Research Article

Catalytic Transfer Hydrogenation of Glucose to Sorbitol with Raney Ni Catalysts Using Biomass-Derived Diols as Hydrogen Donors

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ABSTRACT: The catalytic transfer hydrogenation (CTH) of glucose to sorbitol has been studied using a wide collection of different biomass-derived alcohols and diols as hydrogen donors. Catalytic activity results reflect the feasibility to conduct this transformation in the presence of conventional, commercially available Raney Ni-type sponges as catalysts. Sacrificial diols displayed a superior performance as hydrogen donors as compared to short-chain alcohols, including secondary alcohols. Among them, terminal diols such as 1,4-butanediol and 1,5-pentanediol were revealed as excellent hydrogen donors, providing a high selectivity in the conversion of glucose into sorbitol. As for the catalysts, molybdenum promotion provided a very high catalytic activity to sponge nickel catalysts, even under mild temperature conditions. The transformation was also studied in a fixed-bed reactor under continuous-flow operation conditions. Results demonstrate that the catalysts are highly stable and able to operate for at least 550 h on stream with a high selectivity in the CTH of glucose to sorbitol.

KEYWORDS: Raney nickel, catalytic hydrogen transfer, sacrificial diols, biomass, bioproducts, glucose, sorbitol
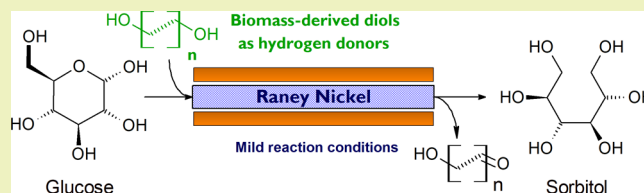
INTRODUCTION

The valorization of different biomass fractions to chemicals has received notable attention during the last decade. This is not only caused by the important environmental benefits related to the use of a renewable raw material of large availability and wide geographical distribution, as opposed to crude oil, but also because of the possibility to produce a wide variety of chemicals difficult to be obtained from other sources. Sugar alcohols constitute a group of bioproducts arising high interest from industry, in which these products find direct application as low-glycemic sweeteners[1] but also as a starting point for the manufacture of interesting derivatives. These include, for instance, sorbitan, which is used as spans in the food industry,[2] and isosorbide, which is used for the preparation of rigid polyesters,[3] both coming from the dehydration of sorbitol, and mono-oxygenated compounds and light alkanes,[4,5] produced by means of hydrogenation/hydrogenolysis among others.

Sugar alcohols are obtained through conventional catalytic hydrogenation processes.[6,7] These usually start from concentrated syrups of sugar monosaccharides and make use of typical hydrogenation catalysts, such as Raney-type nickel catalysts. These materials are robust and cheap catalysts that have taken over most of the hydrogenation industrial processes.[8] Nevertheless, though profitable at an industrial scale, nickel sponges do not lack of problems, such as the leaching of the metal when used in aqueous-phase conditions.[9] This leads to impurification of the product, whose commercialization require its elimination for food and pharma applications.[10,11] In addition, sugar hydrogenation usually requires high hydrogen pressures, typically between 40 and 80 bar, to achieve high

substrate conversion rates.[12] Within this context, numerous investigations have been reported on the development of alternative catalysts, including several noble metals (Ru, Pt, Pd, Rh, and Ir),[13−15] which avoid the problems ascribed to nickel leaching in aqueous solutions but entail a higher cost.

Catalytic transfer hydrogenation (CTH) can be considered as a chemically efficient, environmentally sustainable alternative to conventional hydrogenation.[16,17] CTH avoids several main issues associated with the use of hydrogen under high-pressure conditions. It has proven to be an excellent option for different biomass chemical valorization processes,[18−20] including the hydrodeoxygenation of lignin-derived aromatics,[21] polysaccharide hydrogenolysis,[22] or the reduction of platform molecules.[23] CTH has also been explored in the transformation of glucose to sorbitol,[24−27] although reported results are scarce, compared to hydrogenation, and evidence a low performance in terms of sorbitol productivity. In addition, the reducing nature of glucose makes its disproportionation easy under the reported CTH reaction conditions.[27,28] Enhancing the productivity of glucose to sorbitol CTH requires using hydrogen donors from which hydrogen abstraction is easier as compared to glucose or at least using reaction conditions favoring so. Most of the reported hydrogen donors in biomass

valorization include sacrificial alcohols,[29] formic acid and its esters,[30,31] cyclic ethers and amines,[17] or glycerol.[32,33] On the contrary, the use of diols, despite their good performance as hydrogen donors[34−37] with their dehydrogenation being coupled with some interesting hydrogenation reactions,[38−40] has been barely used in biomass valorization. One of the few examples is the work of Pérez-Ramirez et al.[41] about the reduction of glucose to sorbitol using homemade Ni-Cu-Al$_2$O$_3$ catalysts. These authors reported a 67% sorbitol yield when treating 96 mM glucose at 150 °C with 1,4-butanediol, under continuous operation conditions. Despite the promising results, this strategy has not received much attention—only one sacrificial diol has been reported—and its true potential remains unknown. Here, we report a thorough study on the use of different diols as hydrogen donors for the CTH of glucose to sorbitol in the presence of widely available commercial Raney Ni catalysts. Results evidence a very high potential of alkyl diols as hydrogen donors, especially terminal diols, which lead to almost quantitative yields toward sorbitol using cheap and commercially accessible catalysts based on Mo-promoted Raney Ni. Remarkably, the catalyst did not suffer deactivation after being used on stream for 550 h. Finally, it must be stressed that all of the tested diol hydrogen donors can be derived from biomass resources that enable the CTH reaction here described as a green and sustainable route for the production of sorbitol.

■ EXPERIMENTAL SECTION

Materials and Methods. D-Glucose (≥99.5%), fructose (≥99%), mannose (≥99%), sorbitol (99%), and mannitol (≥98%) were used without previous purification as starting raw materials and standards in the calibration of analytical techniques. Methanol (>99,5%), ethanol (>99,5%), 2-propanol (>99%), ethylene glycol (>99%), 1,2-propylene glycol (>99%), 1,3-propanediol (98%), 1,2- and 1,4-butanediols (98 and 99%, respectively), and 1,2- and 1,5-pentanediols (96 and 98%, respectively) were all purchased from Aldrich and used as hydrogen donors in catalytic transfer hydrogenations as received. Tested catalysts comprise a series of Raney-type sponge nickel catalysts, kindly provided by Johnson Matthey Process Technologies (commercial references A-4000, A-5000, and A-7063). All the catalysts were characterized by means of ICP-OES analysis for quantification of the metal composition. Prior to their analysis, the metal samples were digested to get aqueous solutions, which were analyzed using a Varian Vista AX ICP-OES unit, previously calibrated with standard stock solutions. Textural properties were determined by N$_2$ adsorption/desorption manometric porosimetry using a Micromeritics TriStar 3000 unit. Specific surface areas were calculated using the B.E.T. method, and the total pore volume was assumed to be that recorded at p/p_0 = 0.95 for each sample (see Supporting Information, Table SI-1).

Catalytic Tests. Catalytic transfer hydrogenation assays were carried out in two types of chemical reactors depending on whether batch or continuous-flow operation conditions were used. Experiments under batch conditions were performed in a 100 mL-capacity stainless steel reactor (Autoclave Engineers) fitted with a mechanical stirrer, a temperature controller, and a pressure gauge to monitor the reaction conditions. Typically, catalytic tests were performed starting from 75 mL of a suspension containing an appropriate amount of the catalyst, glucose (90 mM, equivalent to 1.6 wt %), and the hydrogen donor, which also acted as a reaction solvent. This suspension was outgassed by sonication under helium flow prior to the reaction. The autoclave was sealed, and inert conditions were ensured by fluxing the void part of the reactor with nitrogen. The reaction conditions were then set up to the desired temperature (90−130 °C) and stirring rate (500 rpm). All the experiments were performed under autogenous pressure conditions. Sample aliquots of the reaction media were periodically withdrawn for analytical purposes, for a total period time

of 6 h. Afterward, the reactor was cooled down in a water-ice bath, and the catalyst samples were recovered by filtration and stored for further analysis. Catalytic tests performed under continuous-flow conditions were conducted in a tubular fixed-bed reactor, fitted with an HPLC dosing pump. Typically, the catalyst (0.5 g) was loaded in a 1/4″ 316-SS tube and firmly held between silica beads. The temperature of the reaction was controlled through an electric furnace by continuously monitoring the temperature of the fixed-bed reactor. Pressure conditions were manually controlled through a backpressure regulator set at 5 × 10^2 kPa. In a typical experiment, once the temperature and pressure conditions were set, a 90 mM solution of glucose in 1,4-butanediol was dosed to the tubular reactor (t_0 of the experiment) at a given flow rate (typically 0.02 mL/min). These conditions were kept constant for more than 550 h. Sample aliquots were collected from a high-pressure liquid storage reservoir located before the backpressure valve in which the samples were accumulated for several hours (10−12 h). The collected samples were filtered through a 0.45 μm syringe filter and submitted for analysis.

Product Analysis. The analysis of the reaction aliquots was performed by using several chromatographic techniques. High-performance liquid-phase chromatography (HPLC) was used to determine the conversion of the substrate and the yields toward the main products. HPLC was performed using Agilent 1260 Infinity equipment fitted with an ELSD and a UV-DAD. Separations of the reaction mixtures were accomplished using a Hi-Plex Ca, 300 × 7.7 mm column, operating at 80 °C and using 0.6 mL/min of water as a mobile phase. The quantification of the extension of 1,4-butanediol hydrogen donation was performed through the analysis of sample aliquots by means of a Varian CP3900 GC unit fitted with a CP-WAX-52CB column. GC−MS and HPLC−MS were used to identify unknown products and were carried out in a Bruker 320-MS GC quadrupole mass spectrometer fitted with a BR-SWax column (30 m × 0.25 mm, DF = 0.25 μm) and in a Bruker UHPLC-HESI-MS triple quadrupole mass spectrometer, using a Bruker intensity Solo 2 C18 100 × 2.1 mm column. The results of the catalytic tests are expressed in terms of substrate conversion (X_i) and product yields (Y_i), which were calculated as follows

$$X_i = \frac{\left(\begin{array}{c}\text{initial moles of} \\ \text{the substrate in the reactor}\end{array}\right) - \left(\begin{array}{c}\text{final moles} \\ \text{of the substrate}\end{array}\right)}{\left(\begin{array}{c}\text{initial moles of} \\ \text{the substrate in the reactor}\end{array}\right)} \times 100 \tag{1}$$

$$Y_i = \frac{\left(\begin{array}{c}\text{final moles} \\ \text{of the product } i\end{array}\right)}{\left(\begin{array}{c}\text{initial moles of} \\ \text{the substrate in the reactor}\end{array}\right)} \times 100 \tag{2}$$

The repeatability of the catalytic tests was evaluated through a black box procedure in which the overall uncertainty was calculated based on the repetition of the same catalytic test four times. Uncertainties for substrate conversion and product yields are, all, below 2.5%.

■ RESULTS AND DISCUSSION

CTH with Short-Chain Monoalcohols. Raney-type nickel catalysts have been selected to drive the catalytic transfer hydrogenation of glucose to sorbitol due to their low cost, high versatility, and widespread use in industrial processes. Preliminary results on glucose CTH with sponge Ni catalysts were accomplished in the presence of short-chain alcohols, and these are summarized in Table 1.

The analysis of the reaction products confirmed the presence of several C6 sugar isomers after the CTH tests. Glucose, fructose, and mannose were all present in the reaction

Table 1. Preliminary Results from the Catalytic Transfer Hydrogenation of Glucose with Several Hydrogen Donors in the Presence of a Raney-Type Ni Sponge

no.[a]	H donor	X (%)	$Y_{Fructose}$ (%)	$Y_{Mannitol}$ (%)	$Y_{Sorbitol}$ (%)
1	methanol	64.5	18.7	0.0	21.6
2	ethanol	83.7	3.4	0.9	58.2
3	1-propanol	72.5	7.4	0.2	43.1
4	2-propanol	78.7	8.9	5.3	48.8
5	1-butanol	63.1	25.8	0.0	11.8
6	2-butanol	67.5	19.8	0.0	16.1

[a]Reaction conditions: reaction volume = 75 mL; [glucose] = 90 mM; catalyst to substrate weight ratio = 1:1; reaction temperature = 130 °C; reaction time = 6 h.

media, though the latter in a very low concentration (typically below 0.5% yield).

These monosaccharides are produced by isomerization of glucose and usually require the presence of Lewis acidic or basic functionalities to occur.[42] Together with the different sugar isomers, two hexitols, sorbitol and mannitol, were also present. Sorbitol is obtained from the reduction of glucose, whereas mannitol evolves from either the reduction of fructose or mannose or from the hydroisomerization of sorbitol (Scheme 1). Finally, regarding the side products, alkyl glycosides produced through the etherification of sugar monosaccharides with the short-chain alcohols, gluconolactone produced through the disproportionation of glucose by autoreduction,[27] or several C2 and C3 glycols and polyols, like ethylene glycol and glycerol, presumably produced from hexitols, were also detected, though in very low concentrations.

Interestingly, none of the tested short-chain alcohols (Table 1) led to the completion of the reaction in terms of substrate conversion. The sacrificial hydrogen donors providing larger substrate consumption (>80%) were ethanol and 2-propanol, which are usually described as efficient hydrogen donors.[29] As for the product distributions, a correlation between the size of the alkyl chain and the extension of the different reactions was observed. Results prove that the shorter the alkyl chain, the lower the extension of glucose isomerization and the higher the sorbitol yield. This occurs for all the tested alcohols, aside from methanol, which is not easily dehydrogenated under the tested reaction conditions, thus providing poor CTH product yields.

Ethanol yielded almost 60% of the starting glucose as sorbitol, with a minimum formation of side products (2.5 and 0.9% fructose and mannitol yields, respectively). On the contrary, 1-propanol and 1-butanol, tested under the same reaction conditions, produced 43.1 and 11.8% sorbitol yields, which in the case of 1-butanol, the result is less than half of the sorbitol yield provided by ethanol. On the other hand, these alcohols yielded fructose in 7.4 and 25.8%, which are substantially higher productions than those occurring in an ethanol medium.

Comparison between primary and secondary alcohols reflected slightly better performance of the latter in terms of sorbitol production, a fact usually ascribed to the easier dehydrogenation of secondary alcohols.[43] However, the observed differences in product distributions, when comparing reactions performed in the presence of alcohols with a different number of carbon atoms, are greater than those shown by alcohol isomers. In this way, the size of the alkyl group seems to be the most influential variable determining the efficiency of the sacrificial alcohol as a hydrogen donor, most probably because it also conditions the adsorption of the alcohol on the catalyst surface and its dehydrogenation. DFT molecular simulations have predicted that the interaction of an alcohol with Ni(111) surfaces occurs through the O atom, with the alkyl chain close to the surface, enabling the weakening of the O−H and C−H at the hydroxyl α-carbon bond.[44,45] This is a key step in the CTH transformation, the dehydrogenation of the sacrificial alcohol. However, a large concentration of the hydrogen donor could make this configuration difficult, as the oxygen atoms would preferentially interact with the metal surface, displacing the alkyl chain of other alcohol-adsorbed molecules to an upward configuration. This phenomenon would make the dehydrogenation of the alcohol with larger alkyl chains less favorable, thus depressing the extension of hydrogen transfer reactions with the selectivity of the process displaced toward the formation of side products, such as fructose or alkyl glucosides. In order to check this hypothesis, two catalytic tests were performed using a second solvent to dilute the diol used as a hydrogen donor. For this purpose, THF was selected due to its inability to transfer hydrogen or to undergo hydrogenolysis under the tested reaction conditions. In a similar way, 1-propanol was chosen as a hydrogen donor,

Scheme 1. Main and Side Reactions Occurring in the CTH Reduction of Glucose to Sorbitol with Short-Chain Alcohols in the Presence of Raney Nickel Catalysts
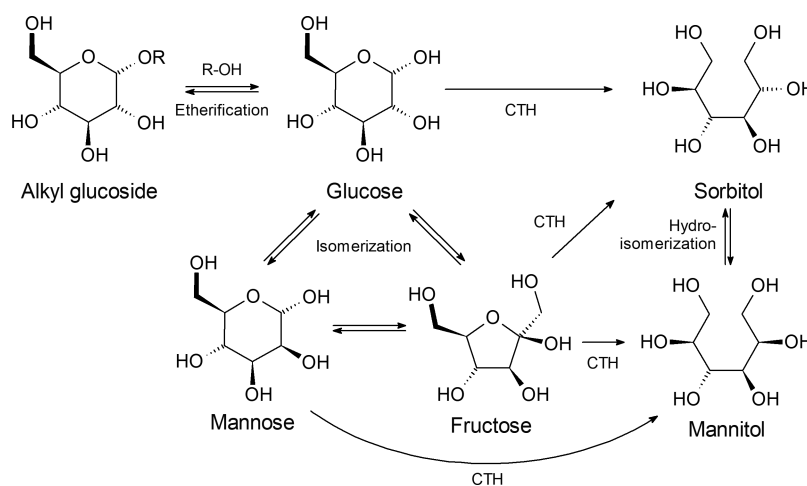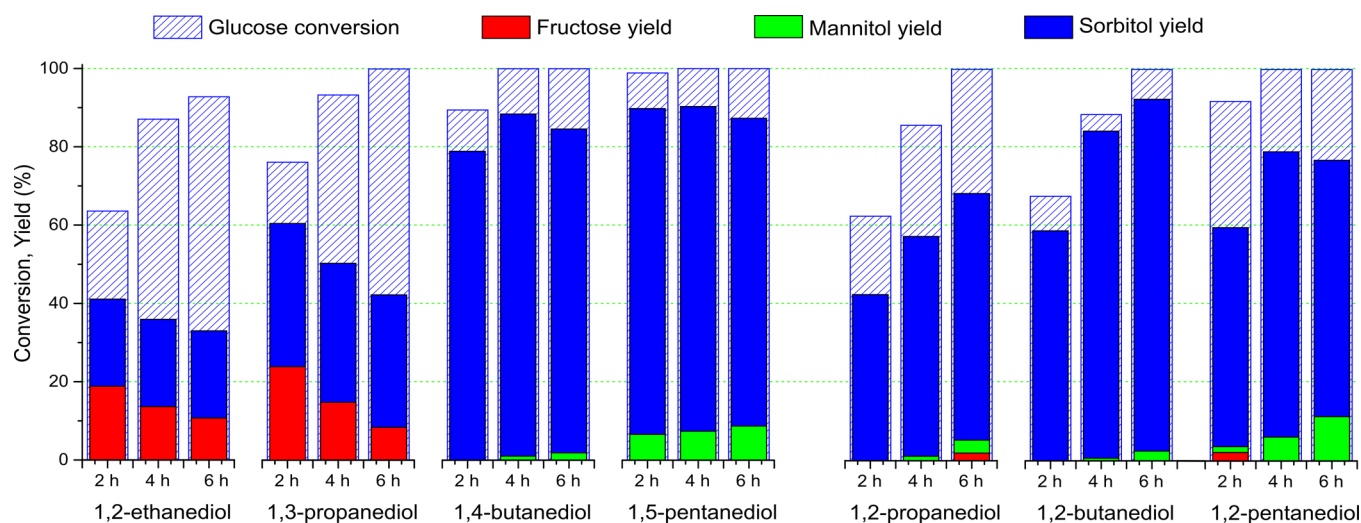
Figure 1. Results achieved in the catalytic transfer hydrogenation of glucose in the presence of different diols used as hydrogen donors after 2, 4, and 6 h. Reaction conditions: reaction volume = 75 mL; [glucose] = 90 mM; catalyst to substrate weight ratio = 1:1; temperature = 130 °C.

which evidences lack of performance as a sacrificial alcohol, and thus, there is some space for improvement. Two THF:1-propanol mixtures were tested (50:50 and 90:10 vol) to check the influence of the concentration of the alcohol on its ability to transfer hydrogen (see Supporting Information, Figure SI-1). The presence of THF exerted a strong influence on the product distribution achieved from glucose, as high yields toward fructose were detected in the presence of this cosolvent. As for the influence of the concentration of the hydrogen donor on the CTH reduction of glucose, the catalytic test performed using a 50:50 vol THF:1-propanol mixture provided a sorbitol yield close to that previously achieved within the test conducted in pure 1-propanol at 6 h (36.5% vs 43.1% sorbitol yield, respectively). However, kinetic curves point to a faster production of sorbitol during the early beginning of the catalytic test when THF-diluted 1-propanol (50:50 vol) was used as the reaction medium. This result supports the conclusion about the saturation of the nickel surface by a high concentration of the hydrogen donor diminishing its ability to conduct the catalytic transfer hydrogenation of glucose to sorbitol. A reaction in the presence of a 90:10 vol mixture of THF:1-propanol provided poor sorbitol yields (7.2% at 6 h), probably because of the excessive dilution of the hydrogen donor, but demonstrated that the CTH reduction of glucose was possible even using dilute hydrogen donors.

CTH with Diols: Screening of Hydrogen Donors. The use of short-chain alcohols, despite being a simple pathway for the conversion of glucose to sorbitol, evidences important drawbacks related to the ability of these alcohols to function as hydrogen donors. Bearing in mind these limitations and based on previous works on the use of diols for the catalytic transfer hydrogenation of various substrates,[36,41,46] several organic diols have been tested as hydrogen donors. The existence of the two hydroxyl groups in the same molecule allows for a closer interaction between the hydrogen donor and the catalyst surface[47] and thus a higher extension of its dehydrogenation, thus providing more hydrogen to the reaction media. Results achieved with selected diols are depicted in Figure 1.

Two sets of diols have been tested: diols showing primary/terminal hydroxyl groups and 1,2-glycols. The selected diols have been chosen from those liable to be produced from

lignocellulosic biomass, for instance, through hydrogenolytic pathways,[48−51] thus ensuring the complete renewability of the used chemicals. The selection includes 2 to 5 carbon diols, aiming to evaluate not only the influence of the relative position of hydroxyls but also the effect of the size of the hydrogen donor.

In the case of diols with terminal hydroxyl groups, 1,2-ethanediol and 1,3-propanediol yielded fructose and sorbitol as the main products, as well as minor quantities of glycosides through the reaction of monosaccharides with the sacrificial diols. The rapid production of fructose suggests a lack of performance of the C2 and C3 terminal diols in hydrogen transfer reactions. Indeed, these produced limited sorbitol yields (21.8 and 34.7%, respectively), and only during the early beginning of the reaction, they remained unaltered for the rest of the reaction time. This suggests the inhibition, as a function of time, of the hydrogen transfer capability of the catalyst.[21] Larger diols with terminal hydroxyl groups, e.g., 1,4-butanediol and 1,5-pentanediol, provided fast conversion of glucose, together with a high selectivity toward sorbitol. Moreover, no inhibition of the catalyst activity was observed in transfer hydrogenation.

As for the side products, 1,4-butanediol and 1,5-pentanediol did not produce glucose isomerization or etherification derivatives but mannitol, some other polyols, and bulky condensation-derived products. Since the formation of mannitol occurs at long reaction times, once monosaccharides are fully converted, its formation seems to proceed via sorbitol hydroisomerization (Scheme 1). On the other hand, GC−MS and HPLC−MS revealed the presence of C2 and C3 glycols as well as some bulky compounds showing C4 and C5 alkyl moieties. The C2 and C3 glycols can be ascribed to the hydrogenolysis of sorbitol, whereas bulky side products may evolve from condensation reactions, being the most plausible causes for the reduction of sorbitol yield observed at long reaction times. Treating sorbitol with 1,4-butanediol in the presence of Raney Ni catalysts confirmed the occurrence of these side reactions.

The detection of side products coming from hydro-isomerization and hydrogenolysis, two hydrogen-related reactions, which could be considered within this work as two forms of sorbitol overhydrogenation, evidences the plenty
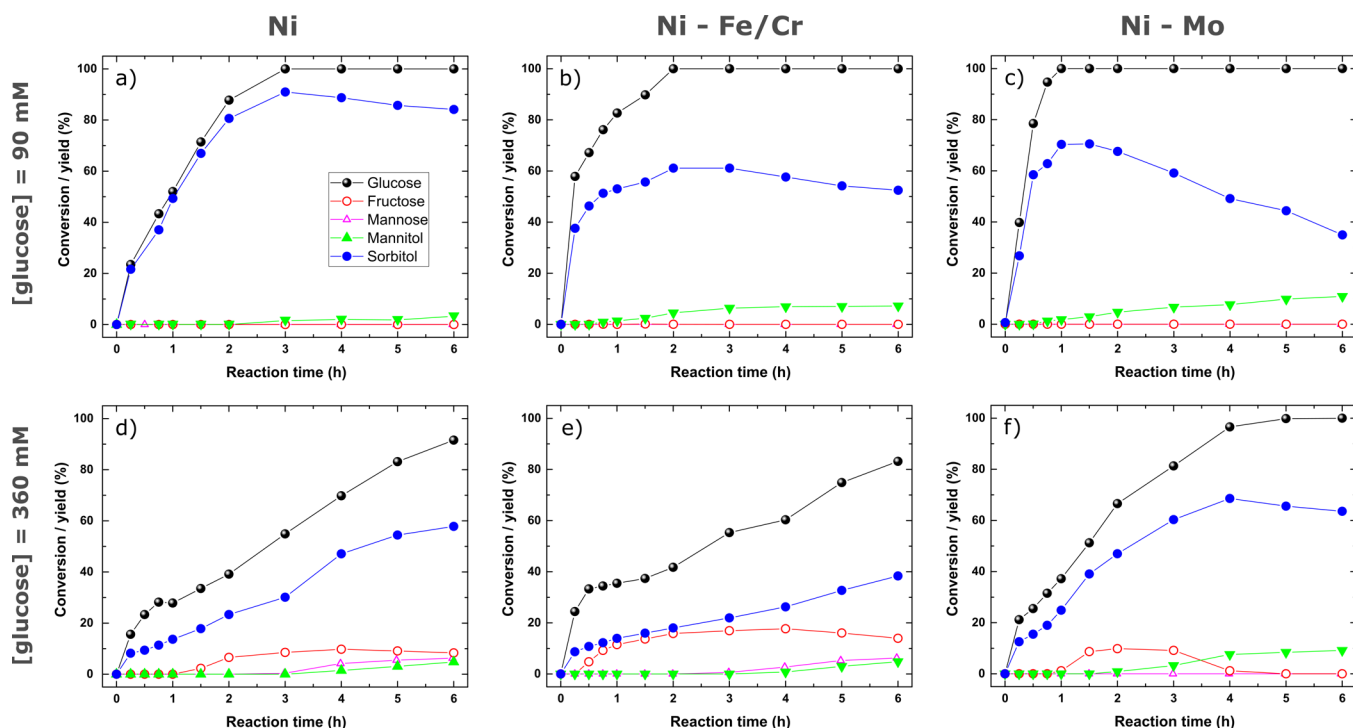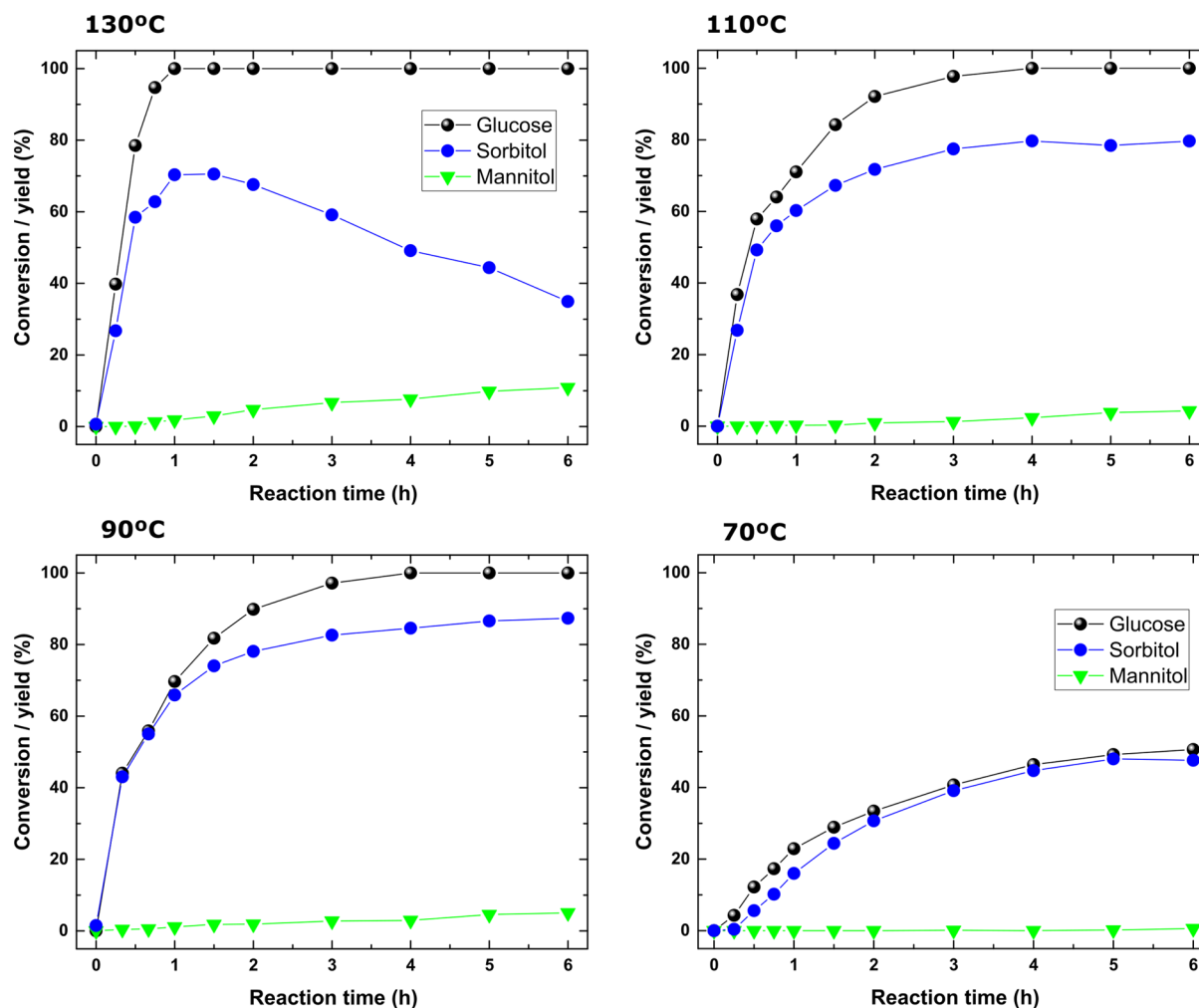
Figure 2. Results achieved in the catalytic transfer hydrogenation of glucose in 1,4-butanediol, at two different concentrations (90 and 360 mM), in the presence of Raney-type nickel catalysts showing different activity promoters: (a,d) unpromoted nickel catalyst, (b,e) Fe/Cr-promoted catalyst, and (c,f) Mo-promoted catalyst. Reaction conditions: reaction volume = 75 mL; [glucose] = 90 and 360 mM; catalyst loading = 1.65 g; reaction temperature = 130 °C.

availability of hydrogen onto the surface of the catalysts. This confirms the good performance of both 1,4-butanediol and 1,5-pentanediol as hydrogen donors. This behavior could be ascribed to the ability of the hydroxyaldehydes evolving after the dehydrogenation of terminal diols to form cyclic hemiacetals since the alkyl chains of these C4 and C5 diols are long enough to bend to provide the corresponding cyclic hemiacetals. These are expected to mildly interact with the catalyst surface because of a lower polarity, thus allowing fast replacement by the starting diol molecules. It is noteworthy that 2-oxolanol (the hemiacetal produced by cyclization of 5-hydroxypentanal evolving from the dehydrogenation of 1,5-pentanediol) has been reported to undergo a second dehydrogenation step to produce δ-valerolactone (see Supporting Information, Scheme SI-1).[52] This leads to a greater availability of hydrogen in the reaction media, but under our reaction conditions, this step barely occurs with the ether coming from the condensation of the cyclic hemiacetals with the diol hydrogen donor, the main product derived from 1,4-butanediol and 1,5-pentanediol (see Supporting Information, Scheme SI-2). Nevertheless, the reactions undergone by the hydroxyaldehyde avoid the reversibility of the transformation by rehydrogenation of the carbonyl groups, which is conducive to a higher availability of hydride groups for the reduction of the sugar molecules. This possibility does not occur in the case of simple alcohols, and thus, the reversibility between the sacrificial alcohol and the resultant carbonyl compound could make monoalcohols less efficient as hydrogen donors than diols with terminal hydroxyl functionalities.

As for 1,2-alkyl glycols, all of them displayed good performance as hydrogen donors, providing complete substrate conversion after 6 h, with sorbitol being the main reaction product, and a minimum formation of mannitol at long reaction times. As in the case of terminal diols, the rate of the substrate conversion increased with the size of the alkyl chain at the hydrogen donor, probably because of the same reasons mentioned above. One-to-one comparison between regioisomers of the hydrogen donors (terminal and 1,2-alkyl diols) suggests that glycols lead to slower substrate conversion than terminal diols but to a higher selectivity to sorbitol, altogether with a minimum formation of side products coming from glucose isomerization or etherification. This is especially evident in the case of C3 diols (Figure 1), in which 1,2-propanediol provided fructose and sorbitol yields of 2 and 65.4%, respectively, after 6 h, whereas 1,3-propanediol yielded the same products with 9.2 and 34.7% yields. 1,2-Butanediol and 1,2-pentanediol provided faster glucose conversion and higher sorbitol yields (90.8 and 68%, respectively, at 6 h) as compared to 1,2-propanediol. As for the lower sorbitol yield obtained for 1,2-pentanediol at 6 h, this is most probably due to its transformation through the sorbitol-consuming pathways involving hydroisomerization and hydrogenolysis, as suggested by the increasing yields obtained toward mannitol and C2 and C3 glycol-derived products.

Regarding the products coming from the sacrificial alcohol, 1,2-diols yielded, upon dehydrogenation, preferentially 1-hydroxy alkyl-2-ketones and minor quantities of 2-hydroxy aldehydes. This suggests that the dehydrogenation of the sacrificial glycol preferentially occurs on the secondary hydroxyl group, not on the terminal alcohol. In order to get a better insight into the better performance of sacrificial diols with pendant secondary hydroxyl groups, a new experiment, using 2,3-butanediol as a hydrogen donor, was performed (see Supporting Information, Figure SI-2). This hydrogen donor is able to provide very high yields of sorbitol, comparable to those obtained with its regioisomers 1,4-butanediol and 1,2-

Figure 3. Results achieved in the catalytic transfer hydrogenation of glucose in 1,4-butanediol (90 mM), in the presence of Mo-promoted Raney nickel catalysts at different reaction temperatures. Reaction conditions: reaction volume = 75 mL; [glucose] = 90 mM; catalyst loading = 1.65 g; reaction temperature = 70−130 °C.

butanediol but at a substantially higher rate. The fast reduction of sorbitol indicates that the dehydrogenation of the sacrificial diol occurs in a very fast manner, thus providing support to the conclusion about the better performance of the secondary hydroxyl functionalities as hydrogen donors.

From the previous results, it can be concluded that the sacrificial diol showing the best performance as a hydrogen donor for the catalytic transfer hydrogenation of glucose to sorbitol in the presence of the Raney nickel catalyst is 1,4-butanediol. The fast substrate conversion, together with a high selectivity for the desired hexitol, makes this diol the best option among the tested hydrogen donors. Nevertheless, despite the good catalytic performance shown by the tested Raney nickel catalyst, it still requires several hours to complete the reaction.

CTH with Promoted Raney Ni Catalysts. Aiming to increase the production rate for sorbitol under CTH conditions, we have explored the use of Fe/Cr- and Mo-promoted Raney-type nickel catalysts, which have also demonstrated catalytic activity in CTH reactions.[53] Doping Raney nickel catalysts with Fe/Cr and Mo species provides Lewis acidity to the resultant alloys, making them more oxophylic,[54] thus increasing their capability to interact with carbonyl groups such as those at the glucose substrate.

Figure 2 depicts the results achieved in the catalytic transfer hydrogenation of glucose with 1,4-butanediol in the presence of unpromoted and Fe/Cr- and Mo-promoted Raney nickel catalysts.

Catalytic tests performed with 90 mM glucose solutions revealed strong differences between the tested catalysts. Thus, Ni-Fe/Cr or Ni-Mo catalysts provided faster substrate conversion than the unpromoted catalyst but also a poor selectivity toward sorbitol. Both Ni-Fe/Cr and Ni-Mo catalysts produced a maximum sorbitol yield during the first 2 h of the reaction (61.1 and 70.5%, respectively), but afterward, it diminished until the end of the reaction. The decrease in sorbitol yield is accompanied by the production of significative amounts of mannitol (up to 10.9% in the case of the molybdenum-promoted catalyst). However, in this case, mannitol production and fructose consumption simultaneously occur, meaning that at least a fraction of mannitol is produced through the reduction of fructose (Scheme 1). Sorbitol consumption can be ascribed to the abovementioned hydroisomerization, hydrogenolysis, and condensation side reactions, which are extensive in the case of the promoted catalysts. The observed differences in terms of sorbitol production found between the tested catalysts can be ascribed to the different ability of the same catalyst in the dehydrogenation of 1,4-

butanediol used as a hydrogen donor. The results achieved in the presence of the different Raney-type catalysts (see Supporting Information, Figure SI-3) make the superior ability of molybdenum-promoted Raney nickel to get hydrogen from 1,4-butanediol evident followed by the unpromoted nickel sponge, with the Fe/Cr-promoted catalyst being the one showing a lower activity. The formation of 1,4-butanediol-derived products seems to proceed in a parallel way to the production of sorbitol and mannitol, as shown in Figure 2. In this way, it seems that the process is controlled by the first stage, the dehydrogenation of the diol, rather than by the hydrogenation of glucose.

Looking for the enhancement in the productivity of the process, we have explored a higher concentration of the substrate. Experiments performed with 360 mM glucose solutions pointed to, though magnified, the same differences already described between the tested catalysts. Under these conditions, the unpromoted nickel catalyst was not able to complete the reaction in terms of substrate conversion, yielding 57.8% of the starting glucose as sorbitol. Together with this hexitol, the nickel catalyst produced fructose and mannose in quite large yields (8.3 and 6.3%, respectively). The formation of these sugar isomers, which are not present in dilute catalytic tests, revealed the strong dependence of the glucose isomerization rate on its concentration. A similar profile was also observed for the Ni-Fe/Cr catalyst, though this material displayed a poor catalytic performance in CTH as compared to the unpromoted catalyst, with 38.4% sorbitol at 6 h. In contrast, the isomerization of the starting glucose was extensive. Both fructose and mannose were produced in appreciable yields (14.0 and 6.3%, respectively, at 6 h) in the presence of the iron/chromium-doped nickel catalyst. Glucose isomerization can be promoted by Lewis acids, and the presence of doping agents, like Fe and Cr, provides Lewis acidity to promote this side reaction. Finally, the Ni-Mo catalyst was the only catalyst able to fully convert the starting substrate while providing high sorbitol yield (68.6% at 4 h), evidencing its superior catalytic activity in the tested reaction. Fructose was also produced, not mannose, but it was fully converted during the course of the reaction, yielding sorbitol and mannitol. However, the Ni-Mo catalyst also leads to, if treating dilute glucose solutions, a high extension of the sorbitol-consuming hydroisomerization and hydrogenolysis side reactions. On the other hand, when starting from more concentrated glucose solutions, the enhancement of glucose isomerization leads to higher yields toward mannitol because of the reduction of the evolving fructose. Bearing this in mind, we conducted additional experiments with the molybdenum-promoted Raney catalyst, under dilute reaction conditions to prevent glucose isomerization, at different reaction temperatures, aiming to depress the extension of the sorbitol-consuming side reactions.

Figure 3 depicts the kinetic profiles recorded for glucose reduction to sorbitol with 1,4-butanediol, in the presence of Mo-promoted nickel catalysts, at different reaction temperatures. Substrate conversion was complete in the majority of the cases, though longer times were required as the applied temperature decreased. On the contrary, sorbitol yield increased when decreasing the reaction temperature, reaching an 87.3% sorbitol yield after 6 h at 90 °C. Cooling down the reaction temperature to 70 °C did not produce a higher yield of sorbitol because substrate conversion abruptly dropped to 47.6%, but under these conditions, the selectivity of the

conversion of glucose to sorbitol was almost complete. These experiments demonstrate the existence of a limit in the reaction temperature in which the CTH transformation can be applied.

The high selectivity of the transformation of glucose to sorbitol at 90 °C is the consequence of the depression of the hydrogenolytic and condensation side reactions at low temperatures. This suggests that the side reactions of sorbitol are more sensitive to temperature changes than the catalytic transfer hydrogenation of glucose and that their extension can be limited, as demonstrated, by operating at lower reaction temperature conditions. Nevertheless, decreasing the reaction temperature leads to a substantially lower rate in the conversion of the substrate, and thus, the productivity of sorbitol is also reduced. The reasons behind the high dependence of the CTH extension on temperature can be found in the dehydrogenation rate of 1,4-butanediol. Figure SI-5 displays the conversion of 1,4-butanediol and the dehydrogenation-derived products. Results reveal a dramatic influence of the temperature on the ability of the molybdenum-promoted nickel sponge to conduct the dehydrogenation of 1,4-butanediol, with its conversion above 10% at 130 °C but below 1.0% at 70 °C. Nevertheless, these results also revealed the high efficiency of the catalyst to transfer hydrogen from 1,4-butanediol to glucose, even at low temperature conditions.

In order to explore different alternatives to expand the productivity of the catalytic transfer hydrogenation of glucose to sorbitol in the presence of 1,4-butanediol, continuous-flow operation conditions were explored by conducting the catalytic test in a fixed-bed reactor. These new experiments have allowed not only to evaluate the possibility to carry out the desired transformation under continuous operation conditions but also to evaluate the existence of eventual catalyst deactivation phenomena, hidden under batch conditions, and the stability of the catalytic system.

CTH of Glucose under Continuous-Flow Operating Conditions. Figure 4 depicts the results achieved in the experiments performed in a fixed-bed reactor using Raney Ni and Mo-promoted Raney Ni catalysts under different temperature conditions. The experiments were carried out using a single catalyst loading (typically 0.5 g), without previous or intermediate catalyst treatment. As observed, these catalytic tests were conducted for several hundreds of hours of time on stream. A spatial velocity of 0.04 min^{-1} was used in all the experiments.

Results from the catalytic tests performed in the presence of the unpromoted sponge Raney Ni catalyst (Figure 4A) makes the low catalytic performance of this material evident in the CTH of glucose. Initially, the experiment was conducted at 110 °C for 250 h. Substrate conversion was quite reduced, below 20.4%, which was accompanied by a quite low sorbitol yield, too (ca. 17−20%). The selectivity of the transformation was high, above 90%, due to the negligible formation of fructose or mannitol, probably because of the low temperature conditions. However, the catalytic performance of the Raney Ni catalyst was partially reduced in so far as the reaction proceeded, as it is evident from the decreasing glucose conversion and sorbitol yields achieved at long time on stream values. The analysis of the reaction aliquots by means of ICP-OES reflected negligible nickel leaching, so the catalyst deactivation must be probably caused by the blockage of the catalytic sites by organic deposits. An attempt to compensate the catalytic activity loss detected at 110 °C was carried out by
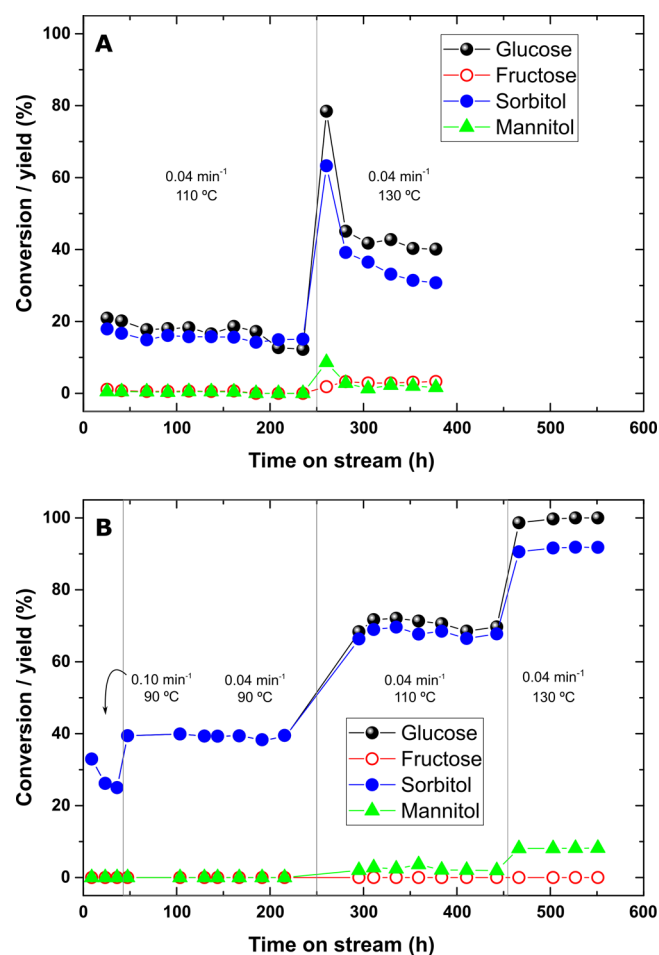
Figure 4. Reaction profiles (substrate conversion and product yields) achieved from the CTH reduction of glucose to sorbitol in the presence of (A) unpromoted and (B) molybdenum-promoted Raney-type Ni sponges. Reaction conditions: [glucose] = 90 mM; catalyst loading = 0.5 g; reaction temperature = 90−130 °C.

increasing the reaction temperature to 130 °C. Nevertheless, this modification of the temperature conditions resulted in the opposite to that of expected. Right after increasing the reaction temperature to 130 °C, the substrate conversion increased to 80%, accompanied by a high sorbitol yield of 63%. However, few hours after this enhancement in the productivity of sorbitol, both the substrate conversion and sorbitol yield abruptly dropped to 45 and 39%, respectively. The loss of catalytic activity continued with time, and it was even more evident than that observed at 110 °C. Simultaneously to the reduction in the conversion of the substrate and the yield of sorbitol, the difference between these two parameters increased with time, meaning that the selectivity of the transformation of glucose to sorbitol decreased. In this way, both fructose and mannitol side products evolved from the reactor in quantifiable amounts (above 5%). These results confirm the conclusion extracted from reactions performed in batch conditions about the higher sensitivity of side reactions to the reaction temperature, being favored in so far as the temperature increased.

Fixed-bed experiments were completed by conducting similar experiments to those above described by using the Mo-promoted Nickel catalyst (Figure 4B). Reaction conditions were quite similar to those previously applied for the

unpromoted catalyst, though in this case, bearing in mind the superior catalytic performance demonstrated by this material under batch reaction conditions, that is, a higher spatial velocity (0.1 min^{-1}) and lower reaction temperature conditions (90 °C) were initially assayed. Under these conditions, low sorbitol yields were produced (ca. 30%), in a very high selective manner, close to 100%. However, in order to perform a suitable comparison of the catalytic performance with the unpromoted catalysts, the space velocity was readily reduced to 0.04 g min^{-1}. Under these conditions, the molybdenum-doped nickel catalyst displayed a much higher catalytic performance than the bare one, providing a 40% sorbitol yield for a similar substrate conversion value and a negligible formation of side products. The catalyst remained stable for at least 150 h, evidencing the robustness of the system and the resistance against deactivation phenomena. Afterward, the reaction temperature was set up to 110 °C to assay the very same reaction conditions already used for the unpromoted material. Under these conditions, the molybdenum-doped material evidenced the superior catalytic performance, more than three-fold higher than that of the unpromoted material, which was already observed in batch reactors. Thus, a substrate conversion of 70−71% was accompanied with sorbitol yield values in the range of 66−69%. Together with the main reactants, the presence of mannitol was quantified in low yields (2−4%), with its origin being the hydroisomerization of the main polyol product, as already explained. Finally, in order to explore the limits of the operation and the resistance of the Mo-doped catalyst against deactivation, the reaction temperature was finally increased to 130 °C. Under these conditions, a complete substrate conversion was achieved together with a 100% selectivity to hexitols, being distributed as 90% sorbitol and 10% mannitol. No other side products were observed, whereas the conversion and product yields remained stable for at least 100 h, totaling 550 h of operation time on stream. These results evidence the very high catalytic activity, stability, and resistance against deactivation of the Mo-promoted Raney-type nickel sponge catalytic system in the CTH reduction of glucose to sorbitol, using 1,4-butanediol as a hydrogen donor.

In order to explore the reasons for the different stability of the bare Raney nickel and molybdenum-promoted Raney nickel, samples of the spent catalysts were analyzed by means of thermogravimetric and nitrogen adsorption−desorption analyses (Supporting Information, Figure SI-5). TGA results evidence the presence of organic deposits onto the surface of the spent catalysts, both pure nickel and molybdenum-doped nickel, though in the first case, the amount of organic deposits is much higher. These deposits have an outstanding influence on the textural properties of the metal sponges, as it is evident in the nitrogen adsorption−desorption isotherms collected for fresh and spent samples of these two catalysts. These results support our claim about the blockage of the porous structure because of deposition of organics onto the surface of the spent catalysts, which seems to take place in the presence of the conventional Raney nickel catalyst in a higher extension than when using the molybdenum-doped counterpart. This behavior could be related to the existence of side reactions taking place in the presence of Raney nickel, which are minimized when using Mo-Raney nickel because of the higher catalytic activity of the latter in hydrogen transfer reactions.

CONCLUSIONS

The catalytic transfer hydrogenation of glucose to sorbitol has been efficiently performed in the presence of conventional Raney nickel catalysts. The study on the feasibility of this transformation has reflected the superior performance of alkyl diols as hydrogen donors, as compared to short-chain monoalcohols, including secondary alcohols like *iso*-propanol or *sec*-butanol. Different types of diols have been tested as sacrificial hydrogen donors; however, diols showing C4 and C5 alkyl chains have provided better results in the reduction of glucose to sorbitol as compared to shorter-chain analogues. This result involves an additional advantage from a sustainability point of view since the tested butyl- and pentyl-derived diols can be produced from biomass sources. As for the catalyst, molybdenum promotion of the nickel sponge leads to a highly active, efficient catalyst able to conduct the catalytic transfer hydrogenation of glucose to sorbitol even under mild temperatures. Finally, the catalytic system and the studied transformation have been proven to work properly in a fixed-bed reactor under continuous-flow operation for 550 h, yielding quantitative conversion of glucose into hexitols, with the selectivity of the transformation to sorbitol being above 90%. The catalyst was stable during all the continuous-flow experiments showing no evidence of deactivation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.1c04957.

> Physicochemical properties of Raney nickel catalysts used in this work, reaction schemes for the transformation of C4 and C5 hydroxyaldehydes derived from terminal diols used as hydrogen donors and related derived products, influence of the concentration in reaction media of 1-propanol as a hydrogen donor in glucose CTH, comparison between butanediol regioisomers as hydrogen donors in glucose CTH, 1,4-butanediol conversion and derived product yields achieved in glucose CTH driven by different Raney-type nickel-based catalysts at different temperatures, and thermogravimetric analysis and nitrogen adsorption/desorption isotherms recorded for spent Raney Ni and Mo-doped Raney Ni catalysts after use in fixed-bed reactors (PDF)

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Author Contributions

J.I. and J.M. conceptualized the study and designed the research; J.I. and M.L.G. acquired funds for the investigation; B.G., A.O.S., and M.L.G. conducted the catalytic experiments; J.I., J.M., and M.L.G. supervised the work. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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REFERENCES

(1) Grembecka, M. Sugar Alcohols—Their Role in the Modern World of Sweeteners: A Review. *Eur. Food Res. Technol.* **2015**, *241*, 1−14.

(2) Glittenberg, D. Starch-Based Biopolymers in Paper, Corrugating, and Other Industrial Applications. In *Polymer Science: A Comprehensive Reference, 10 Volume Set*; Elsevier, 2012; Vol. 10, pp 165−193, DOI: 10.1016/B978-0-444-53349-4.00258-2.

(3) Delbecq, F.; Khodadadi, M. R.; Rodriguez Padron, D.; Varma, R.; Len, C. Isosorbide: Recent Advances in Catalytic Production. *In Molecular Catalysis* **2020**, *482*, 110648.

(4) Vilcocq, L.; Cabiac, A.; Especel, C.; Guillon, E.; Duprez, D. Transformation Du Sorbitol En Biocarburants Par Catalyse Hétérogène: Considerations Chimiques et Industrielles. *Oil Gas Sci. Technol.* **2013**, *68*, 841−860.

(5) Zada, B.; Chen, M.; Chen, C.; Yan, L.; Xu, Q.; Li, W.; Guo, Q.; Fu, Y. Recent Advances in Catalytic Production of Sugar Alcohols and Their Applications. *Sci. China Chem.* **2017**, *60*, 853−869.

(6) Zhang, J.; Li, J. B.; Wu, S.; Bin; Liu, Y. Advances in the Catalytic Production and Utilization of Sorbitol. *Ind. Eng. Chem. Res.* **2013**, *52*, 11799−11815.

(7) Delgado Arcaño, Y.; Valmaña García, O. D.; Mandelli, D.; Carvalho, W. A.; Magalhães Pontes, L. A. Xylitol: A Review on the Progress and Challenges of Its Production by Chemical Route. *Catal. Today* **2020**, *344*, 2−14.

(8) Schiweck, H.; Bär, A.; Vogel, R.; Schwarz, E.; Kunz, M.; Dusautois, C.; Clement, A.; Lefranc, C.; Lüssem, B.; Moser, M.; et al. Sugar Alcohols. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH − Co. KGaA: Weinheim, Germany, 2012, DOI: 10.1002/14356007.a25_413.pub3.

(9) Kusserow, B.; Schimpf, S.; Claus, P. Hydrogenation of Glucose to Sorbitol over Nickel and Ruthenium Catalysts. *Adv. Synth. Catal.* **2003**, *345*, 289−299.

(10) ESFA Panel on Contaminants in the Food Chain. Scientific Opinion on the Risks to Public Health Related to the Presence of Nickel in Food and Drinking Water. *EFSA J.* **2015**, *13*, 1−202.

(11) European Medicines Agency - Committee for Human Medicinal Products. *Guideline for Elemental Impurities*; 2019; Vol. Q3D(R1).

(12) Moreno, J.; Iglesias, J.; Blanco, J.; Montero, M.; Morales, G.; Melero, J. A. Life-Cycle Sustainability of Biomass-Derived Sorbitol: Proposing Technological Alternatives for Improving the Environ-

mental Profile of a Bio-Refinery Platform Molecule. *J. Cleaner Prod.* **2020**, *250*, 119568.

(13) Negoi, A.; Triantafyllidis, K.; Parvulescu, V. I.; Coman, S. M. The Hydrolytic Hydrogenation of Cellulose to Sorbitol over M (Ru, Ir, Pd, Rh)-BEA-Zeolite Catalysts. *Catal. Today* **2014**, *223*, 122−128.

(14) Zhang, X.; Durndell, L. J.; Isaacs, M. A.; Parlett, C. M. A.; Lee, A. F.; Wilson, K. Platinum-Catalyzed Aqueous-Phase Hydrogenation of D-Glucose to D-Sorbitol. *ACS Catal.* **2016**, *6*, 7409−7417.

(15) Melero, J. A.; Moreno, J.; Iglesias, J.; Morales, G.; Fierro, J. L. G.; Sánchez-Vázquez, R.; Cubo, A.; García, B. Ru-ZrO2-SBA-15 as Efficient and Robust Catalyst for the Aqueous Phase Hydrogenation of Glucose to Sorbitol. *Mol. Catal.* **2020**, *484*, 110802.

(16) Wang, D.; Astruc, D. The Golden Age of Transfer Hydrogenation. *Chem. Rev.* **2015**, *115*, 6621−6686.

(17) Baráth, E. Hydrogen Transfer Reactions of Carbonyls, Alkynes, and Alkenes with Noble Metals in the Presence of Alcohols/Ethers and Amines as Hydrogen Donors. *Catalysts* **2018**, *8*, 671.

(18) Jin, X.; Yin, B.; Xia, Q.; Fang, T.; Shen, J.; Kuang, L.; Yang, C. Catalytic Transfer Hydrogenation of Biomass-Derived Substrates to Value-Added Chemicals on Dual-Function Catalysts: Opportunities and Challenges. *ChemSusChem* **2019**, *12*, 71−92.

(19) Gilkey, M. J.; Xu, B. Heterogeneous Catalytic Transfer Hydrogenation as an Effective Pathway in Biomass Upgrading. *ACS Catal.* **2016**, *6*, 1420−1436.

(20) Shivhare, A.; Kumar, A.; Srivastava, R. An Account of the Catalytic Transfer Hydrogenation and Hydrogenolysis of Carbohydrate-Derived Renewable Platform Chemicals over Non-Precious Heterogeneous Metal Catalysts. *ChemCatChem* **2021**, *13*, 59−80.

(21) Kennema, M.; De Castro, I. B. D.; Meemken, F.; Rinaldi, R. Liquid-Phase H-Transfer from 2-Propanol to Phenol on Raney Ni: Surface Processes and Inhibition. *ACS Catal.* **2017**, *7*, 2437−2445.

(22) Liang, G.; He, L.; Cheng, H.; Li, W.; Li, X.; Zhang, C.; Yu, Y.; Zhao, F. The Hydrogenation/Dehydrogenation Activity of Supported Ni Catalysts and Their Effect on Hexitols Selectivity in Hydrolytic Hydrogenation of Cellulose. *J. Catal.* **2014**, *309*, 468−476.

(23) Scholz, D.; Aellig, C.; Hermans, I. Catalytic Transfer Hydrogenation/Hydrogenolysis for Reductive Upgrading of Furfural and 5-(Hydroxymethyl)Furfural. *ChemSusChem* **2014**, *7*, 268−275.

(24) van Hengstum, A. J.; Kieboom, A. P. G.; van Bekkum, H. Catalytic Transfer Hydrogenation of Glucose-Fructose Syrups in Alkaline Solution. *Starch-Starke* **1984**, *36*, 317−320.

(25) Kieboom, A. P. G.; van Bekkum, H. Aspects of the Chemical Conversion of Glucose. *Recl. des Trav. Chim. des Pays-Bas* **1984**, *103*, 1−12.

(26) Kobayashi, H.; Matsuhashi, H.; Komanoya, T.; Hara, K.; Fukuoka, A. Transfer Hydrogenation of Cellulose to Sugar Alcohols over Supported Ruthenium Catalysts. *Chem. Commun.* **2011**, *47*, 2366−2368.

(27) García, B.; Moreno, J.; Iglesias, J.; Melero, J. A.; Morales, G. Transformation of Glucose into Sorbitol on Raney Nickel Catalysts in the Absence of Molecular Hydrogen: Sugar Disproportionation vs Catalytic Hydrogen Transfer. *Top. Catal.* **2019**, *62*, 570−578.

(28) Komanoya, T.; Kobayashi, H.; Hara, K.; Chun, W. J.; Fukuoka, A. Simultaneous Formation of Sorbitol and Gluconic Acid from Cellobiose Using Carbon-Supported Ruthenium Catalysts. *J. Energy Chem.* **2013**, *22*, 290−295.

(29) Panagiotopoulou, P.; Martin, N.; Vlachos, D. G. Effect of Hydrogen Donor on Liquid Phase Catalytic Transfer Hydrogenation of Furfural over a Ru/RuO2/C Catalyst. *J. Mol. Catal. A: Chem.* **2014**, *392*, 223−228.

(30) Shen, Z.; Zhang, Y.; Jin, F.; Zhou, X.; Kishita, A.; Tohji, K. Hydrogen-Transfer Reduction of Ketones into Corresponding Alcohols Using Formic Acid as a Hydrogen Donor without a Metal Catalyst in High-Temperature Water. *Ind. Eng. Chem. Res.* **2010**, *49*, 6255−6259.

(31) López Granados, M.; Moreno, J.; Alba-Rubio, A. C.; Iglesias, J.; Martín Alonso, D.; Mariscal, R. Catalytic Transfer Hydrogenation of Maleic Acid with Stoichiometric Amounts of Formic Acid in Aqueous

Phase: Paving the Way for More Sustainable Succinic Acid Production. *Green Chem.* **2020**, *22*, 1859−1872.

(32) Sung, K.; Lee, M. H.; Cheong, Y. J.; Jang, H. Y. Ir(Triscarbene)-Catalyzed Sustainable Transfer Hydrogenation of Levulinic Acid to γ-Valerolactone. *Appl. Organomet. Chem.* **2021**, *35*, No. e6105.

(33) Ainembabazi, D.; Wang, K.; Finn, M.; Ridenour, J.; Voutchkova-Kostal, A. Efficient Transfer Hydrogenation of Carbonate Salts from Glycerol Using Water-Soluble Iridium N-Heterocyclic Carbene Catalysts. *Green Chem.* **2020**, *22*, 6093−6104.

(34) Kijeński, J.; Ruszczyński, J.; Knedler, I.; Gliński, M. Polyhydroxy Alcohols as Hydrogen Donors in Catalytic Transfer Reduction of Carbonyl Groups over MgO. *React. Kinet. Catal. Lett.* **1993**, *49*, 287−291.

(35) Maytum, H. C.; Tavassoli, B.; Williams, J. M. J. Reduction of Aldehydes and Ketones by Transfer Hydrogenation with 1,4-Butanediol. *Org. Lett.* **2007**, *9*, 4387−4389.

(36) Maytum, H. C.; Francos, J.; Whatrup, D. J.; Williams, J. M. J. 1, 4-Butanediol As a Reducing Agent in Transfer Hydrogenation Reactions. *Chem. - An Asian J.* **2010**, *5*, 538−542.

(37) Wakeham, R. J.; Morris, J. A.; Williams, J. M. J. Alternative Hydrogen Source for Asymmetric Transfer Hydrogenation in the Reduction of Ketones. *ChemCatChem* **2015**, *7*, 4039−4041.

(38) Marčec, R. Reduction of Carbonyl Compounds by Catalytic Hydrogen Transfer from 1, 4-Butanediol. *Zeitschrift fur Naturforsch. - Sect. B J. Chem. Sci.* **1984**, *39*, 1823−1824.

(39) Wang, H.; Ding, G.; Li, X.; She, H.; Zhu, Y.; Li, Y. Sustainable Production of γ-Valerolactone and δ-Valerolactone through the Coupling of Hydrogenation and Dehydrogenation. *Sustain. Energy Fuels* **2021**, *5*, 930−934.

(40) Bhanushali, J. T.; Prasad, D.; Patil, K. N.; Reddy, K. S.; Rama Rao, K. S.; Jadhav, A. H.; Nagaraja, B. M. Simultaneous Dehydrogenation of 1,4- Butanediol to γ-Butyrolactone and Hydrogenation of Benzaldehyde to Benzyl Alcohol Mediated over Competent CeO2−Al2O3 Supported Cu as Catalyst. *Int. J. Hydrogen Energy* **2020**, *45*, 12874−12888.

(41) Scholz, D.; Aellig, C.; Mondelli, C.; Pérez-Ramírez, J. Continuous Transfer Hydrogenation of Sugars to Alditols with Bioderived Donors over Cu-Ni-Al Catalysts. *ChemCatChem* **2015**, *7*, 1551−1558.

(42) Delidovich, I.; Palkovits, R. Catalytic Isomerization of Biomass-Derived Aldoses: A Review. *ChemSusChem* **2016**, *9*, 547−561.

(43) Jalid, F.; Khan, T. S.; Haider, M. A. Insights into the Activity and Selectivity Trends in Non-Oxidative Dehydrogenation of Primary and Secondary Alcohols over the Copper Catalyst. *Catal. Today* **2021**, *370*, 151−160.

(44) Tereshchuk, P.; Silva, J. L. F. D.; Postal, C.; Postal, C. Ethanol and Water Adsorption on Close-Packed 3d , 4d , and 5d Transition-Metal Surfaces : A Density Functional Theory Investigation with van Der Waals Correction. *J. Phys. Chem. C* **2012**, *116*, 24695−24705.

(45) Costa-Amaral, R.; Silva, J. L. F. D. The Adsorption of Alcohols on Strained Pt3Ni(111) Substrates: A Density Functional Investigation within the D3 van Der Waals Correction. *Phys. Chem. Chem. Phys.* **2018**, *20*, 24210−24221.

(46) Garduno, J. A.; García, J. J. Nickel-Catalyzed Transfer Hydrogenation of Benzonitriles with 2-Propanol and 1,4-Butanediol as the Hydrogen Source. *ACS Omega* **2017**, *2*, 2337−2343.

(47) Mendes, P. C. D.; Costa-Amaral, R.; Gomes, J. F.; Da Silva, J. L. F. The Influence of Hydroxy Groups on the Adsorption of Three-Carbon Alcohols on Ni(111), Pd(111) and Pt(111) Surfaces: A Density Functional Theory Study within the D3 Dispersion Correction. *Phys. Chem. Chem. Phys.* **2019**, *21*, 8434−8444.

(48) Xu, W.; Wang, H.; Liu, X.; Ren, J.; Wang, Y.; Lu, G. Direct Catalytic Conversion of Furfural to 1,5-Pentanediol by Hydrogenolysis of the Furan Ring under Mild Conditions over Pt/Co2AlO4 Catalyst. *Chem. Commun.* **2011**, *47*, 3924−3926.

(49) Ooms, R.; Dusselier, M.; Geboers, J. A.; Op De Beeck, B.; Verhaeven, R.; Gobechiya, E.; Martens, J. A.; Redl, A.; Sels, B. F. Conversion of Sugars to Ethylene Glycol with Nickel Tungsten

Carbide in a Fed-Batch Reactor: High Productivity and Reaction Network Elucidation. *Green Chem.* **2014**, *16*, 695−707.

(50) Wang, X.; Liu, X.; Xu, Y.; Peng, G.; Cao, Q.; Mu, X. Sorbitol Hydrogenolysis to Glycerol and Glycols over M-MgO (M = Ni, Co, Cu) Nanocomposite: A Comparative Study of Active Metals. *Cuihua Xuebao/Chinese J. Catal.* **2015**, *36*, 1614−1622.

(51) Murillo Leo, I.; López Granados, M.; Fierro, J. L. G.; Mariscal, R. Selective Conversion of Sorbitol to Glycols and Stability of Nickel-Ruthenium Supported on Calcium Hydroxide Catalysts. *Appl. Catal. B Environ.* **2016**, *185*, 141−149.

(52) Zhao, J.; Hartwig, J. F. Acceptorless, Neat, Ruthenium-Catalyzed Dehydrogenative Cyclization of Diols to Lactones. *Organometallics* **2005**, *24*, 2441−2446.

(53) García, B.; Moreno, J.; Morales, G.; Melero, J. A.; Iglesias, J. Production of Sorbitol via Catalytic Transfer Hydrogenation of Glucose. *Appl. Sci.* **2020**, *10*, 1843−1854.

(54) Hoffer, B. W.; Crezee, E.; Devred, F.; Mooijman, P. R. M.; Sloof, W. G.; Kooyman, P. J.; Van Langeveld, A. D.; Kapteijn, F.; Moulijn, J. A. The Role of the Active Phase of Raney-Type Ni Catalysts in the Selective Hydrogenation of D-Glucose to D-Sorbitol. *Appl. Catal. A Gen.* **2003**, *253*, 437−452.