



Short Communication

Liquid-phase transfer hydrogenation of furfural to furfuryl alcohol on Cu–Mg–Al catalysts



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ABSTRACT

The liquid-phase transfer hydrogenation of furfural on Cu-based catalysts was studied. Catalysts were prepared by incipient wetness impregnation (Cu/SiO₂) and co-precipitation (Cu–Mg–Al). The effect of metal-support interaction, hydrogen donor, copper loading and temperature on catalytic performance was evaluated. Small particles, strongly interacting with a spinel-like matrix, had higher capability for transferring hydrogen than large ones having low interaction with support. An important increase in reaction rate was observed when temperature was raised from 110 to 150 °C. Thus, it was possible to attain complete furfural conversion to furfuryl alcohol with Cu(40%)–Mg–Al after 6 h at 150 °C.

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1. Introduction

Furfural (FAL) is a biomass-derived platform molecule very important for the production of a great number of chemicals [1]. Conversion of FAL in the presence of H₂ and metallic catalysts can lead to a complex reaction network [2]. Among the possible products, furfuryl alcohol (FOL) is one of the most interesting and valuable compounds since it can be used for the production of resins, synthetic fibers, farm chemicals, foundry binders, adhesives and some fine chemicals products such as vitamin C, lysine and tetrahydrofurfuryl alcohol [1–3]. FOL is produced industrially with copper chromite (Cu–Cr) catalysts, which are active for the selective FAL hydrogenation with gaseous H₂ but can cause severe environmental pollution due to the high toxicity of Cr⁶⁺ ion [1]. For this reason, different research groups have performed a great effort to develop Cr-free catalysts. With this objective in mind, the liquid-phase selective hydrogenation of FAL to FOL has been investigated employing different catalysts based on noble metals, like Pt [4], and non-noble metals, like Cu [2,5], Cu–Ni [3], Ni [6–8] and Co [9].

Besides direct hydrogenation with gaseous H₂, FAL can be selectively converted to FOL by transfer hydrogenation from an organic molecule that acts as hydrogen donor in the presence of a catalyst. This process normally involves the simultaneous hydrogenation of FAL and dehydrogenation of H donor [10–13]. In comparison with conventional

hydrogenation, this process has some important advantages as to avoid the use of gaseous H₂ and the reduction in production costs [14]. Transfer hydrogenation of aldehydes and ketones, e.g. acetophenone and cyclohexanone, in liquid and gas phase has been investigated using different alcohols as hydrogen sources and distinct Cu [14], Ni [15–17], MgAlOx [18] and MgO [19] catalysts. It was determined that secondary alcohols, like 2-propanol, 2-butanol, 2-pentanol, 2-heptanol or 2-octanol, gave higher yields in hydrogen transfer reactions than primary alcohols like ethanol, 1-propanol or 1-butanol. In particular 2-propanol showed to be a proper hydrogen donor for a wide number of organic molecules [13,15–18].

Gas-phase transfer hydrogenation of FAL has been studied by several authors using Cu-based catalyst and cyclohexanol and 1,4-butanediol as hydrogen sources [10–12]. High conversion of FAL (60–90%) and selectivity to FOL (99–100%) were reported. Instead, to our knowledge, there are few works dealing with the liquid-phase transfer hydrogenation of FAL [13,20,21]. Scholz et al. [13] used Cu/, Ni/ and Pd/Fe₂O₃ as catalysts and 2-propanol as hydrogen donor. Despite catalytic tests were performed at high temperature (180 °C), low conversion of FAL (35–45%) and selectivity to FOL (≈ 75%) were obtained with Cu and Ni/Fe₂O₃. Instead, 100% conversion of FAL was reached with Pd/Fe₂O₃, but selectivity to FOL was only 35–65% due to hydrogenolysis of FOL into 2-methylfuran. Panagiotopoulou et al. [20] used a Ru/RuO₂/C catalyst and different alcohols as hydrogen donors obtaining 2-methylfuran as main product (yield ≈ 76%), as well. He et al. [21] got high yield (≈ 96%) in FOL but using Au-based catalysts and aqueous HCOOK solution as hydrogen donor.

In a previous work, we showed that Cu–Mg–Al catalyst, prepared by the co-precipitation method, was more active than a Cu–Cr catalyst for

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the selective hydrogenation of FAL to FOL at 10 bar H₂ and 110 °C [2]. The aim of this work is to determine the feasibility of performing the selective liquid-phase transfer hydrogenation of FAL into FOL employing Cu-based catalysts free of Cr, as Cu–Mg–Al catalysts, with 2-propanol as hydrogen donor. The influence of metal-support interaction, hydrogen donor nature, copper loading and reaction temperature on catalytic performance was evaluated.

2. Experimental

2.1. Catalyst preparation

Cu–Mg–Al catalysts, with copper loadings from 20 to 40 wt.%, were prepared by the co-precipitation method at 60 °C and pH = 10 ± 0.2, following the procedure described elsewhere [2,22]. It was checked by atomic absorption spectrometry (AAS) that no significant amounts of Cu²⁺, Mg²⁺ and/or Al³⁺ were present in the mother liquor after the co-precipitation step was over. This is indicative of complete precipitation of these cations. The hydrated precursors were then decomposed in N₂ flow at 500 °C for 5 h to obtain the corresponding mixed oxides. Besides, a Cu/SiO₂ was prepared by the incipient wetness impregnation method. Copper was deposited on a commercial SiO₂ (Sigma-Aldrich grade 62, 99.7%) by adding dropwise a 2.3 M aqueous solution of Cu(NO₃)₂·3H₂O (Merck, 98%). The solid was dried at 100 °C overnight and then decomposed in air flow at 500 °C for 5 h.

2.2. Catalyst characterization

The identification of polycrystalline species, formed before and after thermal decomposition, was carried out by X-ray diffraction (XRD) using a Shimadzu XD-1 diffractometer and Ni-filtered Cu-K α radiation with a scan speed of 2°·min⁻¹. Specific surface area (Sg) was measured by N₂ physisorption at -196 °C in a Quantochrome Autosorb I sorptometer. Temperature-programmed reduction (TPR) experiments were performed using a 5% H₂/Ar gaseous mixture (60 mL min⁻¹). Oxide samples (100 mg) were heated at 10 °C min⁻¹ from 25 to 550 °C. Hydrogen concentration in the effluent was measured by mass spectrometry (MS) in a Baltzers Omnistar unit. Elemental analysis was carried out by atomic absorption spectroscopy (AAS) using an Espectr mter Perkin Elmer PinAAcle 900T.

2.3. Catalytic tests

The liquid-phase transfer hydrogenation of FAL (Aldrich, 99%) was carried out in a 100 ml autoclave (Parr 4565), equipped with a mechanical stirrer and magnetic drive, at 110–150 °C and using 60 ml of ethanol (ETA, Cicarelli, 99.5%), n-propanol (n-PA, Anedra, 99.9%) or 2-propanol (IPA, Merck, 99.5%) as solvents. Prior to catalytic tests, samples were activated ex-situ in H₂ flow (60 mL min⁻¹) at 300 °C for 2 h. Then, the ex-situ reduced sample (0.2 g, dp ≤ 100 μm) was transferred to the reactor under inert atmosphere (N₂). The reaction system was stirred at 650 rpm or higher and heated up to reaction temperature at 2 °C min⁻¹. Once reaction temperature was reached, 1.00 ml of FAL was injected into the reactor. The absence of mass transfer limitations was verified using the quantitative criteria described by Ramachandran and Chaudhari [23], which has been successfully employed for liquid-phase hydrogenation reactions [24,25].

Evolutions of FAL and product concentrations with reaction time were followed by ex-situ gas chromatography using an SRI chromatograph, equipped with flame ionization detector and a 30 m HP-Innowax capillary column. Liquid samples were withdrawn from the reactor and collected every 15–30 min by using a loop under pressure in order to avoid sample flushing. The reactant conversion (X_{FAL} , mol of FAL reacted/mol of FAL fed) was calculated as $X_{\text{FAL}} = (C_{\text{FAL}}^0 - C_{\text{FAL}}) / C_{\text{FAL}}^0$, where C_{FAL}^0 is the initial FAL concentration and C_{FAL} is the FAL concentration at reaction time t .

3. Results and discussion

3.1. Catalysts characterization

The X-ray diffractogram for Cu/SiO₂ hydrated precursor prepared by impregnation fitted very well with the XRD pattern of Cu(NO₃)₂·3H₂O (JCPDS 14–415). Instead, a hydrotalcite-like (HC) phase (JCPDS 14–191) was identified by XRD in all of the Cu–Mg–Al hydrated precursors obtained by coprecipitation at constant pH. The X-ray diffractograms of oxides precursors, obtained after thermal decomposition of the former hydrated precursors, are shown in Fig. 1. Thermal decomposition of Cu(NO₃)₂·3H₂O, deposited on SiO₂ surface, led to a polycrystalline phase with tenorite-like structure (CuO, JCPDS 5–0661), as shown in Fig. 1, diffractogram a. Instead, not-well-ordered tiny crystallites (≈ 5 nm) with spinel-like structure were observed by XRD after thermal treatment of samples prepared by coprecipitation (Fig. 1, diffractograms b–d). This spinel-like phase was assigned to a magnesium aluminate-like phase (MgAl₂O₄, JCPDS 21–1152), obtained at temperatures lower or equal to 500 °C by pseudomorphic decomposition of the HC phase [26,27]. Assignment to CuAl₂O₄ (JCPDS 78–1605), having a similar X-ray diffraction pattern to MgAl₂O₄, was initially discarded since temperatures higher than 600 °C are necessary to form this mixed oxide [28]. No significant segregation of crystalline CuO was detected in these Cu–Mg–Al mixed oxides, thereby indicating that Cu²⁺ ions are probably highly dispersed in the spinel-like matrix. Only some broadening of diffraction peaks for sample Cu40MgAl was detected. Then, it is possible that some segregation of small CuO particles from the spinel-like matrix occurred. In all of the cases, the specific surface area (Sg) of the oxide precursors was between 220 and 290 m² g⁻¹.

The results corresponding to the reducibility of the oxide precursors are shown in Fig. 2 and Table 1. The TPR profile for the Cu/SiO₂ oxide precursor exhibited only a broad peak between 240 and 360 °C, with the maximum H₂ consumption at 310 °C, arising from the reduction of the tenorite-like phase (Fig. 2, profile a). This broad peak has been previously assigned to the reduction of CuO particles with a broad distribution in size [22]. For Cu–Mg–Al oxide precursors, the maximum H₂ consumption shifted to temperatures 50–60 °C lower, what is normally attributed to reduction of CuO highly dispersed in a spinel-like matrix [29]. No peak between 450 and 500 °C due to CuAl₂O₄ reduction was detected [29]. The last is in agreement with the previous assignation of Cu–Mg–Al diffraction peaks to the formation of a magnesium

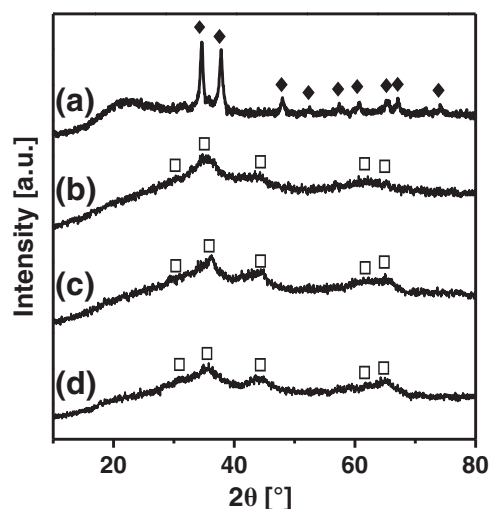


Fig. 1. Characterization of samples. X-ray diffraction patterns [Ni-filtered Cu-K α , scan speed: 2°·min⁻¹]: (a) Cu/SiO₂; (b) Cu40MgAl; (c) Cu30MgAl; (d) Cu20MgAl. Phases: (◆) CuO (tenorite-like); (□) spinel-like.

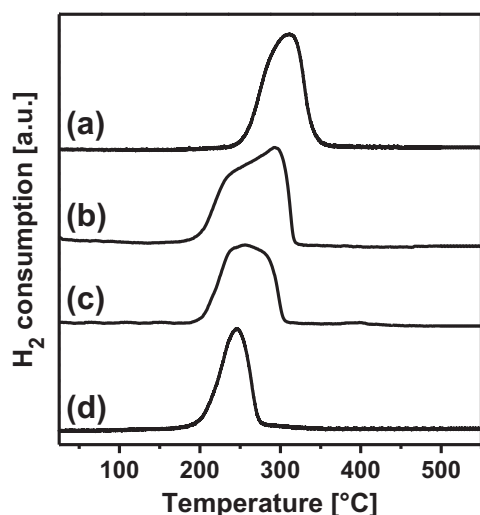


Fig. 2. Characterization of samples. TPR profiles [$\text{H}_2(5\%) / \text{Ar}, 60 \text{ mL min}^{-1}$, heating rate: $10^\circ \text{C min}^{-1}$]: (a) Cu/SiO_2 ; (b) Cu40MgAl ; (c) Cu30MgAl ; (d) Cu20MgAl .

aluminate phase at low temperature. A single reduction peak, with a maximum around 245°C , was observed for the sample Cu20MgAl (Fig. 2, profile d), due to reduction of CuO highly dispersed in the mixed oxide matrix [28,29]. This peak was also observed for samples Cu30MgAl and Cu40MgAl (Fig. 2, profiles b and c). However, as the Cu content was raised, it is clear that a second peak was developed that is overlapped to the one at 245°C , which can be due to reduction of segregated CuO particles. These particles must be some larger than those reduced at 245°C [29], but the crystallite domains are small enough ($<4 \text{ nm}$) as not to be detected by XRD. For sample Al, the maximum of the second peak was at a temperature closer to that one observed in the TPR profile of Cu/SiO_2 sample (Fig. 2, curves a and b). These results indicate that very small CuO crystallites, highly dispersed in the Mg–Al spinel-like matrix, are formed at Cu loadings lower or equal to 40 wt.%. By numerical integration of the TPR profile, the H_2 consumption was determined for all samples. From these values, and assuming a stoichiometry $\text{H}_2/\text{Cu} = 1$, the amount of Cu^{2+} ions reduced after treatment in H_2 was determined (Table 1). These results confirm that, in all of the cases, Cu^{2+} ions can be totally reduced to Cu^0 . In summary, the reducibility of oxide samples follows the pattern: $\text{Cu20MgAl} > \text{Cu30MgAl} > \text{Cu40MgAl} > \text{Cu/SiO}_2$.

Characterization results clearly indicate the influence of the preparation method on the type of catalytic precursor obtained and the interaction between oxidized copper and support matrix. Thus, it is expected that, after reduction, Cu/SiO_2 sample would be composed of large metal copper particles with low interaction with the support. In contrast, Cu-Mg-Al sample would be constituted by small metal copper particles strongly interacting with the spinel-like matrix [22].

Table 1
Composition and reducibility of the samples determined by temperature programmed reduction (TPR).

Sample	Cu loading [%] ^a	Cu / (Mg + Al) ratio	H_2 consumption [mmol $\text{g}_{\text{CAT}}^{-1}$]	Cu loading [%] ^b
Cu/SiO_2	30	–	4.98	31.6
Cu20MgAl	20	0.4	3.57	22.7
Cu30MgAl	30	0.8	4.51	28.6
Cu40MgAl	40	1.2	6.48	41.2

^a Nominal amount of Cu, expressed in wt.%.

^b Amount of Cu determined from H_2 consumption calculated by numerical integration of TPR profiles.

3.2. Catalytic tests

3.2.1. Influence of Cu-support interaction

Firstly, transfer hydrogenation of FAL using IPA as hydrogen donor was carried out at 110°C over Cu/SiO_2 and Cu30MgAl , which have similar content of Cu but different physicochemical properties. It was observed that Cu/SiO_2 was not active for transfer hydrogenation of FAL with IPA. In contrast, a FAL conversion of around 30% was reached after 8 h reaction with Cu30MgAl catalyst (Fig. 3). The only product detected under these experimental conditions was FOL. On the other hand, Cu30MgAl mixed oxide, i.e. sample after thermal decomposition in N_2 without further treatment in H_2 , was tested under the same reaction conditions. No transfer hydrogenation of FAL was observed after 6 h, which indicates that metal copper is necessary for this reaction to take place.

A Cu–Cr sample, previously prepared and reported [2], having approximately a 40 wt.% Cu load and copper chromite structure, was also tested in the FAL transfer hydrogenation with IPA at 110°C . It was verified that this Cu–Cr sample was much less active than Cu30MgAl (Fig. 3).

According to these results, it can be concluded that a phase formed by small metal copper particles, highly dispersed in the Mg–Al spinel-like matrix, is active for liquid-phase transfer hydrogenation of FAL with IPA under mild conditions. In a previous work, we suggested that FAL can be adsorbed on-top through carbonyl group over Lewis acid sites, i.e. Mg^{2+} and/or Al^{3+} , which are on the surface of the spinel-like matrix [2]. As well, in other works, it was reported that IPA is dissociatively chemisorbed over metal Ni particles and thus catalyzes the H transfer from IPA to acetophenone [17,30]. It is likely that small metal copper clusters, interacting with Mg–Al spinel-like matrix, can activate IPA molecules in a similar way than metal nickel particles and this favors H transfer to carbonyl group, which is activated on Mg^{2+} and/or Al^{3+} sites. Instead, large metal Cu particles, interacting weakly with the support, have not the capability to activate IPA molecule and then H transfer to FAL is not feasible [30].

We also studied the catalytic behavior of Cu30MgAl on the FAL transfer hydrogenation at 110°C using different hydrogen donors, like ETA, n-PA and IPA. The conversion attained with linear alcohols (ETA and n-PA) as solvents was much lower ($X_{\text{FAL}} < 10\%$ at 8 h) than with IPA ($X_{\text{FAL}} \approx 30\%$ at 8 h), as shown in Fig. 4A. In all of the experiments, the selectivity to FOL was 100%. It is also clear that the initial reaction rate with IPA was one order of magnitude higher than that with ETA or n-PA as hydrogen sources (Fig. 4B). Thus, the pattern for hydrogen transfer is: $\text{IPA} > \text{n-PA} > \text{ETA}$. These results are consistent with those

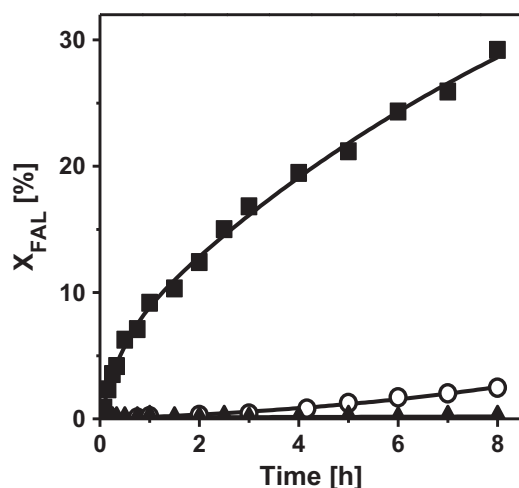


Fig. 3. Liquid-phase transfer hydrogenation of FAL. Conversion as a function of time, (\blacktriangle) Cu/SiO_2 ; (\circ) Cu–Cr; (\blacksquare) Cu30MgAl [$T = 110^\circ \text{C}$; $m_{\text{CAT}} = 0.20 \text{ g}$; $C_{\text{FAL}}^0 = 0.2 \text{ M}$; $V_{\text{SOLV}} = 60 \text{ mL (IPA)}$].

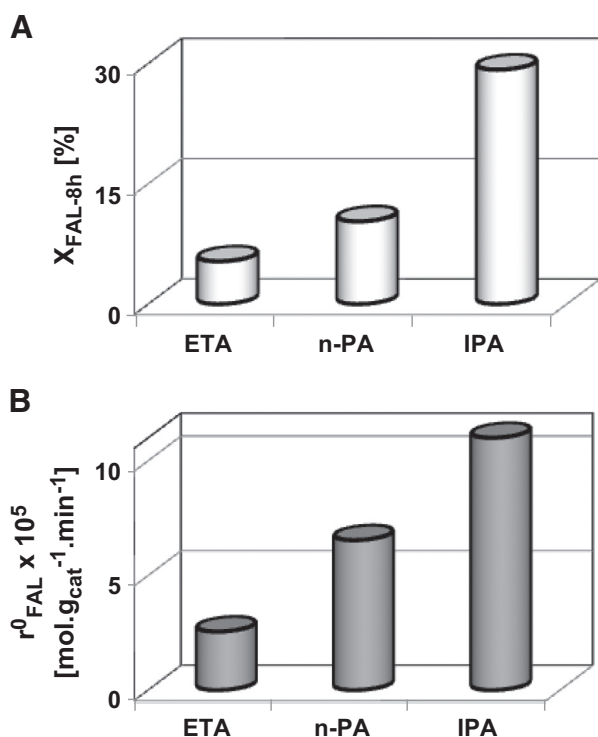


Fig. 4. Influence of hydrogen donor (ETA, n-PA and IPA) in liquid-phase transfer hydrogenation of FAL on Cu30MgAl catalyst. A) FAL conversion at 8 h; B) Initial reaction rate [T = 110 °C; $m_{\text{CAT}} = 0.20$ g; $C_{\text{FAL}}^0 = 0.2$ M; $V_{\text{SOLV}} = 60$ mL].

obtained in previous works for other reaction systems [13,17]. Thus, IPA was chosen as the best hydrogen donor among the alcohols tested in this work.

3.2.2. Influence of Cu loading

Cu–Mg–Al catalysts with different amounts of Cu were tested in the transfer hydrogenation of FAL employing IPA as hydrogen donor. The reactions were performed at 130 °C with Cu20MgAl, Cu30MgAl and Cu40MgAl catalysts. It was found that the catalytic activity for hydrogen transfer increased with Cu loading (Table 2). Thus, Cu40MgAl catalyst was the most active, attaining a 70% FAL conversion at 130 °C after 8 h reaction. In all of the cases, the selectivity to FOL was 100%. Besides, as the Cu loading was raised from 20 to 40 wt.%, the initial reaction rate per gram of catalyst increased linearly with Cu content. However, the initial reaction rate per gram of copper was very similar for all of the Cu–Mg–Al catalysts. These results are indicating that the intrinsic activity of metal copper phase is almost the same for all of the Cu–Mg–Al catalysts.

Transfer FAL hydrogenation with IPA was studied at three different temperatures (110, 130 and 150 °C) using Cu40MgAl as catalyst and results are shown in Fig. 5. It was determined that complete FAL hydrogenation was reached at 150 °C after 6 h reaction. From these curves, the initial reaction rate ($t = 0$) was determined by numerical differentiation and the results are summarized in Table 3. Assuming an Arrhenius type dependence, the apparent activation energy (E_a) was estimated as

Table 2
Influence of Cu load on liquid-phase transfer hydrogenation of furfural (FAL) [T = 130 °C, $m_{\text{CAT}} = 0.20$ g, $C_{\text{FAL}}^0 = 0.2$ M and $V_{\text{SOLV}} = 60$ mL (IPA)].

Catalyst	$X_{\text{FAL}} [\%]$ (t = 8 h)	$r_{\text{FAL}}^0 \times 10^4$ [$\text{mol}_{\text{FAL}} \text{g}_{\text{CAT}}^{-1} \text{min}^{-1}$]	$r_{\text{FAL}}^0 \times 10^3$ [$\text{mol}_{\text{FAL}} \text{g}_{\text{Cu}}^{-1} \text{min}^{-1}$]
Cu20MgAl	55.2	1.9	0.95
Cu30MgAl	61.3	2.9	0.96
Cu40MgAl	73.1	4.3	1.1

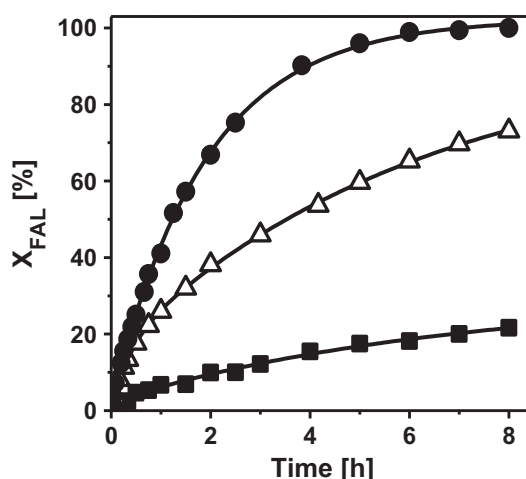


Fig. 5. Effect of temperature in liquid-phase transfer hydrogenation of FAL on Cu40MgAl catalyst. (■) 110 °C; (Δ) 130 °C; (●) 150 °C [$m_{\text{CAT}} = 0.20$ g, $C_{\text{FAL}}^0 = 0.2$ M, $V_{\text{SOLV}} = 60$ mL (IPA)].

66 kJ mol⁻¹. This value is in the range of E_a reported in previous works for the same reaction using other catalysts. For example, Scholz et al. [13] determined an $E_a = 47$ kJ mol⁻¹ for transfer hydrogenation of FAL to FOL on a 2 wt.% Pd/Fe₂O₃ catalyst.

In summary, hydrogen transfer from isopropanol to furfural in liquid phase can be efficiently performed using a solid catalyst constituted by a metal copper phase highly dispersed in a magnesium aluminate-like matrix. To our knowledge, this is the first time that the liquid-phase transfer hydrogenation of carbonyl compounds over a chromium-free copper-based catalyst, under mild conditions, is reported. This can become very important in the chemical industry due to both economic and environmental aspects.

4. Conclusions

We showed that Cu–Mg–Al catalysts, prepared by coprecipitation at constant pH, are active and highly selective for liquid-phase transfer hydrogenation of furfural to furfuryl alcohol using 2-propanol as H donor. Instead, Cu/SiO₂ and Cu–Cr, with similar metallic contents, have none or little activity for this reaction under similar conditions. This is because metal particle size and metal-support interaction have a strong influence on the copper capability for favoring hydrogen transfer from 2-propanol to furfural. Thus, small metallic particles, interacting with a Mg–Al spinel-like matrix, are very active for transferring hydrogen from 2-propanol to furfural. On the contrary, large metal particles, having low interaction with support, are not able for 2-propanol activation.

A 100% conversion of furfural to furfuryl alcohol can be attained at 150 °C with a Cu–Mg–Al catalyst containing 40 wt.% of Cu. For Cu–Mg–Al catalyst, the rate for transfer hydrogenation increases linearly with Cu content. However, furfural hydrogenation rate per gram of metal copper is the same for all of the Cu–Mg–Al catalysts.

Table 3
Influence of reaction temperature on liquid-phase transfer hydrogenation of furfural (FAL) using Cu40MgAl catalyst [T = 110–150 °C, $m_{\text{CAT}} = 0.20$ g, $C_{\text{FAL}}^0 = 0.2$ M and $V_{\text{SOLV}} = 60$ mL (IPA)].

Temperature [°C]	$X_{\text{FAL}} [\%]$ (t = 8 h)	$r_{\text{FAL}}^0 \times 10^4$ [$\text{mol}_{\text{FAL}} \text{g}_{\text{CAT}}^{-1} \text{min}^{-1}$]	$r_{\text{FAL}}^0 \times 10^3$ [$\text{mol}_{\text{FAL}} \text{g}_{\text{Cu}}^{-1} \text{min}^{-1}$]
110	21.7	1.4	0.3
130	73.1	4.3	1.1
150	100	9.7	2.4

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.catcom.2014.08.021>. These data include MOL files and InChiKeys of the most important compounds described in this article.

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