



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, CH₄, and CO₂. 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 H-transfer 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/granted 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-butanediol, 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 non-reactive 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, decarbonylation, 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

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].

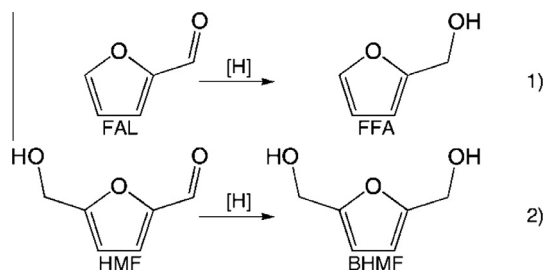
Here, we report on the reduction of FAL and HMF to the corresponding unsaturated alcohols, FFA and BHMF, using a simple procedure which enables selective HT from methanol to reactants, with MgO as the HT catalyst. The reaction is carried out in a liquid monophasic system, in which methanol also acts 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(NO₃)₂·6H₂O (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° 2θ, with acquisitions of 10 s every 2θ 0.1°). The surface area of MgO (125 m²/g) was measured using a Fisons Sorptly 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 N₂ (20 bar) and then pressurized at 1 bar (N₂). The temperature was increased up to 160 °C and the reaction mixture was stirred at



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

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