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Methanol as a clean and efficient H-transfer reactant for carbonyl reduction: Scope, limitations, and reaction mechanism



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ABSTRACT

The previously unexplored use of methanol as a H-transfer agent for the Meerwein–Ponndorf–Verley reduction of aromatic aldehydes and aryl ketones is described. Furfural, 5-hydroxymethylfurfural, benzaldehyde, and acetophenone were selectively reduced to the corresponding alcohols in mild conditions. The reaction mechanism was elucidated by means of reactivity tests and DFT calculations. It was found to include the highly efficient H-transfer with the formation of formaldehyde, which further reacted with excess methanol to generate the adsorbed hemiacetal. In turn, the latter reduced carbonyl, with the formation of methylformate, which further decomposed into CO, CH_4 , and CO_2 . Compared to the alcohols typically used for carbonyl reductions, methanol showed the advantage of producing gaseous components as the only co-products, which are easily separated from the reaction medium. In the case of furfural, a 100% yield to furfuryl alcohol was obtained, using the high-surface area MgO as the easily recoverable and reusable catalyst.

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1. Introduction

The reduction of carbonyl groups using alcohols as hydrogen sources, i.e. the Meerwein-Ponndorf-Verley (MPV) reaction, offers an alternative approach to work under hydrogen pressure with supported precious metal catalysts [1–8]. Using appropriate conditions, the reaction can be highly chemoselective toward carbonyl groups. The MPV is usually carried out through homogeneous catalysis by using Lewis acids such as Al, B, or Zr alkoxides (isopropoxide); other catalysts are based on precious metals such as Pd, Rh, Ru, and Au. However, the MPV reaction usually requires a large amount of alkoxide in order to obtain an acceptable yield, and often, the procedure used for catalyst recovery ends up leading to non-reusable compounds. Alternative homogeneous catalysts have been sought, based on either non-precious metals, such as Fe [9-12], or alkali metal ions, such as Li alkoxides [13,14] or KOH [15]. Nevertheless, alternative catalysts, based on heterogeneous, inexpensive, easily available, and non-toxic materials, are

still being sought with the aim of developing sustainable hydrogenation protocols.

Within this framework, several different solid catalysts have been reported in the literature, mostly based on alkali and alkaline earth oxides, as well as zeolites or mesoporous materials, sometimes incorporating metal ions acting as Lewis acid sites. More specifically, examples include the following: (a) MgO, either doped or as is, and Mg/M mixed oxides, used for the reduction of substrates such as citral [16,17], cyclohexanone [18–20], acrolein [21], acetophenone [22,23], hexenone [24–26], mesityl oxide [27–30], acetone [31], benzaldehyde [32,33], crotonaldehyde [34], furfural [35,36] and, in general, various aliphatic aldehydes and ketones [37-43] or aralkylketones [44,45], in most cases using isopropanol as the Htransfer reactant, with a few exceptions in which ethanol [31,33], methanol [22], or other C₄ alcohols [32] were used; (b) ZrO₂ and hydrous zirconia, either doped or as is [46–53], anchored/grafted Zr over supports [54–57], and Zr-beta [58,59], for the reduction of the same substrates as for MgO, again using isopropanol; (c) zeolites such as H-beta [60-63] and alumina [64] using isopropanol, ethanol, or cyclopentanol; (d) CuO- [65-69] and MnO₂-based [70] catalysts, with cyclohexanol, 1,4-butandiol, or ethanol; and (e) Ti or Sn incorporated in MCM or beta zeolite [71–74], with isopropanol or 2-butanol as the reducing agents.

Among the various carbonyl-bearing substrates, furfural (FAL) and 5-hydroxymethylfurfural (HMF) are important renewable



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building blocks, as key precursors for the production of biofuels and chemicals [75–79]. The upgrading of these molecules includes, among others, the hydrogenation of carbonyl groups to the corresponding aromatic alcohols, furfuryl alcohol (FFA), and 2,5-bis(hydroxymethyl)furan (BHMF), respectively (Scheme 1).

FFA is used as a modifier for phenolic and urea resins, as a nonreactive solvent in the production of epoxy resins, as a chemical intermediate for producing lubricants, and for the synthesis of lysine, vitamin C, and tetrahydrofurfuryl alcohol. It is industrially produced through the hydrogenation of FAL, which is carried out in either the vapor or the liquid phase. The industrial catalyst is made of a mixed Cu-Cr oxide [80,81]; in general, Cu-based catalysts catalyze the gas-phase hydrogenation of FAL to FFA with good selectivity [65,82-86]. Indeed, hydrogenation may lead to several compounds, because of the hydrogenolysis of the C-O bond, decarbonvlation, hydrogenation, and furan ring opening; therefore, alternative. Cr-free, highly-selective catalysts that can operate at mild conditions have been sought. Alternative catalysts studied include the following: (a) systems based on Ni or Co-Raney, and Ni or Co alloys with Cu, Fe or Ce, for liquid-phase hydrogenation, which may reach 98% selectivity to FFA [87,88]; Ni-B and Co-B amorphous alloys [89–92] are some examples. On the other hand, undoped silica-supported Ni mainly catalyzes the formation of ring-opening products (butanal, butanol, and butane); (b) supported Pt and Pt/Sn-based systems, also containing various promoters [93,94]; (c) supported Ru [95] and Ru(II) bis(diimine) homogeneous complexes [96]; and (d) supported Ir [97]. Conversely, silica-supported monometallic Pd and bimetallic Pd-Cu mainly catalyze the formation of the decarbonylation product, furan [98]. Recently, Hermans reported that Fe₂O₃-supported Cu and Ni catalysts permit over 70% selectivity to FFA at moderate FAL conversion, with isopropanol as the H-transfer reagent; however, Pd/Fe₂O₃ exhibited extraordinary activity in the further hydrogenolysis to methylfuran, to the ring-hydrogenated compound, and to furan, with a combined yield of 62% under continuous flow conditions. A similar performance was shown with HMF [99].

The reduction of HMF to BHMF (or to the saturated molecule, 2,5-bis(hydroxymethyl)tetrahydrofuran, DHMTHF) has been studied previously in the literature by a number of authors (see the recent review on the reduction of FAL and HMF [100]). For example, catalysts based on Ni, Cu, Pt, Pd, or Ru in a neutral solution have made it possible to obtain aromatic compounds, whereas when used in acidic solution, the main products were ring-opened compounds. Ni–Pd bimetallic catalysts gave primarily DHMTHF (selectivity 96%) [101,102].

As for the catalytic HT aimed at the reduction of FAL and HMF, the reduction of the latter into BHMF has recently been achieved with an excellent yield using formic acid (which is used as a source of H₂) [103,104] and various catalysts based on Ir or Ru complexes. This reaction was carried out at mild conditions, at 40 °C, in THF solvent; the presence of a base greatly accelerated the reaction rate [105]. Conversely, hydrogen donors traditionally used for HT



Scheme 1. Hydrogenation of FAL and HMF to FFA and BHMF, respectively.

catalysis in organic synthesis, for example alcohols, resulted in a substantial decrease in activity. For example, FAL was totally reduced to 2-methylfuran by contact with 1,4-butanediol, using a Cu–Zn–Al catalyst at 225 °C, but the reaction needed the presence of a large excess of H₂ [69,106]. Nagaraja et al. [68] showed that Cu–MgO catalysts made possible the reduction of FAL to FFA with cyclohexanol as the HT agent in the 200–300 °C *T* range, without needing the H₂ input, but with a yield of FFA no higher than 60%. Recently, a 99% yield of FFA was achieved using isopropanol as the HT alcohol, with a Ru carbene complex as the catalyst, KOtBu, KOH, and THF as the solvent, at 60 °C and 24 h reaction time [107]. The catalytic conversion of HMF to dimethylfuran, dimethyltetrahydrofuran, and 2-hexanol was obtained over Cu-doped metal oxides in supercritical methanol [108].

Here, we report on the reduction of FAL and HMF to the corresponding unsaturated alcohols, FFA and BHMF, using a simple procedure which enables selective HT from methanol to reactants, with MgO as the HT catalyst. The reaction is carried out in a liquid monophasic system, in which methanol also acts as a fully recyclable solvent, since the only co-products obtained in methanol transformation are gaseous compounds, i.e. CO, CO₂, and CH₄. Moreover, we extended the procedure to other aldehydes and ketones, in order to demonstrate the general soundness of the approach used. The further aim of the present work was to assess the reaction mechanism, through the validation of the reactivity experiments by means of DFT calculations. This allows the identification of validity boundary conditions and limitations of the method used for carbonyl reduction.

2. Materials and methods

2.1. Catalyst preparation and reactivity experiments

MgO was prepared by means of thermal decomposition of brucite. Brucite was synthesized following the conventional co-precipitation method reported in the literature [109,110]. A $Mg(NO_3)_2 \cdot 6H_2O$ (Sigma-Aldrich) aqueous solution was added dropwise into a solution containing 1 M NaOH (Sigma-Aldrich). While the brucite was precipitating, the slurry was maintained at 55 °C and pH 10.5. At the end of the precipitation, an 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 2 L water per gram of solid. Lastly, brucite was dried at 70 °C in static air overnight. The precursor obtained was calcined in air at 450 °C for 5 h. Both phases of the precursor and magnesium oxide were characterized by means of X-ray diffraction, using a Bragg/ Brentano X'pertPro PANalytical diffractometer (5-80° 20, with acquisitions of 10 s every 2θ 0.1°). The surface area of MgO $(125 \text{ m}^2/\text{g})$ was measured using a Fisons Sorpty 1750 CE instrument (single point BET method). The analysis was conducted after dry-treating the sample at 120 °C.

The following reagents and products were used for reactivity experiments: furfural (FAL) (Sigma–Aldrich), 5-hydroxymethylfurfural (HMF) (Sigma–Aldrich), furfuryl alcohol (FFA) (Sigma– Aldrich), and 2,5-bis(hydroxymethyl)furan (BHMF) (Toronto Research Chemicals). The hydrogenation of FAL and HMF was carried out using a Parr Instrument 4561 autoclave reactor (300 mL capacity). The reaction was carried out in methanol, using the appropriate amount of catalyst. If not otherwise indicated, each test was conducted for 3 h at 160 °C, with the following amounts of reagents: 50 mL methanol; 1.21 mmol FAL or HMF; 0.5 g MgO; 1 bar of nitrogen. After loading the methanol, reactant, and catalyst, the autoclave reactor was purged 3 times with N_2 (20 bar) and then pressurized at 1 bar (N_2). The temperature was increased up to 160 °C and the reaction mixture was stirred at 400 rpm for the time needed. At the end of the reaction, the reaction mixture was cooled in an ice bath and the MgO was separated by filtration.

Preliminary experiments were carried out in the aim of finding the lowest stirring rate to apply in order to avoid mass transfer limitations. Results of experiments are reported in Fig. S1, plotting yield to FFA (which corresponds to FAL conversion, being FFA selectivity equal to 100%) in function of the stirring rate, at 130 °C. From these results, we decided to use a stirring rate of 400 rpm for catalytic experiments.

Liquid products were analyzed by means of HPLC (Agilent Technologies 1260 Infinity), using a 50 × 4.6 mm C-18 core–shell column using an 80% solution of 0.01 M H₃PO₄ and 20% acetonitrile as the mobile phase. The gas phase was collected and analyzed with an Autosystem XL (Perkin Elmer) GC equipped with a 30 mm × 0.32 mm Elite Plot Q capillary column attached to a methanizer assembly flame ionization detector (FID). Compounds were identified by calibration using reference commercial samples, and by means of NMR. NMR analyses were performed using a 400 MHz NMR instrument.

2.2. Modeling approach

Gas-phase electronic structure calculations were carried out using the Gaussian09 [111] suites of codes and the B3LYP [112,113] density functional theory (DFT), including all the electrons in the calculations. The basis set employed was 6-31++G(d,p). The presence of methanol as the solvent was modeled using the PCM model with the appropriate dielectric constant, as necessary.

MgO nano-crystals were modeled using a cluster approach that was previously benchmarked for structure, energetics, and spectral properties [114,115], by evaluating possible size effects on adsorption energies and structures by increasing the number of atom clusters while maintaining the overall species neutrality. The geometrical parameters of the MgO (cubic, d_{MgO} = 2.1084 Å) clusters were kept frozen in all calculations, as one would expect minor effects for them [116] as well as for energetic quantities. Geometries for the adsorbed species and reaction-relevant structures (i.e. aldehydes, methanol, hemiacetals, transition states, TSs) were fully optimized and the stationary points found were characterized by means of frequency calculations. Putative structures for energy minima were built using literature data [117,118] followed by a complete geometrical relaxation keeping the MgO cluster constrained. On the other hand, TS geometries were often built using relaxed scans along the reaction coordinates (e.g. C–H distances); the latter approach helped in locating sensible initial structures with small forces as well as the correct local curvatures of the potential energy surface (PES). In order to propose possible reactive H-transfer pathways, we exploited both the formal similarity between the β -hydride transfer (β HT) termination reaction typical of olefin polymerization with the reduction of aldehydes (furfural and formaldehyde) and previous studies on the MPV reaction in homogeneous [117,119,120] and heterogeneous [121] catalysis. The only deviation from the procedures just discussed is the optimization of hemiacetal, which was spontaneously obtained while attempting to minimize the structure of a system made of both formaldehyde adsorbed on the corner Mg (Mg3C) of MgO and a methanol molecule adsorbed onto a vicinal-face Mg (Mg5C).

As the transferring atom is light, harmonic frequency calculations may be needed in order to account for possible differences in vibrational zero point energy (ZPE) properties between minimum and TS structures. In this respect, such correction is found to lower the electronic energy barrier by roughly 1 kcal/ mol for all species due to the similar structure of carbonyl and alcoholic parts of reactants, TSs, and products. Therefore, no strong substituent effects are found with respect to the vibrational modes entailed in these reactions.

3. Results and discussion

3.1. Furfural and 5-hydroxymethylfurfural reduction with methanol as HT agent

Fig. 1 reports the FAL conversion and selectivity to FFA for fixed reaction conditions (3 h reaction time, 160 °C), as a function of the catalyst amount. It is shown that under the conditions chosen, 100% yield to FFA was obtained using 1.0 g MgO; the C balance, as well as a careful analysis of the reaction mixture by means of both HPLC and NMR, confirmed the total yield to FFA. However, a lower catalyst amount led to a partial FAL conversion only, but still with 100% selectivity. It is worth noting that the methanol was both HT reagent and solvent, which may explain the complete FAL conversion experimentally observed.

Table 1 summarizes the results obtained after changing the reaction temperature. The table also shows the values of TON and TOF, calculated by assuming that all the surface basic sites, previously determined by means of CO_2 -TPD [109,110], contribute to the reaction; this assumption clearly leads to an underestimation of the TON and TOF values.

With regard to the effect of temperature, when using less mild reaction conditions (entries 5–7 in Table 1), it was possible to decrease both reaction time and catalyst amount, while obtaining a significant FFA yield, still with 100% selectivity. On the other hand, when a lower temperature was used (entries 1 and 2 in Table 1), the selectivity to FFA was not total; in fact, in addition to a 55% yield to FFA, a 2% yield to the acetal formed by reaction between FAL and methanol was also obtained at 130 °C. At 100 °C, the acetal was the only product, obtained with a 15% yield in 3 h reaction time; at 160 °C and above, the acetal did not form at all. Therefore, under our conditions, methanol reacts with the carbonyl moiety at low temperatures, whereas a temperature higher than 130 °C is needed to activate methanol for the HT reaction. However, it is worth noting that the formation of the acetal might derive from acid impurities present in FAL.

TOF showed an exponential increase when the temperature was raised. In general, TON and TOF values were low, mainly because of both the high catalyst amount and the low FAL concentration used. On the other hand, under the assumptions made, the calculated turnover values demonstrate that the reaction was catalytic in nature. At 230 °C, 86% FAL conversion (corresponding to a TOF value



Fig. 1. FAL conversion (\blacksquare) and FFA selectivity (\Box) as a function of catalyst amount in the reaction of FAL reduction over MgO in methanol. Reaction conditions: FAL 1.21 mmol, methanol 50 mL, reaction time 3 h, temperature 160 °C.

Entry	Temperature (°C)	Time (h)	FAL (mmol)	MgO (g)	FFA yield, FAL conv. (%)	TON ^a	$TOF^{b}(h^{-1})$
1	100	3	1.21	0.5	0, 15	0	0
2	130	3	1.21	0.5	55, 57	3.7	1.2
3	150	3	1.21	0.5	90, 90	6.0	2.0
4	160	3	1.21	0.5	97, 97	6.5	2.2
5	210	0.75	1.21	0.25	51, 51	6.9	9.1
6	230	0.5	2.42	0.1	43, 43	28.9	57.8
7	230	1	2.42	0.1	86, 86	57.8	57.8

Effect of the reaction temperature on catalytic performances of MgO catalyst in FAL reduction with methanol.

All experiments were conducted using 50 mL methanol.

^a TON expressed as mol FFA produced per basic site; the number of basic sites is assumed to coincide with the number of moles of CO₂ adsorbed during CO₂-TPD experiments [109,110].

^b TOF = TON/reaction time.

Table 1

close to $58 h^{-1}$) was achieved after 1 h reaction time, still with 100% selectivity to FAA (entry 7 in Table 1).

The absence of condensation compounds might be due to the low concentration of FAL in methanol; however, experiments carried out at higher substrate concentrations (see below) still led to a fairly significant yield to FFA with 100% selectivity, with an acceptable TON value.

Fig. S2 shows FAA yield (coincident with FAL conversion, since at conditions used, selectivity was always 100%) and TOF values plotted in function of reaction time, at 160 °C; the test carried out at 3 h reaction time corresponds to entry 4 in Table 1. An increase in reaction time led to an increase of FFA yield (with an obvious analogous increase of TON value), whereas the TOF declined.

The effect of FAL concentration on FFA yield (once again, yields were coincident with FAL conversion, because of the 100% selectivity achieved) is shown in Fig. 2, for experiments carried out at 160 °C. It is shown that the reaction rate was positively affected by FAL initial concentration, even though a decline of FFA yield indicates a surface saturation effect.

Fig. 3 shows the results obtained in HMF reduction (HMF conversion and selectivity of BHMF), in conditions similar to those used for FAL reduction. In this case, also, total selectivity to the corresponding alcohol was obtained at every level of reactant conversion; the NMR analysis of the reaction mixture confirmed the formation of BHMF as the only product (Figs. S3–S5). It is worthy of note that similar reactant conversion (and alcohol yield) values were obtained from either HMF or FAL, when the same values of substrate/catalyst (mol/wt) ratio were used. This indicates that the reaction rate is not affected by the type of



Fig. 2. FFA yield (\blacksquare), TON (\blacktriangle) and TOF (\blacklozenge) values as a function of FAL initial amount in the reaction of FAL reduction over MgO in methanol. Reaction conditions: MgO 0.5 g, methanol 50 mL, reaction time 3 h, temperature 160 °C. TON expressed as mol FFA produced per basic site; the number of basic sites is assumed to coincide with the number of moles of CO₂ adsorbed during CO₂-TPD experiments [109,110]. TOF = TON/reaction time.



Fig. 3. HMF conversion (\blacksquare) and BHMF selectivity (\Box) as a function of catalyst amount in the reaction of HMF reduction over MgO in methanol. Reaction conditions: HMF 1.21 mmol, methanol 50 mL, reaction time 3 h, temperature 160 °C.

 $CH_{3}OH \rightarrow H_{2}CO + H_{2}$ $H_{2}CO \rightarrow CO + H_{2}$ $2 H_{2}CO \rightarrow CH_{3}OC(O)H$ $CH_{3}OC(O)H \rightarrow CO_{2} + CH_{4}$

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

substrate and that the rate-determining step of the process involves the activation of the HT agent; experiments aimed at determining the amount of active hydrogen species generated by methanol transformation will confirm this hypothesis (see below).

With respect to the amount of active hydrogen species involved in the HT reaction, we noted that the only products of methanol transformation were CO, CO₂, and CH₄, while we did not detect the formation of partially dehydrogenated or dimerization compounds, such as formaldehyde, methylformate, formic acid, the hemiacetal or the acetal, dimethoxymethane. We did not even detect the formation of molecular hydrogen. This strongly suggests that the HT, from methanol to the substrate, generates formaldehyde, which either also acts as a HT reagent (with the ultimate co-production of CO), or dimerizes to yield methylformate, which, however, is rapidly decomposed into CH₄ and CO₂. As for this, Scheme 2 gives a formal set of reactions that would account, at least in principle, for both the reduction capability of methanol and gaseous by-products (vide infra for a more detailed analysis based on modeling results) and would also allow for hydrogen mass balance calculation. As shown in Fig. 4, which reports the number of moles of CO, CH₄, and CO₂ formed based on the time



Fig. 4. FFA yield (**■**) and number of moles of CO (\diamond), CO₂ (\bigcirc) and CH₄ (\triangle) generated as a function of reaction time in the reaction of FAL reduction over MgO in methanol. Reaction conditions: FAL 1.21 mmol, MgO 0.5 g, methanol 50 mL, temperature 150 °C.



Fig. 5. Number of moles of FFA produced (\blacksquare) and theoretical number of H₂ moles generated by methanol dehydrogenation (\diamondsuit) (calculated taking into account the number of moles of CO and CO₂ generated during reaction, see text for explanation), as a function of time in the reaction of FAL reduction over MgO in methanol. Reaction conditions: FAL 1.21 mmol, MgO 0.5 g, methanol 50 mL, temperature 150 °C.

in FAL reduction, the number of CH_4 and CO_2 moles generated was identical, thus supporting the hypothesis of a rapid methylformate decomposition; both were approximately half the number of CO moles.

When the number of H₂ molecules theoretically used for the reduction of the substrate, produced during methanol transformation into formaldehyde and then into CO - this value was calculated from the sum of the number of CO and CO2 moles as determined by analysis of the gas phase, both multiplied by 2 (see Scheme 2) - were plotted in function of reaction time, we obtained the plot shown in Fig. 5; the figure also reports the number of FFA moles generated. Since neither H₂ nor formaldehyde, the hemiacetal or methylformate was found either in gas or in liquid phase, this implies that all the hydrogen atoms in converted methanol (with the exception of those finally contained in methane) were used for the reduction of the carbonyl moiety in FAL. Therefore, the two curves reported in Fig. 5 should be coincident, which in fact was the case. The overall selectivity to the hydrogen incorporated in the substrate, calculated with respect to the converted methanol, was about 45%, because of the unproductive formation of CH₄. Therefore, our method made possible the reduction (with 100% yield with respect to the substrate and 45% selectivity with respect to hydrogen atoms in converted methanol) under mild reaction conditions, i.e. in the liquid phase under autogenous pressure and with temperatures in the range of 130–160 °C, without the need for H_2 input.

The comparison between MgO catalyst maximum productivity in FAL reduction by means of selective HT (entries 6 and 7 in Table 1) and the best results reported in the literature obtained by means of liquid-phase FAL hydrogenation with H_2 (Fig. S6) indicates that the best productivity obtained under MgO-catalyzed HT conditions was the same order of magnitude as those reported for supported noble metal catalysis, under H_2 pressure.

We also carried out experiments recovering and recycling the used MgO catalyst (Fig. S7); we found that the MgO catalyst can be recovered by filtration and recycled without a significant loss of activity, but a thermal treatment at 450 °C for 5 h in air is required to regenerate the partially deactivated catalyst.

Concerning the use of methanol as a HT agent for a MPV-type reduction, very few examples are reported in the literature. Aramendia et al. [22] reported on the reduction of acetophenone with MgO and Mg phosphate catalysts using methanol as the reagent. In previous papers, we reported that in basic-catalyzed vapor-phase methylation of phenol with methanol, at temperatures over 300 °C, the dehydrogenation of methanol led to the *in situ* generation of formaldehyde, which reacted with the activated phenolic compound to produce a hydroxymethylphenol compound. The latter compound was either dehydrogenated into the corresponding aldehydic compound and then reduced by methanol to yield the methyl group, or directly reduced by the formaldehyde generated *in situ* [122–127]. The ultimate product of the reaction was the corresponding ring-methylated phenol (o-cresol).

Other examples are reported in which, over MgO-based catalysts also with acid features, the *in situ* dehydrogenation of methanol generates formaldehyde, which then reacts with activated C—H-containing compounds (nitriles, ketones, ethers) to form α , β -unsaturated compounds via aldol condensation and dehydration [128,129]; in these cases, however, methanol was not reported to act as a H-transfer reagent.

The present work results demonstrate that it is possible to reduce FAL and HMF to FFA and BHMF, respectively, using mild reaction conditions, an MgO catalyst, and methanol as a HT reagent, achieving 100% yield to the alcohol within a few hours' reaction time, at a temperature of 160 °C, and under autogenous pressure. Methanol also acts as a solvent. The co-products of methanol transformation are exclusively light molecules which are transferred into the gas phase under reactor depressurization and, in the end, easily separated from the liquid mixture.

3.2. Other carbonyl substrates

Table 2 shows the results obtained with benzaldehyde and acetophenone as substrates (1.21 mmol), using methanol (50 mL) as the HT reagent and MgO as the catalyst. It is shown that other aromatic aldehydes could be reduced with methanol, although under more demanding reaction conditions than for FAL and HMF. In fact, either longer reaction times (for benzaldehyde) or the combination of longer times and higher temperature (for acetophenone) was required in order to achieve good conversion to the corresponding alcohol. At 160 °C, for instance, acetophenone conversion was very low. With both substrates, the selectivity was not total, because of the formation of the acetal in the case of benzaldehyde and of 1-phenylpropanone in the case of acetophenone. As also reported by Aramendia et al. [22], the formation of 1-phenylpropanone occurs by aldol condensation between the formaldehyde generated in situ and the ketone, followed by dehydration and hydrogenation. Therefore, it is apparent that the use of methanol as a selective H-transfer agent is possible only with substrates, which do not bear activated C-H bonds.

Table 2 Reactivity of other aldehydes for reduction with methanol.

Substrate, conversion (%)	Product, yield (%)	T (°C), t (h), MgO amount (g)	By-product
Benzaldehyde, 12	Benzyl alcohol, 12	160, 3, 0.25	None
Benzaldehyde, 90	Benzyl alcohol, 52	160, 6, 0.50	Benzaldehyde acetal
Acetophenone, 52	1-Phenylethanol, 38	210, 6, 0.50	1-Phenylpropanone

We also tested the reactivity of crotonaldehyde and butyraldehyde; however, in this case, not only the formation of dimerization and aldol condensation compounds was observed, but also the conversion was very scarce.

3.3. The mechanism of HT with methanol

The reaction mechanism for the homogenous Al-alkoxy MPV reaction involves a cyclic six-membered transition state in which both the reducing alcohol and the carbonyl compound are coordinated to the same metal center. The reaction proceeds by a hydride transfer from the alcohol, bound to the metal center as an alkoxide. to the carbonyl (Scheme 3, left). On strong Lewis basic sites M=O, the reducing alcohol adsorbs with the oxygen and hydrogen to the metal ion and the oxo-ion site, respectively. The carbonyl group coordinates by hydrogen-bonding to this surface hydroxyl group rather than to the metal; the reaction proceeds again via a cyclic seven-membered transition state (Scheme 3, right). As an exception, a single electron transfer pathway was observed for alkali-catalyzed MPV reductions [130]; metal hydrides are only formed during hydrogenations catalyzed by transition metals such as ruthenium [131].

Analogous mechanisms involving a six-membered cyclic transition state are also suggested for heterogeneous catalysis, but reaction may also occur on Brønsted acid sites, Lewis acid sites, and basic sites [5,20,46,48,63,71,72]. The cooperation of acid-base pairs is believed to contribute in the activation of the two reactants [16,18,28,29,31,33,34,41]; in this case, the HT is thought to take place again via a concerted process involving a six-center transition state, with the alcohol and carbonyl compound adsorbed on a surface acid-base pair. If the HT takes place on a flat surface, the rate-determining step might be the interaction of the alcohol with the acid-base site and thus related to the catalyst basicity. However, methanol is known to dissociate on less coordinated sites [132] (vide infra), a finding suggesting that the HT may be the kinetic bottleneck in these alternative situations. However, it seems that these ideas should be taken as sensible indications rather that proven facts in view of the lack, for instance, of any quantitative support from theoretical modeling.

Bearing in mind what is suggested in the literature as well as the fact that the experiments in this work did not reveal any molecular hydrogen in the gaseous products developed during



Scheme 3. Sketch of the transition state for H-transfer as proposed in the literature.

211

the reaction, we opted for directing our modeling effort toward low-coordination defective sites such as a tri-coordinated vertex Mg (Mg3C). On these, the reaction can take place via direct atomic transfer without imposing strong geometrical constraints on the various species, as suggested for the mechanism of the MPV reaction with homogeneous [4,121,133] and heterogeneous [134] catalysts (a hydride transfer from the OH-bearing carbon in the alcohol to the carbonyl one). There are also strong similarities with the β-hydride transfer (βHT) termination reaction of Ziegler–Natta olefin polymerization [135–139]. In both cases, six-center TSs are invoked, with one of the centers being a cationic Lewis acid. Despite such structural similarities, however, it is stressed that the assistance of transition metal *d* orbitals in stabilizing the partial negative charge [135] on the transferring H atoms is not available in the six-center transition state for MPV when the Mg cation is involved. Thus, the energetic cost required for inducing the bond restructuring should be expected to be higher in the latter case. This observation provides additional support to the idea that the Mg3C site may play a key role as a reactive defect, as it is expected to provide regions of higher electrostatic potential than in the vicinity of edge (Mg4C) or terrace (Mg5C) sites [122-126,135,140]. In fact, Mg3C is known to be the most stabilizing adsorption location for many adsorbates [125].

To test this idea, we have verified that this is also the case for formaldehyde. In fact, our results suggest a decrease of roughly 20 kcal/mol for the CH₂O adsorption energy on Mg4C compared to the Mg3C site on the largest of our MgO models (Mg₁₃O₁₃, see Table 3). The structure of the latter and of $Mg_{10}O_{10}$, the two most frequently used MgO models in this work, is shown in Fig. 6. The latter have been previously used to study molecular adsorption energies and have shown to provide a sufficiently accurate description even in cases when dissociative chemisorption takes place [124-126,140].

Note that, at least in principle, H₂ could be formed (see Scheme 2) and spontaneously dissociated over the MgO surface as already discussed [115]. However, the temperature in the reactor is sufficiently high to force H₂ desorption [115], so that the direct hydride transfer appears as to be the most sensible pathway to explore. To test the generality of the identified pathway, we opted to investigate the energy profile for the hydride transfer to all the mentioned carbonyl-containing compounds and also to formaldehyde. The results for the latter species should provide the data for a quantitative comparison among differently substituted aldehvdes.

Table 3 lists adsorption energies for a few of the species involved in MPV reactions - namely methanol, formaldehyde, and furfural - on the Mg3C site for the two aforementioned cluster sizes; the structures of the minima obtained are shown in Fig. 6. Note that one strong reason for using such a large MgO model is based both on the size of the substituted aldehydes and on the need to limit effects due to edge or vertex polarization that may introduce artefacts when studying reactivity.

From the structures shown in Fig. 6, it can be seen that the adsorbed methanol dissociates when transferring the OH acid proton onto vicinal O4C oxygen in the MgO cluster as previously sug-

Table 3

Electronic adsorption energies (Ead, kcal/mol) for methanol, formaldehyde and furfural on the vertex of the MgO clusters used to model the defective Mg3C site at the B3LYP/6-31++G(d,p) level. Methanol dissociates while transferring the hydroxyl proton to a vicinal O4C site. The value in parentheses is for formaldehyde on the Mg4C site.

E _{ad} (kcal/mol)	Methanol	Formaldehyde	Furfural
Cubic Mg ₁₀ O ₁₀	40.4	27.0	33.5
Cubic Mg ₁₃ O ₁₃	38.2	23.7 (3.4)	28.5



Fig. 6. MgO cluster models used in this work (d(MgO) = 2.168 Å). The structure of $Mg_{10}O_{10}$ (a) the adsorbed methanol (b), formaldehyde (c, on MgC4; d, on MgC3), and furfural (e) on the largest cluster ($Mg_{13}O_{13}$) tested in this study are also shown here.

gested [117], thus confirming its basicity. The formation of a stabilizing hydrogen bond between the transferred proton and the just-formed methoxide is worthy of note, as well as the fact that CH₂O and FAL are found with the aldehydic H atom pointing toward the O4C site. The latter finding suggests the presence of both a partial positive charge on the H atoms and a quadrupolar charge distribution on the aldehydic oxygen. The acidic dissociation of methanol ought to be considered as preparatory for the possible hydride shift, as the negatively charged oxygen would represent the source of electrons for the post-transfer formation of the carbonylic double bond.

From the quantitative standpoint, methanol adsorption is more exothermic than that of the two aldehydes, a finding explained by its weak proton-donating ability. Additionally, we found that FAL releases more energy upon adsorption than CH₂O, likely due to the electron donating capability of the furanyl ring. Also, it is possible to see the weak dependency ($\Delta E_{ad} \sim 2 \text{ kcal/mol}$) on the cluster size observed for the adsorption energy of methanol, and the slightly more marked decrease ($\Delta E_{ad} 3-5 \text{ kcal/mol}$) for the aldehydes; the latter is probably due to a weak termination effect influencing the Mg3C and O4C charge distributions. Despite this effect, the Mg₁₀O₁₀ model seems to provide reasonably accurate results at a reduced computational cost; thus we opted to use the latter as a testing ground for our mechanistic study.

Table 4 shows the TS energy barrier (E^{\ddagger}) for the hydride shift to the species found to be reactive, and E_{ad} for a molecule adsorbing onto a Mg3C site already bearing a dissociated methanol molecule. The stationary points found during the optimization process of the reactants and TS geometries are shown in Fig. 7.

In commenting the results in Table 4, we begin by noticing that there is a clear reduction of E_{ad} for a second molecule adsorbing onto a Mg3C site already bearing a methanol molecule if compared with the results in Table 3. Nevertheless, adsorption of the second molecules on Mg3C still remains energetically advantageous for the system by roughly 17.7 kcal/mol for methanol, 10 and 13.5 kcal/mol for CH₂O and the remaining species. Similar values for the adsorption of methanol and carbonyl-bearing compounds are indeed a prerequisite for the hydride transfer to take place,

Table 4

TS energy barrier (E^{\ddagger} , kcal/mol) for the hydride transfer between methanol and the reactive carbonylic species; reactants coordinated on the Mg3C vertex of the Mg₁₀O₁₀ cluster modeling site; B3LYP/6-31++G(d,p) level. The last column gives the energy released by adsorbing a second molecule (either methanol or a carbonyl compound) on the Mg3C site already occupied by a dissociated methanol molecule.

Electronic E [‡]	Second molecule E_{ad}
No reaction	17.9
14.0	10.0
27.5	13.5
25.3	13.4
27.8	13.3
	Electronic E [‡] No reaction 14.0 27.5 25.3 27.8

as it is necessary for the latter to bind on the same acid center of the dissociate methanol to react. This quantitative observation also explains the increase in TON seen as the concentration of FAL (Table 1) in the reaction mixture is increased, as it pushes the equilibrium toward the formation of doubly-occupied methanol/FAL Mg3C sites fostering the reactivity of the aldehyde.

Turning to the reaction barriers, the energetic effect of the substitution on the carbonyl moiety is very clear. The net influence of both aromatic and aliphatic substituents causes the deactivation of the carbonyl group with respect to hydride transfer: a finding mainly connected to the reduction of the partially positive charge on carbonyl carbon due to the electron donor character of the substituents. Nevertheless, the barrier heights remain sufficiently low to support the idea that the related TSs are sensible stationary points along the reaction pathways. In fact, when comparing the energy barriers in Table 4 with the MPV and β HT ones in the literature, we can see that the barrier for the CH₂O reduction (i) is similar to the one for β HT when the latter is a very efficient chain termination process [138], (ii) is 2 kcal/mol lower than for MPV catalyzed by Sn or Zr [72] in zeolites, and (iii) is more than 6 kcal/ lower than in the case of Al bi-naphtolate [121] (20.4 kcal/mol) or bis-cyclopentadienyl Ti(IV) (26.3 kcal/mol) complexes, which are known to be active with respect to BHT. The latter species appears to induce a TS barrier similar to the one found for aromatic species in Table 4, thus suggesting that TSs obtained in this study



Fig. 7. Reactant and TS structures for species (b and c, methanol/formaldehyde; d and e, methanol/FAL; f and g, methanol/benzophenone; h and i, methanol/benzaldehyde) involved in the hydrogen transfer reaction between methanol and the tested carbonylic species. Also, panel (a) shows two methanol molecules co-adsorbed on the same Mg3C site.

are likely to represent the kinetic bottleneck of the MPV process over MgO.

As for the TS structures obtained, it is worth pointing out that reactants remain close to the C₃ axis passing through the Mg3C site of the Mg₁₀O₁₀ cluster and away from its lower edges: a situation that should reduce any bias due to size-related polarization effects and thus support the validity of our initial choice for the cluster size. On comparing TS geometries and barriers found for the methanol-based reduction processes and a few previously studied β HT [135,138,139] and MPV hydride transfers [121,134], it can be seen that the TS structure of the MPV reduction conforms to the B-type TS discussed by Talarico and Budzelaar [138] for β HT in homo- and hetero-olefins. This is characterized by a longer distance between metal and hydride than between the metal and the C atoms involved in the transfer; this finding supports the lack of hydride-metal interaction mediated by metal orbitals (*vide*

supra). These features appear to be present even when Ti [138] and Zr are involved in the reaction instead of Al [135] or Sn [134]. Unlike many cases studied so far, we must also point out that our TS geometries are strongly unsymmetrical (e.g. in terms of the C—H distance) due to substantially different local molecular environments. In particular, the hydride-receiving carbon distance is ~0.4 Å shorter than the other one, thus indicating a late TS and the need for injecting energy into the methanol C—H vibration to facilitate the reaction. It is also evident from Fig. 7 that the developing formaldehyde has increased its O—Mg3C distance thanks to an incipient hydrogen bond formed with the proton sitting on O4C. The latter interaction is, in fact, sufficiently strong to make possible the migration of the forming CH₂O away from the Mg3C site, as evidenced by the post-TS reaction pathway in all cases.

Having shed some light on a few mechanistic aspects of the reduction of aromatic carbonyls by methanol, we now focus on clarifying the fate of the produced CH_2O , with an eye on the gaseous by-products methane, carbon dioxide, and carbon monoxide. In this, we are helped by the spontaneous (and serendipitous) formation of a hemiacetal molecule by adding a methanol molecule to formaldehyde. This was obtained while trying to optimize a system with methanol adsorbed onto a Mg4C site in $Mg_{13}O_{13}$ and CH_2O previously adsorbed onto Mg3C. At first, the minimization led the alcohol molecule to transfer its OH proton onto a vicinal O4C site, with the negatively charged methanolate subsequently binding to the carbonylic carbon. The structure of the methoxy methanol (hemiacetal) adduct is shown in Fig. 8; note that the hemiacetal is 12.1 kcal/mol below the parent species with methanol and CH_2O co-adsorbed onto the Mg3C site. Also, this finding contributes to some extent to explaining the formation of acetal compounds reported above for some species.

As the hemiacetal is a fairly reactive species, its formation may, at least in principle, open a few reactive channels. Perhaps more interesting for our work, the hemiacetal may subsequently react with another aldehyde (whether CH_2O or one of the aromatic species is inconsequential, *vide infra*), reducing the latter via hydride transfer. If the transfer occurred from the di-oxo methylene, it would produce methyl formate (Scheme 4, top); alternatively, if it occurred from the methyl group, it would generate a methanal dimer that should decompose quickly (Scheme 4, bottom).

The TS leading from the hemiacetal to the methyl formate via hydride transfer was located (see Fig. 8), and it required surmounting a ZPE-uncorrected barrier of 13.6 kcal/mol (11.8 kcal/mol if ZPE-corrected). Note that this value is slightly lower than the one for the hydride transfer from the methoxy species coordinated to Mg3C, in agreement with the presence of two partially negative O atoms capable of donating electrons to the incipient electronpoor carbon. Clearly, one would expect a higher barrier for transferring the hydride to aromatic species than for formaldehyde; whether the latter reaction is active or not, it is of limited practical consequence for the overall process, as the formaldehyde consumed in the former transformation would come from the oxidation of methanol. The hydride transfer from the methyl group to formaldehyde was also studied and found to require at least 38 kcal/mol of energy; this result indicates that such a process is almost irrelevant in this context. A similar conclusion was reached with respect to the possible decomposition via SN2-type intramolecular hydride transfer from the methyl group onto the di-oxo methylene producing CH₂O through four-atom TS, which we were not able to locate despite several attempts. Finally, it is also worth mentioning that the possible dimerization of formaldehyde directly producing methyl formate should be expected with a very high barrier (49.3 kcal/mol in gas phase [141], vide infra, for solvent and surface effects).

The possible formation of methyl formate gives us the chance to explain the presence of gaseous products. Indeed, the thermal chemistry of methyl formate, either on its own [141,142] or on basic oxides such as MgO [143], is known to produce both methanol and CO, or CO₂ and methane via monomolecular rearrangements. It is worth noting that gas-phase processes require rather high temperatures to occur [141,142], while the decarbonylation of ester is already active at 100 °C [143] in the presence of activated MgO. Thus, it is clear that the oxide surface plays a key role in increasing the decomposition rate by catalyzing the otherwise kinetically demanding step. According to the gas-phase TSs for both decarbonylation and CO₂ elimination of methyl formate, the four-center TS for the latter process should be more affected by the presence of an acid site such as Mg3C due to the very long distance between the O atom in the ester bond and methyl carbon, a structure that requires stabilization of a partially negative charge present on the detaching oxygen [141,142]. Thus MgO should be expected to lower the TS for CO₂ more than for decarbonylation, which does not have a polar TS. Indirect support to these theories comes from the de-carboxylation of carboxylic acids, which appears to be active already around 150 °C [144]. Conversely, a more direct support comes from TS barriers in the presence of methanol, a polar molecule that is in clear excess in the reaction environment, obtained using the model PCM. In fact, the computed TS barrier for CO₂ loss decreases from 77.8 to 72.8 kcal/mol while going from the gas phase to the model solvent. Conversely, the same quantity slightly increased from 66.1 to 69.7 kcal/mol for decarbonylation, in agreement with what has just been discussed. Clearly, similar barrier heights would make CO₂ loss a competitive process with respect to CO loss. We also located TSs for two decomposition channels in the presence of MgO (see Fig. 9), and a similar effect was indeed seen. However, the two barriers (65.2 and 83.0 kcal/mol for CO₂ and CO loss, respectively) still seem too high to lead to gaseous products in reaction conditions. As a possible reason for these findings, we suggest that oxygen vacancies may play a role, as previously found for the decomposition of formic acid on MgO [145]. Given the previous experimental evidences of methyl formate decomposition on metal oxides which supported our interpretation of the MPV results, we feel that testing whether or not this is the case would be best left for a more focused study including details on how the decomposition depends on the defective nature of MgO.

3.3.1. Comparison of reactivity between aromatic and aliphatic aldehydes

As indicated in the section describing the results for other aldehydes, aliphatic species were scarcely reactive with respect to accepting a HT from methanol. The latter is expected to be a



Fig. 8. Hemiacetal formed by the spontaneous reaction between methanol placed on the Mg4C site and formaldehyde adsorbed on the corner Mg (a); hemiacetal and formaldehyde co-adsorbed on Mg3C (b); TS for the hydrogen transfer from the di-oxo methylene part of the hemiacetal to the carbonyl carbon in formaldehyde (c).



Scheme 4. The H-transfer from hemiacetal to formaldehyde leading either to methylformate and methanol (top), or to a dimer which quickly decomposes to formaldehyde (bottom).



Fig. 9. Methyl formate adsorbed onto the corner Mg and produced by HT from hemiacetal to formaldehyde (a); CO loss TS onto Mg3C (b); CO2-loss TS onto Mg3C (c).

weaker reducing agent than primary or secondary alcohols (e.g. isopropanol) due to the stabilization permitted by aliphatic chains to the forming carbonyl group; thus, the reason for this difference may be related to the thermodynamics of processes. As a first step to investigate possible reasons for the experimental results, TS energy barriers for the reduction of crotonaldehyde and butyraldehyde with methanol on $Mg_{10}O_{10}$ were calculated, and these were roughly 23 and 25 kcal/mol, i.e. slightly lower than the aromatic species in Table 4. With TS and reactant geometries being similar to those found for aromatic species, this finding clearly indicates that a kinetic hurdle should not be expected to be present for aliphatic aldehydes and that these experimental results may either be due to alternative reactivity or related to energy issues.

To verify whether or not the latter case may provide sound evidence, we computed the energy change ΔE for the reduction of all the tested carbonyl species with methanol in the gas phase, and assuming that product and reactants are adsorbed on the MgO surface. Data are shown in Table 5. As can be seen, all reactions are energetic (by 6–17 kcal/mol), both in the gas phase and on the MgO surface. Furthermore, it should be noted that – in the gas phase – the lowest ΔE is the one for the non-conjugated aldehyde butyraldehyde, thus suggesting that breaking the conjugation of carbonyl with a double bond or an aromatic group destabilizes the aldehyde. However, the effect related to adsorption for aromatic species is clearly substantial (ΔE is lowered by up to 3 kcal/mol, the smallest change being for acetophenone) and works

Table 5

Gas-phase and surface-adsorbed electronic ΔE (kcal/mol) for the hydride transfer between methanol and carbonylic species tested in this work; reactants and products are considered to be coordinated on the most stable site of the Mg₁₀O₁₀ cluster (usually the corner); B3LYP/6-31++G(d,p) level.

Carbonyl species	Gas-phase ΔE	Surface ΔE
Furfural	8.7	7.3
Benzaldehyde	9.4	6.4
Acetophenone	11.5	11.2
Crotonaldehyde	9.6	16.9
Butyraldehyde	5.9	11.7

in the direction of reducing the energetic request for the HT; the opposite is true for aliphatic species (increasing by 6–7 kcal/mol), whose reduction becomes more energetically demanding than for aromatic species.

In this case, the different behavior is explained by the structure of the adsorbed products shown in Fig. 10; there, it can be seen that the electron cloud of the π system in aromatic rings interacts directly with the dissociated proton bearing a partial positive charge. Such interaction reduces, for example, the energy of the adsorbed benzyl alcohol by roughly 9 kcal/mol, compared to a conformer where the ring points away from the proton. In conclusion, it seems that the lower activity with respect to reduction by HT of alignatic aldehydes may be explained by the thermodynamics of

the process; nevertheless, alternative reaction channels might also provide some contribution to a different behavior.

In conclusion, Fig. 11 summarizes the reaction pathway, and Scheme 5 shows a simplified picture of the sequential steps in the reduction of FAL into FAA. The reaction energy profile assumes as energy zero a doubly-ligated Mg3C bearing two methanol molecules, the latter being present in much higher abundance than other chemicals, plus the two molecules involved in the redox process via HT. While the first step describes the energetic change upon methanol substitution by FAL on Mg3C, the second describes the HT through a TS state 27.5 kcal/mol higher than the coadsorbed reactants. Note the substantial decrease in energy upon substituting the produced formaldehyde with methanol in the third step, as well as the energetic cost of desorbing the formed FFA due to the previously discussed effect of the aromatic ring. In conclusion, it can be seen that the HT is slightly endothermic due the cost of desorbing redox products, supporting the experimental evidence indicating that the somewhat limited requirement for the reaction temperature derives from the HT step.

Scheme 5 explicitly indicates the possible formation of methyl formate via HT transfer from methoxy methanol (the hemiacetal) and its two decomposition channels. In this respect, one might wonder if a similar channel is also open for FAL, which would lead to the formation of both the methyl ester of furoic acid and, perhaps, the relevant decomposition products also. As for this, the experimental results discussed for FAL suggested that the

equilibrium involved in forming acetal and hemiacetal may be in favor of the reactants and fairly sensitive to thermal effects, so that the hemiacetal from FAL should be present in low concentrations. if any. To verify whether this may be the case, we computed the change in gas-phase energy upon forming the methoxy hemiacetal for both formaldehyde and FAL, obtaining respectively -14.6 and -2.8 kcal/mol. These results clearly indicate a net disparity in reaction energy and that – even at the lowest temperature explored in our experiments – entropic effects should tilt the balance in favor of free FAL, due to the net decrease in the number of molecules upon hemiacetal formation. Conversely, the stronger energy decrease estimated for formaldehyde would be expected to bias the equilibrium toward the formation of methoxy methanol, a process facilitated by the presence in MgO of Mg acting as a Lewis acid (vide supra) even at low formaldehyde concentrations. Note that our results are in line with thermodynamic data reported in the literature [146], which indicate a less negative (by 2–3 kcal/mol) acetal formation enthalpy for aromatic species than for aliphatic ones, probably due to the stabilization effects induced by the conjugation with aromatic substituents, and a very low equilibrium constant (7.4×10^{-3}). Thus FAL hemiacetal should not be expected to play any substantial role in the reaction environment.

To conclude our discussion on the reaction processes involved in FAL reduction, it may be useful to mention that there are other alternatives that might explain the gaseous by-products, in addition to the decomposition channels discussed above. These



Fig. 10. Product alcohols adsorbed on the corner Mg: (a) butanol; (b) crotylic alcohol; (c) benzylic alcohol; (d) furfuryl alcohol; (e) 1-phenyl ethanol. Note the orientation of the dissociated proton with respect to aromatic rings.



Fig. 11. Reaction energy profile for FAL reduction by methanol on MgO. Note that energy zero has been chosen in order to have reactants in their most stable form (e.g. FAL in solution and two coordinated Mg3C sites).



Scheme 5. The simplified sequence of reactions occurring at the adsorbed state between FAL and methanol.

are the Cannizzaro-type disproportionation of formaldehyde leading to formic acid and methanol, and a direct HT from formaldehyde to FAL producing FFA and CO. In the first process, which would allow formic acid decomposition into CO and H₂O [145], oxygen from a water molecule is required. This makes this process unlikely, as H₂O is not among the reactants introduced into the reactor. Moreover, it may be expected that the mechanism for the Cannizzaro reaction would follow closely what was proposed for the methyl formate formation (i.e. via HT) [147] with the substitution of methanol by water, so that the latter species should be favored due to the large methanol excess. As for the second possibility, it seems unlikely that the process transferring hydrogen from formaldehyde to FAL could have a TS barrier as low as the one found for methoxy methanol, due to the absence of positive charge-stabilizing groups such as the coordinated O^- in methoxy methanolate, OH, or the methoxy group. In conclusion, we feel the methyl formate route is the most likely pathway along which gaseous products are formed.

4. Conclusions

The liquid-phase reduction of furfural and of 5-hydroxymethylfurfural, catalyzed by high-surface-area MgO, was carried out with 100% yield into furfuryl alcohol and bis(2,5-dihydroxymethyl)furan, respectively, using methanol as both the H-transfer reagent and the reaction solvent, under mild conditions (T 160 °C), with autogenous pressure, within a few hours' reaction time. The reaction co-products were exclusively gaseous compounds - CO, CO₂, and CH₄ - which were easily removed during reactor depressurization at room temperature. The use of methanol, as an unconventional H-transfer reagent, proved to be possible under generally mild reaction conditions, but only with aromatic aldehydes and ketones, because of thermodynamic constraints which limit the reaction in the case of aliphatic substrates, and with substrates not bearing α -activated H atoms. The reaction mechanism was investigated in detail, and proved to consist of a rate-determining step of H-transfer from methanol to carbonyl through a six-center TS involving the aldehyde and alcohol coordinated onto a Mg3C site. Other significant steps in the mechanism are represented by the adsorption of FAL onto Mg3C and the desorption of FAA from it, both presenting a positive energy requirement. With our modeling, we were also able to investigate gaseous by-product formation, which led us to suggest methyl formate decomposition as the most likely pathway. The ester is thought to form via HT transfer by a hemiacetal formed from formaldehyde and methanol to another aldehyde.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2014.06.023.

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