

Catalytic hydrothermal conversion of CO₂ captured by ammonia into formate using aluminum-sourced hydrogen at mild reaction conditions

Juan I. del Río ^{a,b}, Eduardo Pérez ^a, David León ^a, Ángel Martín ^a, María D. Bermejo ^{a,*}

^a BioEcoUva Research Institute on Bioeconomy, High Pressure Process Group, Department of Chemical Engineering and Environmental technology, Universidad de Valladolid, Valladolid, 47011, Spain

^b Grupo Procesos Químicos Industriales, Facultad de Ingeniería, Universidad de Antioquia UdeA, calle 70 # 52-21, Medellín, Colombia

*Corresponding author Tel.: +34 983 18 40 77

E-mail address: mdbermejo@iq.uva.es (María Dolores Bermejo)

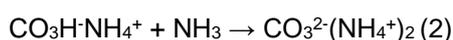
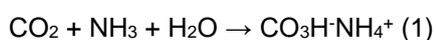
Abstract

The catalytic conversion of CO₂ captured in aqueous media into formate was studied using aluminum-sourced hydrogen in a batch reaction system. To do so, the main ammonia-based CO₂ absorption derivatives: ammonium carbamate, carbonate and bicarbonate and sodium bicarbonate were selected as CO₂ source. The performance of the different species was determined under mild hydrothermal reaction conditions (120 °C), using Pd/C 5 wt% catalyst. In these conditions, the formate yield and selectivity increase in the order ammonium bicarbonate < sodium bicarbonate < ammonium carbonate < ammonium carbamate. Ammonium bicarbonate and sodium bicarbonate reagents needed higher temperature (250 °C) for an increased yield. Results with ammonium carbamate as starting material indicate a significant effect of time and catalyst content on formate yield, which ranged between 4 and 38%. Experiments with gaseous H₂ showed that a comparable yield with Al can be obtained at a similar level of pressure. The reutilization and characterization of the reaction solid, comprising exhausted aluminum and Pd/C catalyst, showed that the aluminum was not completely oxidized up to the 5th re-use, and Pd can play a reducing role through the formation of palladium hydride species. The process can be improved by operating at higher pressure and lower temperature, to avoid loss of yield by dehydration of formate.

Keywords: CO₂ utilization, hydrothermal reduction, Formic Acid, ammonium carbamate, aluminum-water splitting

1. Introduction

The concentration of greenhouse gases, mainly CO₂ from burning fossil fuels, has increased the global concern for climate change [1]. The Paris Agreement has the objective of limiting global warming to less than 2 °C above the temperature in pre-industrial times by reducing CO₂ emissions, and pursuing efforts to limit the temperature increase to 1.5 °C [2]. To achieve it, the European Union and the rest of the international community encourage the use of renewable energies, but it can be foreseen that for many years it will still be necessary to use fossil fuels for the production of electricity and as fuel in the automotive industry [3-5]. Therefore, other solutions are considered, such as CO₂ capture and storage technologies (CCS) [6], and the Carbon Capture Utilization (CCU), which would significantly reduce the CO₂ emissions of thermal power stations and chemical industries such as ammonia, hydrogen, steel and cement production [7]. The amine based CCS technology is one of the most attractive solutions nowadays, but the high cost of the desorption step entails to consider further possibilities. Recently, the French company Alston developed a technology known as "Chilled Ammonia", based on a similar principle [8]. Instead of using an amine aqueous solution, combustion gases are absorbed into an ammonia aqueous solution (28 %wt) at low temperature (2-10 °C). CO₂ is then immobilized by forming ammonium bicarbonate (1), carbonate (2), and carbamates (3) [9].



Typically, 0.33-0.67 mol CO₂/mol NH₃ can be absorbed [10]. As in the case of amines, regeneration is produced by desorption at temperatures between 100-150 °C, and pressures between 0.3-13.6 MPa. This process has the advantage that the heat of absorption is much lower than in the case of amines, and therefore the regeneration is cheaper economically and energetically, but it presents the disadvantage of using considerable cooling.

The European Union has launched the SET Plan (Strategic Energy Technology Plan) to encourage the use of CO₂ as a source of carbon for the production of fuels, chemicals and energy storage, in search for a CO₂ zero emission cycle [11]. Considering this approach, the CO₂ should not be seen as a residue but as a renewable

resource and a sustainable C1 building block in organic synthesis because of its abundance, low cost, non-toxicity, and non-flammability [12]. Nowadays, one of the most developed processes of CO₂ conversion is the production of polycarbonates by copolymerization of CO₂ with epoxides [13].

Conversion of carbon dioxide, C (IV) into other chemical or fuels requires reduction of carbon in one or several steps. The reduction steps for C1 species are: CO₂ (IV) → Formic acid (II) → Formaldehyde (0) → Methanol (-II) → Methane (-IV) (Roman Numerals refer to oxidation states). Different methods of reduction have been investigated, including photochemical reduction, electrochemical reduction and hydrogenation of CO₂ [14]. The final reduced species produced depends on the reaction conditions and the catalyst used.

The production of formic acid (FA) by catalytic CO₂ hydrogenation was first proposed nearly a century ago [15]. Since the 70's the reduction of CO₂ has been studied with homogeneous catalysts, due to their high performances [16]. It was only in the 80's that Pd/C catalyst was introduced for synthesizing formate from H₂ and bicarbonate [17-19]. The uses of formic acid include food additive, preservative, insecticide, industrial material for synthetic processes and hydrogen storage. In the recent years, formic acid has been presented as a promising media for hydrogen storage, to be used in direct liquid fuel cells, owing to its relatively high hydrogen content (4.4 wt%) and higher energy density [20], where the fuel cell runs successfully over formic acid concentrations between 5 and 20 mol L⁻¹ [21]. Other advantages are: (1) it is nontoxic and biodegradable, (2) it is liquid at ambient conditions, and (3) it is easy to store and transport [16].

The hydrothermal reduction can be a feasible alternative to overcome the thermochemical stability of CO₂, taking as reference the abiotic formation of organic compounds in Earth, where the CO₂ and/or CO is reduced by H₂ on a catalytic surface in hydrothermal media [22, 23]. Although the use of gaseous hydrogen is currently based on a non-sustainable economy, it can be potentially obtained by environmentally friendly and economically hydrogen production technologies like the Aluminum-water splitting, see reaction (4). In this reaction, hydrogen can be produced *in situ* in a safe way, getting advantage of the water present in the reaction media [24]. The hydrogen formed as free radicals in water at high temperature is more active than the so-called dry hydrogen (molecular H₂), which is much more chemically stable [25, 26]. In spite of the need of further economic assessments to ensure feasibility of aluminum as feedstock, the process is promising in terms of sustainability, owing to the recyclability of aluminum from scrap using renewable energy [27], as aluminum can be regenerated through a solar thermochemical cycle [28-30]. Besides, the hydrogen mass yield of the Aluminum-water splitting of 11.1% is competitive with other renewable sources of hydrogen like

steam gasification of biomass (hydrogen yield potential of 7.6-12.6%), and can be obtained under milder reaction temperature, where gasification requires above 700 °C [31].

CO ₂ source	Hydrogen source/reducing Agent	Temperature (°C)	Time (h)	Catalyst	Formate Yield (%)	Ref.
Sodium bicarbonate	Zn/ZnO	225	0.5-4	Ni powder	81	[33]
Sodium bicarbonate	Al	250-325	2	-	64	[35]
Sodium bicarbonate	Al	260-320	0.5-3	Pd/C (5%wt)	70	[39]
Sodium bicarbonate	Zn	250-325	0-10	-	80	[36]
Sodium bicarbonate	Zn	250-400	0-3	-	75	[37]
Sodium bicarbonate	gaseous-H ₂	Room	24-46	Pd/C (5 wt%)	54	[18]
Sodium bicarbonate	2-pyrrolidone	250-350	0.5-2.5	Pd/C (5 wt%)	30	[41]
Sodium bicarbonate	glucose	300	3	-	60*	[38]
Sodium bicarbonate	isopropanol	260–320	0.5-2.5	-	70	[48]
Carbonates and bicarbonates of Na, K, Ca and NH ₄	gaseous-H ₂	200	2	NiNPore	0-92	[40]
Carbonates and bicarbonates of Na, K, and NH ₄	gaseous-H ₂	20-80	1-15	Palladium Nanocatalysts	95.6	[47]
Potassium carbonate	Ni, Fe	200-350	1-6	Ni	25	[32]
Ammonium carbamate/carbonate	gaseous-H ₂	20-60	1-8	Pd/C (5 wt%)	92	[42]
Ammonium carbonate	NaBH ₄	90	0.1	-	75	[44]
CO ₂ gas	Fe nanoparticles	80-200	5-200	Fe nanoparticles	8.5**	[34]



Table 1. Overview of the catalytic hydrothermal conversion of CO₂ into formate using different sources of hydrogen in batch reactors.

* With respect to the initial molar concentration of glucose

** Units are in mmol*L⁻¹

Table 1 summarizes the yields reported in the literature as function of reaction conditions for the hydrothermal conversion of CO₂ into formate. In most cases, sodium bicarbonate has been preferred as the starting material for the hydrothermal reduction of CO₂, using Ni [32, 33] and Fe [34] catalysts, and/or reductants like Al, Mg, Mn and Zn. Metals like Zn and Al produce the highest yields [33, 35, 36]. In our previous research, the use of zinc allowed to obtain a yield of 75% of formic acid from the reduction of sodium bicarbonate in batch system at 300 °C and 2 h [37]. Also, the use of biomass derivatives (glucose) allowed reducing sodium bicarbonate in hydrothermal media with efficiencies of up to 60%, in batch system at 300 °C and 3 h [38]. Zhong *et al.* [39] studied the catalytic reduction of sodium bicarbonate with palladium supported on carbon (5 wt%), using Aluminum-water splitting as source of hydrogen, obtaining formic and acetic acid at temperatures of 260-320 °C and in reaction times of 0.5-3 hours. Wang *et al.* [40] conducted experiments to obtain formate from several carbonates and bicarbonates of Na, K, Ca and NH₄, under high pressure of gaseous hydrogen, at 200 °C, while testing several catalysts. In general, Na and K bicarbonates showed higher FA yield (86-92%) than its carbonates (71-76%). The ammonium bicarbonate had a negligible performance (6.5%) compared to the previous ones. Yao *et al.* [35] studied the production of formic acid from the reduction of CO₂ by using as well aluminum water splitting. They obtained a formic acid yield of 64% with near 100% selectivity, in a batch reactor with a temperature range of 250 and 350 °C, operating for 2 hours (pressure was not reported). Takahashi *et al.* [32] studied the effect of Fe-powder and Ni-powder as reducing agents of gaseous CO₂ in hydrothermal media, using a micro batch autoclave at 70% filling, between 200 and 350 °C and reaction times ranging from 1 to 6 hours. The main product obtained was methane (a maximum of 94% at 350 °C), because of the hydrogenating effect of Ni, except when K₂CO₃ was used as a carbon source, which generates basic conditions and mainly produces formic acid, increasing its performance with high temperatures, up to a yield of 25% at 300 °C. The mild reaction conditions on the hydrothermal reduction of CO₂, catalyzed by Pd/C (5 wt%), were studied by Stalder *et al.* [18]. They used sodium bicarbonate (concentration of 1.0M) as carbon source, a pressure of 1.0-1.7 atm of hydrogen and room temperature, obtaining sodium formate with final concentration up to 0.5 M, but the reaction time was too long (24-46 hours). Likewise, He *et al.* [34] reduced CO₂ in hydrothermal media in presence of iron nanoparticles acting both as reductant and as catalyst, using batch reactors pressurized between 0.14 and 1.4 MPa of CO₂, temperatures between 80 and 200 °C and times between 5 and 200 hours. It was concluded that by increasing time and temperature the yield of both formic acid and acetic acid was improved. Nevertheless, the final concentration of formic acid was low, of 8.5 mmol/L. Zhu *et al.* [41] reduced sodium bicarbonate with 2-pyrrolidone as a reducing agent to obtain formic acid in

batch system at 250-350 °C and 0.5-2.5 hours, using Pd/C (5 wt%) catalyst. Other metals like Co, Ni, Cu, Cr, Mo, and NiAl alloy were tested as catalyst, but only Cr showed similar performance as Pd/C.

Many works attempted the reduction of CO₂ in the form of sodium or potassium bicarbonate, which corresponds to the product from capturing CO₂ into NaOH and KOH aqueous solutions, respectively. Not much research has been done in reducing CO₂ captured in ammonia and amines, even though these derivatives (carbamates and carbonates) can be more easily hydrogenated at mild temperatures than bicarbonates (in ethanol-rich solutions), and are more reactive than carbonates and bicarbonates of inorganic cations [42, 43]. As example, Su et al. [42] reduced ammonium carbamate to formic acid in hydrothermal media, aided by ethanol co-solvent, using Pd/C catalyst at room temperature with gaseous hydrogen. They showed that the higher reactivity of bicarbonates is conditional and solvent-dependent. Pulidindi *et al.* [44] hydrothermally reduced ammonium carbonate using NaBH₄ as reducing agent, in batch reaction using a domestic microwave oven as heating system (2.45 GHz, 1100 W at 100% power), under atmospheric pressure in the presence of air, obtaining a yield of 75 wt% of formate with an irradiation time of 5 min at 90 °C.

However, in none of these reports, the comparison of ammonia-based CO₂ absorption derivatives (ammonium carbamate, carbonate and bicarbonate) has been studied as starting materials for the hydrothermal production of formic acid under mild reaction conditions using aluminum water-splitting reaction as hydrogen source. Not much research has been done in reducing CO₂ captured in ammonia and amines, even though its derivatives can be more easily hydrogenated at mild temperatures. This route is important because it allows obtaining value-added chemicals like formic acid, without separation, purification or compression steps between the CO₂ capture and its conversion, thus involving a safer and efficient way of producing hydrogen from aluminum. In this work, the implementation of a commercial catalyst allowed lowering the temperature of the reduction process in search for mild reaction conditions. This approach allowed selecting the best starting material for a parametric study to determine the effect of the main process variables on the yield, selectivity and conversion in the formic acid production. The evaluation of the chemical-state evolution and reusability of the resulting reaction solid allowed determining the reducing species available in the synergy Al powder-Pd/C catalyst, based on thorough characterization.

2. Materials and methods

2.1 Chemicals

Ammonium carbamate (AC) (99%), ammonium carbonate (ACA) ($\geq 30.0\%$ NH_3 basis), ammonium bicarbonate (AB) ($\geq 99.0\%$) and sodium bicarbonate (SB) (100%) were used as carbon source, and diluted in deionized water. Fine powder of commercial Pd/C catalysts of 5 wt% of metal loading was used as received. Aluminum fine powder (Al) ($< 5\mu\text{m}$, 99.5%) was employed as source of hydrogen. All reagents, except aluminum and sodium hydroxide pellets (Panreac) and sodium bicarbonate (COFARCAS-Spain), were purchased from Sigma-Aldrich. Hydrogen (99.99%) was provided by Linde. All chemicals were used without further purification.

2.2 Catalytic experiments

Hydrothermal reactions for the reduction of the ammonia-based CO_2 captured species, using Al powder as hydrogen source and Pd/C as catalyst, were conducted in a stainless steel stirred reactor from Parr Instruments (Series 4791 Micro Stirred Reactors of 25 mL, maximum pressure of 200 bar, and maximum temperature of $350\text{ }^\circ\text{C}$), at 500 RPM, with autogenous pressure and heating at a ramp of $14\text{ }^\circ\text{C}/\text{min}$ using a band heater. The pressure meter device had an error of ± 2 bar. Before each run, all the solids were weighed (Al, catalyst and the respective carbon source) and diluted/suspended in water. Once the reactor was sealed, a gentle flow of nitrogen was passed through the head-space to purge the remaining air out of the system. After the reaction, the vessel was rapidly immersed in a cold water bath. Then, the liquid sample was collected and filtered through a 0.22 mm filter, while the solid was stored under N_2 atmosphere for characterization.

It was established a reference central point of reaction conditions, comprising the values: $120\text{ }^\circ\text{C}$, 2 h (constant temperature), Al:Carbon Source molar ratio of 6:1, 15 wt% catalyst with respect to the initial weight of carbon source, and 70% of reactor filling in volume at room temperature. Then, the effect of the process variables on the production of formic acid (FA) from ammonium carbamate was assayed by varying the reaction conditions as follows: temperature ($80\text{-}300\text{ }^\circ\text{C}$), reaction time (0.5-5 h), Al:AC molar ratio (1.5:1 - 9:1), catalysts content (7.5-60 wt%), calculated as grams of catalyst/grams of carbamate), liquid filling (50-85% of the total volume of the vessel), using an initial concentration of carbamate of 0.5 M (initial pH=9.2).

All the carbon sources were evaluated in order to determine their reactivity as starting material for the production of formic acid at the central point of reaction conditions and at $250\text{ }^\circ\text{C}$. Sodium bicarbonate was used as reference feedstock, given its wide use as carbon source.

The effect of alkalinity of the initial reaction solution of carbamate was evaluated at the central point conditions by adding NaOH before the reaction, until reaching pH of 10.1 and 12.5, separately. Experiments with AC at the central point were also carried out with gaseous hydrogen as the reducing agent, for contrasting the performance of aluminum. To do it so, the reactor was charged with the corresponding amount of AC, water and catalyst, followed by a gentle flow of hydrogen passed through the head-space to purge the remaining air out of the system, and finally pressurized with hydrogen.

The evaluation of the reutilization of the resulting solid after reaction (a mixture of exhausted aluminum and Pd/C catalyst) was done through 5 reuses at the central point, using carbamate. Before every reuse, the solid was filtered and dried in-situ in the reactor, by attaching a vacuum pump to the reactor, while passing nitrogen at 50 °C for 30 min.

2.3 Product analyses

The liquid samples were analyzed by HPLC (Waters, Alliance separation module e2695) using an Aminex 87H (Bio-Rad) column with RI detector (Waters, 2414 module). The mobile phase was 5 mM H₂SO₄ with a flow rate of 0.6 mL/min. The temperatures of the column and the detector were 60 °C and 30 °C, respectively. The yield and selectivity to formic acid, as well as conversion of the carbon source were calculated as shown in equations 5 to 7.

$$Y_{FA} = \frac{C_{FA,f}}{C_{cs,i}} \times 100 \quad (5)$$

$$X_{CS} = \frac{C_{cs,i} - C_{cs,f}}{C_{cs,i}} \times 100 \quad (6)$$

$$S_{FA} = \frac{Y_{FA}}{X_{CS}} \times 100 \quad (7)$$

Where $C_{FA,f}$ is the final molar concentration of formic acid, $C_{cs,i}$ is the initial molar concentration of carbon source and $C_{cs,f}$ is the final molar concentration of carbon source.

In order to measure the concentration of H₂ in the gas phase at the end of reaction, the reactor was cooled down and the gas collected using a Tedlar® bag. The sample was injected to a Bruker 430 GC-TCD (Palo Alto, USA) equipment, with water trap and a CP-Molsieve 5A (15 m × 0.53 mm × 15 μm) and a CP-Pora BOND

Q (25 m × 0.53 mm × 15 μm) columns. The injector, detector and oven temperatures were maintained at 150 °C, 175 °C and 40 °C, respectively. Helium was used as the carrier gas at 13.7 cm³/min.

2.4 Solid Characterization

The solid samples were dried in an oven under vacuum overnight at 45 °C, to remove the remaining moisture. They were analyzed by X-ray diffraction (XRD), using a BRUKER D8 DISCOVER A25 equipment, with 3 kW Generator, 2.2 kW type FFF Cu-ceramic tube, LynxEye Detector, operating at 40 kV and 30 mA. The database used for identifying the phases was the PDF-2 Released 2013 (ICDD). For evaluating the oxidative stability of the catalyst after reaction at the central point, first and last reutilization, Temperature Programmed Reduction (H₂-TPR) was conducted using the commercial Micromeritics TPD/TPR 2900 unit. Firstly, the sample was loaded into a U-shaped quartz cell (100 mm × 3.76 mm i.d.) and heated at 10 °C/min to 150°C and maintained for 1 h under a flow of 50 cm³/min of pure nitrogen (99,999%, Air Liquide), in order to remove air and moisture. Afterwards, the temperature was returned to ambient and then ramped up to 900 °C under a flow of H₂/N₂ (5% v/v; 50 cm³ min⁻¹, Air Liquide) at a rate of 10 °C·min⁻¹. Hydrogen consumption was monitored by a thermal conductivity detector (TCD) with data acquisition/manipulation using the ChemiSoft TPX V1.03™ software. Before the detector, an ice trap was used to retain any water formed in the analyses. Transmission electron microscopy (TEM) was performed to determine possible changes in the particle size distribution and shape of the Pd/C catalyst after the hydrotreatment. For that, the samples were ultrasonically dispersed in water-MilliQ and suspended on a copper grid before the analysis, and analyzed in a JEOL JEM-1011 HR equipment (JEOL, Tokyo, Japan) at 100kV.

3. RESULTS AND DISCUSSION

3.1 Comparative results using different sources of carbon.

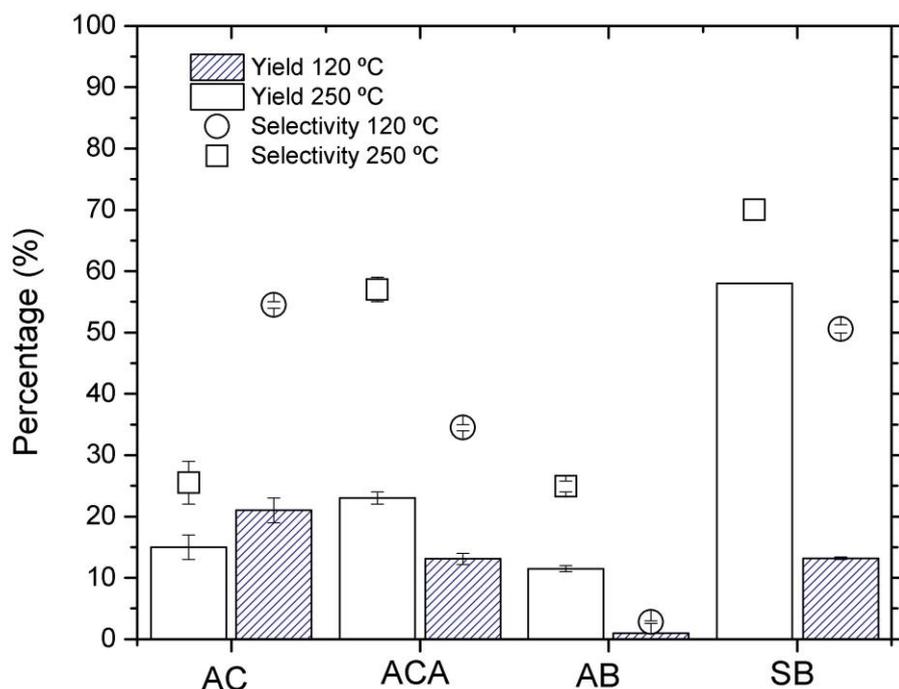


Fig. 1. Performance comparison of different carbon source at 120 and 250 °C. Reaction conditions: 2 h, Al:carbon source molar ratio of 6, 15% catalyst, 70% of filling and 0.5 M of initial concentration. (AC: ammonium carbamate, ACA: ammonium carbonate, AB: ammonium bicarbonate and SB: sodium bicarbonate).

Fig. 1 shows the results of the reactivity of the different carbon sources at 120 °C and at 250 °C. Highest yield (20%) and selectivity (55%) towards formate were obtained with carbamate at 120 °C, while carbonate displays a similar selectivity but at a higher temperature (250 °C), with slightly increased yield of 24%. It is worth noting that AB showed the worst performance at any temperature, with a maximum yield of 11% and selectivity of 25%, while SB only reached its highest performance at 250 °C, with a yield and selectivity of 57% and 72%, respectively. The results indicate that under mild hydrothermal reaction conditions, using *in-situ* produced hydrogen, the FA yield and selectivity increase in the order AB<SB<ACA<AC, where AB and SB reagents need higher temperature (250 °C) for a better yield. Equilibrium constants were computed and used for estimating the concentration of each species of the ammonium speciation in water, for a given temperature, according to the work of Ahn et al. [45]. This shows that the fact that AC and ACA are more reactive as starting materials at mild temperature is probably because in water as solvent at 120 °C, AC and ACA generate 27% more concentration of HCO_3^- anion (0.42 mol/L) in the equilibrium than that obtained from AB (0.33 mol/L) [45]. Moreover, ammonium bicarbonate decomposes into ammonia and CO_2 presenting more loss of the anion to

yield a higher concentration of gaseous CO_2 (0.17 mol/L) than for AC and ACA (0.08 mol/L). The similar activity of carbamate and carbonate is because they both easily decompose into HCO_3^- (see Fig. 2), which is the reducible species, and that happens because the ammonium cation (NH_4^+) can donate its proton (H^+) to other species due to its weak acid nature [46]. HCO_3^- is the reducible species as suggested in the mechanism of hydrogenation of NaHCO_3 by water splitting with Al by Yao et al. [35]. High temperatures are not favorable to carbamate and carbonate because the reduction competes with a thermal decomposition step.

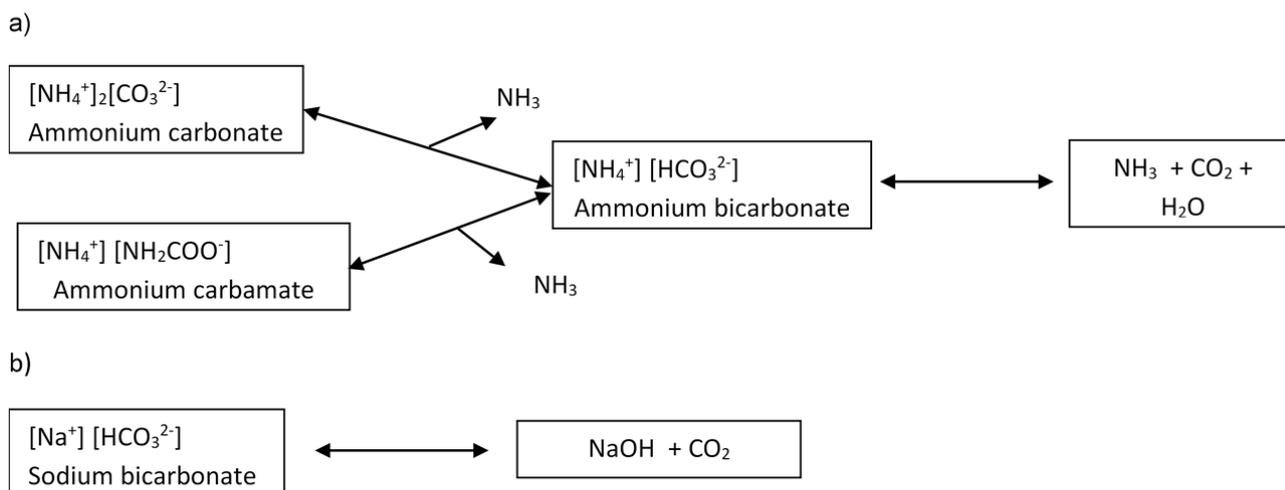
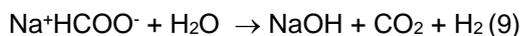


Fig. 2. Decomposition equilibria of a) ammonia-based CO_2 absorption derivatives and b) sodium hydroxide-based CO_2 absorption derivatives.

It is worth noting that a significant yield of 57% was obtained from reducing SB at an increased temperature of 250 °C, while at this temperature AB only yields 11% of FA, in accordance with Wang et al. [40], who obtained higher FA yield out of SB (86.6%) than AB (7.2%). This is because the concentration of HCO_3^- (the reducible species) is higher when we use Na^+ than NH_4^+ at elevated temperatures (200 °C), as shown in the calculated equilibrium between HCO_3^- and CO_3^{2-} with sodium cation, using the aforementioned model of Ahn et al. [45]. HCO_3^- concentration from sodium bicarbonate is not affected by the temperature increase, in the range of 0 to 350 °C, whereas ammonium bicarbonate is more affected by thermal decomposition. i.e. Reaction b in Fig. 2 is less favored. On the contrary, high temperature may favor the reduction step. Na^+ and K^+ cations does not promote the hydrogenation of carbonates and bicarbonates at low temperature [47], but the reduction

of NaHCO₃ can be handled up to 300 °C before affecting the formate concentration, as shown by Shen et al. [48].

In general, the lower yield of formate obtained from ammonium salts may be owed to the high yield of hydrogen coming from dehydration reaction of ammonium formate at the tested reaction temperature of 120 °C, in accordance to Su *et al.* [47]. However, this can be made up by the fact that, as hydrogen storage method, it is desired to produce formate with NH₄⁺ counteraction rather than with Na⁺, because the volumetric hydrogen density is expected to be higher, as it depends on the solubility of the salt. Thereby, the solubility of ammonium formate (~22 mol/L) is nearly double of sodium formate (~12 mol/L) at room temperature. What is more, higher yields (>90%) of hydrogen as fuel, from the decomposition of ammonium formate, are obtained, owing that NH₄⁺ easily donates H⁺ protons to complete the reaction (8), while for the sodium formate is more difficult as the proton must be taken from the H₂O, reaction (9), making it more stable to temperature [47, 49]. Another advantage is that the ammonium formate can be utilized in solid state, so its decomposition for producing hydrogen will leave no residue.



3.2 Experimental results for ammonium carbamate

3.2.1 Influence of temperature

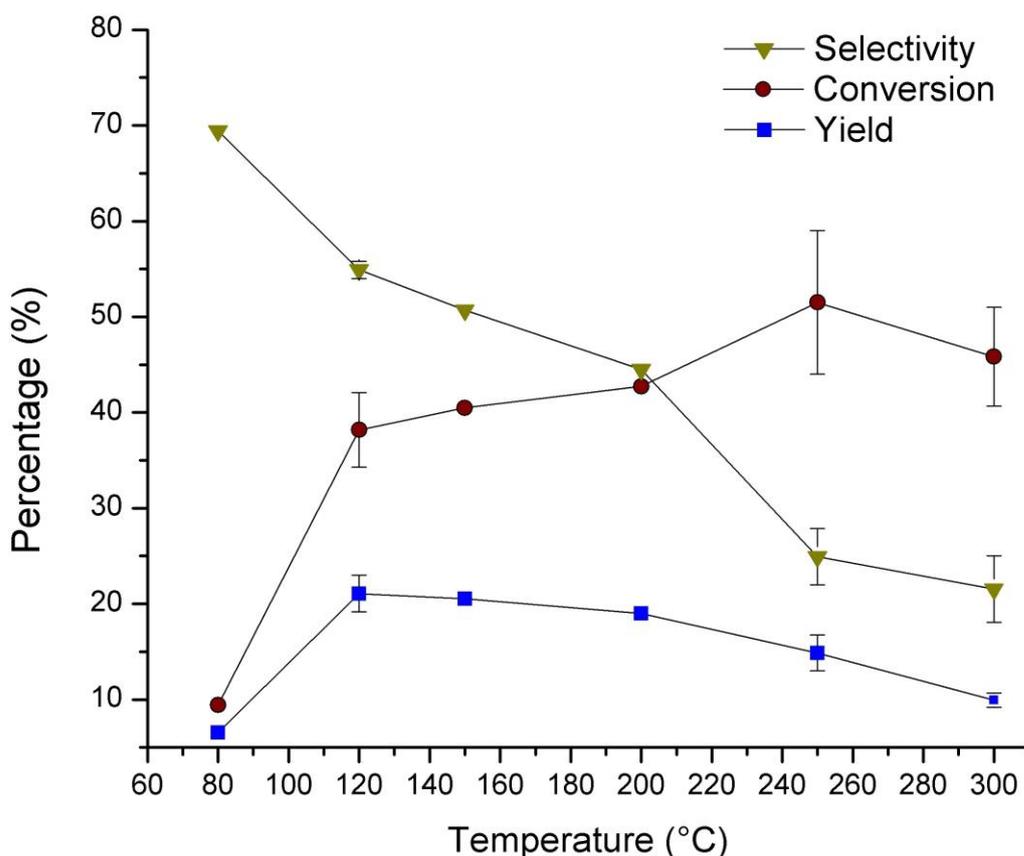


Fig. 3. Effect of temperature over yield, conversion and selectivity. Reaction conditions are: 2 h, Al:AC molar ratio of 6, 15% catalyst, 70% filling and 0.5 M of AC initial concentration.

Fig. 3 depicts the results of yield, conversion and selectivity as a function of the reaction temperature. It can be appreciated that a minimum yield (4%) is obtained at the lowest temperature of 80 °C, with the highest selectivity (70%), but low conversion (10%). In the region 120-200 °C the yield stabilizes around 20%, but higher temperature makes the yield and selectivity to decrease, owing to the thermal decomposition of AC to CO₂ and ammonia, and the ammonium formate to CO₂, ammonia and H₂ [42, 50]. The increase of conversion can be attributed to decomposition of HCO₃⁻ that becomes gaseous CO₂ (detected by GC-TCD) which is a by-product along with formaldehyde and methanol (detected by HPLC).

At 300 °C the dry-based gas composition was 66.7% H₂, 30.2% N₂, 1.1% CO₂, 1.97% O₂ and traces of CH₄ (<0.005%). At 120 °C was 73.2% H₂, 25.4% N₂, 0.67% CO₂ and 0.67% O₂ (other components are not identified by the chromatographic system). Given that NH₃ decomposition into N₂ and H₂ is a high temperature process (usually above 400 °C for complete conversion [51, 52]), the nitrogen reported in the gas phase corresponds

to the purge done before reaction. The lower concentration of hydrogen in the gas phase at 300 °C, compared to 120 °C (central point), can be explained by the fact that the aluminum-water splitting reaction has an optimum temperature of 70-90 °C, in which the highest rate of hydrogen production is reached [53]. Likewise, at higher temperature the availability of dissolved hydrogen in the liquid phase for the reduction of HCO_3^- ions is lower, and the ammonium-formate dehydration rate is accelerated, thus contributing to the observed drop of FA yield at 300 °C. Both the hydrogen production using aluminum and the selectivity towards formic acid (HCOO^- stability) are improved by alkaline conditions [32, 36, 54, 55], so high temperatures should be avoided because the alkalinity is reduced by NH_4^+ dissociation into NH_3 and H^+ . Likewise, He et al. [34] concluded that slightly acidic media does not favor the reduction of CO_2 , probably due to low solubility in water.

3.2.2 Influence of reaction time

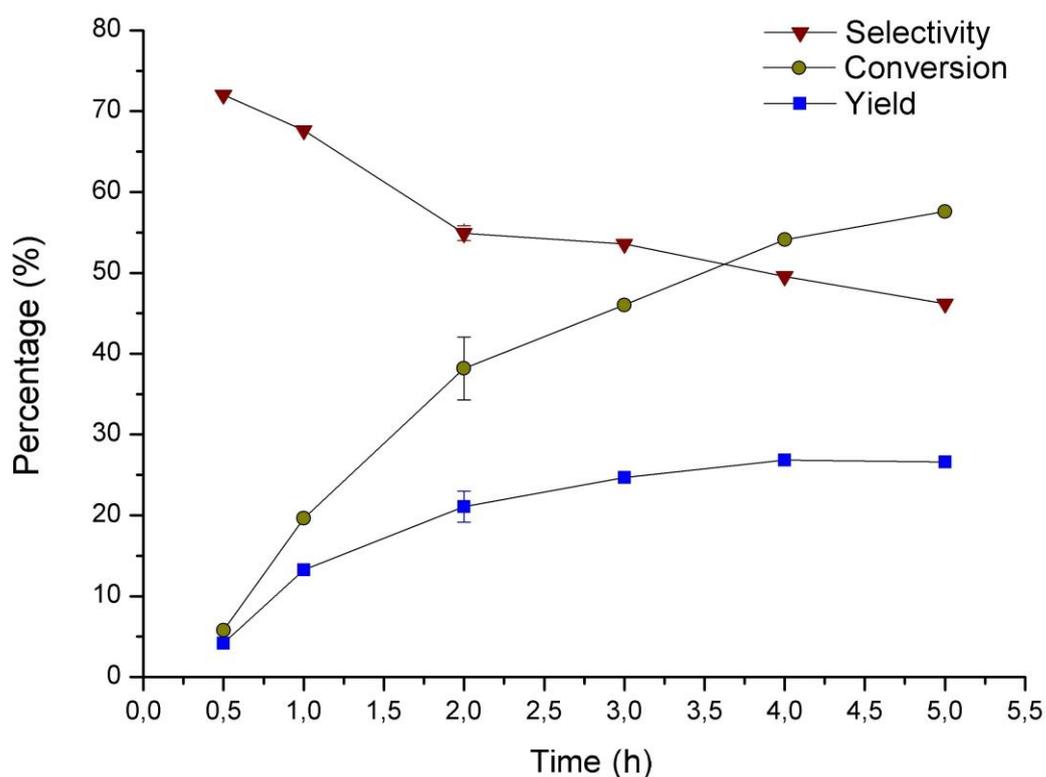


Fig. 4. Effect of time over yield, conversion and selectivity. Reaction conditions are: 120 °C, Al:AC molar ratio of 6, 15% catalyst, 70% filling and 0.5 M of AC initial concentration.

The influence of time in the reaction at 120 °C is presented in Fig. 4. A high selectivity (72%) is achieved at 0.5 h, indicating that the FA is formed faster than other possible products. In general, previous authors [35,

39], who studied the reduction of sodium bicarbonate during up to 3 hours using aluminum as reductant, found that the conversion was promoted by an increase of reaction time. Similarly, in our study the conversion is still increasing after 4 hours, but toward undesired products. However, it is clear that the selectivity decreases proportionally to time, so it is not convenient to increase time because the parameters to be optimized are yield and selectivity.

3.2.3 Influence of catalyst content

A reaction blank, using activated carbon powder instead of catalyst (0% of Pd load), showed a negligible yield of 2%. A reaction using Pd powder (without activated carbon) at the central point of reaction conditions, keeping the proportion of metal with respect to the initial weight of carbon source (11% mol) as in the test of 15% wt Pd/C content, yielded less than 1% of FA. This supports the following facts: a) the hydrogenation/reduction of ammonia-based CO₂ captured species in hydrothermal media requires the presence of a selective catalyst such as Pd/C, b) The active site of the catalyst is the Palladium and c) the dispersion of Pd into a matrix increases greatly the contact area and mass transfer. It seems that Pd/C and aluminum powder conform a good catalytic system for the reduction of SB at 250 °C (FA yield of 57% as aforementioned), given that when using Pd/C with a liquid reductant (pyrrolidone), even at higher temperature of 300 °C and 2 h, the yield is only 17.8%, and 30% at 350 °C [41]. Likewise, when reducing SB without catalyst, and only with 6 mmol of Al at 250 °C for 2 h the yield is 19% [35]. In a recent work by Zhong et al. [33], the addition of Ni powder as catalyst in the reduction of SB with Zn/ZnO yielded 81% of formate at 225 °C. This support the need of a selective catalyst for an increased yield under a moderate temperature.

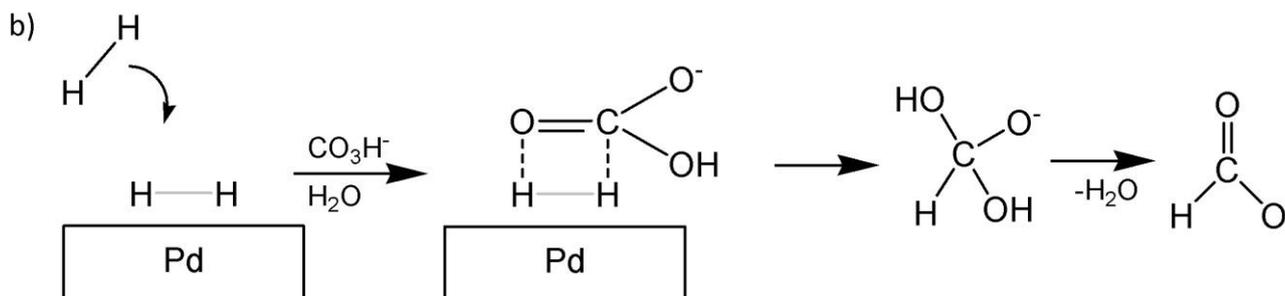
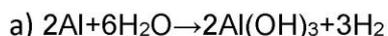


Fig. 5. a) Hydrogen production from aluminum-water splitting, and b) Reaction pathway for the reduction of ammonium carbamate over Pd/C catalyst surface.

These results confirm that the reaction mechanism occurs in two steps: the reduction of water to obtain H₂ by oxidizing Al, followed by a reduction of bicarbonate heterogeneously catalyzed by Pd⁰. A reaction pathway is proposed in Fig. 5. The first reaction (a) describes the production of molecular hydrogen from the water splitting using aluminum. In the second one (b), is described the reduction of bicarbonate ion in aqueous media, starting with the H₂ adsorption into a surface-palladium site of the catalyst composite, followed by the weakening of the H-H bond that allows the hydrogenation and the loss of one mole of water to yield the formate.

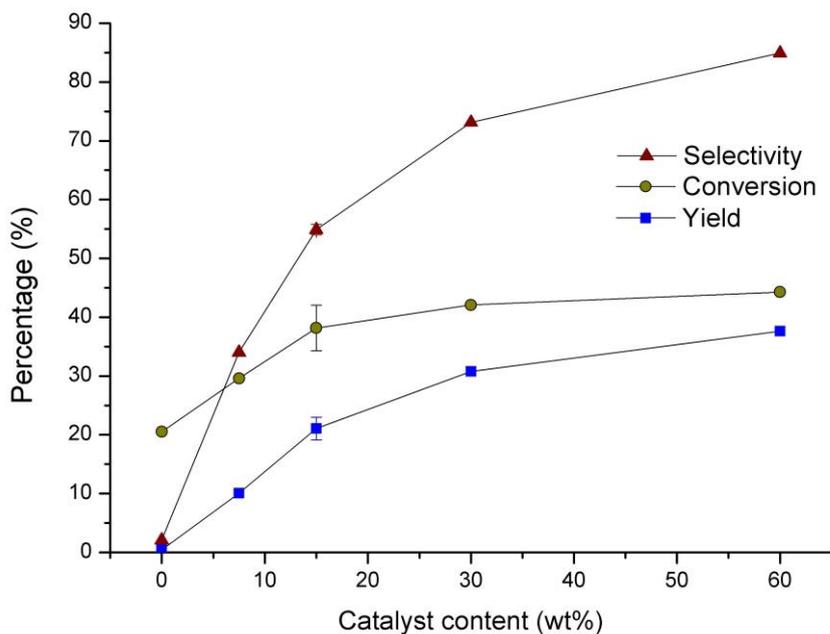


Fig. 6. Effect of catalyst Pd/C 5wt % content with respect to ammonium carbamate. Reaction conditions are: 120 °C, 2 h, Al:AC ratio of 6, 70% filling and 0.5 M of AC initial concentration.

Fig. 6 shows the influence of the amount of catalyst in the reduction of AC at 120 °C. When no catalyst is used, the yield and selectivity is almost zero, indicating that the mild reaction conditions of carbamate reduction are feasible only through an active and selective catalyst like Pd/C. However, the conversion is 20% because the carbamate is thermally decomposed into NH₃ and CO₂. The response variables are linearly proportional to the catalyst content, and start to level off above 30% with respect to carbamate (0.02 g catalyst/mL of reaction solution). This is in accordance with Wiener et al. [19], who reduced sodium and potassium bicarbonate in batch system with dry hydrogen (7 atm), employing Pd/C (5%wt) catalyst, and observed that the rate of reaction rose linearly up to a certain amount of catalyst (in this work, 0.03 g catalyst/mL of reaction solution). The results

at 60% of catalyst show that Pd/C is highly selective toward FA (85%), while the yield is of ca. 40%, and the conversion tends to stabilize in 45%.

3.2.4 Influence of filling percentage

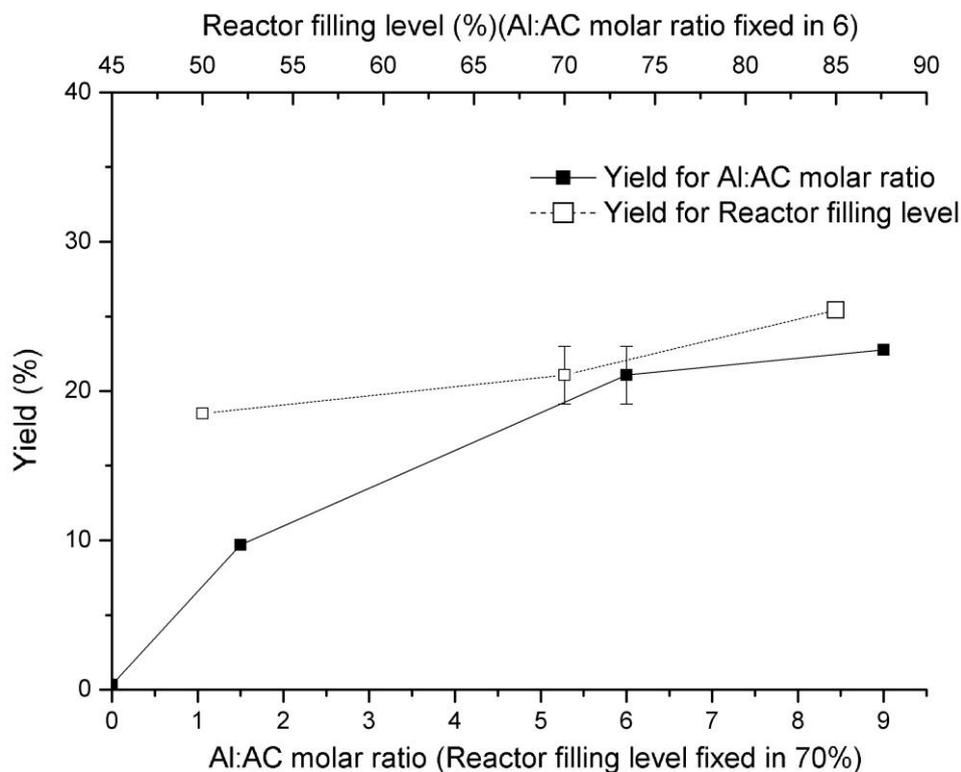


Fig. 7. Effect of filling and Al:AC molar ratio over FA yield. Reaction conditions are: 120 °C, 2 h, and 0.5 M of AC initial concentration.

As the reactor works with autogenic pressure, the final pressure can be increased by increasing the percentage of volume filled in the reactor with the liquid phase. The concentration of carbamate is kept constant at 0.5 M by recalculating the amount needed for the varying liquid phase volume. In Fig. 7 can be appreciated that the liquid filling has a modest effect over FA yield at a filling percentage of 85%, related to the higher pressure produced of 1.1 MPa that accounts for dissolved hydrogen of 8.4×10^{-6} mol H₂/g H₂O, compared to the central point of reaction conditions of 70% with a pressure of 0.6 MPa that accounts for 4.6×10^{-6} mol H₂/g H₂O, according to the solubility data generated by Wiebe *et al.* [58]. Nevertheless, the effect is more clear when using zinc as reductant, as modelled in our previous research at 300 °C and 75% of filling [37], owing to the higher pressure produced of 21 MPa, which accounts for dissolved hydrogen of 1.6×10^{-4} mol H₂/g H₂O.

3.2.5 Influence of Al:AC molar ratio

The Al:AC molar ratio had a remarkable effect over FA yield in the range 1.5-6 (see Fig. 7), which represents an excess of 2.25 and 9 times the stoichiometric ratio of Al:H₂ of 0.67 (based on Fig. 5), respectively. The yield is not significantly improved when the Al:AC molar ratio is increased up to 9, which represents an excess of 13.5 times the stoichiometric ratio, most probably because of the large amount of solids inside the reactor which are out of the working range of the agitator. A previous work with sodium bicarbonate by Zhong et al. [39], also reported that the excess of aluminum promoted the formation of formic acid using catalyst Pd/C (5 wt%).

3.2.6 Reduction with gaseous-H₂

The behavior of aluminum, as hydrogen source, against gaseous-H₂ in the reduction of AC was analyzed at different stoichiometric excesses of the reaction 10, where the stoichiometry is 1:1. For reduction with hydrogen generated by aluminum, the excesses were calculated as the molar ratio Al:AC (1.5 and 6) divided by 0.67 (moles of aluminum per mole of hydrogen, see reaction 4), thus yielding hydrogen excesses of 2.25 and 9 over the stoichiometric amount. For reduction with gaseous-H₂ low stoichiometric excesses of 0.35, 1 and 2.25 were selected owing to hydrogen safety and below maximum pressure of the reactor, representing initial pressures at room temperature of 0.4, 1.15 and 2.6 MPa, respectively.



Table 2. Comparison results of experiments with gaseous H₂ and aluminum as reducing agents. Reaction conditions are (Central point): 120 °C, 2 h, Al:AC ratio of 6, 15% of catalyst (Pd/C 5wt %), 70% filling and 0.5 M of AC initial

Hydrogen source	Hydrogen Stoichiometric excess	Final Absolute Pressure (MPa)**	Yield (%)
gaseous H ₂	0.35	0.5	15.6 ± 1.0
	1	1.1	30.2 ± 1.0
	2.25	2.4	56.3 ± 1.0
aluminum	2.25	0.3	9.7 ± 1.9
	9	0.6	21.1 ± 1.9

*This experiment was at 85% filling

** Water vapor pressure at 120 °C = 0.2 MPa (absolute)

Table 2 shows the yield results for both reductants. It is observed that yields using Al (9.7%) are lower than using H₂ (56.7%), at equal hydrogen excess of 2.25. If instead comparing data with the same excess over the stoichiometric amount, data with a similar level of pressure are compared: data with 0.35 excess over the stoichiometric (yield =15.6%) for gaseous-H₂ and excess of 9 for Al (yield=21.1) the yield is slightly higher for Al experiments, but the yields are comparable.

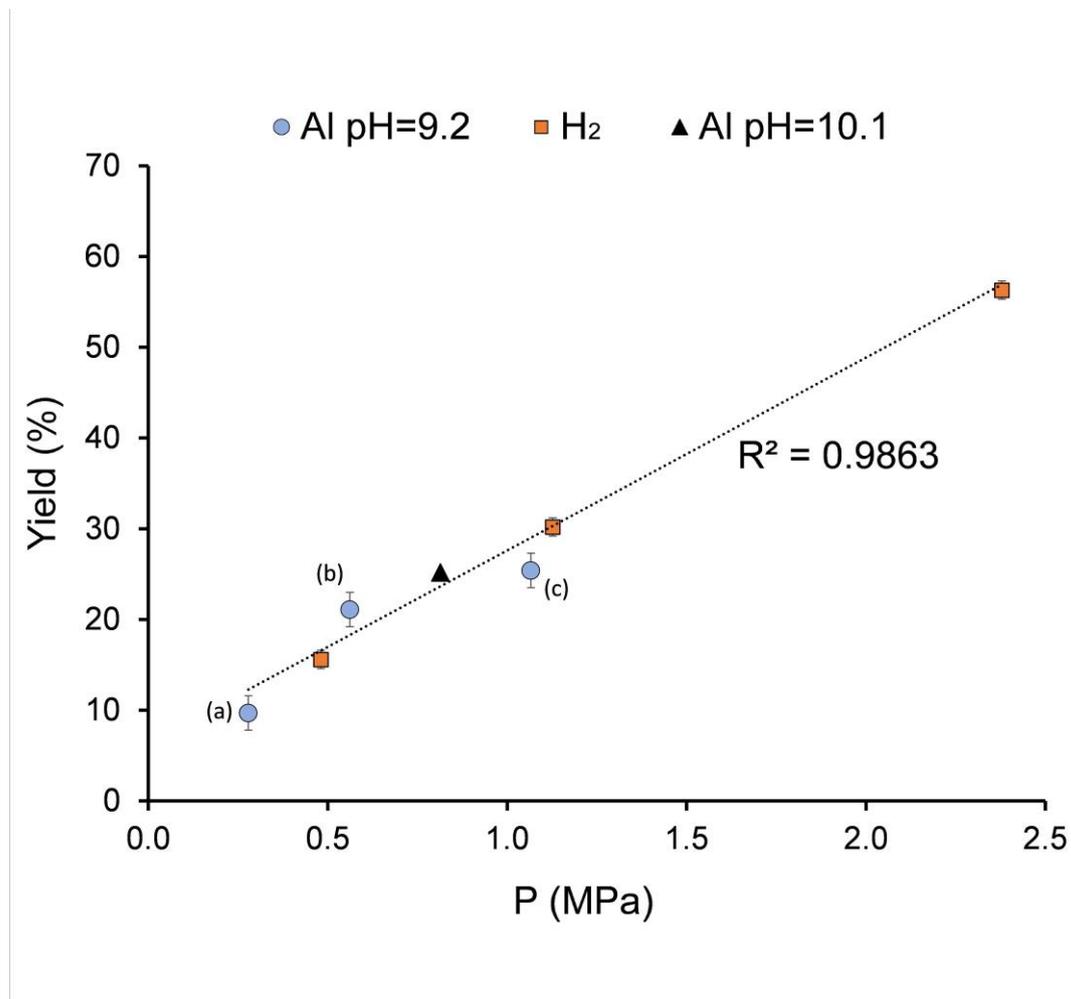


Fig. 8. Proportionality of yield to pressure using Aluminum and hydrogen as reducing agents. (Data of Al pH= 9.2 are at stoichiometric excesses of 2.25 (a), 9 (b) and 9* (c)).

Fig. 8 indicates that using both sets of data the yield is linearly proportional to pressure ($R=0,986$), which is produced by gaseous H₂. This can be indicative that, in both cases H₂ is the reductant, and the only role of Al

would be releasing H₂. In this way it is different from other hydrothermal reduction processes using Zn as reductant in which the reduction yields more than twice the reduction using gaseous H₂ [36]. Secondly, the slow release of H₂ from Al makes that the pressure is lower than using gaseous H₂, and thus, decrease the solubility of H₂ in the liquid phase penalizing in this way the reaction rate. From the results of yield in Table 2, it is clear that a high excess of aluminum is not sufficient to release enough H₂ to reach the performance showed by gaseous H₂ in batch. To improve this process, efforts must be directed to increase the operational pressure. One solution is to speed up the release of H₂, for example, increasing the pH to release the H₂ faster. According to the results shown in table 3, in which the pH is increased by adding NaOH, the increase of pH from 9.2 to 10.1, increases Yield from 19.2 to 25.2 with an increment of pressure of 0.2 MPa. Nevertheless, at pH 12.5 the yield decreased dramatically although the pressure is almost three times that of pH=10.1 (see Table 3). This could be explained by the fact that at pH=12.5 the chemical equilibrium favors the formation of carbonate instead of HCO₃⁻ (the reducible specie), according to the model of Ahn et al. [45]. This results are in good agreement with Onoki *et al.* [59], who found that pH should be kept below 11, so an excessive addition of NaOH inhibits reduction from HCO₃⁻ to useful carbonic compounds like CH₄ and HCOO⁻ under the hydrothermal conditions.

Table 3. Results of different initial pH of carbamate solution using aluminum as reductant. Reaction conditions are (Central point): 120 °C, 2 h, Al:AC ratio of 6, 15% of catalyst (Pd/C 5wt %), 70% filling and 0.5 M of AC initial concentration.

pH	Final Absolute Pressure (MPa)	Yield (%)
9.2	0.6	19.2 ± 1.9
10.13	0.8	25.2 ± 1.0
12.5	2.0	3.43 ± 1.0

Another solution to improve the process using Al, could be the use of a more suitable reaction system. Using a continuous reaction system has the advantage that pressure can be controlled independently of the filling of the reactor or Al content, thus a higher working pressures for increasing the solubility of H₂ would be achievable, and may allow optimizing two temperature zones for the aluminum-water splitting and formate

formation. In addition, the continuous flow would allow the instantaneous removal of the hydrolysis product (aluminum hydroxide) that covers on the aluminum surface and inhibits the H₂ release [55].

3.3 Solid characterization

In our previous experience with Zn as reductant of sodium bicarbonate in hydrothermal media, this metal is completely oxidized in the early stages of the reaction [37]. In order to verify if the Al behaves similarly, a set of reutilization cycles were performed. Owing to the configuration of the reactor it is not possible to isolate the exhausted aluminum from the catalyst. The resulting solid from the reaction, comprising partially oxidized aluminum and Pd/C catalyst, was recovered and reutilized without washing. Based on Table 4, a certain amount of aluminum was consumed in the first use, as the yield dropped from 22.7 to 9.5% obtained in the first re-use (second use). However, Al it is not totally oxidized since, even up to the 5th re-use, the reductant is able to yield 4.8% of formate, suggesting that hydrogen is still produced but in a deficient amount with low pressure, limiting its solubility in water, as discussed before. This is in agreement with the low pressure found in the experiments with aluminum compared to an equivalent amount of H₂, as explained in section 3.2. It is also consistent with the observations of Setiani *et al.* [60] who found that the aluminum was only partially reacted for reactions at ≤ 270 °C after 24 h reaction, generating 30 mmol of hydrogen over the theoretical maximum of 60 mmol.

Table 4. Reutilization results (%wt) of reaction solid (Al+Pd/C)

Re-use	Yield (%)	Conversion (%)	Selectivity (%)
0*	22.7	42.1	53.9
1	9.5	26.9	35.5
2	7.4	28.5	26.0
3	6.6	24.0	27.6
4	6.0	25.3	23.7
5	4.8	23.4	20.6

* Fresh aluminum powder and catalyst. Reaction conditions are (Central point): 120 °C, 2 h, Al:AC ratio of 6, 15% of catalyst (Pd/C 5wt %), 70% filling and 0.5 M of AC initial concentration.

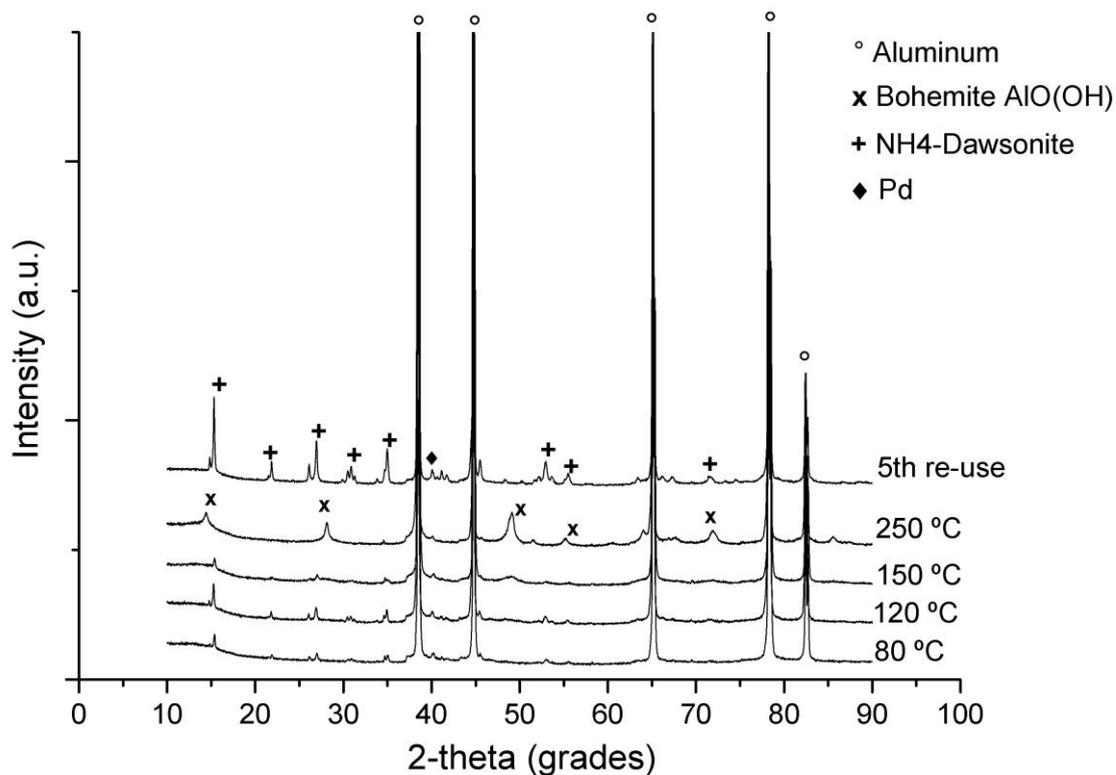


Fig. 9. Comparative XRD patterns of reaction solid at different temperatures and after five reuses

Fig. 9 shows the XRD patterns of the remaining solid after reaction, at different temperatures and after the 5th re-use. At 40° there is an appreciable peak, corresponding to Pd (PDF 00-046-1043). At every reaction temperature tested, the cubic structure of aluminum powder, with diffraction peaks at $2\theta = 38, 45, 65$ and 78° , is present [61, 62] confirming that is not completely exhausted. However, there is also evidence of aluminum oxidation, reflected by peaks at $2\theta = 14.5, 28, 49, 55$ and 72° , which corresponds mostly to bohemite $\text{AlO}(\text{OH})$ (PDF 00-021-1307) [63].

The presence of the by-product ammonium aluminum carbonate hydroxide ($\text{NH}_4\text{Al}(\text{OH})_2\text{CO}_3$) (or NH_4 -dawsonite) (PDF 76-1923) (known as a potential precursor in the field of alumina synthesis [64]) is detected after the 5th re-use. It seems that after oxidation, Al (III) precipitates with CO_3^{2-} and NH_4^+ anions present in the medium to form this new compound. Therefore, the drop of yield and selectivity in table 4 is mostly due to the oxidation of the aluminum.

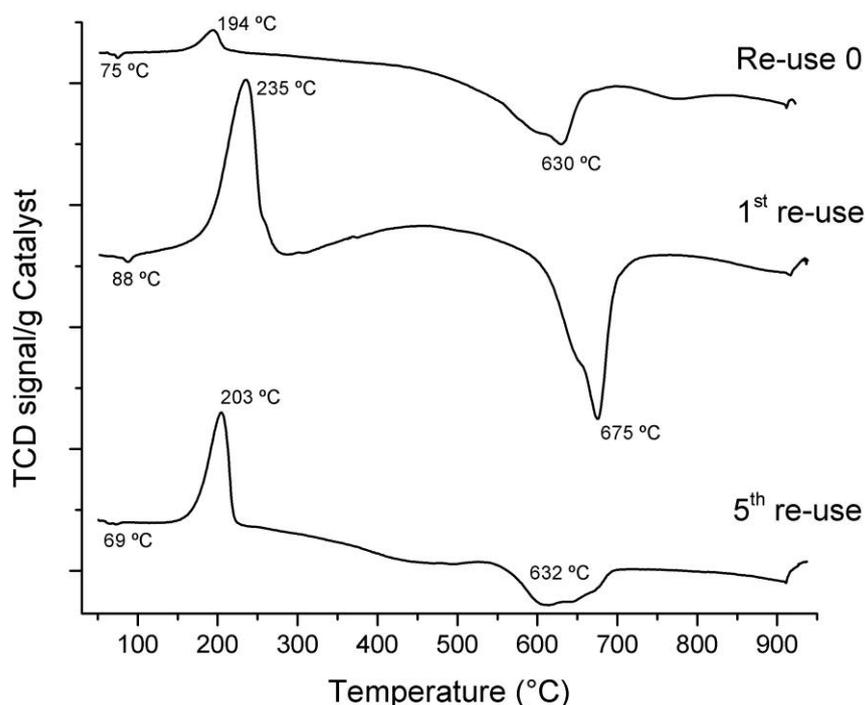


Fig. 10. TPR profile of resulting solid (Al+Pd/C 5 wt%) after central point of reaction conditions (Re-use 0), 1st and 5th re-use.

The temperature programmed reduction (TPR) technique allows determining the reduction temperature of metallic oxides of a catalyst, and the amount of hydrogen consumed, revealing its reducibility [65]. In this work the TPR analysis is presented for the resulting solid after the central point of reaction conditions (Re-use 0), for the 1st re-use and the 5th. In Fig. 10 a first small negative peak appears at the low temperature in the range of 69-75 °C, characteristic of decomposition of superficial palladium hydride specie (β -PdH_x, where $x > 0.6$) [66-69], tentatively formed during the hydrothermal process and/or at ambient temperature under H₂/N₂ flow of the TPR experiment. This phenomena of H₂ adsorption into palladium as hydride specie has been thoroughly studied [70]. The positive peak present in the three samples in the range 194-235 °C corresponds to hydrogen consumption of the PdO species strongly interacting with the support [71], where a complete reduction of Pd²⁺ to Pd⁰ takes place [72]. This represent a catalyst depletion and is more evident in the reactions where the solid is re-used, as the PdO reduction peak is larger. Since Al, as the main reductant, is depleted, Pd can play that role instead. This can explain the residual yield observed in the reutilization studies. Because Pd facilitates the H atom migration to the carbon support [73], the negative peak present in the three samples in the range 630-675 °C can be explained by the desorption of adsorbed hydrogen on the carbon support (following the reaction Pd-H_x → Pd + x/2H₂). This high temperature hydrogen evolution is promoted by the PdO strongly bonded to

the support that in turn follows the reaction $(2+x)/2 \text{ H}_2 + \text{PdO} \rightarrow \text{Pd-H}_x + \text{H}_2\text{O}$ that occurs at ambient temperature. The asymmetry of this hydrogen desorption peaks correspond with distinct desorption stages, depending on the proximity of palladium hydride specie to the surface [74]. The formation of aluminum hydride during the hydrothermal process and/or TPR analyses should be discarded, given that its decomposition temperature (negative peak) is usually between 150-170 °C [75].

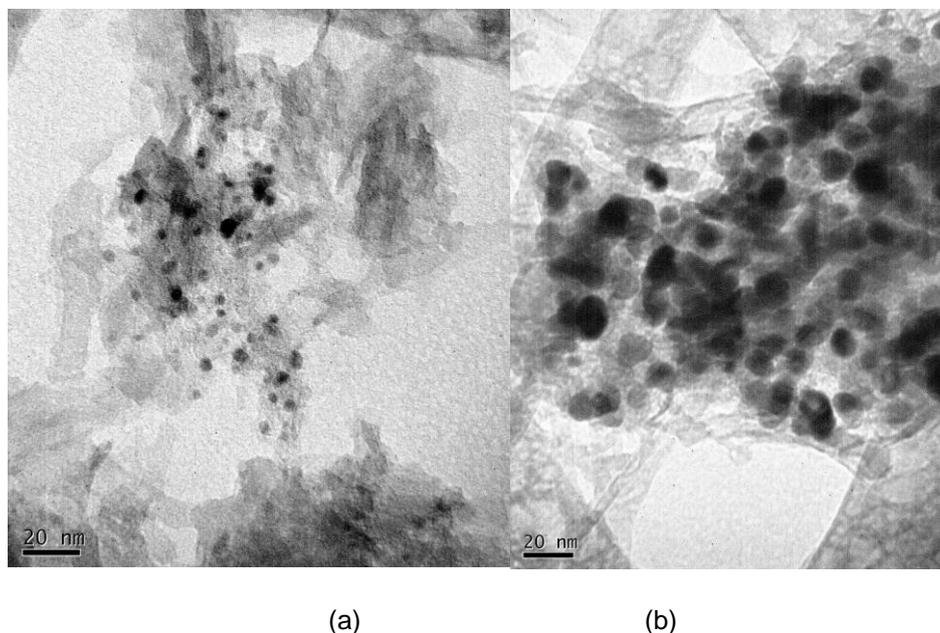


Fig. 11. TEM image of resulting solid, a) after reaction in the central point (20 nm), b) after 5th re-use (20 nm)

The morphology of the reaction solid was analyzed by Transmission Electron Microscopy (TEM). From Fig. 11a it can be observed at 20 nm the nano-particles of Pd (5 wt%) active sites, well distributed, with an average particle size of 4.3 ± 1.0 nm, calculated with the software ImageJ 1.52a. From Fig. 11b it can be observed at 20 nm that the metallic dispersion of the catalyst after the 5th re-use has not been seriously compromised, but grain growing of Pd particles is warned, making the average particle size to increase to 7.6 ± 3.1 nm, which may have consequences over the catalytic performance.

4. Conclusions

In the process to obtain formic acid from the catalytic conversion of CO₂ captured in aqueous media, ammonium carbamate showed the best performance under mild reaction temperature (120 °C) as starting material, while ammonium carbonate, ammonium bicarbonate and sodium bicarbonate reagents need higher temperature (250 °C) for an increased yield. Time variable had a significant effect and after 4 h of reaction the yield stabilized in 27%. The response variables are proportional to the catalyst content, and start to level off

above 30% of Pd/C with respect to carbamate, obtaining a yield of ca. 40%. The increase of autogenic pressure of 1.1 MPa, by increasing the liquid filling up to 85% of reactor's volume, had a modest effect over FA yield. Although an excess of aluminum is required, the formate yield is not significantly improved at the highest Al:AC ratio of 9. The process can be improved by operating at higher pressure and lower temperature, to avoid loss of yield by dehydration of formate. Experiments using gaseous H₂ as reductant, showed higher yield of formate, but also higher pressure inside the reactor. When comparing data with a similar level of pressure the yield is slightly higher for Al experiments, but the yields are comparable. The slow release of H₂ from the Aluminum hinders the process. The reutilization and characterization of the reaction solid, comprising exhausted aluminum and Pd/C catalyst, showed that most of the aluminum was consumed in the first use, but XRD analyses confirmed it was not completely oxidized up to the 5th re-use. Pd can play a reducing role through the formation of palladium hydride species, as it was observed through the TPR analyses.

Declaration of competing interest

None.

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