

Communication

Synthesis of Furfuryl Alcohol from Furfural: A Comparison between Batch and Continuous Flow Reactors

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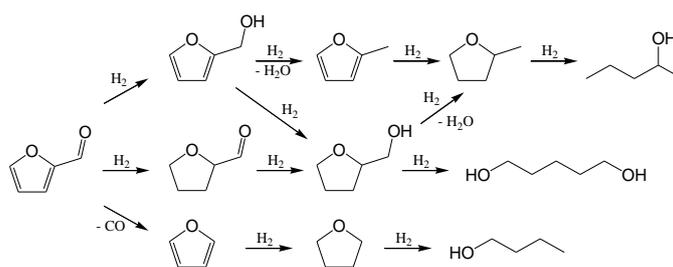


Abstract: Furfural is a platform molecule obtained from hemicellulose. Among the products that can be produced from furfural, furfuryl alcohol is one of the most extensively studied. It is synthesized at an industrial scale in the presence of CuCr catalyst, but this process suffers from an environmental negative impact. Here, we demonstrate that a non-noble metal catalyst (Co/SiO₂) was active (100% conversion of furfural) and selective (100% selectivity to furfuryl alcohol) in the hydrogenation of furfural to furfuryl alcohol at 150 °C under 20 bar of hydrogen. This catalyst was recyclable up to 3 cycles, and then the activity decreased. Thus, a comparison between batch and continuous flow reactors shows that changing the reactor type helps to increase the stability of the catalyst and the space-time yield. This study shows that using a continuous flow reactor can be a solution to the catalyst suffering from a lack of stability in the batch process.

Keywords: continuous flow; batch reactor; furfural; furfuryl alcohol; hydrogenation

1. Introduction

Motor fuel components and fine chemicals can be produced from non-edible plant-based feedstocks using catalytic processes. Among all available starting materials, furfural is one of the most promising compounds, as it is a platform molecule for the synthesis of a high number of chemicals for a wide range of applications [1–4]. Furfural production is based on acid hydrolysis of hemicellulose [5]. One interesting reaction from furfural is the hydrogenation reaction, which is the most significant process in the furfural conversion. The hydrogenation of furfural leads to the production of valuable chemicals, such as furfuryl alcohol (FOL), 2-methylfuran (2-MF), tetrahydrofurfuryl alcohol (THFA), and so on. Currently, around 50% of furfural production is employed for the synthesis of furfuryl alcohol (FA), which can be used for resins, flavors, as components of motor fuels (alkyl levulinates), and in the pharmaceutical industry (ranitidine), biochemistry, and so on. During the hydrogenation of furfural to FOL many side reactions can occur, such as the formation of THFA, 2-methylfurane, and so on (Scheme 1). Precise control of the selectivity of the reaction by using an appropriate and stable catalyst is in high demand.



Scheme 1. Hydrogenation of furfural.

Copper-chromium (CuCr) alloy is the catalyst used on an industrial scale to produce FOL, with a high yield (98%) [5]. This catalyst has some drawbacks, such as, for instance, the presence of chromium, which can contaminate FOL and hamper its use in pharmaceutical industry. Moreover, chromium-containing catalysts can be deactivated due to shielding of copper by chromium [6]. Many studies have been devoted to the replacement of this catalyst by catalysts based on noble metals such as Pt and Pd [7–11], leading to an increase in the process cost. Furthermore, FOL selectivity is lower in the presence of these catalysts than in the presence of chromium–copper systems. To increase the selectivity to FOL, the addition of metals such as Cu to Pd based catalysts results in the improvement of the selectivity to FOL (98% of FOL was obtained) [12]. Non-noble metals catalysts were also studied in the selective hydrogenation of furfural to FOL, such as supported Ni, Cu, Fe, Mo, Zn, and so on [13–18]. Various methods were used for the synthesis of catalysts, additives, process conditions, and various solvents in the case of a liquid phase process [19–21]. Several drawbacks are present using this system: deactivation due to the sintering of active species; poisoning of the catalyst surface by coke formation; low selectivity of FOL; and high temperature and pressure. Up to now, several studies of selective hydrogenation of furfural to FOL have been performed in the liquid phase in batch reactors using different solvents, but very little attention has been paid to the process in a flow system [22–26]. To this aim, hydrogenation of furfural to FOL was studied in the presence of Co/SiO₂ catalyst in batch and in continuous flow reactors. We demonstrate here that, despite the high selectivity and activity of the Co/SiO₂ catalyst in the hydrogenation of furfural in the batch reactor, the reaction performed in a continuous flow reactor led to a higher space time yield (STY = quantity of FOL produced per unit volume unit per time unit). STY was three times higher when the hydrogenation of furfural was performed in a continuous flow reactor than in a batch process. The selectivity was slightly lower in a continuous flow reactor than in a bath reactor, but the activity was similar. The catalyst was more stable in the flow reactor than in the batch reactor.

2. Materials and Methods

Catalyst preparation: The Co₃O₄/SiO₂ material, with a metal loading of 10 wt.% was prepared using incipient wetness impregnation method as described previously [27] using Co(NO₃)₂ and aerosil silica (380). The dry solid was calcined at 500 °C for 6 h to obtain the Co₂O₃/SiO₂ sample. Co₂O₃/SiO₂ (around 100 mg) was reduced under hydrogen flow (3 L·h⁻¹) at 500 °C for 10 h.

Catalyst characterizations: Co/SiO₂ catalyst was characterized by ICP-OES, XRD analysis, N₂-physisorption, transmission electronic microscopy (TEM), thermal analysis. A Perkin Elmer Optima 2000 DV instrument was used for ICP analysis. The catalysts were first dissolved in a mixture of HF and HCl under microwaves for digestion before analysis. X-Ray Diffraction (XRD) analysis is performed using a Bruker Empyrean with a Co cathode. N₂-physisorption experiments were obtained on an Autosorb 1-MP instrument, at 77 K. The catalysts were treated under vacuum à 350 °C for 3 h and the surface area, the pore size as well as the pore volume were determined as described previously [27]. Transmission Electron Microscopy (TEM) experiments were performed on a JEOL 2100 UHR (Ultra High Resolution) instrument operated at 200 kV, equipped with a LaB6 source and a Gatan ultra scan

camera. Thermogravimetric analysis (TGA) was performed using a TA instrument (SDTQ 600) under air flow of $100 \text{ mL}\cdot\text{min}^{-1}$ from $25 \text{ }^\circ\text{C}$ to $800 \text{ }^\circ\text{C}$.

General procedure for the hydrogenation of furfural in a batch reactor: in a typical experiment, 1 g of furfural was added to 9 g of ethanol and 50 mg of catalyst was added in a batch reactor (75 mL). The hydrogen pressure was fixed to the desired one. Then, the temperature was increased up to the desired reaction temperature, i.e., $150 \text{ }^\circ\text{C}$. At the end of the reaction, the reactor was cooled down to room temperature, and liquid phase was analysed.

General procedure for the hydrogenation of furfural in flow reactor: The experiments were carried out in H-Cube ProTM Flow Reactor ThalesNanoTM, Hungary, connected to an HPLC pump to supply a continuous feed of 10 wt.% furfural in ethanol. A 70 mm catalyst cartridge (0.88 mL empty volume) catalyst was packed with 260 mg catalyst by applying vacuum suction at the bottom of the cartridge. The total flow through volume (including feed, reactor, and product sections) was 6 mL. First, pure ethanol was pumped through the system, and then the feed was changed to the furfural-ethanol mixture. The flow was continued until the desired temperature and hydrodynamic pressurization (20–60 bar) of the reactor module were reached. Depending on the flow rate used ($0.2\text{--}0.5 \text{ mL}\cdot\text{min}^{-1}$), the reaction time was set (20–50 min) before collecting the first sample (time zero). The samples were collected after regular time intervals.

Analytical methods: yields to furfuryl alcohol and conversion of furfural were determined by external calibration at $25 \text{ }^\circ\text{C}$ using HPLC equipped with a nucleosil 100–5 C18 column (250 mm and diameter of 4.6 mm), a Shimadzu LC-20AT pump, and a Shimadzu RID-10 A detector using acetonitrile/water (10:90) as the mobile phase ($0.6 \text{ mL}\cdot\text{min}^{-1}$).

Continuous flow results were detected on a gas chromatograph (HP, 14009 Arcade, New York, United States) coupled with a Flame Ionization Detector (FID) detector equipped with a Supelco 2-8047-U capillary column (15 m \times 0.25 mm i.d. and 0.25 μm film thickness, Alltech Part No.31163-01). The flow rate of the carrier gas (H_2) was $1 \text{ mL}\cdot\text{min}^{-1}$. The injector temperature was $250 \text{ }^\circ\text{C}$ and the oven started at $70 \text{ }^\circ\text{C}$ for 1 min. The temperature was then increased up to $250 \text{ }^\circ\text{C}$ at a rate of $20 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$, and then maintained at $250 \text{ }^\circ\text{C}$ for 10 min.

2.1. Catalyst Characterizations

The catalyst was prepared using the Incipient Wetness Impregnation (IWI) method. After calcination of the solid at $500 \text{ }^\circ\text{C}$ under air, oxide precursor, $\text{Co}_3\text{O}_4/\text{SiO}_2$, is obtained, confirmed by XRD analysis (Figure 1), with the presence of peaks corresponding to the awaited position (PDF file 01-1152). Considering the width of the reflections, the cobalt crystal size is relatively low ($<10 \text{ nm}$). This result confirms that when using this impregnation method, high dispersion of the cobalt oxide phase can be achieved. The loading of cobalt was evaluated by ICP-OES and was of 9 wt.%.

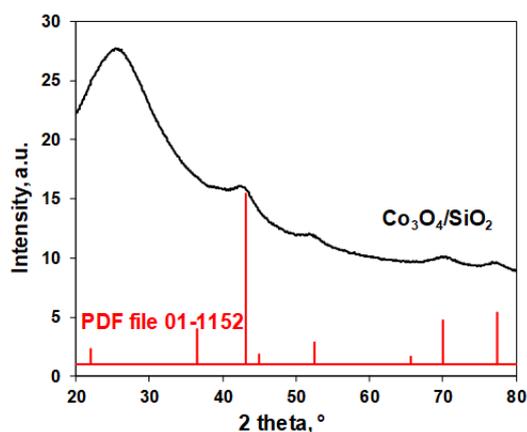


Figure 1. X-Ray Diffraction analysis of non reduced Co/SiO_2 catalyst (vertical bars, Co_3O_4 reference PDF file 01-1152).

The catalyst was reduced under H₂ flow at 500 °C for 10 h prior to catalytic test leading to a large surface area and large pore diameter, suitable for liquid phase hydrogenation reaction. Moreover, the limited evolution of the textural properties indicates adequate stabilities of the support (Table 1).

Table 1. Main characteristics of the Co₃O₄/SiO₂ and reduced Co/SiO₂ materials.

Characteristics	Co ₃ O ₄ /SiO ₂	Co/SiO ₂
XRD phase	Poorly crystallized Co ₃ O ₄	n.d. ^[a]
D _{part.} / ^[b] nm	n.d. ^[a]	Aggregates 10 to > 100 nm Crystals < 20 nm
SBET/ ^[c] m ² ·g ⁻¹	185	169
V _p / ^[c] m ³ ·g ⁻¹	0.71	0.63
D _p / ^[c] nm	15.0	14.7

[a] n.d.: not determined; [b] mean particle size obtained by TEM image observation; [c] surface area (S_{BET}), pore volume (V_p) and pore diameter (D_p) issued from N₂ physisorption at 77K.

Figure 2 shows that the particle sizes and localization throughout the support porosity are not homogeneous and aggregates of cobalt nanoparticles are observed throughout the surface of the silica with a size of 20–100 nm. Energy dispersive x-ray spectroscopy (EDS) showed that dark mark are cobalt particle and hexagonal cobalt phase was observed using electron diffraction.

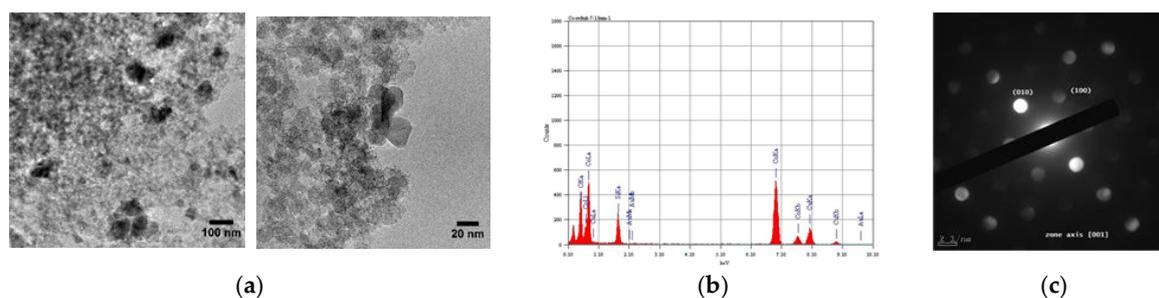


Figure 2. Transmission electronic microscopy (TEM) images recorded for reduced Co/SiO₂ catalyst (a), energy dispersive x-ray spectroscopy (EDS) (b) and electron diffraction analysis (c).

2.2. Hydrogenation of Furfural in Batch Reactor

The hydrogenation of furfural was performed in a batch reactor starting from 1 g of furfural in 9 g of ethanol in the presence of 50 mg of catalyst (Table 2).

Table 2. Hydrogenation of furfural in a batch reactor ¹. FOL; furfuryl alcohol, STY; space time yield.

	Reaction Time (h)	P _{H2} (bar)	Temperature (°C)	Conversion (%)	Selectivity to FOL (%)	STY (g·L ⁻¹ ·h ⁻¹)
entry 1	1	20	150	100	100	13.2
entry 2	1.5	20	150	100	65	5.9
entry 3	1	40	150	100	85	11.4
entry 4	1	20	180	100	80	10.8

¹ Furfural = 1 g, ethanol = 9 g, Co/SiO₂ = 50 mg

We were pleased to see that furfural conversion reached 100% at 150 °C after 1h of reaction, with a FOL yield of 100% (Table 2, entry 1). By prolonging the reaction time, the yield of FOL decreased from 100% to 65% due to further hydrogenation of FOL to THFA (Table 2, entry 2). This result shows that Co/SiO₂ was active and selective in the hydrogenation of furfural to FOL. An increase in hydrogen pressure led to a decrease in FOL yield due to the further hydrogenation of FOL to THFA that can be favored by a higher solubility of hydrogen than at lower pressure of hydrogen (Table 2, entry 3).

In both conditions, FOL was further hydrogenated to THFA. A similar trend was observed with an increase of the temperature from 150 to 180 °C. With the increase of the temperature, THFA was also observed as a by-product and the selectivity of FOL decreased on the benefit of the formation of THFA. Based on these results, it is of prime importance to control the kinetic of the reaction in order to prevent further hydrogenation of FOL to THFA.

The recyclability of the catalyst was then studied under the optimum conditions (150 °C, 20 bar of hydrogen, 1 h of reaction). This is a key parameter, as in a batch liquid phase reactor catalysts used in the literature suffer from leaching and from deposition of furanic derivatives on the catalytic sites, preventing the reuse of the catalyst. The recycling of the catalyst was performed by recovering the solid, owing to its magnetic properties. It was then reused without any treatment. The amount of furfural used was always 1 g for each cycle in 9 g of ethanol. Four cycles were performed under 20 bar of hydrogen for 1 h of reaction at 150 °C (Figure 3).

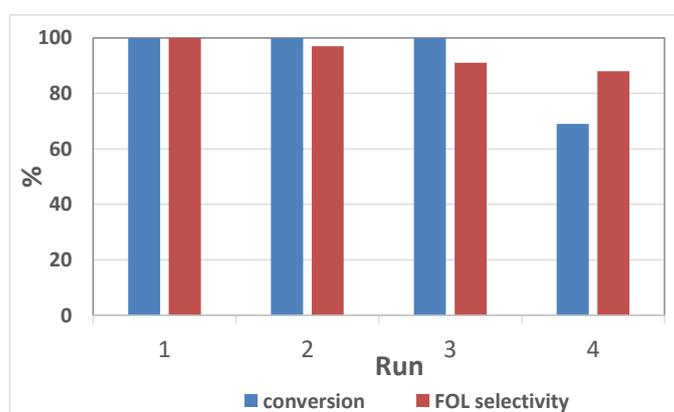


Figure 3. Recycling of Co/SiO₂. 1 g of furfural, 9 g of ethanol, T = 150 °C, 20 bar of hydrogen, 1 h of reaction.

FOL selectivity and conversion of furfural slightly decreased after the third cycle, which can be ascribed to the work up process. However, after the fourth cycle, the conversion of furfural dropped from 100% to 69% and the selectivity to FOL also decreased (88%). This could be due to the poisoning of cobalt in the solution, as this is already mentioned in the literature, or to the leaching of cobalt, [24,26] leading to the formation of by-products such as THFA and other unidentified by-products. To confirm these hypotheses, TGA analysis of the spent catalyst were performed and compared to the TGA analysis of the fresh catalyst (Figure 4).

It was shown that 18% of the weight was lost during the TGA analysis of the spent catalyst, whereas only 7% was lost during the fresh catalyst analysis. This increase in weight loss could be due to the deposition of carbon species on the catalyst due to the sorption of furanic compounds. To confirm this hypothesis, TEM analysis of the spent catalyst was performed (Figure 5).

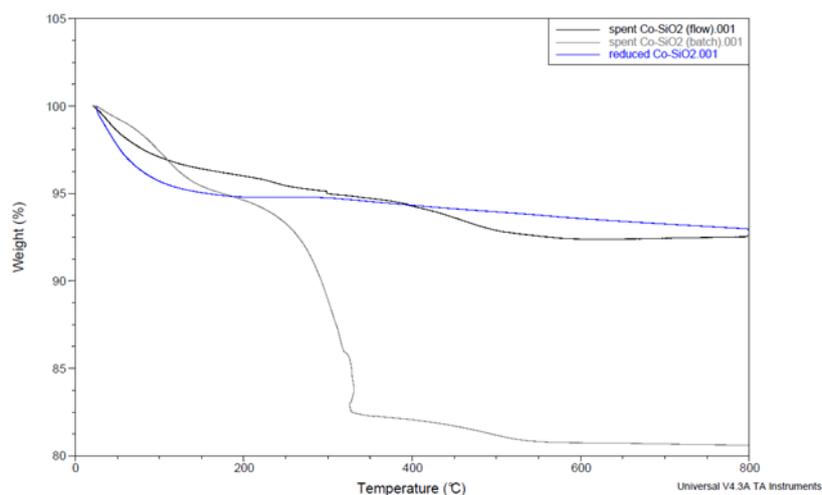


Figure 4. TGA analysis of the reduced Co/SiO₂ catalyst before reaction and after reaction under batch and flow conditions.

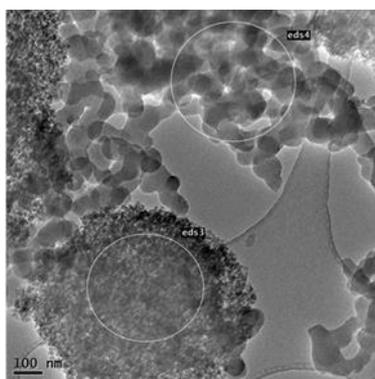


Figure 5. TEM images recorded for reduced Co/SiO₂ catalyst after reaction under batch reaction and EDS analysis.

It was clearly shown using EDS that carbon was deposited on the catalyst surface, leading to less accessibility of furfural to active sites and a decrease of the selectivity to FOL. Several zones of the catalyst contained carbon deposited. In order to prevent this deactivation, hydrogenation of furfural was performed in the continuous flow reactor.

2.3. Continuous Flow Reactor

The hydrogenation of furfural was performed while keeping the concentration of furfural used for batch experiments (5 g of furfural in 45 g of ethanol) and the catalyst amount of 260 mg to fill the catalyst cartridge. In the first set of experiments, the flow rate of the alcoholic solution of furfural was studied. To this aim, the flow rate was increased from 0.2 to 0.5 mL·min⁻¹ (Figure 6).

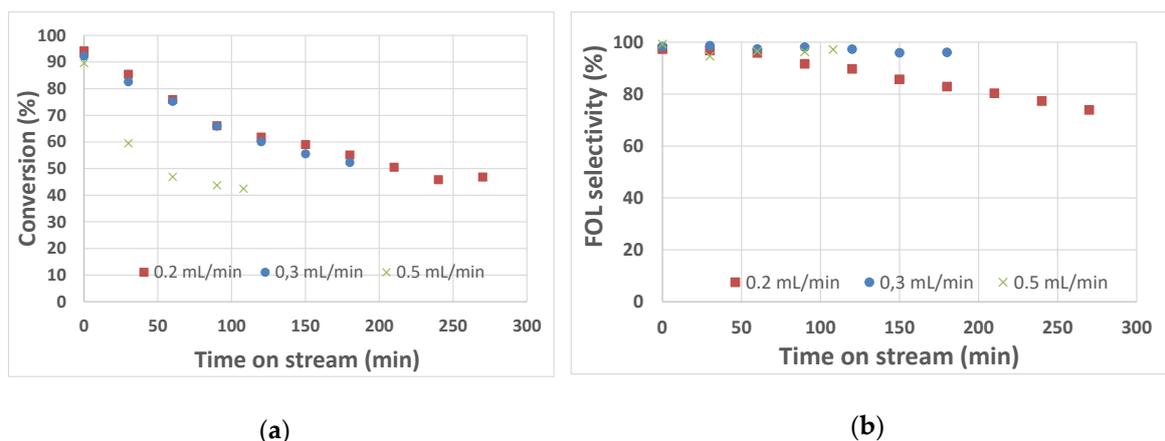


Figure 6. Effect of the alcoholic furfural solution (5 g of furfural in 45 g of ethanol) flow rate. 150 °C, 20 bar of hydrogen in the presence of 260 mg of Co/SiO₂. (a) conversion vs. Time On Stream (TOS). (b) FOL selectivity vs. TOS.

When the flow rate of the furfural solution increased from 0.2 to 0.3 mL·min⁻¹, similar trend in the conversion of furfural was obtained, a drop of the conversion from 94% to 50% being observed in the function of TOS (Time On Stream) from 0 to 180 min. The selectivity was maintained at around 97% for 0.3 mL·min⁻¹ whereas under 0.2 mL·min⁻¹ of furfural solution, the selectivity to FOL decreased from 97 to 74%, which is due to the increase of residence time that favored the formation of THFA.

A further increase of the furfural solution flow rate up to 0.5 mL·min⁻¹ led to a significant drop of furfural conversion from 90% to 40% after 110 min of reaction. The FOL selectivity was kept constant. Based on these results, it was decided to keep the flow rate at 0.3 mL·min⁻¹ for the following experiments. The effect of the pressure of hydrogen was then studied from 20 to 60 bar (Figure 7). Increasing the pressure of hydrogen led to an increase of the conversion of furfural from 92 to 100%. It was interesting to see that under 60 bar of hydrogen the conversion was always 100% when TOS increased up to 180 min, whereas at lower pressure a slight decrease of the conversion was observed. Concerning the selectivity, it was kept constant independently of the hydrogen pressure, but the selectivity to FOL was lower under 60 bar of hydrogen due to the formation of THFA as a by-product. This can be explained by a higher solubility of hydrogen due to its pressure, as previously shown in batch reactions.

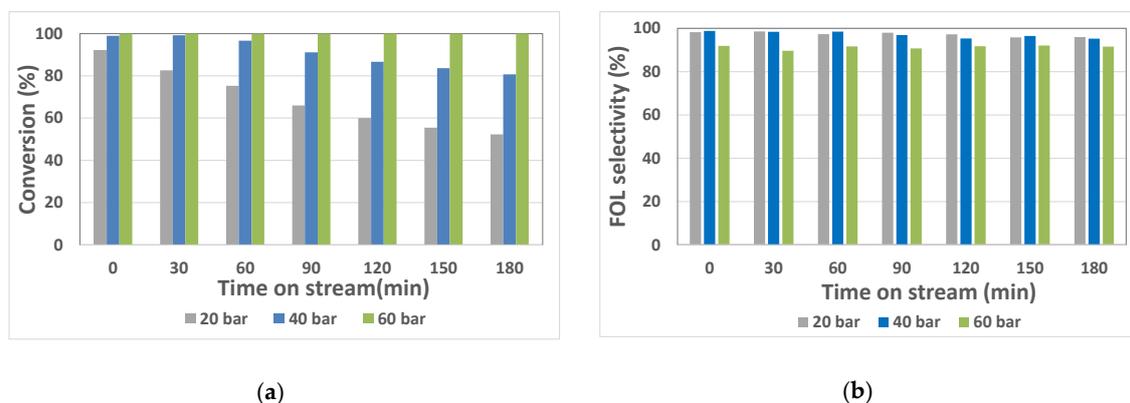


Figure 7. Effect of the hydrogen pressure. 5 g of furfural in 45 g of ethanol at 0.3 mL·min⁻¹ flow rate. 150 °C in the presence of 260 mg of Co/SiO₂. (a) conversion vs. TOS. (b) FOL selectivity vs. TOS.

3. Discussion-Conclusion

Our results suggest that hydrogenation of furfural to FOL in a batch reactor in the presence of Co/SiO₂ catalyst is efficient at 150 °C under 20 bar of hydrogen using a solution of furfural of

10 wt.% in ethanol. However, the stability of the catalyst is not optimal, as shown by the catalyst recycling. TGA and MET analysis showed that carbon was adsorbed on the catalyst surface due to the sorption of furanic molecules in batch reactions, as has already been mentioned in the literature [28]. The recyclability of the catalyst was thus hampered by this coke formation on the catalyst surface.

The hydrogenation of furfural to FOL in a continuous flow reactor can afford a high conversion of furfural with a selectivity higher than 90% under 60 bar of hydrogen at 150 °C. This means that the catalyst was not poisoned when a hydrogen pressure of 60 bar was used, but the selectivity was slightly lower due to further hydrogenation to THFA. From an industrial point of view, it can be interesting to see the space time yield of the reaction (Table 3). The space time yield (STY) was calculated and it was higher if the hydrogenation of furfural was performed in a continuous flow reactor than in a batch reactor. Thus, under similar conditions of pressure and temperature, the STY was 13.2 g·L⁻¹·h⁻¹ for the batch reaction versus 16.6 g·L⁻¹·h⁻¹ for the continuous flow reaction. By increasing the hydrogen pressure, the STY increased in the continuous flow reaction from 16.6 to 30.6 g·L⁻¹·h⁻¹. These results show that using a same catalyst, the hydrogenation of furfural to FOL was more performant in the continuous flow reactor than in the batch reactor.

Table 3. Hydrogenation of furfural: effect of the reactor ¹.

Reactor	P _{H2} (bar)	Conversion (%)	Selectivity to FOL (%)	STY (g·L ⁻¹ ·h ⁻¹)
Batch ²	20	100	100	13.2
Flow ³	20	52	50	16.6
	40	81	77	26.6
	60	100	92	30.6

¹ furfural in ethanol 10 wt.%, Co/SiO₂ = 5 wt.% of furfural solution, 150 °C. ² reaction time = 1 h.

³ time on stream = 3 h; flow rate of alcoholic solution of furfural = 0.3 mL·min⁻¹

In order to go deep in the comparison of these two processes, it was interesting to compare the stability of the catalyst. In the batch reactor, the catalyst was recyclable up to 3 times and lost its activity, but the selectivity was kept constant. This was due to an adsorption of the furanic molecules on the catalyst surface. For the continuous flow reactor, TGA analysis was performed on the spent catalyst and only a slight difference in the weight loss was observed between the fresh and the spent catalyst (Figure 4). The specific surface area was similar before and after the reaction. ICP analysis of spent catalyst showed that there was no leaching of cobalt (9 wt.% before and after reaction). TEM showed that the particle size did not change after the reaction, and that no carbon was formed on the catalyst surface (Figure 8).

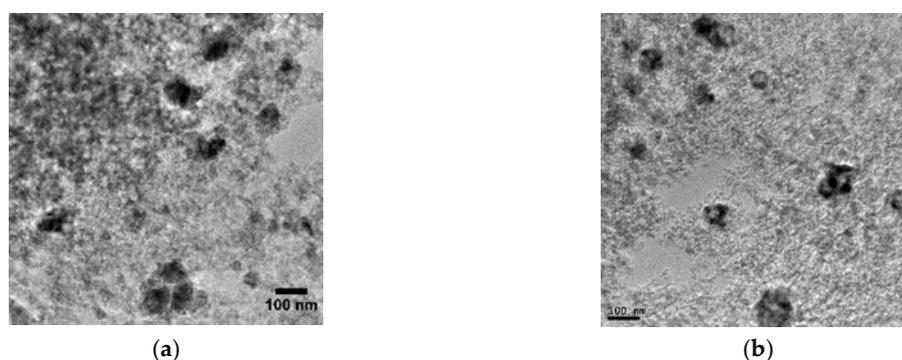


Figure 8. TEM images recorded for Co/SiO₂ catalyst before (a) and after reaction (b) under continuous flow.

The difference between the two processes is the sorption of furanic compounds on the catalyst. In batch processes the catalysts were in contact with the reactant and the products formed, which led to a higher contact time between the furanic molecules and the catalysts than in the continuous flow

process. With these results, it is clearly demonstrated that the stability of the catalyst is higher under continuous flow processes than under batch processes.

In the continuous flow reactor, it was interesting to see that by increasing the hydrogen pressure it was possible to maintain the activity of the catalyst for at least 3 h and that the selectivity was kept constant above 90%. This could be due to an increase in the hydrogen solubility, which was also observed during the hydrogenation in the batch reactor, since FOL produced was then hydrogenated to THFA with an increase of the hydrogen pressure from 20 to 40 bar.

In conclusion, this study shows that using a continuous flow reactor can be a solution when a catalyst suffers from poisoning during batch processes due to sorption of molecules (reactants or products). The optimization of the reaction conditions which are not the same in both processes has to be performed in order to reach similar conversion of furfural and selectivity to FOL.

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