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Selective Hydrogenation of Furfural to Furfuryl Alcohol in the Presence of a Recyclable Cobalt/SBA-15 Catalyst

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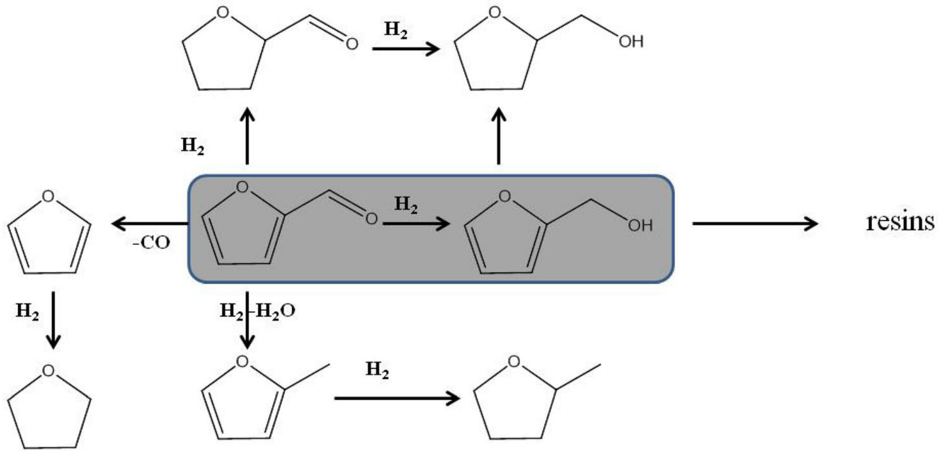
The hydrogenation of furfural to furfuryl alcohol was performed in the presence of a Co/SBA-15 catalyst. High selectivity (96 %) at a conversion higher than 95 % is reported over this catalytic system. As the conversion of furfural to furfuryl alcohol occurs over metallic Co sites, the effect of reduction temperature, H_2 pressure, and reaction temperature were studied. Optimum reaction conditions were: 150 °C, 1.5 h, 2.0 MPa of H_2. The catalyst was recyclable, and furfuryl alcohol was recovered with a purity higher than 90 %. The effect of the solvent concentration was also studied. With a minimum of 50 wt % of solvent, the selectivity to furfuryl alcohol and the conversion of furfural remained high (both over 80 %). Likewise, the activity of the catalyst is maintained even in pure furfural, which confirms the real potential of the proposed catalytic system. This catalyst was also used in the hydrogenation of levulinic acid to produce γ-valerolactone selectively.

Introduction

The concept of biorefinery is the use of biomass as a renewable feedstock for the production of fuels and fine chemicals. Lignocellulosic biomass is made of polymeric components such as cellulose, hemicellulose, and lignin. After the fractionation of biomass, these three main components can be isolated and converted to commodities. Among the molecules that can be obtained from biomass, furanic compounds are of prime industrial interest. In particular, the hydrogenation of furfural (FAL; obtained by the hydrolysis/isomerization/dehydration of hemicellulose) is a relevant reaction that gives access to furfuryl alcohol (FOL), a valuable chemical used in the production of liquid resins, fine chemicals, lysine, vitamin C, lubricants, dispersant agents, and fibers.[1,2] FAL is industrially available with a production of 400 000 t per year. In principle, FOL can be produced selectively through the catalytic hydrogenation of the C=O bond of FAL. However, many side compounds (Scheme 1) are often produced simultaneously from secondary or side reactions (e.g., hydrogenation to tetrahydrofurfuryl alcohol (THFA), hydrogenolysis of FAL to methylfuran, decarbonylation of FAL to furan).[3–5] Consequently, the development of an efficient catalytic system for the selective production of FAL is challenging.



Scheme 1. Hydrogenation of FAL.

FOL is mainly produced by the hydrogenation of FAL in either gas- or liquid-phase processes. The gas-phase hydrogenation of FAL has two main drawbacks: the amount of byproducts is higher than that in the liquid-phase process and it has a high energy consumption because of the need to vaporize FAL.[6] In the liquid phase, solvent and high H_2 pressures are generally required for the hydrogenation of FAL to FOL with high selectivity.[7,8] In this context, copper chromite (Cu-Cr) catalysts are the most widely used commercial catalysts for the hydrogena-

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tion of FAL. Conversions and selectivities to FOL of 98% and 35–98% were claimed in liquid- and gas-phase reactions, respectively.[7]

However, the toxicity of Cu-Cr catalysts that can cause environmental pollution after the final disposal of the catalyst represents a serious shortcoming.[8] In addition, although these catalysts are very selective to FOL, they exhibit moderate activity.[9] Consequently, the liquid-phase hydrogenation of FAL has been studied using catalysts based on Ni, Co, Ru, Pt, and Pd as alternatives to the Cu-Cr catalytic system.[2c,4,10–14] However, a major disadvantage of the proposed catalytic systems is that they always promote side reactions and are difficult to recycle. In most cases, the use of promoters is required to improve the activity and/or selectivity of these catalysts.[15,16] For example, Chen et al.[12] used a Mo-doped Co-B amorphous catalyst (Co-Mo-B) prepared by the chemical reduction of mixed $CoCl_2$ and Na_2MoO_4 with KBH_4 in aqueous solution. This catalyst exhibited excellent activity and nearly 100% selectivity to FOL in the liquid-phase hydrogenation of FAL at 100 °C under 1.0 MPa of H_2. This high selectivity and activity is rarely observed in the presence of a monometallic catalyst. Clearly, the design of non-noble monometallic catalysts able to hydrogenate FAL to FOL selectively in the liquid phase with an acceptable activity remains an important issue.

Herein, we demonstrate that monometallic non-noble Co-based nanoparticles confined in the mesopores of SBA-15 silica are active and selective in the hydrogenation of FAL to FOL at a moderate reaction temperature (150 °C) and H_2 pressure (2.0 MPa). An important benefit of the use of such confined catalysts is the control of the stability of the nanoparticles because of the special microenvironment of SBA-15 nanopores that inhibits their growth during high-temperature catalyst activation and/or catalytic reaction.[17–19] The effects of reduction temperature of the catalyst, H_2 pressure, reaction time, and reaction temperature were investigated specifically. Catalytic results showed that the proposed catalytic system is recyclable, and the reaction can take place either in ethanol or under solvent-free conditions. At the end of the reaction, the purity of FOL was higher than 90%, which facilitates downstream purification. Moreover, the Co/SBA-15 catalyst was active in the hydrogenation of levulinic acid to γ-valerolactone (GVL) to lead to a selectivity of 88% to GVL.

Results and Discussion

Oxide material properties

The catalytic material consists of 10 wt% equivalent Co metal dispersed over the SBA-15 silica support, a content verified by inductively coupled plasma optical emission spectroscopy (ICP-OES). The catalyst was prepared by an incipient wetness impregnation (IWI) route proposed previously as this process ensures the homogeneous infiltration of the precursors inside the pores without a significant enrichment of active phase on the external silica surface.[17] XRD analysis of the calcined precursor shows the presence of a Co_3O_4 crystalline phase (Figure S1) with an average crystallite size of 10.9 nm as evaluated by the Scherrer equation. As expected, TEM analysis demonstrates the formation of oxide nanoparticles confined in the mesopores with only the minor formation of external aggregates (Figure 1 a and c).

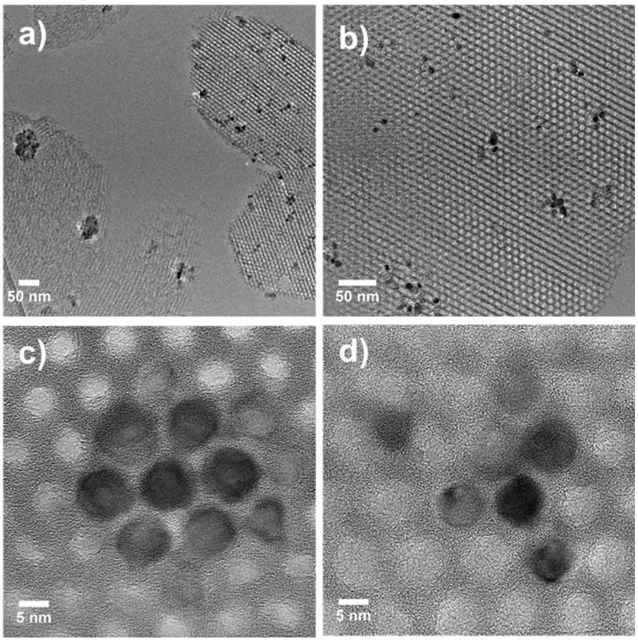


Figure 1. Representative TEM images recorded of a, c) calcined Co_3O_4/SBA-15 and b, d) Co^0/SBA-15 obtained by reduction at 800 °C.

N_2 adsorption/desorption isotherm measurements performed on the calcined Co_3O_4/SBA-15 exhibit a type IV isotherm with an H1 hysteresis loop comparable with that recorded for the SBA-15 support (Figure S2). Pore periodicity seems to be unaltered upon preparation, as confirmed by low-angle XRD analysis (Figure S1). Sensible decreases in specific surface area and total pore volume are observed upon impregnation and calcination (Table S1). Such a result is consistent with pore filling by a secondary phase to result in a partial plugging of the intrawall micropores and mesopores that occurs if particles grow to a size comparable with the pore size of the SBA-15 host (Figure S2).[17–20] Based on these characterization results, we can conclude that the oxide material consists of homogeneously size-distributed cobalt oxide nanoparticles confined in the SBA-15 main mesochannels.

Reducible properties of the cobalt oxide particles confined in the channels of SBA-15

The reducibility of the cobalt oxide was monitored by H_2 temperature-programmed reduction (TPR), and the crystal structure evolution under a reducing atmosphere was followed by in situ XRD (Figure 2). The TPR profile exhibits three distinct reduction stages (Figure 2 A) as reported previously.[19–21] Below 350 °C, the reduction of large, mesopore-confined Co_3O_4 particles in two steps ($Co^{3+}\rightarrow Co^{2+}\rightarrow Co^0$) is supposed to occur. Small Co_3O_4 particles, with a moderate interaction with the support, are supposed to reduce at higher temperatures, with

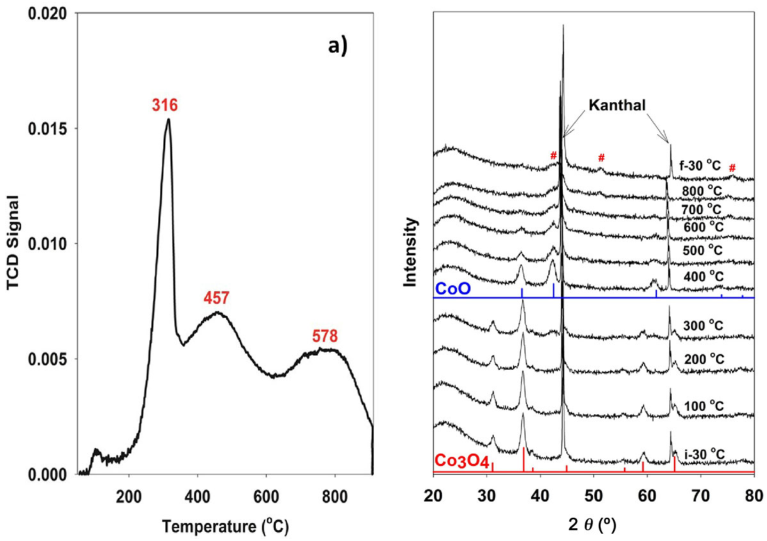


Figure 2. a) Reducible properties of calcined Co_3O_4/SBA-15 and b) Co structure evolution under a reducing atmosphere (vertical bars: Co_3O_4 ICDD 42-1467; CoO, ICDD 02-8505; #, metallic Co, ICDD 15-0806).

a maximum H_2 consumption at 457 °C. Finally, the reduction at high temperature, above 600 °C, suggests the formation of a third fraction of Co species that interact strongly with the support, such as that in phyllosilicate phases.[22] Reduction processes were further validated by in situ XRD (Figure 2 B). The in situ XRD experiment showed that the Co_3O_4 phase is observed until reduction at 300 °C. Above 300 °C, the Co_3O_4 phase signal decreases along with the appearance of characteristic reflections of the CoO phase. The CoO signal decreases progressively in intensity along with the appearance of weak Co^0 phase signals (ICDD 15-0806) at high temperatures. Characterization of the material by TEM, after reduction at 800 °C, evidenced the formation of Co^0 metallic particles of a comparable size to that of precursor oxide particles that remain confined in the support channels (Figure 1 b and d).

Impact of the reducing conditions on activity

FAL of high purity (≥99 %) was used in the experiments. If an ethanolic solution of FAL (10 wt %) was heated at 150 °C under 2.0 MPa of H_2 without any catalyst, a FAL conversion of 13 % was obtained and no production of FOL was observed (Table 1, entry 1). Similar results were obtained in the presence of neat SBA-15. In both cases, the low conversion of FAL was attributed to the acetalization of FAL with ethanol, as shown by MS and NMR spectroscopy (Figures S3 and S4). The hydrogenation reaction was next investigated in the presence of 5 wt % Co/SBA15 reduced at 500 °C under 3 L h^{-1} of H_2 for 10 h. After 90 min, 92 % conversion of FAL was obtained along with a selectivity to FOL of 96 % (Table 1, entry 6).

Table 1. Hydrogenation of FAL. Effect of the Co reduction conditions.[a]

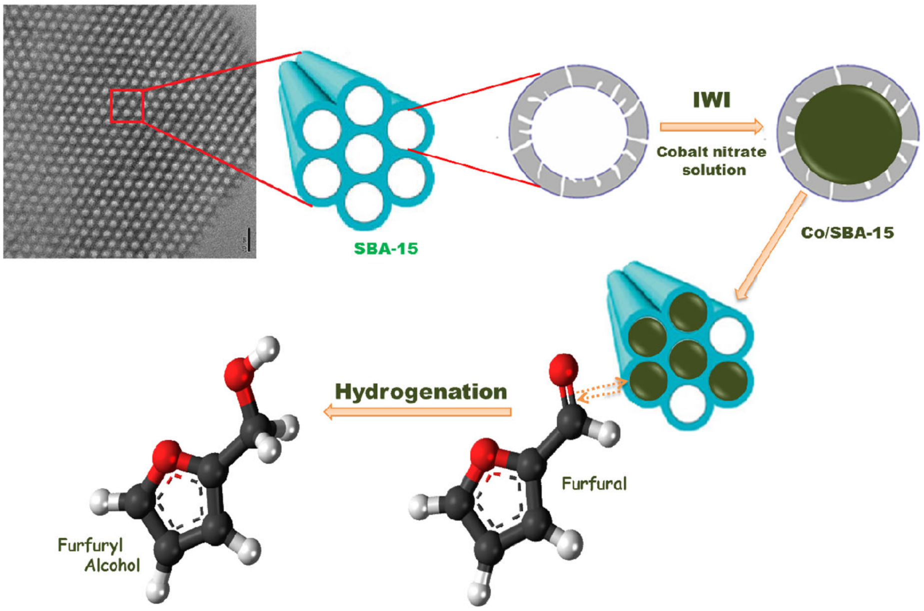
Entry	Reduction temperature [°C]	FAL conversion [%]	FOL selectivity [%]	FOL yield [%]
1[b]	–	13	–	–
2[c]	–	15	–	–
3	NR[d]	18	–	–
4	150	20	–	–
5	300	75	88	66
6	500	92	96	88

[a] Conditions: 9 g of ethanol, 1 g of FAL, catalyst = 5 wt %, 150 °C, 2 MPa of H_2, 90 min. [b] Reaction without catalyst. [c] Reaction in the presence of neat SBA-15. [d] NR = not reduced.

The conversion of FAL remained very low (18 %) and no formation of FOL was observed if the reaction was performed over the oxide form (Co_3O_4) of the catalyst (Table 1, entry 3). The only product obtained was always the acetal formed by the reaction between FAL and ethanol. If the catalyst was reduced at low temperature (Table 1, entry 4), below the temperature needed to form metallic species, the conversion of FAL remained low and no FOL was produced. A minimal reduction temperature of 300 °C is needed to convert FAL into FOL significantly (Table 1, entry 5). At this reduction temperature, H_2-TPR and in situ XRD results suggest the formation of metallic Co sites, although the reduction was still not complete (Figure 2). As expected, the best results were obtained in the presence of Co/SBA15 reduced at 500 °C. This catalyst presented the highest degree of reduction and thus had the highest number of active sites (Table 1, entry 6). Together, these results showed that:

- reduced Co species are required for the hydrogenation of FAL,
- FAL can be hydrogenated selectively to FOL in the presence of metallic Co sites without the addition of a promoter (Scheme 2).

Two mechanism pathways can occur during this reaction after the adsorption of the carbonyl group on the metallic Co species. Hence, a hydroxyalkyl species can be formed by H attack on the O atom of the carbonyl group or an alkoxy intermediate can be obtained by H attack on the C atom of the carbonyl group. In the literature, the formation of a hydroxyalkyl intermediate is favored in the presence of a Cu/SiO_2 catalyst based on the stabilization of this intermediate by the furanic ring.[22] In this study further investigations are performed to determine the exact mechanism of the hydrogenation of FAL in the presence of Co/SBA-15.



Scheme 2. Hydrogenation of FAL to FOL.

Table 2. Effect of H_2 pressure and reaction temperature on the hydrogenation of FAL to FOL.[a]

Entry	T [°C]	P_{H_2} [MPa]	t [h]	FAL conversion [%]	FOL selectivity [%]	FOL yield [%]
1	150	2.0	2	100	76	76
2		2.0	1.75	99	84	83
3		2.0	1.5	92	96	88
4		2.0	1	80	96	77
5	150	5.0	1	100	78	78
6		5.0	2	100	75	75
7		5.0	4	100	40	40
8		1.0	2	81	95	77
9		1.0	3	88	84	74
10	140	2.0	2	97	85	83
11	130	2.0	2	76	87	66
12	120	2.0	2	71	89	63
13	110	2.0	2	34	76	26
14	100	2.0	2	20	90	18
15	100	2.0	6	51	88	45

[a] Conditions: 9 g of ethanol, 1 g of FAL, 5 wt% catalyst reduced under H_2 flow at 500 °C.

In subsequent experiments, the reduction temperature was kept at 500 °C.

Effect of reaction time

The effect of the reaction time on the hydrogenation of FAL (150 °C, 2.0 MPa of H_2, 5 wt% catalyst) is presented in Table 2 (entries 1–4). If the reaction time was decreased from 2 to 1.5 h, the conversion decreased from 100 to 92%. However, a beneficial effect on the FOL selectivity was observed (from 76 to 96%). This can be ascribed to the limitation of secondary reactions that can occur during the hydrogenation of FAL upon prolonged reaction time because of the stability of FOL in the reaction media. Hence, there are several compounds derived from side reactions (i.e., the hydrogenation of the furan ring to THFA, hydrogenolysis of the C=O bond to methylfuran, decarbonylation to furan, and further hydrogenation to THF (Scheme 1).[3,6,23] Resinous material and ring-decomposed products are also produced.[24] If the reaction time was further decreased to 1 h, the conversion was only 80% and the selectivity remained higher than 95%. From these results, it is clear that a maximum reaction time of 1.5 h is required for FAL hydrogenation to FOL under 2.0 MPa of H_2 at 150 °C. The purity of the FOL obtained was higher than 90%.

Effect of H_2 pressure

An increase of the H_2 pressure was beneficial for the conversion of FAL. Indeed, after 1 h of reaction at 150 °C, the conversion of FAL was complete under 5.0 MPa of H_2 (Table 2, entry 5) versus only 80% under a H_2 pressure of 2.0 MPa (Table 2, entry 4). However, an increase in the H_2 pressure led concomitantly to a decrease in the FOL selectivity from 96 to 75% as supported by the formation of dark brown products. This decrease of selectivity can be ascribed to i) the formation of polymers from the polymerization of FOL or FAL or ii) the degradation of FOL or FAL, which can be favored at high H_2 pressure as described previously.[15,16] In evidence, if the reaction was continued after the complete conversion of FAL from 2 to 4 h at 5.0 MPa of H_2 (Table 2, entries 6 and 7), the selectivity to FOL decreased significantly from 75 to 40%, which supports the relative instability of FOL under a high pressure of H_2. Hence, byproducts of the condensation of FOL can be produced as shown previously. This result was further confirmed by conducting experiments at only 1.0 MPa of H_2 (Table 2, entries 8 and 9). Under 1.0 MPa of H_2, the conversion of FAL was incomplete even after 2 h of reaction (81%), and the selectivity to FOL reached 95%. At this pressure, the increase of the reaction time from 2 to 3 h led to an increase of the conversion of FAL from 81 to 88%, along with a decrease of the selectivity to FOL from 95 to 84% (Table 2, entries 8 and 9). Therefore, in the presence of monometallic Co/SBA-15, FAL can then be converted selectively to FOL even under a pressure of 1.0 MPa H_2.

Table 3. Hydrogenation of FAL. Effect of the catalyst and FAL content.[a]

Entry	FAL content [wt %]	Catalyst content [wt %]	FAL conversion [%]	FOL selectivity [%]	FOL yield [%]	Productivity [$mol_{FOL}\,mol_{Co}^{-1}\,h^{-1}$]
1	10	5	100	76	76	46
2	10	3	63	87	55	56
3[b]	10	3	84	85	71	48
4	30	5	100	88	88	161
5	50	5	90	78	70	214
6	100	5	37	84	31	190

[a] Conditions: 150 °C, 2.0 MPa of H_2, $t=2$ h. [b] $t=3$ h.

Effect of reaction temperature

The reaction was performed at temperatures lower than 150 °C (Table 2 entries 10–15). A decrease of the reaction temperature from 150 to 140 °C led to 97 % conversion of FAL with a selectivity to FOL of 96 % after 2 h of reaction versus 1.5 h at 150 °C (Table 2, entry 3). If the reaction temperature was further decreased from 140 to 130 and 120 °C, the conversion decreased logically from 97 to 76 and 71 % with a similar selectivity to FOL (around 87 %; Table 3, entries 10–12). At lower temperatures of 110 and 100 °C, a significant decrease of the FAL conversion was observed (20 % after 2 h). At such low temperatures, the conversion can be increased by increasing the reaction time. For instance, the conversion of FAL increased from 20 to 51 % if the reaction time was increased from 2 to 6 h (Table 3, entry 15). The selectivity to FOL remained high (around 90 %), which shows that side reactions are limited at low reaction temperatures.

Stability in reaction

The recyclability of the catalyst is a key aspect for the viability of a heterogeneously catalyzed pathway. The catalyst was recycled after the reaction performed at 150 °C under 2.0 MPa of H_2 for 1.5 h. The catalyst was recovered simply based on its magnetic properties and was reused without washing and/or reactivation. The weight percentage of fresh FAL added was always 10 wt % in EtOH. The amount of FAL was not adjusted during the recycling process. A decrease in the conversion from 92 to 81 % was observed between the two first runs (Figure 3). Thereafter, the conversion remained almost constant (around 80 %) during the next two runs. After the fourth cycle, the conversion decreased slightly run by run. However, the conversion of FAL remained higher than 70 % up to the ninth cycle. In all runs, the selectivity to FOL was similar. These results show that the performances of the active sites are maintained under recycling, despite the slight progressive decrease in conversion. To elucidate this point, the leaching of Co during the reaction was evaluated. Co in solution at the end of each run was ~10 ± 2 ppm. Hence, Co leaching can be the origin of the loss of activity as after 11 runs approximately 110 ppm of Co is lost from the catalyst surface. However, to validate that the process is purely heterogeneous (i.e., Co in solution is not responsible for FAL conversion in a homogeneous process), an additional test was performed. Thus, the catalyst was removed from the reaction media when the conversion reached 50 %. After the removal of the catalyst, H_2 was reintroduced and the reaction was performed for a further hour. No additional conversion of FAL was observed, which shows that Co in solution did not allow the formation of FOL. This is probably because Co in solution has a cationic character, which is inactive for the hydrogenation reaction.

The activation of the catalyst after the fifth cycle was performed by calcination under air for 6 h at 100 °C and then reduction under H_2 for 10 h at 500 °C. This activated catalyst was used in the hydrogenation of FAL to FOL at 150 °C under 2.0 MPa of H_2 for 1.5 h. A FAL conversion of 90 % and a selectivity to FOL of 96 % were obtained, which shows that this catalyst can be reactivated.

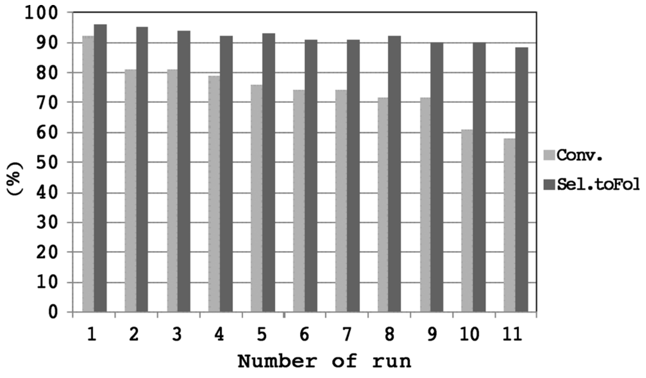


Figure 3. Evolution of FAL conversion and FOL selectivity during recycling tests over Co/SBA-15 (10 wt % of FAL in ethanol, 150 °C, 2.0 MPa of H_2, 1.5 h).

Optimization studies

The catalyst content can be decreased without affecting the selectivity to FOL. Indeed, with a catalyst content as low as 3 wt %, the FAL conversion was 84 % with 85 % selectivity to FOL (Table 3, entries 1–3). The productivity was similar for both catalyst contents (around 50 $mol_{FOL}\,mol_{Co}^{-1}\,h^{-1}$). The effect of the FAL/solvent ratio on the FAL conversion and selectivity to FOL was studied. Several reactions were performed (5 wt % catalyst, reaction temperature 150 °C, 2.0 MPa of H_2, 2 h; Table 3, entries 1 and 4–6). The conversion of FAL remained above 90 % and the selectivity to FOL is around 80 % up to 50 wt % FAL content. In addition, if FAL was used without solvent (100 wt %), the selectivity remained unchanged, and a conversion of 37 % was measured. This is clear evidence that this catalytic system can work without solvent and maintain a high productivity to FOL. Hence, the productivity was 161 $mol_{FOL}\,mol_{Co}^{-1}\,h^{-1}$ for 30 wt % of FAL and increased up to 214 $mol_{FOL}\,mol_{Co}^{-1}\,h^{-1}$ for 50 wt % of FAL. We were pleased to see that a productivity of 190 $mol_{FOL}\,mol_{Co}^{-1}\,h^{-1}$ was obtained in the absence of solvent, which shows the excellent productivity that can be obtained using this catalyst.

Hydrogenation of levulinic acid to GVL

We were interested to study the use of this catalyst in another hydrogenation reaction. With this aim, the hydrogenation of levulinic acid was performed in the presence of Co/SBA-15 catalyst to produce GVL. GVL, a frequently used food additive, exhibits the most important characteristics of an ideal sustainable liquid, which include the possibility to be utilized in the production of energy or carbon-based consumer products.[25] The reaction was performed under 2.0 MPa of H_2 at 150 °C for 2 h in the presence of 1 g of levulinic acid in 9 g of ethanol. A selectivity to GVL of 88 % was obtained at 89 % levulinic acid conversion (Table 4, entry 2). Ethyl levulinate was observed as a byproduct (Figure S5). If the reaction time was prolonged to 4 h, the conversion was complete but the selectivity to GVL decreased from 88 to 69 % (Table 4, entry 1) because of the formation of ethyl valerate, as shown by GC–MS analysis (Figure S6), along with traces of ethyl levulinate.[26] If the pressure of H_2 was decreased from 4.0 to 2.0 MPa at 150 °C for 2 h, the selectivity to GVL was 73 % for a conversion of levulinic acid of 81 % (Table 4, entry 3). These results show that Co/SBA-15 can be used in the hydrogenation of levulinic acid to obtain GVL with a selectivity of 88 %.

Table 4. Hydrogenation of levulinic acid.[a]

Entry	Reaction time [h]	Levulinic acid conversion [%]	GVL selectivity [%]	GVL yield [%]
1	4	100	69	69
2	2	89	88	78
3[b]	2	81	73	59

[a] Conditions: 150 °C, 5.0 MPa of H_2. [b] 150 °C, 2.0 MPa of H_2.

Conclusions

Herein, we have demonstrated that furfuryl alcohol (FOL) can be produced selectively from the hydrogenation of furfural (FAL) in the presence of a monometallic Co/SBA-15 catalyst. The presence of a metallic Co species is required for the hydrogenation of FAL to FOL. The effect of the reaction conditions (temperature, pressure, reaction time) was studied. Optimal conditions to achieve high conversions and selectivity were 150 °C under 2.0 MPa of H_2 for 1.5 h. The catalyst was recyclable, with a limited decrease in activity in up to nine cycles. The effect of the FAL to EtOH ratio was also studied. The catalyst works even without solvent. Despite the decrease in conversion, selectivity remains high (above 80 %) and productivity to FOL can be increased significantly. Co/SBA-15 can be considered as a promising catalyst for FOL production and also for γ-valerolactone production from levulinic acid with a low environmental impact as processes with limited solvent consumption that function at low temperature and H_2 pressure can be designed. Moreover, compared to other systems, a similar yield of FOL can be obtained without the promotion of another metal, and Co-SBA-15 can be recovered easily and recycled, which is of prime interest in such reactions.

Experimental Section

Catalyst preparation

The SBA-15 support was synthesized according to the procedure used by Zhao et al.[27] Pluronic P123 ($PEO_{20}PPO_{70}PEO_{20}$, MW = 5800 g mol^{-1}, 4 g) and HCl (1.6 M) were stirred at 40 °C until the complete dissolution of the templating agent. The silica source, tetraethyl orthosilicate (8.5 g), was added dropwise, and the mixture was stirred for 24 h. The resulting gel was submitted to hydrothermal treatment for 48 h at 100 °C. The SBA-15 support was obtained by calcination at 550 °C for 6 h in a muffle oven (heating ramp 1.5 °C min^{-1}). Freshly calcined support was impregnated with an aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$ (0.8 mol L^{-1}). The volume of solution was adjusted to obtain a metal loading of 10 wt %. Under these conditions, the volume of impregnation solution ensures the complete wetting of the support (IWI[28]). The impregnated powder was dried at 120 °C for 12 h in stagnant air and was calcined at 500 °C in a muffle oven (heating ramp 1.5 °C min^{-1}).

Physicochemical characterization of Co/SBA-15

Materials were characterized by ICP-OES, XRD, TEM, N_2 physisorption, H_2-TPR, and in situ XRD after programmed reduction. A description of the procedures is provided in the Supporting Information.

Hydrogenation of FAL

The hydrogenation of FAL was performed in the liquid phase by using a batch reactor. In a typical experiment FAL (1 g) was added to ethanol (9 g), and Co/SBA-15 (5 wt %) was added to the solution. The reactor was then filled with the desired pressure of H_2 (e.g., 5.0 MPa) at RT, and the temperature was increased to 150 °C. The reaction time was 1–4 h. At the end of the reaction, the liquid phase was recovered and analyzed by HPLC. FAL and FOL were quantified by external calibration at 25 °C using HPLC equipped with a nucleosil 100–5 C_{18} column (250 × 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 mL min^{-1}). The productivity [$mol_{FOL}\,mol_{Co}^{-1}\,h^{-1}$] was evaluated by the ratio of the moles of FOL produced over the moles of Co species per hour.

Hydrogenation of levulinic acid

The hydrogenation of levulinic acid was performed in the liquid phase by using a batch reactor. Typically, levulinic acid (1 g) was added to ethanol (9 g), and Co/SBA-15 (5 wt %) was added to the solution. The reactor was then filled with the desired pressure of H_2 (5.0 or 2.0 MPa) at RT, and the temperature was increased to 150 °C. The reaction time was 2–4 h. Levulinic acid and GVL were quantified by external calibration at 25 °C by using HPLC equipped with a nucleosil 100–5 C_{18} column (250 × 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 mL min^{-1}).

Recycling experiments

The recycling tests were performed by recovering the catalyst at the end of each cycle magnetically. The catalyst was reused without washing or thermal treatment. Fresh FAL (10 wt%) was added to ethanol (90 wt%), and the recovered catalyst (5 wt%) was introduced. The reactor was then filled with the desired pressure of H_2 (2.0 MPa) at RT, and the temperature was increased to 150 °C. The reaction time was 1 h 30. After the reaction, the catalyst was recovered, and the liquid phase was analyzed by HPLC.

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Keywords: biomass · cobalt · heterogeneous catalysis · hydrogenation · supported catalysts

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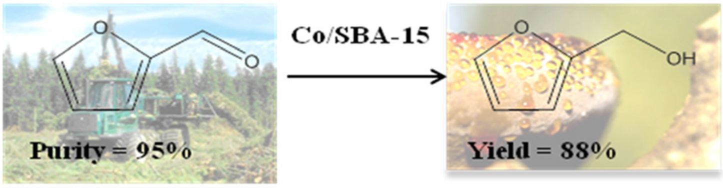
■■–■■

Selective Hydrogenation of Furfural to Furfuryl Alcohol in the Presence of a Recyclable Cobalt/SBA-15 Catalyst



The fast and the furfural: Furfuryl alcohol is produced from furfural with a yield of 88 % in the presence of a recyclable and stable Co/SBA-15 catalyst at 150 °C under H_2 pressure in ethanol. This catalyst is also active and selective in the hydrogenation of levulinic acid to γ-valerolactone.