CaO as a cheap, eco-friendly material for the continuous-flow, gas-phase, catalytic transfer hydrogenation of furfural with methanol

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ABSTRACT

The hydrogenation of biomass-derived molecules is a key reaction in upgrading 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 under high pressure and precious noble metal catalysts. In this work, the continuous-flow, selective conversion of biomass-derived furfural (FU) into furfuryl alcohol (FAL) was investigated, using methanol as the H-transfer agent and CaO-based catalysts. CaO is easily prepared by thermal decomposition of the carbonate precursor and has proved to be a suitable material for the reduction of furfural into its unsaturated alcohol, thus allowing selective H-transfer from methanol to the substrate with relatively good conversion and very high selectivity. The decomposition temperature of the precursor is one of the fundamental parameters which allows the obtainment of the catalyst, albeit with a low surface area, which maintains an adequate number of defects and basic sites on the surface. The feed composition rich in methanol allows to avoid saturation of the active sites by the substrate to minimize the oligomerization reactions which decrease the selectivity and deactivate the catalyst. Dedicated characterizations have proven the *in-situ* formation of a partially carbonated CaO phase during the first hour of time on stream. The presence of the two phases improves the catalyst activity and stability leading, in the best reaction conditions, to high FAL productivity ($5.37 \bullet 10^{-4}$ mol$_{FAL}$/h m^2).

1. Introduction

Catalytic conversion of bio-derived building blocks molecules for the production of high-added value chemicals represents one of the most important approaches to efficiently reduce the dependence on fossil resources [1,2]. In the last years, furfural (FU) has been considered one of the most attractive platform molecule deriving from renewable lignocellulose feedstock due to the possibility to upgrade it to a wide plethora of products and intermediates with application in both fuel manufacturing and polymer production [3,4]. FU is one of the most accessible bioderived molecules, since it is produced at large scale through well-established industrial processes [3,5–7]. FU upgrading strategies includes the hydrogenation of its carbonyl group into the corresponding furfuryl alcohol (FAL), which is used in both the polymer and intermediate industries [8], and into 2-methylfuran (MF) (Scheme 1).

The so-called Meerwein–Ponndorf–Verley (MPV) mechanism, may allow the highly chemo-selective reduction of the carbonyl groups of bio-based substrates using light alcohols as hydrogen donors, becoming an alternative methodology to the traditional hydrogenation with high-pressure molecular hydrogen [9–12].

CTH (catalytic transfer hydrogenation) is an emerging approach for the selective reduction of furfural to FAL and MF, since good selectivities of the two products can be achieved, by using an alcohol as reducing agent without interfering with the chemical structure of the furanic ring during the upgrade [13,14]. Indeed, one of the major issues related to the use of traditional H_2-mediated reduction processes is related to the low control of the selectivity, which leads to the undesired reactions, such as hydrogenation and/or opening of the furanic ring. Thus, the development of effective catalysts for furfural reduction by means of CTH has attracted a big deal of attention in the past years. Several classes of catalyst have been found out to be efficient in the CTH-mediated

upgrade of furfural, such as pure metal oxides, mixed ones and supported precious metals. Metal-oxides as CuO are reported for the CTH of FU using methanol as H-donor [15]. Alkali and alkaline earth oxides (MgO, CaO) [16,17], mixed oxides (Mg/Al, Mg/Ga, Mg/In, Ga/Al, Mg/Al/Zr, Co/ Al, Ni/Al, Cu/Al) [18–23], and amphoteric oxides (Al_2O_3) [24], as well as zeolites or mesoporous materials, sometimes incorporating metal ions acting as Lewis acid sites (Al^{3+}, Zr^{4+}, Sn^{4+}) [25,26] are claimed in literature for this reaction. In particular, MgO, CaO, and SrO are solid-base catalysts used for a number of base-catalyzed reactions: the isomerization of alkenes and alkynes, aldol condensation, Knoevenagel condensation, nitroaldol condensation, Michael addition, conjugate addition of alcohols, nucleophilic ring opening of epoxides, oxidation reactions, and Si-C bond formation [27]. The surface basic strength follows the order MgO < CaO < SrO. Among the former, MgO has been studied most extensively, probably because samples of definite structure with high surface area are prepared much more easily by thermal pretreatment than are CaO and SrO samples [28].

In light of these observations, with the goal to further explore the potential of cheap and easily available CaO in the frame of furfural reduction by means of methanol-mediated CTH, the present work aims to evaluate the use of such material as cheap, non-toxic, catalyst for the continuous gas phase furfural upgrade. Indeed, previous studies have demonstrated the possibility to use MgO-based catalysts in both liquid and gaseous phase, but in this transition a big deal of attention must be devoted to the optimization of the reaction parameters to maximize the yield into the desired products and keep as high as possible the carbon balance. Thus, alongside to the synthesis and characterization of the catalytic materials, a big deal of attention has been devoted to the fine tuning and optimization of the operative conditions to achieve the best catalytic performances of Ca-based materials.

2. Experimental

2.1. Catalyst preparation

Calcium-based materials were prepared by means of thermal decomposition of $CaCO_3$, synthesized by precipitation. In detail, a aqueous solution containing the corresponding metal nitrate (1 M), Ca $(NO_3)_2 \cdot 4H_2O$ (Sigma – Aldrich) was added dropwise into a 1 M Na_2CO_3 (Sigma-Aldrich) solution at controlled temperature and pH (55 °C and 10.5, respectively). During addition, a white precipitate was formed and after the addition of the Ca-containing solution, 1 h aging treatment was carried out in order to increase the crystallinity of the formed phase. The obtained solid was then filtered and washed with warm water (40 °C, 2 L per gram of precipitate) to remove the residual impurities. Lastly, the washed solid was dried at 120 °C in static air overnight and then calcined in static air at temperature between 500 °C and 900 °C (10 °C/ min) in order to obtain the decomposition of the precursor.

2.2. Catalyst characterization and reaction general procedure

Catalysts have been completely characterized by means of powder-XRD, BET, Temperature Programmed Desorption (TPD with NH_3 and CO_2) and thermogravimetric/differential thermal analyses (TGA/ DTA). The methodologies as well as the detailed description of the procedure

of catalytic tests are reported in a dedicated chapter in the electronic Supplementary Information (ESI).

For the sake of clarity, all the reactions were performed in a continuous-flow, fixed-bed, micro-reactor in order to investigate and optimize the effect of the main reaction parameters (i.e. temperature, contact time over the catalysts and long-time stability tests). Finally, FU Conversion, product selectivity, C-loss and product yield were calculated as follows:

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

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

$$C - Loss = 100 - \sum_i ProductSelectivity$$

$$ProductsYield = \frac{\dot{n}^{out}_{product}}{\dot{n}^{in}_{furfural}}$$

3. Results and discussion

3.1. Bulk features of the catalyst

The $CaCO_3$ precursor, prepared according with the procedure reported in the experimental section, was calcined at different temperatures (namely 500, 700 and 900 °C) to obtain catalysts with different chemical and surface properties. Table 1 resumes the characteristics in terms of crystalline phases and surface properties as a function of the calcination temperature.

The evolution of crystalline phases was evaluated by XRD analyses (Fig. 1) which demonstrates that the dried precursor consisted in a mixed phase of two polymorphs of $CaCO_3$, calcite and vaterite. Treatment at 500 °C leads to the complete conversion of the vaterite into the calcite polymorph that is the most thermodynamically stable, in fact it was observed the disappearance of the reflexes related to vaterite with the concomitant growth of the calcite' peaks intensity. This is in agreement with the literature that reports the polymorph conversion at temperature higher than 330 °C [29,30]. The two samples treated at higher calcination temperatures, i.e. 700 °C and 900 °C, are characterized by the presence of highly crystalline CaO (lime). Interestingly, the thermogravimetric analysis (TGA) performed on the $CaCO_3$ precursor (Fig. S1) underline a 44 % of weight loss between 550 °C and 750 °C characterized by an endothermic peak showed by the differential thermal analysis (DTA), characteristic of the decomposition process. This value corresponds to the theoretical CO_2 loss due to the decomposition of the carbonate specie to CaO. This clearly explain the different XRD patterns of the catalysts obtained at calcination temperature higher than 500 °C. The thermal treatment is also responsible of the relatively low SSA (< 5 m²/g). These values are in agreement with those reported in literature for CaO synthesis by decomposition of $CaCO_3$ precursor [31, 32]. Increasing the calcination temperature from 700° to 900°C, a small decrease in surface area was observed which is probably the cause of the marked decrease in basic sites (Table 1). In fact, the increase of the $CaCO_3$ decomposition temperature may allow to a gradual increase in
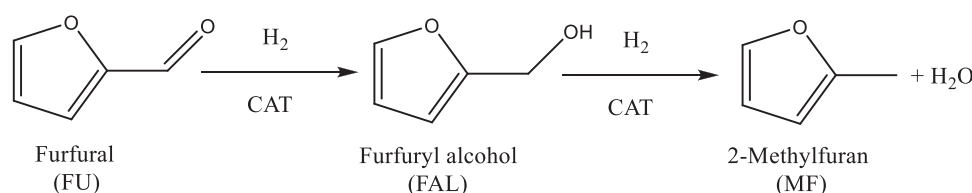
Scheme 1. Conversion of Furfural (FU) into Furfuryl alcohol (FA) and 2-methylfuran (MF).

Table 1

Crystalline phase, specific surface area and acid/base content of the $CaCO_3$ precursors and CaO catalysts calcined at different temperature.

| Material	Calcination Temperature (°C)	Crystalline phase (XRD)	Surface area (SSA) m²/g	Total acidity (mmol/g)[a]	Total basicity (mmol/g)[b]	Total basicity (mmol/g)[c]	CO₂ T desorption (°C)[d]
Precursor	120	CaCO₃ (Vaterite+Calcite)	1.7	0	0	-	-
CaCO₃ 500	500	Calcite (Calcite)	1.4	0	0.22	-	-
CaO 700	700	CaO (Lime)	2.4	0	2.57	2.49	700
CaO 900	900	CaO (Lime)	2.3	0	1.10	1.13	700

[a]Determined by NH3-TPD.
[b]Determined by irreversible adsorption of acrylic acid.
[c]Determined by CO_2-TPD.
[d]Temperature related to the maximum of the desorption peak profile.
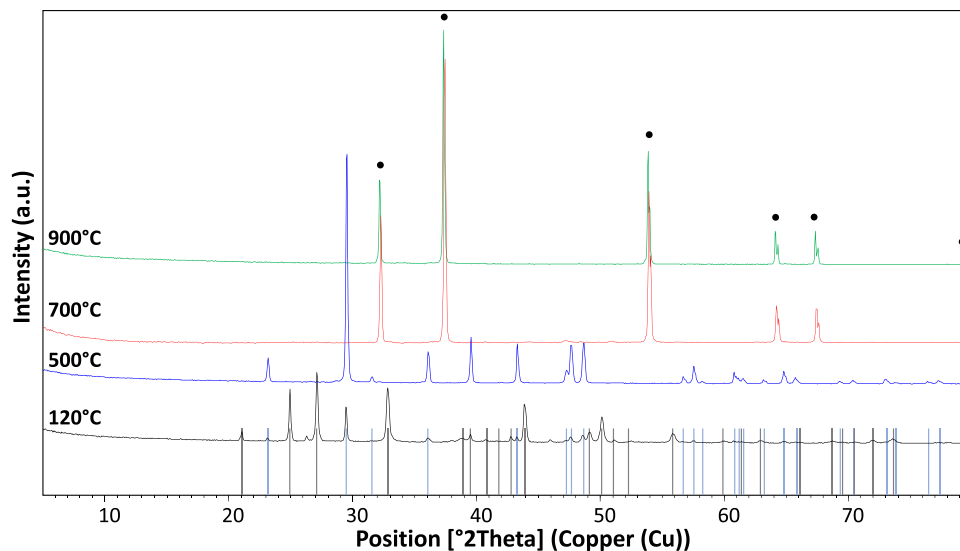
Fig. 1. XRD patterns of the dried CaO precursor and of the samples calcined at different temperature. Reference patterns: (•) CaO, (—) $CaCO_3$ Vaterite, (–) $CaCO_3$ Calcite.

CaO crystallite size with minimum lattice defects and uniform propagation of cubic unit cells throughout the space that results in a decrease of accessible basic sites number [30]. A further confirmation of what has been said can be attributed to the fact that it is only the number of basic sites that changes and not their strength since CO_2 desorption temperature is the same for the samples calcined at 700 and 900 °C respectively.

3.2. Catalytic transfer hydrogenation of furfural over CaO catalyst

The catalytic transfer hydrogenation of FU using methanol as H-donor was carried out testing the synthesized catalysts in a continuous fixed bed tubular reactor.

The precursor calcination temperature plays a role in the amount and distribution of basic active sites on the catalyst surface. For this reason, materials calcined at different temperature were tested in order to identify the best condition to obtain the most active and selective material. The catalytic tests were conducted at 350 °C, contact time of 1 s, atmospheric pressure and with the following feed composition (expressed as mol. %): FU 5 %, CH_3OH 50 %, N 45 % [33]. In Fig. 2, FU conversion, FAL selectivity and yield are plotted as a function of the catalyst calcination temperature. The sample treated at 500 °C, presenting a $CaCO_3$ calcite crystalline structure, shown similar activity in terms of FU conversion compared to CaO (around 15 %) but with very low FAL selectivity (19 %), being predominant the reactants degradation to heavy carbonaceous deposits formed over the catalyst surface. The two samples treated at higher calcination temperature afforded
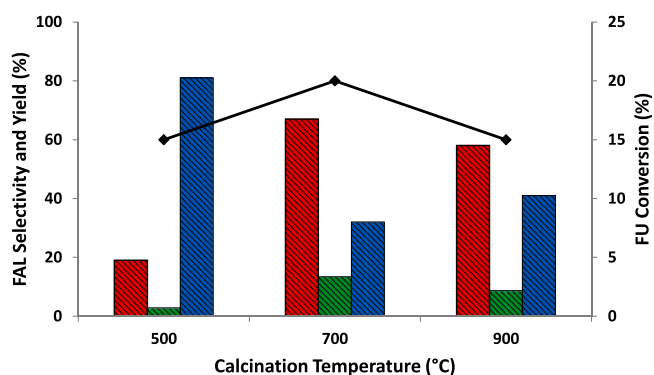

Fig. 2. Obtained trends in terms of FU conversion (secondary axis) and FAL yield and selectivity (main axis) as a function of the calcination temperature. Feed composition (mol. %): FU 5 %, CH_3OH 50 %, N_2 45 %; Pressure 1 atm, reaction temperature 350 °C, overall gas residence time 1.0 s. Symbols: ◆ FU conversion, ■ FAL selectivity, ■ FAL Yield, ■ C-loss.

superior catalytic performances in terms of FAL selectivity and yield. In particular, the catalyst calcined at 700 °C showed the best performances since the highest FU conversion, FAL selectivity and yield were obtained (20 % of FU conversion, 67 % and 13 % of FAL selectivity and yield, respectively). Furthermore, a considerable decrease in carbon loss was observed probably due to the greater basic sites density over the surface, thus enhancing the activation of methanol this way limiting FU

oligomerization. Another aspect that can contribute to the higher activity of the sample calcined at 700 °C is the presence of greater defects (such as kink, step and corner defective sites), which appears to be in fact a consequence of the lower degree of crystallinity. These considerations are fully in agreement with the literature. [34].

This preliminary screening allowed to identify the best decomposition temperature of the precursor for the formation of the most active and selective crystalline phase which was used to study the influence that the different operating parameters have on both FU conversion and products distribution.

3.3. Effect of the reaction temperature

At first it was investigated the effect of reaction temperature in the range between 250 and 400 °C at fixed contact time (1 s) for a time of stream of 6 h. In Fig. 3 are plotted results in terms of FU conversion, MF selectivity, FAL selectivity and yield as a function of reaction temperature. Once the stationary state is reached (after 1 h) the values remain almost constant, therefore the results shown represent the average of the hourly values between the second and sixth hour of reaction. The obtained results showed that at low temperature (250 °C) the transfer hydrogenation reaction does not proceed since no FU conversion happened. By increasing the reaction temperature, the catalyst became able to promote the desired reaction, therefore FU conversion progressively increased up to 42 % registered at 400 °C. However, despite the highest conversion obtained at the highest temperature tested, the results obtained clearly shows that FAL can be further reduced to MF, while very high reaction temperature (i.e. 400 °C) lead to unselective decomposition of the substrate leading again to an increased C-loss.

Interestingly, a complete selectivity to FAL was obtained with CaO by working at 300 °C while, it progressively decreases by increasing the temperature up to 400 °C (being 92 % at 350 °C and 48 % at 400 °C). In these conditions a concomitant increase of the C-Loss was observed. This C-Loss was ascribed to the production of heavy carbonaceous compounds over catalyst surface, which could arise from thermal degradation processes of the furanic intermediates at high temperature. Similar phenomena have been described in our previous works. [35] To further confirm that carbonaceous species are formed over CaO catalyst, TGA/DTA analysis were performed over the spent catalyst used in the reaction at different temperature (Fig. 4).

The thermal analyses showed that the spent catalysts undergo consistent weight loss during thermal analysis if compared to the fresh CaO calcined at 700 °C (black line). Taking into account the exothermic peak registered at the differential thermal analysis coupled with the
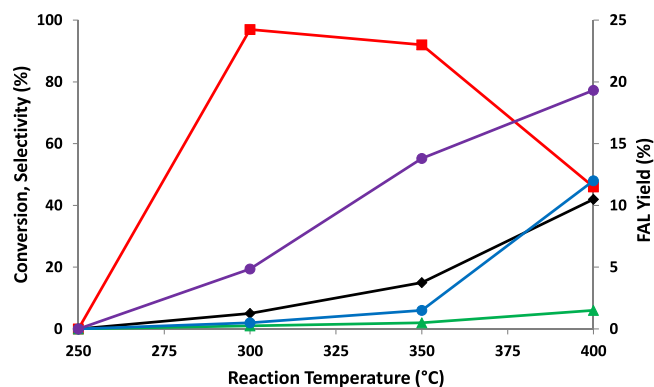

Fig. 3. Effect of reaction temperature over FU conversion FAL selectivity and Yield. Feed composition (mol. %): FU 5 %, CH$_3$OH 50 %, N$_2$ 45 %; Pressure 1 atm, reaction temperature 250÷400 °C, overall gas residence time 1.0 s. Symbols: ◆ FU conversion, – FAL selectivity, ▲ MF selectivity, ● FAL yield, ● C-loss. The values represent the average of the results obtained between second and sixth hour of time-on-stream.
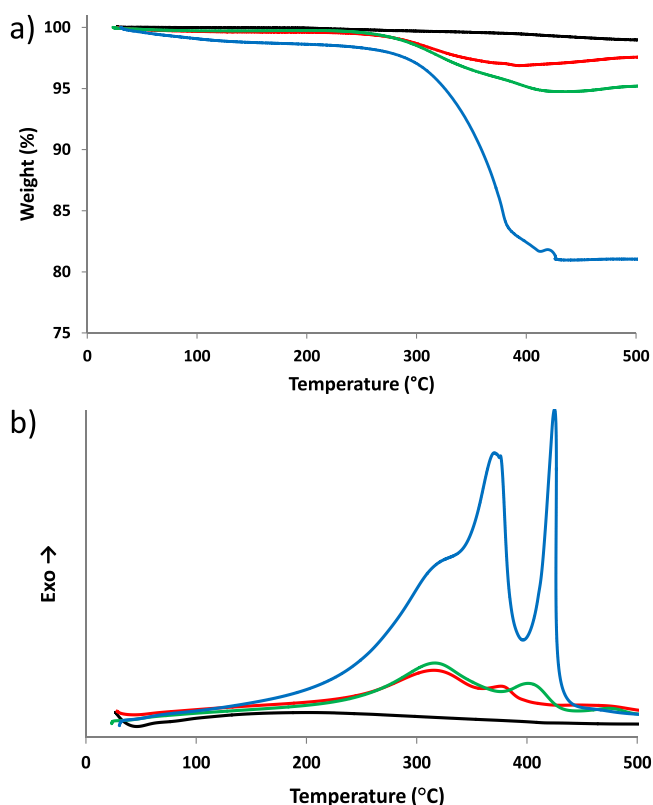

Fig. 4. a) Thermogravimetric analysis (TGA) and b) differential thermal analysis (DTA) performed in air of: (—) fresh CaO calcined at 700 °C; spent CaO used in catalytic test (–) at 300 °C, (–) at 350 °C and (–) at 400 °C.

thermogravimetric analysis, it was possible to conclude that the registered weight loss was related to the combustion of the carbonaceous species formed over the catalyst surface.

Analysing the thermograms it is possible to highlight that, at different reaction temperatures, carbon deposits of different nature are formed. In fact, after six hours of reaction at 300 °C the deposits burn between 300 and 400 °C, index of low molecular weight oligomers; at this temperature it is known that formaldehyde, produced over catalyst surface as a consequence of methanol dehydrogenation, could form some polyoxomethylene oligomers that are removed through combustion at temperature between 250 °C and 350 °C [35]. As the reaction temperature is increased, the progressive formation of two very intense exothermic peaks is observed, one above 380 and the other above 400 °C, index of the formation of polymers with higher molecular weight deriving from condensation reactions of the FU with the FAL [35]. These hypotheses are in agreement with the literature [36] where it is reported that the condensation products of these molecules show combustion peaks between 350 and 460 °C.

As far as the formation of MF is concerned, which is known to be the product of the consecutive hydrogenolysis of FAL, small quantity of this product was detected for reaction temperature equal or higher than 350 °C, being the highest value 6 % obtained at 400 °C.

The reaction temperature of 350 °C appears to be the best in terms of conversion of FU and selectivity to FAL; a further confirmation is given by the test with a contact time of 0.5 s (Fig. S2) in which at 350 °C total selectivity in FAL is reached.

3.4. Effect of the contact time

Following the findings reported in the previous paragraphs, we decided to better investigate the reaction scheme by varying the contact time over the selected catalyst by working at 350 °C. In detail, with the

aim of working with the same linear space velocity of the gaseous stream, the volume of the catalyst was changed accordingly with the desired range of contact time (between 0.5 s and 2.0 s).

FU conversion and products distribution trends on the respect of different contact times are reported in Fig. 5. The data were obtained through the average of results obtained between the 2nd and the 6th hour of time on stream. At the lowest contact time (0.5 s) total FAL selectivity was obtained proving the primary nature of this products. Interestingly, by progressively increasing the contact time, some consecutive reactions kick in leading to a slowly, but progressive decrease of FAL production favoring the formation of both MF (minor contribution, with a selectivity which never exceeds 2 %) and heavy carbonaceous compound over catalyst surface, whose amount increased by increasing the contact time. Indeed, 100 % of FAL selectivity with no C-Loss were obtained at 0.5 s, while a final value of 73 % in FAL selectivity and 25 % of C-Loss were registered at 2.0 s. The reason of this C-Loss increase can be explained by the tendency of FAL to be subject to oligomerization phenomena. [37,38]. Finally, as far as FU conversion is concerned, it has to be highlighted a progressive increase of this parameter by increasing contact time: at 0.5 s the registered conversion was around the 10 % and then increase up to the value of 25 %, registered at the longest residence time (2.0 s).

From the results obtained it is possible to state that the reduction reaction of FU with methanol on CaO can follow the classical MPV (Meerwin-Poondorf-Varley) mechanism (Scheme 2). This mechanism involves the concomitant adsorption and activation of both the carbonyl-containing substrate and the hydrogen donor over different centers of the catalyst surface, via a six-membered ring intermediate that leads to the formation of the target product [39].

In the specific case, it has been also highlighted the consecutive nature of MF and the oligomer derived by FAL degradation, in fact the increase of their selectivity is linear with the residence time increase. Scheme 3 depicts the CTH reaction scheme by working in continuous flow and gas-phase conditions summarizing the main information gathered so far.

3.5. Effect of time on stream

As mentioned above, the steady state is reached in about an hour, therefore, during the reaction time, variations in terms of conversion of FU and selectivity in the products are observed. CaO produced for thermal degradation of the precursor at 700 °C was tested for 6 h at 350 °C and residence time of 1.5 s. The results of this test are reported in Fig. 6. The analysis of this test revealed important features: firstly, catalyst behavior in the first hour of reaction is slightly different if compared to the following hours, showing different trends in conversion
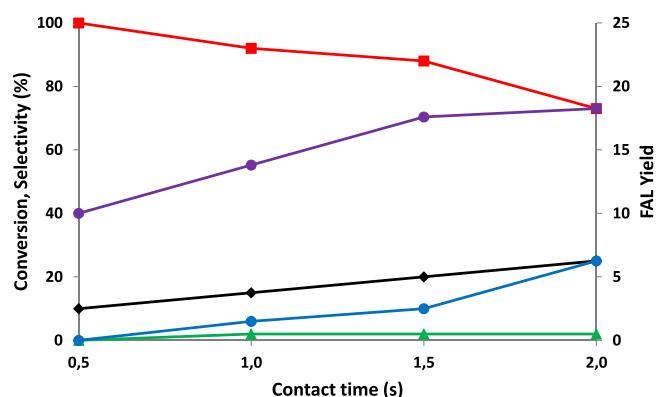

Fig. 5. FU conversion FAL yield and products selectivity as a function of residence time. Feed composition: FU 5 %, CH_3OH 50 %, N_2 45 %; Pressure 1 atm, reaction temperature 350 °C, overall gas residence time 0.5÷2.0 s. Symbols: ◆ FU conversion, ■ FAL selectivity, ▲ MF selectivity, ● FAL yield, ● C-loss.

of reactant and products selectivity. In particular, ~30 % of FU conversion, ~ 60 % of FAL selectivity and 34 % of carbon-loss were initially detected while, starting from the second hour, both a decrease of FU conversion (down to 20 %) and an increased FAL selectivity (85 %) was observed with a concomitant strong decrease of C-loss. This behavior suggests either that a selective deposition of heavy carbonaceous compounds over the most active, defectively coordinated, sites of the catalyst or some other structural changes of the material is rapidly occurring in the first 60 min of reaction. The second important feature revealed by this study is that the catalytic performances were found to be almost constant since the 2nd hour of time on stream. Indeed, products distribution showed very small fluctuation throughout the last 5 h of reaction. The very high stability of the CaO system could be considered a crucial improvement over the behavior showed by an analogous basic material, i.e. MgO, previously tested by our group in similar operative conditions [35]. In particular, the latter was found to be very active and selective in the production of FAL at low-medium temperature, but it also suffered of a progressive deactivation due to the continuous deposition of heavy compounds over the surface.

Interestingly, the peculiar stability of this material was proved also in non-optimized reaction conditions. As an example, Fig. 7 shows the results obtained by working at different contact time at 350 °C. In all the tests performed, FU conversion strongly decreases after the first hour reaching stability since the second hour of reaction. Accordingly, also FAL selectivity of the tests performed at 1.0 and 2.0 s behave at in the same way of the above reported test conducted at 1.5 s with an initial increase until stability is reached after the second hour of reaction. All these results suggested that the catalyst undergoes some changes during the time on stream, as further corroborated by detailed XRD analysis of the spent catalysts.

To investigate in depth the reasons behind this peculiar catalytic behavior, the analytical setup was implemented with an online GC to quantify the evolution of incondensable light products. As a matter of fact, at the reaction conditions applied in the CTH of FU, methanol may undergo to a series of dehydrogenation/dehydration/decomposition reactions as depicted in Scheme 3, finally leading to H_2, CH_4, CO_2 and CO as main products [35,39,40]. Briefly, at high temperature, the endothermic dehydrogenation of methanol can be promoted leading to the formation of formaldehyde and H_2, while the former may behave as both alkylating agent of activated substrate or it may decompose forming both CO and H_2 (Reaction 1 and 2). Otherwise, two adsorbed CH_2O molecules may disproportionate, in the presence of water in the reaction media, to formic acid and methanol (Cannizzaro reaction 6) finally leading to the possible formation of methylformate (reaction 4). The decomposition of both formic acid and methyl formate leads to the production of CO_2 + H_2 (reaction 7) and CO_2 + CH_4 (reaction 5), respectively. Finally, in the presence of a suitable catalyst and water, Water Gas Shift (WGS, reaction 3) and methanol reforming (reaction 8) can play a role in the final products distribution.

$$CH_3OH \rightarrow H_2CO + H_2 \tag{1}$$

$$CH_2O \rightarrow CO + H_2 \tag{2}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{3}$$

$$2CH_2O \rightarrow CO_2 + H_2 \tag{4}$$

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

$$2CH_2O + H_2O \rightarrow CH_3OH + HCOOH \tag{6}$$

$$HCOOH \rightarrow CO_2 + H_2 \tag{7}$$

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \tag{8}$$

In the tests performed with CaO at 350 °C at different contact time
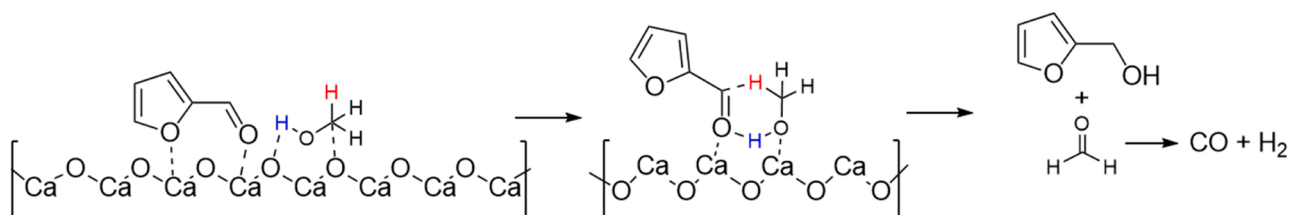
Scheme 2. Proposed reaction mechanism for CTH of Furfural with methanol over CaO catalyst in the gas phase.
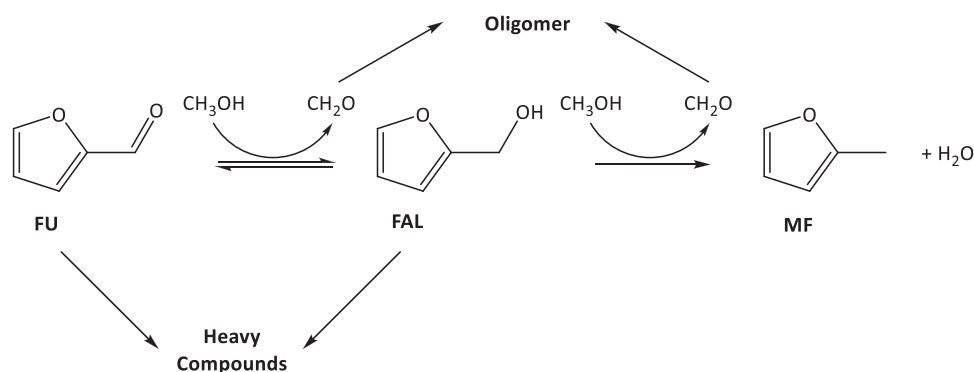
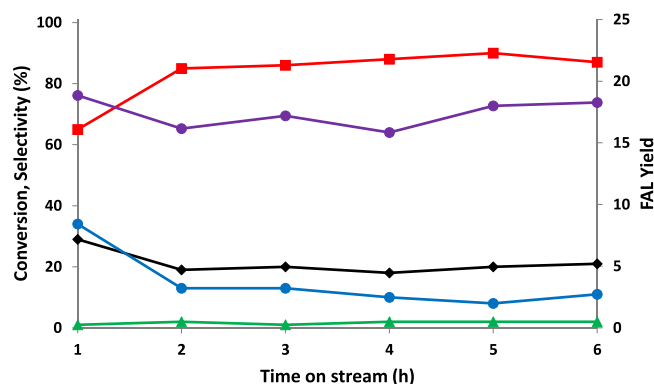**Scheme 3.** FU reduction scheme via CTH with methanol in the gas-phase.

Fig. 6. Effect of the reaction time over FU conversion and products distribution. Feed composition (mol. %): FU 5 %, CH_3OH 50 %, N_2 45 %; Pressure 1 atm, reaction temperature 350 °C, overall gas residence time 1.5 s. Symbols: ◆ FU conversion, – FAL selectivity, ▲ MF selectivity, ● FAL yield, ● C-loss.
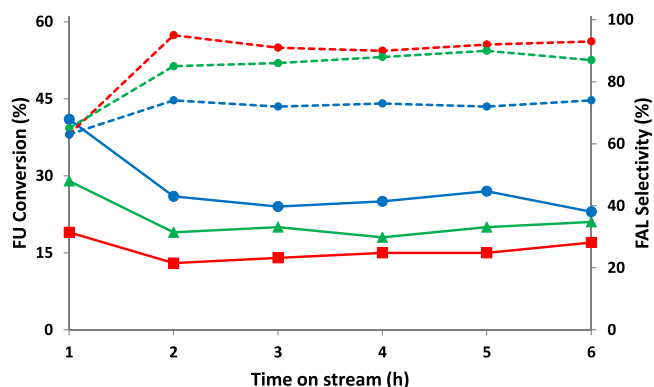
Fig. 7. Effect of the reaction time over FU conversion and FAL selectivity at 350 °C and different contact time. Feed composition (mol. %): FU 5 %, CH_3OH 50 %, N_2 45 %; Pressure 1 atm, reaction temperature 350 °C, overall gas residence time 0.5÷2.0 s. Symbols: FU Conversion (bold line): (–) tau 1.0 s, (–) tau 1.5 s and (–) tau 2.0 s; FAL Selectivity (dotted line): (–) tau 1.0 s, (–) tau 1.5 s and (–) tau 2.0 s.

CO, CO_2, CH_4 and H_2 were detected. In Figure S 3-A, -B, -C are reported the amount of these incondensable products formed as a function of the time on stream at different contact time (1.0, 1.5 and 2.0 s, respectively). The analysis of the plotted results again clearly shows that the catalyst underwent some modification during the first hour of reaction. Indeed, as already discussed for the conversion of furfural and for the condensable products distribution, also the light compounds distribution change between the first and the following hours on stream. Indeed, during the first hour of reaction H_2 was detected as the main light compound, roughly ten times higher compared to any other light products observed. Then, starting from the second hour, product distribution dramatically changed: the detected amount of H_2 dropped, CO and CH_4 were almost produced in the same quantity of the first hour, while the amount of CO_2 progressively grew up very rapidly. Taking into account these information, and considering that CaO is known to interact and absorb carbon dioxide to form carbonate species it could be hypothesized that during the first hour of reaction the catalyst undergoes recabonation process. In detail, CO_2, produced as a by-product of methanol (or formaldehyde) degradation over the catalyst surface,

was trapped by the latter bringing to a structural modification. In order to gain evidence that could corroborate the formulated hypothesis, XRD and TGA analysis were carried out over the used catalyst.

Fig. 8 compares the diffraction patterns of the spent catalyst, unloaded from the reactor after the CTH test perfromed at 350 °C and contact time of 1.5 s with the fresh CaO obtained through the calcination of the precursor at 700 °C in static air. Interestingly, the patterns of the two materials differ significantly. In particular, while the fresh material (in red, Fig. 9) shows the pure CaO structure, the spent material (in dark blue) showed several extra reflexes not detected in the former sample.

The comparison with the JCPD library allowed to conclude that the spent catalyst consisted in a mixed crystalline phase of CaO (lime) and $CaCO_3$ (calcite). To further validate this experimental evidence, the same spent catalyst was also characterized with TGA/DTA analysis (Fig. S4). The spent catalysts showed two main weight loss in the range of temperature analized. The first was registered in the range between 200 °C and 450 °C and could be assigned to the removal of the
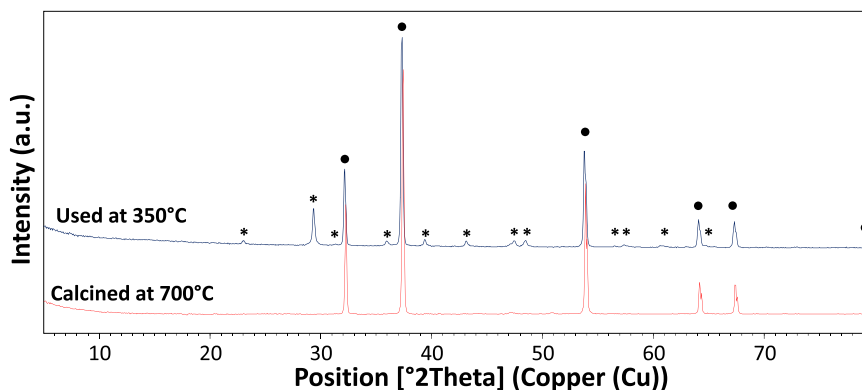
Fig. 8. XRD patterns of CaO calcined at 700 °C (in red) and of the spent sample used in the CTH test performed at 350 °C with a contact time of 1.5 s. Reference patterns: (●) CaO, (*) CaCO₃ Calcite.
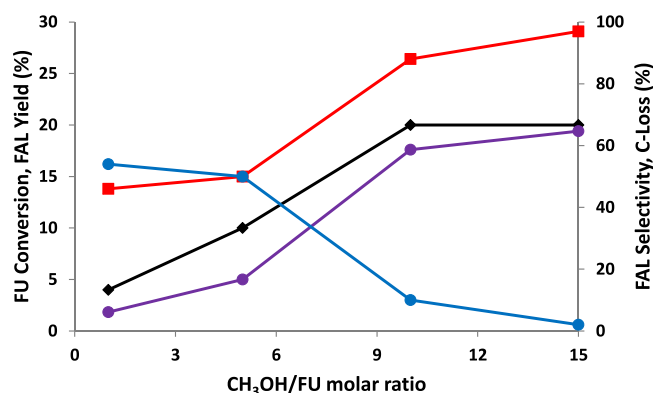

Fig. 9. Effect of the methanol to furfural molar ratio in the feed on products distribution. Feed composition: variable, Pressure 1 atm, reaction temperature 350 °C, overall gas residence time 1.5 s. Symbols: ◆ FU conversion, FAL selectivity, ● FAL yield, ● C-loss.

carbonaceous deposits formed over the catalyst surface during the reaction, considering that this weight loss is correlated to an exothermic peak registered at the DTA. The second was instead detected in the temperature range between 600 °C and 750 °C and was coupled with an endothermic peak at the DTA. Furthermore, comparing the thermograms of the spent catalysts with the CaCO₃ precursor used for the synthesis of our materials, it was noted that the temperature at which the precursor was decomposed to form the oxide structure losing about the 40 % of the initial weight was the same at which the spent catalysts showed the second loss, confirming once again that the catalyst undergoes a recarbonatation process, which probably occuers during the first hour of reaction.

All these findings can explain that the modification catalytic perfomances showed by the catalyst across the time on stream are somehow connected to the carbonatation process. In addition to this, it has also been highlighted that the mixed phase obtained after the partial recarbonatation process was much more selective in the hydrogen transfer process respect to the pure CaO phase. Indeed, similar reasons could be translated also for explanation of the light compounds trend, such as H₂. In particular, the high amount of this species detected in the first hour, was an evidence of the low efficiency in the hydrogen transfer mechanism. Since it is known that the lower is the amount of molecular hydrogen produced during the reaction the higher is the efficiency of the catalyst in hydrogen transfer mechanism [39].

3.6. Effect of feed composition

The effect of the feed composition on FU conversion and FAL yield

and selectivity has been evaluated in the previously optimized reaction conditions over CaO. In a previous study we have demonstrated that the activity of a catalyst with low specific surface area (FeVO₄, 12 m²/g) can be increased by decreasing the organic content present in the feed [33]. Furthermore, as just mentioned above, in literature it is reported that the activity of a basic catalyst in the catalytic transfer hydrogenation was strictly related to the number of basic sites and so, in most of the cases, to the total surface area [39]. In the case of CaO it could be hypothesized that the total organic content present in the feed (55 % molar) was too high if compared to the very low surface area possessed by the catalyst and that for this reason, a high amount of the fed substrates do not have the possibility to interact with the catalyst surface and passed unconverted in the outlet stream. Therefore, dedicated tests were performed under the previously optimized condition by changing the mol % of organic in the feed as well as the FU/methanol molar ratio (Table 2). Interestingly, comparing the results obtained in this study with the ones previously reported it was revealed that the decrease of organic content in the feed do not bring to the expected improvement of the catalytic performance, as reported for FeVO₄ catalyst [33].

The catalytic test performed by feeding a highly diluted FU stream (1 %mol) with a methanol/FU molar ratio of 10 (Table 2 Entry1) a slight increase of substrate conversion was registered (up to 35 %). On the other hand, FAL selectivity was highly affected by this change: indeed, the value obtained in low organic condition was about the half, of that obtained feeding the high organic content (45 % instead of 88 %).

The analysis of these results allowed to hypothesize that the unexpected catalytic behavior showed by the catalyst at the decrease of the organic content present in the feed could be related to a possible FU preferential adsorption over the catalyst surface if compared to methanol. Therefore, dedicated tests were performed to confirm this hypothesis. In particular, by working at constant FU molar percentage (5 mol % in the feed), and progressively changing the excess of methanol, in the range between 5 mol % and 75 mol %, corresponding to a methanol to furfural molar ratio between 1 and 15. Indeed, if FU is preferentially absorbed over catalyst surface respect to methanol, it must be obtained a progressive increase of FU conversion and FAL selectivity as a consequence of the increase of methanol to furfural molar ratio.

The obtained results, showed in both Table 2 (Entries 2, 3, 4 and 5) and Fig. 9, confirm our speculations of a competitive, preferential adsorption of FU compared to methanol over the active sites of the catalyst. Indeed, an increased methanol excess in the feed allowed a progressive boost of FU conversion from 4 %, obtained with the unitary molar ratio, up to 20 % detected with a methanol to FU molar excess equal to 15.

Moreover, higher FU dilution leads to promising results both in terms of FAL selectivity and C-Loss. In particular, FAL selectivity increased from 45 % obtained with the unitary molar ratio to the 97 % detected in

Table 2

Effect of methanol to FU molar ratio and mol. % of organic in the feed on the catalytic results over CaO catalyst. Feed composition: variable, Pressure 1 atm, reaction temperature 350 °C, overall gas residence time 1.5 s the reported results were the average values obtained between the 2nd and the 6th reaction hour.

Entry	Composition of the feed (%mol. %)			Total organic content (mol.%)	CH$_3$OH/FU mol ratio	FU conversion (%)	Selectivity (%)		
	FU	CH$_3$OH	N$_2$				FAL	MF	C-Loss
1	1	10	89	11	10	35	45	1	54
2	5	50	45	55	10	20	88	2	10
3	5	5	90	10	1	4	46	0	54
4	5	25	70	30	5	10	50	0	50
5	5	75	20	80	25	20	97	1	2

the condition of the larger excess of methanol in the feed while the C-loss drops from more than 50 % to almost zero. Therefore, it can be concluded that the composition of the feed, both in terms of total organic content and relative molar ratio between the two organic reagents, is a key parameter to directly and deeply influence the catalytic activity of the catalyst in the CTH process. Finally, tuning the reaction conditions in terms of methanol to substrate molar ratio, it was possible to find the best operative conditions in which the catalyst showed to be totally selective in the formation of FAL as the only reduction product bringing to a crucial improvement of the catalytic performances.

To better highlight the potential of CaO as a catalyst for the reduction reaction of FU to FAL, it is appropriate to consider the differences that exist in terms of activity with respect to MgO, which was studied in a previous work [35]. The main differences between the two catalysts are as follows: i) CaO is active and selective at temperatures about 100 °C higher than MgO (better selectivity at 250 °C where CaO shows no activity); ii) CaO shows a constant activity during the 6 h of reaction unlike MgO which deactivates after only one hour; iii) CaO shows the best FAL selectivity with a methanol/FU molar ratio of 25; while MgO shows similar results with a methanol/FU ratio of 10. These differences can be explained by comparing the chemical-physical characteristics of the two materials (Table S1). In fact, CaO has a much lower surface area than MgO and this may explain why much more methanol needs to be fed than FU. Furthermore, the different stability and resistance to deactivation can be attributed to the different basicity of the two systems. Last but not least, it must be considered that the specific productivity in Fu of CaO is $5.37 \bullet 10^{-4}$ mol$_{FAL}$/h*m^2 which is 27 times greater than that of MgO.

4. Conclusions

Different CaO based catalysts have been obtained through a simple and cheap methodology based on a controlled decomposition of a CaCO$_3$ precursors prepared via a precipitation process. The obtained materials are all characterised by low specific surface area but showed different catalytic behaviour as a function of calcination temperature. However, the relatively high basicity strength promoted methanol conversion and the specific productivity in the FU reduction to FAL. The in-depth investigation of the operating conditions allowed to identify the optimal reaction conditions to reach high FAL selectivity (close to 100 %), minimizing the C-loss and optimising FAL productivity. In particular, by operating at 350 °C with a residence time equal to 1.5 s, a conversion of FU greater than 20 % and a selectivity in FAL greater than 97 % were obtained. It has also been demonstrated that methanol/FU molar ratio play a fundamental role in order to strongly limit both catalysts deactivation and increase FAL selectivity, due to the enhanced dilution of FU obtained with competitive adsorption phenomena over the catalytic surface. All in all, CaO proved to be a very cheap, easy to prepare, non-toxic material with good potential for the catalytic transfer hydrogenation of FU with methanol, showing excellent results also in terms of resistance to deactivation.

CRediT authorship contribution statement

Lorenzo Grazia: Investigation, Metodology, Validation; **Tito Della Rosa:** Investigation, Metodology; **Danilo Bonincontro:** Investigation, Metodology **Tommaso Tabanelli:** Investigation, Metodology, Writing original draft and review and editing; **Nicola Schiaroli:** Investigation, Metodology; **Fabrizio Cavani:** Conceptualization, Supervision; **Carlo Lucarelli:** Supervision, Conceptualization, Methodology, Writing original draft and review and editing; **Stefania Albonetti:** Process administartion, Supervision, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.cattod.2023.02.013.

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