sub> mixture on the K2F conversion and space–time yields (STY).

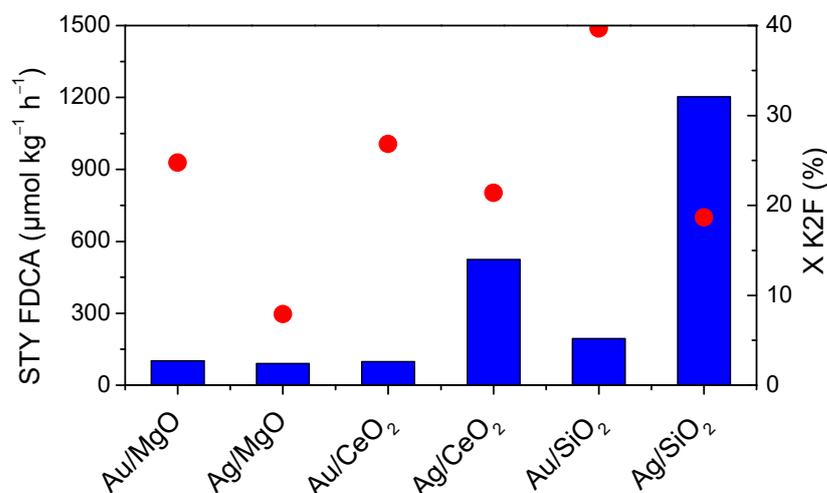
Entry	Catalyst	Temperature (°C)	Conversion (%)	STY <sub>2,5-FDCA</sub> (μmol kg <sup>-1</sup> h <sup>-1</sup> )	STY <sub>DFF</sub> (μmol kg <sup>-1</sup> h <sup>-1</sup> )
1	CdI <sub>2</sub>	200	0	-	-
2	Ag/SiO <sub>2</sub> /CdI <sub>2</sub>	200	51	264	951
3	Ag/SiO <sub>2</sub> /CdI <sub>2</sub>	230	74	145	-
4	Ag/SiO <sub>2</sub> /CdI <sub>2</sub>	260	69	188	-
5	Ag/SiO <sub>2</sub>	200	20	1203	-

Conditions: 17 mg of CdI<sub>2</sub>, 35 mg of K2F, 50 mg of Ag/SiO<sub>2</sub>, F<sub>CO<sub>2</sub></sub> = 45 mL min<sup>-1</sup>, 20 rpm, T = 200–260 °C, t = 20 h.

Using a dual catalytic system seems to open the possibility to significantly decrease the reaction temperature, since the K2F conversion does not show a significant decrease (Table 2, Entries 2 and 4). However, 2,5-FDCA's yield is more affected by using lower temperature. Indeed, at 200 °C, the formation of the 2,5-diformyl furan (DFF) was observed. It was also the major product at this temperature. However, it confirms the beneficial effect of the Ag/SiO<sub>2</sub>, since no activity was observed at 200 °C for CdI<sub>2</sub> alone (Table 2, Entry 1). In addition, Ag/SiO<sub>2</sub> alone already produces 2,5-FDCA, even if the K2F conversion decreases significantly (Table 2, Entry 5).

## 2.3. Effect of the Support

Taking into account good preliminary results obtained with the Ag/SiO<sub>2</sub> (Table 2), the screening of the different supports was performed. Silver and gold catalysts supported on different supports were tested, and the results are shown in the Figure 3.

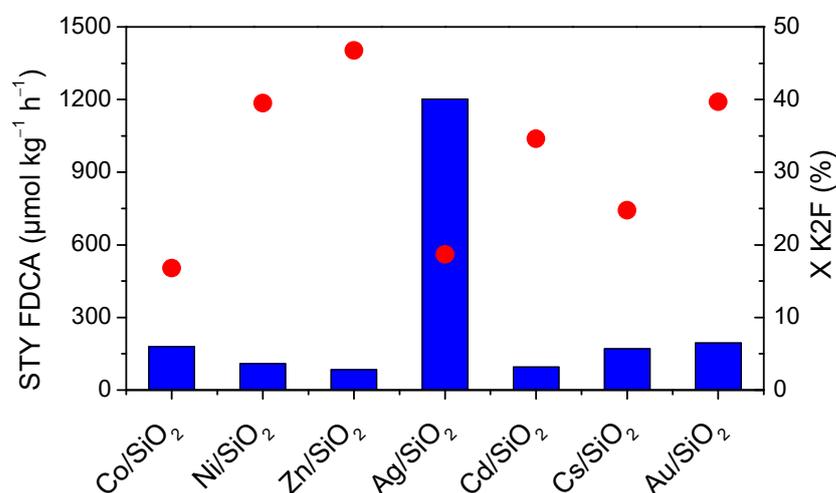


**Figure 3.** Effect of the support on gold and silver catalysts in the K2F carboxylation: K2F conversion (●) and the STY of 2,5-FDCA (■) (Conditions: Substrate/M = 9, F<sub>CO<sub>2</sub></sub> = 45 mL min<sup>-1</sup>, 20 rpm, T = 200 °C, t = 20 h).

Regarding K2F conversion, the use of Au instead of Ag increased the activity, whatever the support. However, a lower 2,5-FDCA yield was obtained by using Au catalysts. Regarding the support, the use of MgO with Au or Ag leads to a low 2,5-FDCA production. On the contrary, Ag/CeO<sub>2</sub> and Ag/SiO<sub>2</sub> catalysts have shown similar activity (~20% of K2F conversion) and promote 2,5-FDCA production up to 524 and 1203  $\mu\text{mol kg}^{-1} \text{h}^{-1}$ , respectively. In order to explain these results, it has to be considered that CeO<sub>2</sub> support has basic and redox properties, while MgO presents high basicity [47]. The redox properties of the CeO<sub>2</sub> could be the reason of an enhanced performance. Indeed, the oxygen vacancies of CeO<sub>2</sub> increase the adsorption capacity of CO<sub>2</sub> [47,48], which could promote the carboxylation reaction. However, the use of SiO<sub>2</sub> has shown a much better yield to 2,5-FDCA than CeO<sub>2</sub>. That could be explained by the presence of acid sites in the support [49].

#### 2.4. Effect of the Metal

Since the SiO<sub>2</sub> support has shown the best performances towards 2,5-FDCA synthesis, it has been selected for the screening of the metal phase in the heterogeneous catalyst. A series of M/SiO<sub>2</sub> catalysts were tested, in similar conditions, for comparison. K2F conversion and 2,5-FDCA space–time yield are shown in Figure 4.



**Figure 4.** Effect of the metal, using SiO<sub>2</sub> supported catalysts on the conversion (●) of K2F and the STY of 2,5-FDCA (■) (Conditions: Substrate/M = 9, F<sub>CO<sub>2</sub></sub> = 45 mL min<sup>-1</sup>, 20 rpm, T = 200 °C, t = 20 h).

High 2,5-FDCA production was observed only for Ag/SiO<sub>2</sub> catalyst with a conversion of 20% (Figure 4). Cs and Co supported on silica showed the lowest conversion values, between 17 and 25%. On the other hand, Zn and Cd supported on silica presented the highest conversion values, which are 47 and 35% respectively. Both metals have already shown promising results in the Henkel reaction, using CdI<sub>2</sub> and ZnCl<sub>2</sub>.

Regarding the metal composition, only the catalyst containing Ag has shown interesting results in 2,5-FDCA synthesis, contrary to the other metals tested. An XRD diffractogram of the Ag/SiO<sub>2</sub> catalyst is shown in Supplementary Materials Figure S4. Diffraction peaks located at 34, 49 and 61° 2 $\theta$  could correspond to Ag<sub>2</sub>O (JCDs ICDD 00-042-9874) or Ag<sub>2</sub>CO<sub>3</sub> (JCDs ICDD 04-017-5597), while the three other peaks at 38.1°, 44.2° and 64.4° 2 $\theta$  are representative of the (111), (200) and (220) planes of metallic Ag (JCDs ICDD 00-001-1164), respectively. The mean crystallite sizes of Ag metallic and Ag<sub>2</sub>O, calculated using Scherrer's equation, were of 25.3 and 9.5 nm, respectively.

One of the main differences between silver and the others metals comes from its particular electronic configuration ([Kr] 4d<sup>10</sup> 5s<sup>1</sup> from group 11), typical from the so-called "coinage metals" group. Furthermore, it has been reported in the literature that Ag(I) salts promote the carboxylation of terminal alkynes [50–52]. The d<sup>10</sup> electronic configuration of silver favors the activation of alkynes through its interaction with the C–C  $\pi$ -bond of alkyne.

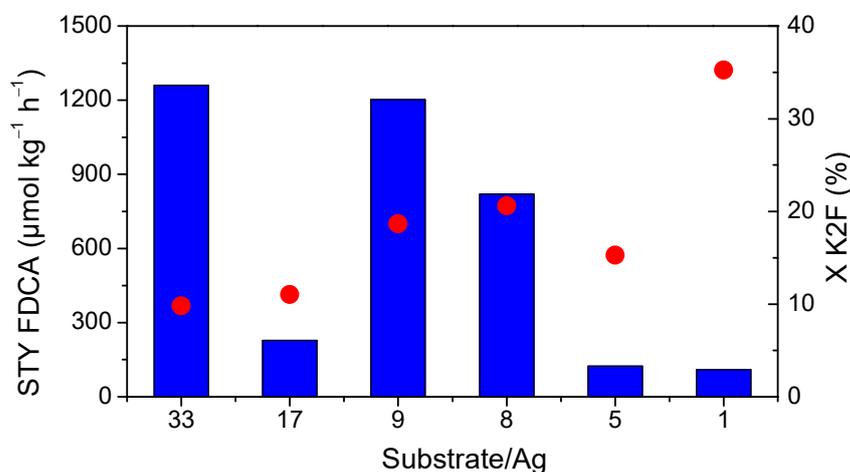
Moreover, Lui et al. [53] have demonstrated that the use of heterogeneous Ag@MIL-101 catalysts promotes the capture and conversion of CO<sub>2</sub>, overcoming the need of strong base or aggressive organometallic reagents to activate the hydrogen of the terminal alkyne. It was also shown that the adsorption of gaseous CO<sub>2</sub> on the Ag surface occurs differently compared to other metals such as Cu or Au. In case of oxidized Ag atoms, surface O atoms interact with gaseous CO<sub>2</sub> and form chemisorbed on the surface of the metal carbonic acid-like species. In these carbonic acid-like species, two oxygen atoms from CO<sub>3</sub><sup>−</sup> are bonded to adjacent Ag bridging sites. The third oxygen atom forms a C double bond (C=O) perpendicular to the surface. This carbonic O=CO<sub>2</sub><sup>δ−</sup> surface specie has a negative charge localized on the two oxygen atoms binding to the Ag surface [54].

The presence of Ag<sub>2</sub>O could explain the 2,5-FDCA formation, which is produced only by using Ag catalysts. As previously reported, the use of Ag(I) promotes alkynes carboxylation. Consequently, in our case 2,5-FDCA formation could come from the interaction of Ag<sup>+</sup> and the reactant. Moreover, this hypothesis could explain the low 2,5-FDCA formation on Au catalysts, which only present metallic gold nanoparticles [55,56]. This parameter would need some deeper investigation to understand the role of silver in the reaction.

In conclusion, an effect of the support was observed from using supports with different acidity and redox properties. Supports with acidic sites and redox properties promote the production of 2,5-FDCA, while basic supports, like MgO, were demonstrated to have the lower catalytic performances. On the other hand, the screening of different metals supported on SiO<sub>2</sub> has shown that only Ag is leading to the formation of 2,5-FDCA, but with less conversion than Au, Zn, Cd and Ni. Therefore, for the optimization of the reaction conditions, the Ag/SiO<sub>2</sub> catalyst was used.

### 2.5. Effect of the Substrate/Metal Molar Ratio

In this section, the substrate/Ag molar ratio from 1 to 33 was studied. The catalytic results (K2F conversion and space–time yield (STY) of 2,5-FDCA) are presented in Figure 5.

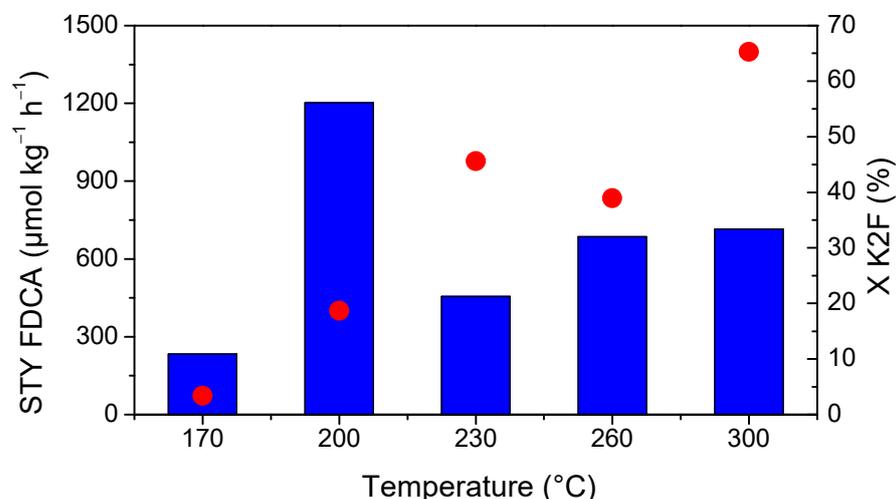


**Figure 5.** Effect of substrate/Ag molar ratio on the conversion of K2F (●) and the STY of 2,5-FDCA (■) (Conditions: Substrate/Ag = 1–33, FCO<sub>2</sub> = 45 mL min<sup>−1</sup>, 20 rpm, T = 200 °C, t = 20 h).

As expected, the K2F conversion increases when the substrate/Ag molar ratio decreases. These results could be directly linked to a limitation of the available active sites on the Ag/SiO<sub>2</sub> catalyst. Regarding the 2,5-FDCA STY, a maximum of 1260 μmol kg<sup>−1</sup> h<sup>−1</sup> is obtained by using a substrate/Ag molar ratio equal to 26. The molar ratio of 9 seems to be an optimum value due to a 2,5-FDCA STY of 1203 μmol kg<sup>−1</sup> h<sup>−1</sup> near to the highest value, and to a K2F conversion of 20% instead of 9% (obtained for the molar ratio of 33). Surprisingly, the 1, 5 and 17 molar ratios have given a very low formation of 2,5-FDCA, which could come from a lack of physical interaction of the mixture, together with a kinetic limitation for the formation of 2,5-FDCA.

### 2.6. Effect of Reaction Temperature

The reaction temperature has been studied from 170 to 300 °C. The conversion and space–time yield are shown in Figure 6.



**Figure 6.** Influence of the reaction temperature on the catalytic performance of Ag/SiO<sub>2</sub> with the conversion of K2F (●) and the STY of 2,5-FDCA (■) (Conditions: Substrate/Ag = 9, F<sub>CO<sub>2</sub></sub> = 45 mL min<sup>-1</sup>, 20 rpm, T = 170–300 °C, t = 20 h).

At 170 °C, a very low conversion of 6% was obtained. An increase of the temperature enhances conversion, with an optimum 2,5-FDCA space–time yield of 1203 μmol kg<sup>-1</sup> h<sup>-1</sup> at 200 °C. Furthermore, between 230 and 300 °C, an increase in K2F conversion to 2,5-FDCA reaching 65% was observed. However, only 715 μmol kg<sup>-1</sup> h<sup>-1</sup> of 2,5-FDCA yield at 300 °C was obtained.

## 3. Materials and Methods

### 3.1. Catalysts Preparation

A series of Au and Ag catalysts with a nominal metal content of 7 wt.% were prepared by wet impregnation, using water as solvent and using commercial SiO<sub>2</sub> (CARiACT Q-10), CeO<sub>2</sub> (Sigma-Aldrich, Saint Louis, MO, USA) and MgO (Sigma-Aldrich, Saint Louis, MO, USA) as support. Typically, for 1 g of catalyst, 10 mL of a 66 mmol L<sup>-1</sup> of AgNO<sub>3</sub> solution (99%, Sigma-Aldrich, Saint Louis, MO, USA) was added to 0.93 g of the support. The mixture was kept under stirring (150 rpm), overnight, and the solvent was evaporated at 90 °C, using a vacuum, prior to a drying step at 80 °C, overnight. The obtained solids were afterwards calcined in air atmosphere for 4 h, at 300 °C.

M/SiO<sub>2</sub> catalyst series with M = Zn, Cs, Cd, Ni and Co were prepared by using the same method, by adjusting the concentration of the precursor solution in order to obtain a 7 wt.% metal content.

### 3.2. Catalytic Test

Potassium 2-furoate (K2F) was prepared by using furoic acid (97%, Sigma-Aldrich, Saint Louis, MO, USA) and KOH (85%, Sigma-Aldrich, Saint Louis, MO, USA) in a 1:1 molar ratio.

2,5-FDCA synthesis was performed in a Glass Oven B-585 Kugelrohr (Büchi), under CO<sub>2</sub> atmosphere. Typically, 1 mmol of K2F was mechanically mixed with 100 mg of Ag/SiO<sub>2</sub> and introduced into a round flask and placed inside the oven. Then, the solid mixture was slowly rotated at 20 rpm, at 200 °C, under a continuous flow of CO<sub>2</sub> (45 mL min<sup>-1</sup>), during 20 h. Afterwards, the setup was cooled down for 1 h. The obtained black solid was dispersed in H<sub>2</sub>O or MeOH, stirred for 1 h and filtered by using PTFE (2 μm), giving a pale-yellow filtrate and the remaining catalyst.

To analyze the reactions reagents and products, a gas chromatograph (GC, Agilent 7890B) apparatus equipped with a CP-Wax 52 CB GC column or a High-Performance Liquid Chromatography (HPLC, Waters 2410 RJ) apparatus equipped with a Shodex SUGAR SH-1011 column and UV detector, using 5 mM of H<sub>2</sub>SO<sub>4</sub> (0.6 mL min<sup>-1</sup>) as a mobile phase, was used. Conversion and STY were calculated by using the following formulas, Formulas (1) and (2), respectively.

$$X_{K2F} = (n_{0K2F} - n_{K2F})/n_{0K2F} \times 100, \quad (1)$$

where  $X_{K2F}$  is the potassium furoate conversion (%), and  $n_{0K2F}$  and  $n_{K2F}$  are the initial and the non-reacted number of moles of potassium furoate, respectively (mol).

$$STY_i = n_i / (m_{catalyst} \times t_r), \quad (2)$$

where  $STY_i$  is the space-time yield of a product  $i$  ( $\mu\text{mol kg}^{-1} \text{h}^{-1}$ ),  $n_i$  is the number of moles of product  $i$  ( $\mu\text{mol}$ ),  $m_{catalyst}$  is the mass of catalyst (kg) and  $t_r$  is the reaction time (h).

#### 4. Conclusions

A dual catalytic system containing a heterogeneous catalyst and CdI<sub>2</sub>, a semi-homogeneous catalyst, was tested. Preliminary results confirmed the possibility to decrease the reaction temperature to 230 °C, obtaining an acceptable conversion (74%). However, a drastic decrease of the 2,5-FDCA STY was observed from 8489 to 154  $\mu\text{mol kg}^{-1} \text{h}^{-1}$ , which could be explained by a high adsorption of the products on the heterogeneous catalyst. It is worth noting that an increase in the temperature of the reaction disfavored the adsorption and favored the catalytic conversion.

Several experiments have been performed to screen a support and a metal which could promote 2,5-FDCA production. SiO<sub>2</sub> support has shown the greatest promotion of 2,5-FDCA synthesis from K2F, contrary to CeO<sub>2</sub> and MgO. In addition, Ag/SiO<sub>2</sub> leads to the highest yields in 2,5-FDCA formation, while other monometallic (Ni, Co, Zn, Cd . . . ) catalysts showed much lower productivities.

**Supplementary Materials:** The following are available online, at <https://www.mdpi.com/2073-4344/11/3/326/s1>. Figure S1: Representative <sup>1</sup>H-NMR of furoic acid (FA). Figure S2: Representative <sup>1</sup>H-NMR of isolated FDCA. Figure S3: Representative <sup>1</sup>H-NMR of crude products obtained from the carboxylation of K2F to FDCA. Figure S4: XRD diffractogram of Ag/SiO<sub>2</sub>.

**Author Contributions:** Conceptualization, F.D., Y.S. and R.W.; methodology, F.D.; formal analysis, F.D. and J.T.-R.; investigation, F.D. and Y.S.; resources, R.W.; data curation, F.D., J.T.-R., I.I.J. and R.W. writing—original draft preparation, F.D., and R.W.; writing—review and editing, F.D.; I.I.J., S.P. and R.W.; visualization, I.I.J. and S.P.; supervision, R.W.; project administration, R.W.; funding acquisition, R.W. All authors have read and agreed to the published version of the manuscript.

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