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Gas-phase cascade upgrading of furfural to 2-methylfuran using methanol as H-transfer reactant and MgO based catalysts

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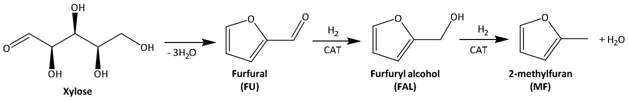
The hydrogenation of biomass-derived molecules is a key reaction in the upgrading of these compounds into chemicals and fuels. The use of catalytic transfer hydrogenation, employing alcohols as hydrogen sources, offers an alternative approach to this process, avoiding the use of H_2 at high pressure and precious metal catalysts. In this work, the gas-phase conversion of biomass-derived furfural into furfuryl alcohol and 2-methylfuran was studied using methanol as the H-transfer agent and MgO-based catalysts. Pure MgO was shown to reduce furfural to the corresponding unsaturated alcohol at low reaction temperatures (lower than 350°C), thus allowing the selective H-transfer from methanol to the substrate. 2-Metylfuran formation, associated with the partial rearrangement of furan ring to ciclopentanones, was observed at high temperatures. Conversely, the distribution of compounds obtained with Mg/Fe/O was significantly different, with prevailing 2-methylfuran formation when the reaction was carried out between 300 and 400°C. In this temperature range, when tuning reaction conditions, a very high yield of 2-metylfuran was produced, thus indicating that the mixed oxide allows efficient sequential transfer hydrogenation/hydrogenolysis reactions. These results highlight the potential application of the H-transfer reaction over MgO-based catalysts, as an efficient process for the selective de-oxygenation of biomass-derived molecules.

1. Introduction

Biomasses are currently the most promising alternative to fossil resources for the production of chemicals and fuels from renewables.[1,2,3] In the transformation of a biomass, an important role is played by furan derivatives.[4,5] For instance, 2-furfural (FU) – which is available on an industrial scale via hydrolysis-dehydration of the hemicellulose part of lignocellulose biomass[6,7] – is a key precursor for the synthesis of derivatives with applications in the fuel and polymer industries.[8] The upgrading of this molecule includes the hydrogenation of the carbonyl group to the corresponding furfuryl alcohol (FAL), used as chemicals in the polymer and intermediate industries,[9] and to 2-methylfuran (MF) (Scheme 1). The production of MF from FU is an extremely interesting route to renewable fuels. Indeed, MF has drawn the attention of researchers as a gasoline alternative due to its very attractive combustion performance in engines.[10] The octane number of MF is higher than that of gasoline (103 vs 96.8 RON), while its energy density is very close (28.5 MJ/L vs 31.9 MJ/L); this meaning that, with the same volume of fuel, MF contains 34% more energy compared to the market-leading biofuel ethanol.[11]



Scheme 1. Production of furfuryl alcohol (FAL) and 2-methylfuran (MF) from xylose and furfural (FU).

For the hydrogenolysis of FU to MF, the H_2 needs to selectively react with the formyl group without opening or hydrogenating the furan rings. Nickel, copper and noble metals based catalysts have been reported to be active towards the conversion of FU to MF.[12,13] Cu-based catalysts (copper chromite, Cu/Al_2O_3) have been extensively used, since they preferentially cleave the carbon-oxygen respect to the carbon-carbon bond or the hydrogenation of the furan ring.[14] Nevertheless, one of the key challenges for upgrading FU is product selectivity; indeed, hydrogenation of FU often results in a mixture of side-chain and ring-hydrogenated products along with ring-opening products.

The reduction of carbonyl groups using alcohols as hydrogen sources, i.e. the Meerwein–Ponndorf–Verley (MPV) reaction, offers an alternative approach to working under hydrogen pressure with supported precious metal catalysts.[15,16,17] Under appropriate

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conditions, the reaction can be highly chemo-selective towards carbonyl groups.

Dumesic and co-workers have demonstrated that ZrO_2 can be used as the catalyst with isopropropanol as the H-donor to hydrogenate levulinc acid and ethyl levulinate for the production of γ-valerolactone; they also reported a systematic computational study on the MPV reaction applied to biomass-derived molecules such us ethyl levulinate and FU.[18]

Additionally, Hermans and co-workers reported that Fe_2O_3-supported Cu and Ni catalysts permitted over 70% selectivity to FAL at moderate FU conversion, with isopropanol as the H-transfer reagent. Moreover, the Pd/Fe_2O_3 system studied showed an interesting activity in the further hydrogenolysis of FAL to MF, to the ring-hydrogenated compound, and to furan, with a combined yield of 62% under continuous flow conditions.[19]

Recently, Vlachos and co-workers demonstrated the catalytic H-transfer to be an effective pathway for converting FU to MF, in batch reactions, when using a mildly oxidized Ru/C catalyst;[20,21,22,23] they suggested the combination of Lewis acid and Ru-based catalyst as a general strategy for performing the upgrading of furans.

Nevertheless, to our knowledge, there are no studies in the open literature on the continuous gas-phase reduction of furanic compounds using solid-base catalysts. The development of a continuous catalytic process, based on non-noble metals, for the production of FAL and MF in a cascade reaction, is an attractive topic, while the tuning of an inexpensive bi-functional catalyst with hydrogenation and de-oxygenation sites would be a good candidate for achieving this goal. In addition, the use of a H-transfer reaction, instead of molecular hydrogen could make it possible to use bio-alcohols as hydrogen donors, thus increasing the sustainability of the entire process.

We recently reported on the use of methanol as a clean and efficient H-transfer reactant for carbonyl reduction in the liquid phase.[24] The selective hydrogenation of FU, 5-hydroxymethylfurfural, benzaldehyde, and acetophenone was described using this alcohol both as hydrogen donor and reaction medium. Compared to other molecules used in H-transfer reaction, methanol showed the advantage of producing gaseous components as the only co-products; these components were easily separated from the reaction medium, thus avoiding undesired reactions involving the products of alcohol transformation. Using high-surface area MgO, as an easily recoverable and reusable catalyst for FU reduction, a 100% yield to FAL was obtained.

Here we report on the gas-phase reduction of FU to FAL and MF. The reaction was carried out in a continuous reactor using a simple procedure, which enables selective H-transfer from methanol to reactants, with MgO-based materials as catalysts.

2. Experimental

2.1. Catalyst preparation

Two catalysts were investigated: MgO and magnesium-iron mixed oxide (sample Mg/Fe/O). MgO and Mg/Fe/O were prepared by the thermal treatment of hydrotalcite-like precursors. The latter were synthesized by precipitation from an aqueous solution containing the corresponding metal nitrates ($Mg(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$, Sigma Aldrich); lastly, filtered samples were dried at 120°C overnight and then calcined in air at 500°C for 6 h. Details regarding the preparation and characterization of catalysts are available in our previous work.[25] Precursors were synthesized using a Mg^{2+}/Fe^{3+} ratio equal to 2, which is within the range of values at which the corresponding hydrotalcite-like material is formed.

2.2. Catalyst characterization

BET Specific Surface Area. The BET surface area of catalysts was determined by N_2 absorption-desorption at the temperature of liquid N_2 using a Sorpty 1750 Fison Instrument. A sample of 0.3 g was typically used for the measurement, and the sample was outgassed at 150°C before N_2 absorption.

X-Ray Diffraction analyses (XRD). XRD powder patterns of the catalysts were recorded with Ni-filtered Cu Kα radiation (λ = 1.54178 Å) on a Philips X'Pert vertical diffractometer equipped with a pulse height analyzer and a secondary curved graphite-crystal monochromator.

Thermogravimetric/differential thermic analyses (TGA/DTA). Using a SDT Q 600 instrument, TG/DT analyses were performed over fresh and spent catalysts in order to identify the amount of heavy compounds absorbed over the catalyst surface. A sample of 5-10 mg was typically employed for the measurement at temperatures from room temperature up to 900°C, with a heating rate of 10°C/min in air.

2.3. Gas-phase catalytic tests

Catalytic tests were carried out in a continuous-flow fixed-bed micro-reactor (Pyrex, length 38 cm, internal diameter 1/3 inch). The catalyst (30-60 mesh particles) was placed in the reactor in the appropriate quantity to vary the contact time from 0.1 to 1.1 s, and then it was heated to the desired reaction temperature (200-500°C) under N_2 flow (26 ml/min). The catalytic reaction was started by the vaporization of methanol (WWR Chemicals) and FU (Sigma-Aldrich) in a 10/1 molar ratio using nitrogen as the carrier gas (26 ml/min). FU was purified via distillation prior to being fed into the flowing gas stream. The total volumetric flow rate through the catalytic bed was held constant at 60 ml/min and the molar concentration of FU, methanol and nitrogen were respectively 5, 50, and 45%. We observed that catalysts deactivate rapidly if they were left exposed to the atmosphere; therefore a freshly calcined catalyst (T=450°C) was always used in each experiment under the different reaction conditions; in all cases, results were taken after 1 h reaction time.

Analyses of reactants and products were carried out as follows: the outlet stream was scrubbed for 1h in cold acetonitrile, which was maintained at -26 °C by a F32 Julabo Thermostat. The condensed products were analyzed by means of HPLC, using an Agilent Technologies 1260 Infinity instrument equipped with a DAD UV-Vis detector and an Agilent POROshell 120 C-18 column. Non-condensable gases (CO, CO_2, and CH_4) were analyzed by sampling the gaseous stream with a syringe at the reactor outlet and by injecting the sample into a Perkin Elmer AutoSystem XL gas chromatograph equipped with a FID detector with methanizer and a PLOT-Q column.

FU Conversion, product selectivity and C-loss were expressed as follows:

$$Furfural\ Conversion = \frac{\dot{n}^{in}_{furfural} - \dot{n}^{out}_{furfural}}{\dot{n}^{in}_{furfural}}$$

$$Products\ Selectivity = \frac{\dot{n}^{out}_{product}}{\dot{n}^{in}_{furfural} - \dot{n}^{out}_{furfural}}$$

$$C - Loss = 100 - \sum_{i} Product\ Selectivity$$

3. Results and discussion

3.1. Bulk features of catalysts

Table 1 shows some results concerning the morphology and structure of the prepared materials after heat treatment.

Table 1. Nature and specific surface area of calcined catalysts.

Catalyst	BET Surface area (m^2/g)	Crystalline phase (XRD)
MgO	172	Periclase
Mg/Fe/O	140	MgO-like mixed oxide

Mg/Fe/O showed a lower surface area than MgO. The TG/DT analysis on MgO and Mg/Fe/O in Figure S1 shows the temperature at which the dried precursors decomposed. A pronounced weight loss in the temperature range between 300 and 400°C was ascribed to the decomposition of brucite (or hydrotalcite-like structure), as also supported by the XRD patterns in Figure 1.

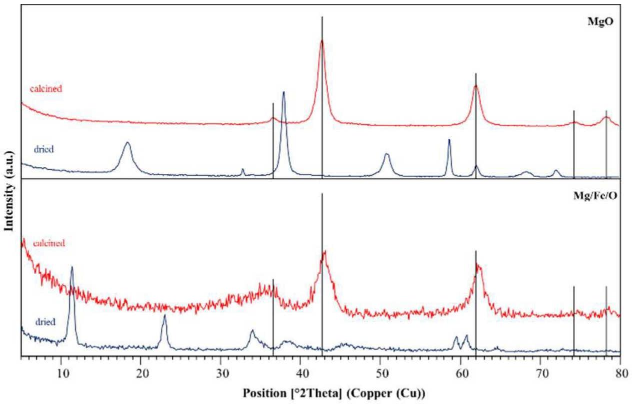


Figure 1. XRD patterns of dried and calcined MgO (top) and Mg/Fe/O (bottom) catalysts. Black lines: Reference pattern of MgO (periclase structure).

The diffractogram for dried MgO showed the typical pattern of brucite $Mg(OH)_2$, and a single well-defined MgO periclase phase after calcination.[26] Conversely, the dried Mg/Fe/O showed a hydrotalcite-like structure, leading after calcination to broad XRD lines, corresponding to a quasi-amorphous MgO phase. The latter XRD pattern well agrees with those reported in literature[27,28,29] for the formation of a Mg/Fe mixed oxide, in which the incorporation of the trivalent Fe^{3+} cation in the MgO lattice generates cationic defects and produces a low degree of crystallinity. No appreciable shifts of XRD reflexes were observed, because the ionic radius of Fe^{3+} (0.69 Å) cation is similar to the radius of Mg^{2+} (0.65 Å).

3.2. Hydrogenation of furfural with MgO catalyst

At first, the hydrogenation of FU was carried out using MgO as catalyst and methanol as the hydrogen donor. Several authors have studied the interaction of methanol with MgO[25,30,31] and it has been well established that MgO catalyzes the dehydrogenation of methanol and H-transfer on carbonyl substrates. Chemisorption occurs via heterolytic dissociation involving the formation of CH_3O^- anions and hydroxyl groups.[32]

In our tests, FAL and MF were the main products detected in the reaction with FU; some cyclopentanones (CPs) (Figure 2) were identified at very high temperatures (450-500°C). These by-products result from the FU rearrangement that occurs under reducing conditions and was previously observed by Hronec and co-workers[33,34] in their studies on FU hydrogenation.

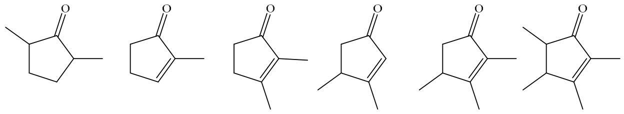


Figure 2. Main cyclopentanones (CPs) identified as by-products.

Figure 3 shows the effect of the reaction temperature, in the range 200-500°C, on FU conversion and products distribution. Previous work[35] involving in-situ IR studies on phenol methylation with methanol demonstrated that CH_3OH interacts with the MgO surface to generate formaldehyde and formate species, thus providing evidence for both the dehydrogenation of methanol and the strong interaction of the resulting products with the MgO basic surface[25].

In the reaction with FU, at low temperature (< 350°C) the catalytic transfer hydrogenation occurred selectively and FAL was the only molecule produced. No products of ring hydrogenation or decarbonylation were detected; moreover, although formaldehyde was supposed to be initially produced, it was never detected in the present experiment; therefore, in addition to the main reaction involving FAL formation, the process was accompanied by the decomposition of formaldehyde to CO and H_2.

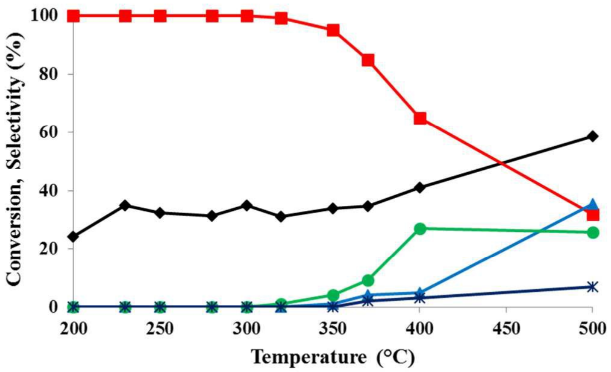


Figure 3. Effect of reaction temperature on FU conversion and products selectivity, catalyst MgO. Feed composition: FU 5%, CH_3OH 50%, N_2 45%; Pressure 1 atm, overall gas residence time 0.5 s, reaction time 1 h. Symbols: ♦ FU conversion, ■ FAL selectivity, ▲ MF selectivity, ∗ CPs selectivity, ● C-loss.

Scheme 2 shows a formal set of reactions that would account, at least in principle, for the transformation of methanol to gaseous by-products[25,35].

$CH_3OH \rightarrow H_2CO + H_2$ (1)

$CH_2O \rightarrow CO + H_2$ (2)

$CO+H_2O \rightarrow CO_2+H_2$ (3)

$2\ CH_2O \rightarrow CH_3O\text{-}C(O)H$ (4)

$CH_3OC(O)H \rightarrow CO_2 + CH_4$ (5)

$2\ CH_2O + H_2O \rightarrow CH_3OH+HCOOH$ (6)

$HCOOH \rightarrow CO_2+H_2$ (7)

$CH_3OH+H_2O \rightarrow CO_2 + 3H_2$ (8)

Scheme 2. Summary of main reactions occurring to methanol over MgO-based catalysts.

The ability of MgO to dehydrogenate methanol was confirmed by tests shown in Figure S2-A, reporting the number of moles of light compounds formed while feeding methanol at 380°C. H_2 and CO, with a molar ratio equal to 2/1, were the only compounds produced, confirming the occurrence of reactions 1 and 2. Alternatively, two adsorbed CH_2O may disproportionate to formate and a methoxy species yielding methylformate (reaction 4) (the latter can also be formed by Tishchenko dimerization), which decomposes at high temperatures to CH_4 and CO_2 (reaction 5)[24]. In the presence of water in the feed, formaldehyde may also produce formic acid and methanol through the Cannizzaro reaction (reaction 6), with formic acid then easily decomposing to CO_2 and H_2 (reaction 7) or CO and H_2O (reaction 9); formic acid may also be formed through the oxidation of formaldehyde by Fe^{3+} redox type cation[25]. Moreover, the role of water in WGS (reaction 3) or methanol reforming (reaction 8) cannot be disregarded.

Figure S2-B shows the number of moles of light compounds, based on time, in the reaction of FU reduction with methanol at 380°C. The main detected products were CO_2, H_2, and CO, while the yield of CH_4 was nil. As a matter of fact, the formation of CO and H_2 can be explained by the contribution of formaldehyde dehydrogenation (reaction 2), while the small amount of CO_2 could be ascribable to the presence of H_2O (reactions 3 and 8), which formed by furfural hydrogenolysis. The lower amount of H_2 detected in this test, compared to the previous one with methanol only (Figure S2-A), confirms the occurrence of the H-transfer from methanol to FU.

Figure 3 shows that the conversion of FU was almost constant at 30-35% in the range of temperatures from 250 to 350°C; it then increased to 40% at 400°C and to 59% when the temperature was raised further to 500°C. The absence of both intraparticle and interparticle diffusional limitations in our conditions was ruled out based on some experiments using either catalysts with different dimensions or different flow rates (Table S1). Therefore, the fact that within a wide range of temperatures the conversion was not affected by temperature might be explained by taking into account that the strong interaction of FU with the catalyst surface would lead to a strongly exoenthalpic adsorption, which might end up resulting in a very low value for the apparent activation energy.

Up to 400°C the main product of the reaction was FAL, while MgO exhibited a limited activity in the further hydrogenolysis to MF. Conversely, at 500°C the activity of the catalyst towards MF production increased and it was possible to obtain a 35% selectivity to this product. The catalyst was still active in the production of FAL (32% selectivity) but the quantity of by-products, such as CPs, increased with the rise in reaction temperature.

Moreover, at high reaction temperatures, poor carbon balance was observed, likely because of the heavy compounds deposition on the catalyst surface. Indeed, Hronec and co-workers reported the possible oligomerization of FAL in similar conditions.[36] Therefore, since MgO alone is inefficient in the further hydrogenolysis of FAL, some parallel reactions, taking place from this molecule, may be produced, leading to the formation of heavy products. The formation of heavy compounds and the deposit of carbonaceous residua on the catalyst surface might also explain the change of surface properties occurring at temperatures higher than 350°C, where a significant increase in FU conversion was also seen.

In order to investigate the presence of carbonaceous components on the catalyst surface, we analyzed the materials tested using TGA/DTA and Raman spectroscopy. Figure 4 shows the weight loss for fresh and used catalysts.

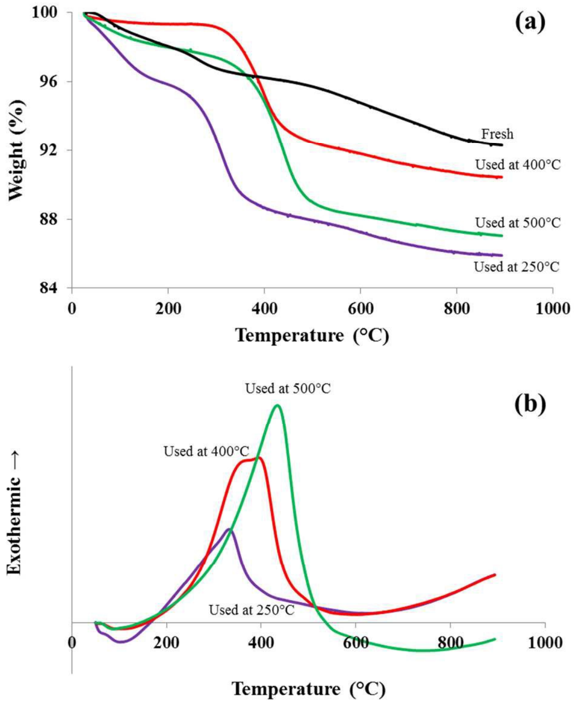


Figure 4. Thermogravimetric (a) and differential thermal (b) analyses (TGA/DTA) in air: (—) fresh MgO calcined at 500°C; MgO used in catalytic test (—) at 250°C, (—) at 400°C, and (—) at 500°C.

The catalyst used at low temperature (250°C) was only slightly off-white in appearance, which suggests that oligomeric compounds were not produced in a significant concentration. Nevertheless, the thermogravimetric profile – which was performed by heating samples from room temperature to 900°C in air – indicated a significant weight loss. As a matter of fact, results revealed an initial marginal weight loss (4-5 wt. %) after heating to 150°C, due to physisorbed water; a further weight loss of 7 wt. % was then registered over the temperature range of 180-380°C. Pristine MgO (calcined at 500°C) also showed a weight loss of 3 wt. % in this temperature range, suggesting that the observed phenomena were related to the decomposition of small amounts of hydroxide and/or carbonate present on the catalyst surface.[37] It is known that MgO surface is very reactive to atmospheric moisture and carbon dioxide, thus its exposure to these gases can lead to the formation of surface hydroxide and carbonate.[38] Nevertheless, its heat flow profile (DTA) exhibited an exothermic peak, which is inconsistent with the solely endothermic decomposition of these compounds. Therefore, the presence of methanol and/or formaldehyde absorbed on the catalyst surface, as is or as oligomers, was suggested. Indeed, the treatment of MgO catalysts at 250°C in the same reaction conditions, but in the absence of FU (Figure S3), led to a similar TGA profile.

Experiments carried out by feeding either FU or FAL with hydrogen or without any co-reactant (Table S2), confirmed that the weight loss shown by the catalyst used at 250°C was due to some carbonaceous species derived from methanol, and not from FU or FAL.

Increasing the reaction temperature gradually increased the TGA temperature at which compounds were removed from the surface of the corresponding used catalyst. This trend, associated with the increase in the exothermicity registered in the DTA thermograms, suggests the deposition of different compounds, derived from FU or FAL, at the highest reaction temperatures. Indeed, with MgO used at 400°C and 500°C, Raman spectra indicated the presence of bands attributable to coke (Figure S4); moreover, under these conditions a significant C-loss was detected (Figures 3 and 5), whereas at low temperature the C-loss was negligible.

In order to gain a better insight into the reaction mechanism occurring in the hydrogenation of FU and hydrogenolysis to MF, we have investigated the effect of contact time on FU conversion and products distribution (Figure 5). A strong effect of this parameter was observed. At 0.1 s contact time, FAL was the main product detected, with 76% selectivity. Increasing the contact time rapidly decreased FAL selectivity and, at 1.1 s, it was produced with 9% selectivity only. Conversely, a significant increase in MF selectivity was observed; the latter was equal to 18% at very low contact time (0.1 s), while at 1.1 s it increased up to 39%. These results indicate that the reaction network for the transformation of FU into MF consists of the direct and rapid transformation of FU into FAL (primary product); then FAL is converted either to MF via hydrogenolysis or to heavy compounds (precursors for coke), the latter being responsible for the increased C-loss value. At high contact time, the highest C-loss was observed, suggesting a significant formation of carbonaceous residua and supporting the hypothesis that these compounds formed on the catalyst surface by the partial polymerization of FAL.[39]

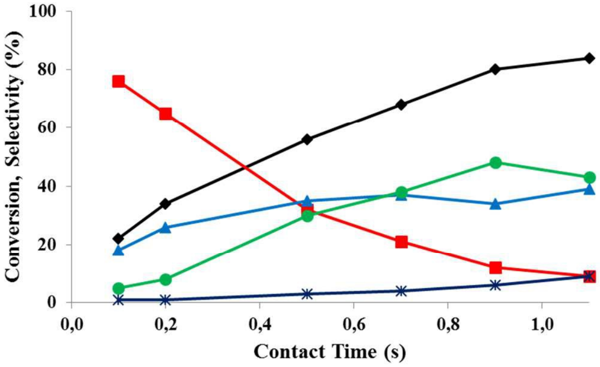


Figure 5. Effect of contact time on FU conversion and products selectivity, catalyst MgO. Feed composition: FU 5%, CH_3OH 50%, N_2 45%; Pressure 1 atm, temperature 500°C, reaction time 1 h. Symbols: ♦ FU conversion, ■FAL selectivity, ▲MF selectivity, ∗ CPs selectivity, ● C-loss.

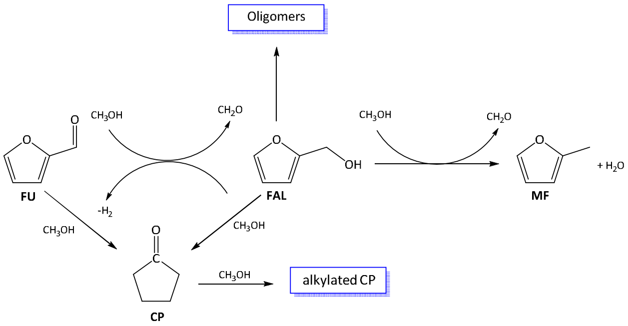
The selectivity to CPs also increased along with the contact time. For a better understanding of the reaction mechanism involved in CPs formation, some catalytic tests were conducted using FU, FAL, MF, and CP as starting reagents (Table 2). First, a preliminary experiment was carried out by reacting FU without any methanol at 500°C (Table 2 – entry 2). This experiment made it possible to ascertain the absence of non-reductive reactions under the conditions used. In fact, FU was partially degraded but neither FAL, MF, nor CPs were observed in these conditions. In order to assess the ability of the catalyst to convert different reaction products into CPs, FAL and MF were used separately as reagents in both the presence and the absence of methanol. The use of FAL in the presence of methanol (Table 2 – entry 3) resulted in the transformation of this compound into MF and CPs. Conversely, neither these products formed in the absence of methanol (Table 2 – entry 4), thus proving that they can be directly derived from FAL reductive transformation. Nevertheless, the transformation of FU to CP could not be ruled out, due to the fact that some FU was formed from FAL.

Table 2. Reactivity experiments from reaction intermediates with MgO catalyst. Feed composition: FU or FAL or CP 5%, CH_3OH 50% , N_2 45% or 95%; pressure 1 atm, temperature 500°C, overall gas residence time 0,5 s, reaction time 1 h.

Entry	Reagents	Detected products			
1	FU + CH_3OH	FU	FAL	MF	CPs
2	FU	-	-	-	-
3	FAL + CH_3OH	FU	FAL	MF	CPs
4	FAL	FU	-	-	-
5	MF + CH_3OH	-	-	-	-
6	MF	-	-	-	-
7	CP + CH_3OH	-	-	-	CPS
8	CP	-	-	-	-

No conversion of MF was shown (Table 2 – entries 5 and 6) in both the presence and the absence of methanol, which confirms that MgO is unable to activate this molecule; moreover, no products of degradation were detected, indicating that MF is stable even at high temperatures. The use of CP as a reagent in the presence of methanol resulted in the methylation of this molecule in different positions, confirming the methylating properties of CH_3OH in the presence of MgO.[25,35,40]

A summary of the main reaction pathways involved in FU transformation using MgO catalyst and methanol as H-transfer agent is shown in Scheme 3.



Scheme 3. Main reaction scheme for FU transformation using MgO catalyst and methanol.

3.3. Hydrogenolysis of furfural with Mg/Fe/O catalyst

The addition of Fe^{3+} to MgO leads to the formation of solid solutions having the general composition $Mg_{1-x}Fe_xO_{1+0.5x}$ and medium-strength basic sites.[35,40] The basic strength decrease is due to the higher electronegativity of Fe^{3+} compared to Mg^{2+}, which decreases the charge density on the neighbouring O^{2-} and makes it less nucleophilic than oxygen atoms in MgO.[41]

The effect of the reaction temperature, in the range 250-500°C, on the catalytic activity of MgO and Mg/Fe/O is compared in Figure 6, while Figure 7 summarizes the effect of the reaction temperature on FU conversion and product distribution for Mg/Fe/O. Both catalysts were active in the catalytic H-transfer reduction of FU, but they led to a very different product distribution. Indeed, with Mg/Fe/O considerable deoxygenation took place, finally resulting in MF, instead of FAL, as the main product even at moderate temperatures. Thus, in this case, the reaction seemed to proceed by rapid reduction of the aldehyde group and then hydrogenolysis of the formed hydroxyl. No subsequent reductions of the furan ring or ring opening were observed during the reaction, while some CPs were identified at high temperatures.

FU conversion increased from 40% to 93% with increasing temperature up to 380°C and then decreased down to 70% at 500°C. Nevertheless, at both low (250°C) and high temperatures (500°C), this catalyst led to the formation of a high quantity of heavy products, consistently with the high C-loss observed. TG/DT analysis (Figure S5) produced results very similar to those obtained with MgO. This confirmed the existence of an optimal reaction temperature (T=380°C) for the reduction of FU with methanol on Mg/Fe/O, since at lower and higher temperatures side reactions were preferred. However, contrarily to MgO which was totally selective to FAL at low temperatures, Mg/Fe/O was very selective in the production of MF, with 79% selectivity at 380°C. FAL selectivity was low (20%) at 250°C, and then decreased further.

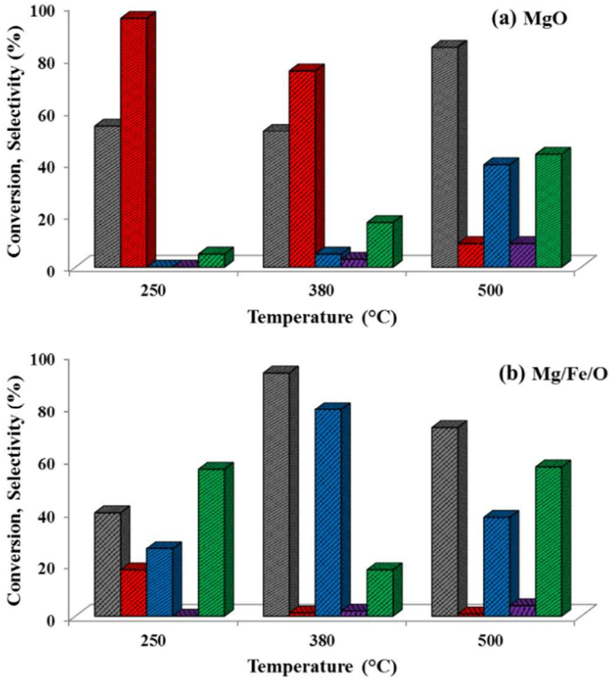


Figure 6. Effect of reaction temperature on FU conversion and products selectivity, catalysts MgO (a) and Mg/Fe/O (b). Feed composition: FU 5%, CH_3OH 50%, N_2 45%; pressure 1 atm, overall gas residence time 1.1 s, reaction time 1 h. Legend: ■ FU conversion, 🟥 FAL selectivity, 🟦 MF selectivity, 🟪 CPs selectivity, 🟩 C-loss.

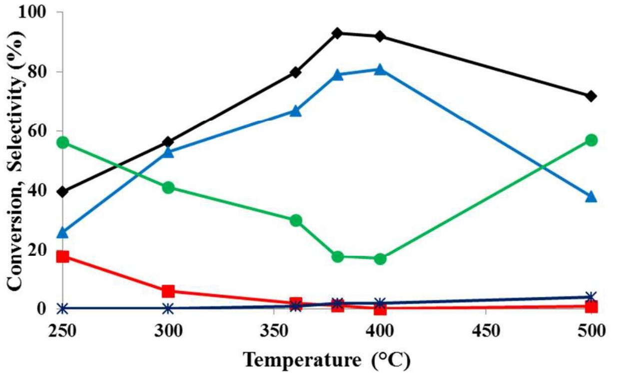


Figure 7. Effect of reaction temperature on FU conversion and products selectivity, catalyst Mg/Fe/O. Feed composition: FU 5%, CH_3OH 50%, N_2 45%; Pressure 1 atm, overall gas residence time 1.1 s, reaction time 1 h. Symbols: ♦ FU conversion, 🟥FAL selectivity, ▲ MF selectivity, ✱ CPs selectivity, ● C-loss.

Concerning the side reactions occurring on methanol with Mg/Fe/O, we detected large amounts of formaldehyde decomposition products (H_2, CO, CH_4 and CO_2), already at low temperature. Methanol conversion, calculated by summing up the yields of C-containing light products at 380°C, was 55%, higher than that registered with MgO at the same conditions (15%). Moreover, as a general remark, higher yields of both CO_2 and CH_4 were observed compared to MgO; these compounds formed in amounts comparable to CO (Figure S6), also accompanied by a significantly increased yield of H_2. Indeed, Mg/Fe/O proved to be very active in the dehydrogenation of methanol to formaldehyde and in the subsequent dehydrogenation of the aldehyde to CO.[25] Moreover, this material showed the ability to catalyze the reaction of formaldehyde dimerization to yield methylformate, and the following decomposition into CH_4 and CO_2. Formic acid may also form, either through the Cannizzaro reaction or through the oxidation of formaldehyde by Fe^{3+} cations, but with formic acid being then easily decomposed to CO_2 and H_2. The progressive decrease in H_2 and CO_2 formation, shown in Figure S6, confirmed the initial presence of this latter reaction, being however less and less important over time, due to the progressive reduction of Fe^{3+} to Fe^{2+}.

The effect of contact time on FU conversion and products distribution was investigated in order to identify primary and secondary reaction pathways; results at 380°C are shown in Figure 8.

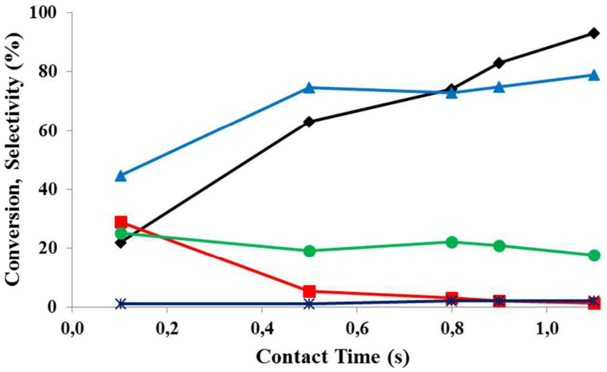


Figure 8. Effect of contact time on FU conversion and products selectivity, catalyst Mg/Fe/O. Feed composition: FU 5%, CH_3OH 50%, N_2 45%; pressure 1 atm, temperature 380°C, reaction time 1 h. Symbols: ♦ FU conversion, ■ FAL selectivity, ▲ MF selectivity, ∗ CPs selectivity, ● C-loss.

On Mg/Fe/O, as also observed for MgO, the main primary product was FAL; its selectivity, however, rapidly declined because it was converted to MF even with a low contact time. CPs were detected only at high contact time, but with a selectivity lower than 2%.

Although in the liquid phase the production of FAL using noble metal-based catalysts is quite common,[42,43,44] only a few studies report on the selective formation of MF from the hydrogenolysis of FU,[19,23,45] while none reports on a continuous gas-phase process using inexpensive solid base catalysts. Very recently, Vlachos and coworkers[20-23] studied the catalytic hydrogenation of FU by means of H-transfer over Ru-based catalysts; they determined the effect of alcohols as reacting solvents on the production of MF and performed DFT studies to explore reaction mechanisms. Moreover, they studied the liquid-phase reduction of FU over homogeneous Lewis acid-Ru/C catalysts.

Our results, obtained using inexpensive Mg/Fe/O catalysts, confirm the possibility of setting up a cascade upgrading of FU to MF by using a continuous system and avoiding noble metal catalysts.

It is well known that the hydrogenation of the aldehydic group can occur on basic catalysts through the H-transfer reaction. On homogeneous, strong Lewis basic sites, the reducing alcohol adsorbs with oxygen and hydrogen atoms to the metal ion and oxo-ion site, respectively. The carbonyl group coordinates by hydrogen-bonding to this surface hydroxyl group rather than to the metal, and the reaction proceeds via a cyclic seven-membered transition state;[3,24] an analogous mechanism was also suggested to occur with heterogeneous catalysis.[46]

Thus, in our conditions, MgO easily carries out the reduction of FU to FAL via the MPV reaction, consistently with the published data in liquid phase. In addition, the catalytic activity of MgO for the hydrogenolysis of FAL to MF is significantly enhanced with the addition of Fe. In particular, at 380°C MF selectivity increases from 2 to 79%. The previously reported characterization of Mg/Fe/O[40] indicated that this catalyst shows Lewis-type acid features, associated with the presence of guest Fe^{3+} metal cation. Moreover, this material shows a strong dehydrogenating capacity.

Therefore, it can be hypothesized that the excellent performance of Mg/Fe/O in FU reduction to MF may be correlated with its higher dehydrogenation properties[25] and Lewis acidity, both properties having been introduced in MgO because of Fe addition[40].

Also in this case, experiments were carried out by feeding either FU or FAL with H_2 or without any co-reactant (Table S3). Results demonstrate that the Lewis acidity shown by Mg/Fe/O might be responsible for the formation of heavy compounds; in fact, the feeding of FU only led to a non-negligible FU conversin, but with formation of heavy compounds only (C-loss was 100%). This confirms that the accumulation of carbonaceous residua observed during FU reduction with methanol was also due to FU transformation into heavy compounds. However, when also H_2 was co-fed, some FU was converted to MF, although with 25% selectivity only. In the case of the experiment carried out by co-feeding FAL and H_2, conversion of FAL was total, with 42% selectivity to MF and 53% C-loss.

Preliminary experiments were carried out aimed at understanding the role of the Fe-containing phase; the catalytic behavior of MgO and Mg/Fe/O was compared with that of Fe_2O_3 and of a catalyst prepared by mixing MgO and Fe_2O_3, with Mg/Fe atomic ratio equal to 10; results of catalytic tests carried out at 380°C are shown in Table S4. Hematite turned out to be an active catalyst, but quite unselective, with most of FU converted to heavy compounds (C-loss 88%, with FU conversion 73%). However, the catalyst prepared by mixing MgO and Fe_2O_3 showed a catalytic behavior similar to that of Mg/Fe/O (with Mg/Fe atomic ratio 10). This suggests that the incorporation of Fe in the structure of MgO is not a necessary requisite to prepare an active and selective catalyst for FU reduction to MF with methanol.

3.4. Catalyst stability

Catalyst stability has been examined by conducting catalytic tests on both MgO and Mg/Fe/O for 3 h at the optimized temperature (250°C and 380°C, respectively); moreover, the regeneration of catalysts was studied by means of thermal treatments. Figures 9 and 10 summarize the results obtained.

On MgO (Figure 9a), FU conversion significantly decreased during the first hour of reaction (from 54% to 44%), then a much slower reduction was observed. Conversely, FAL selectivity remained almost constant; no other product was formed, and the selectivity to FAL slightly lower than 100% after 1 h, was due to a small C-loss (5%). The deactivation observed on this catalyst may have different explanations. First, it may be related to a change in the surface area; indeed, we observed a decreased surface area with time of stream from 173 m^2/g to 163 m^2/g. Moreover, based on the TGA/DTA and Raman results previously reported, this decreased activity might, in part, be ascribed to the adsorption of some methanol/formaldehyde oligomers onto the catalyst surface. Since the efficiency of the H-transfer reaction is related to the presence of basic sites in the catalyst, the interaction of these molecules with MgO may decrease the reaction activity.[47]

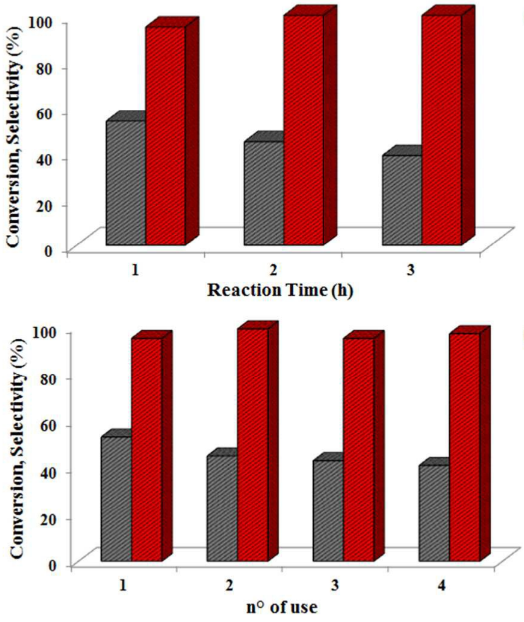


Figure 9. Effect of the reaction time (a) and regeneration treatment (b) on FU conversion and products selectivity with MgO. Feed composition: FU 5%, CH_3OH 50%, N_2 45%; pressure 1 atm, temperature 250°C, overall gas residence time 1.1 s. Legend: ■ FU conversion, 🟥 FAL selectivity. In the case of Figure (b) results were taken after 1 h reaction time.

After the reaction carried out at 250°C for 3 h, the reaction feed was switched to flowing air and the catalyst was heated for 2 h at 450°C in order to perform MgO regeneration. After treatment, the system was switched back again to the reaction feed at 250°C. Figure 9b shows FU conversion and FAL selectivity in the four regeneration tests performed on MgO. FU conversion was reduced by 9% following the first regeneration treatment (2nd use), thus suggesting the presence of a partial irreversible deactivation phenomenon which is probably connected with the loss of surface area. Further increasing the number of regeneration treatments did not lead to a further decline of conversion. Also in this case, FAL was the only product formed, and slight differences in FAL selectivity, shown in Figure 9b, were due to small variations in C balance (C-loss between 0 and 4%). In conclusion, with the exception of a slight irreversible deactivation, MgO resulted stable and the slight deactivation observed could be partly overcome with the catalyst regeneration.

The effect of reaction time on Mg/Fe/O performance is shown in Figure10a, which illustrates the time-on-stream behaviour. During the first hour of reaction, the reduction of FU generated MF as the predominant product with only traces of FAL. The material showed very high conversion, but a significant deactivation of the catalyst was observed and FU conversion decreased rapidly from the initial value of 93% down to 42%, which was registered in the third hour of reaction. As expected for a consecutive reaction pattern, deactivation caused an increase in selectivity to the kinetically primary product, FAL, and a corresponding decrease in selectivity to the secondary product, MF. C-loss was close to 20% during all the experiment time.

Causes of catalyst deactivation may include collapse of the surface area, coking, or basic sites poisoning. Nevertheless, in our case, the previously reported TG analysis suggests that deactivation may be attributed mainly to the deposition of carbonaceous residua on the surface of the catalyst.

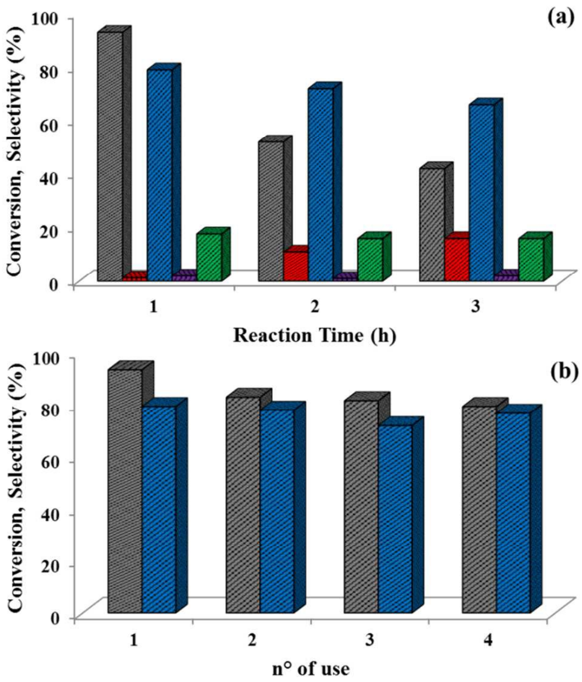


Figure 10. Effect of the reaction time (a) and regeneration (b) on FU conversion and products selectivity with Mg/Fe/O. Feed composition: FU 5%, CH_3OH 50%, N_2 45%, pressure 1 atm, temperature 380°C, overall gas residence time 1.1 s. Legend: ■ FU conversion, 🟥 FAL selectivity, 🟦 MF selectivity, 🟪 CPs selectivity, 🟩 C-loss. In the case of Figure (b) results were taken after 1 h reaction time.

In order to verify the possibility to regenerate the material and recovery the initial activity, catalytic tests were conducted on the used catalyst after the regeneration treatment, carried out with air at 450°C for 2 h. The data reported (Figure 10b) indicate that the treatment led to an almost complete recovery of the original catalytic behaviour. Also in this case the major variation in activity was shown after the 1st use; after the 2nd use, in fact, both FU conversion and MF selectivity at the start of the next cycle were similar to those observed during the previous cycle.

Conclusions

Biomass-derived FU was converted to MF, using methanol as the hydrogen source, via a tandem MPV reaction involving hydrogenation and hydrogenolysis in sequence. MgO and Mg/Fe/O catalysts were active for the H-transfer reaction in the gas-phase with a continuous-flow system; MgO was selective to FAL, whereas Mg/Fe/O was shown to be highly active and selective for MF production. Using Mg/Fe/O, the quantitative conversion of FU with 83% yield of MF was obtained. Due to their high activity, MgO and Mg/Fe/O offer an alternative to FAL and MF production from FU without the need for high pressure H_2 and precious metal catalysts.

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HIGHLIGHTS:

The one-pot hydrogenolysis of furfural to 2-methylfuran in the gas-phase is catalysed by Mg/Fe mixed oxide using methanol as the H-transfer reactant.