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Hydrogenolysis of sorbitol into valuable C3-C2 alcohols at low H₂ pressure promoted by the heterogeneous Pd/Fe₃O₄ catalyst

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Abstract

The hydrogenolysis of sorbitol and various C5-C3 polyols (xylitol; erythritol; 1,2- 1,4- and 2,3-butandiol; 1,2-propandiol; glycerol) have been investigated at low molecular hydrogen pressure (5 bar) by using Pd/Fe₃O₄, as heterogeneous catalyst and water as the reaction medium. Catalytic experiments show that the carbon chain of polyols is initially shortened through dehydrogenation/decarbonylation and dehydrogenation/retro-aldol mechanisms followed by a series of cascade reactions that include dehydrogenation/decarbonylation and dehydration/hydrogenation processes. At 240°C, sorbitol is fully converted into lower alcohols with ethanol being the main reaction product in liquid phase.

1. Introduction

In the last decade, a growing attention has been devoted to the production and the utilization of bio-sugars and bio-alcohols obtainable from renewable cellulose, hemicellulose and lignin (the main fractions of lignocellulosic biomasses) [1, 2]. To this regard, cellulose and hemicellulose derived sorbitol (C6 polyol), xylitol (C5 polyol) and glycerol (C3 polyol) have been inserted in the list of top 12 biomass-based building blocks [3–5] representing key renewable resources for modern biorefineries.

With a global market expected to overcome 2.3 Mt/year, sorbitol is attracting intense industrial and research interests [6, 7]. At present, it is mainly produced by hydrogenation of glucose [5, 6, 8] (easily obtained by the hydrolysis of cellulose [9–15]) and largely used in pharmaceutical, food and cosmetic industries [16]. Moreover, it has been proposed as building block for production of biofuels, chemicals [17–19] and renewable hydrogen (through aqueous-phase reforming reactions - APR) [17, 20–24]. Xylitol (C5 polyol) is commonly produced by catalytic hydrogenation of xylose as well as from the hydrogenation of hemicellulose and it is widely applied as sweetener and inhibitor for the development of bacteria in foods [16, 25]. Erythritol (C4 polyol) is the main starting substrate for the synthesis of butanediols (BDOs), that are widely employed as precursors of polyester resins, polyurethanes and polymers such as polybutylene-terephthalate (PBT) [16, 25]. Glycerol (C3 polyol) is cheaply available in continuously growing quantities, being the main by-product in bio-diesel production. The selective hydrogenolysis of glycerol can lead to 1,2-propanediol (1,2-PDO), that is a useful compound in several industrial fields [4]. The shortest polyol is ethylene glycol (EG, C2 polyol), which is typically used as antifreeze agent and as a precursor of polyesters, such as polyethylene terephthalate (PET) and polyethylene-naphthalate (PEN). Catalytic epoxidation of ethylene is presently the main technology applied in the production of EG, although industrial processes to obtain it directly from cellulose are in continuous development [1]. **Among others, a valuable desirable product from C6-C2 polyol is surely ethanol, that is currently extensively produced through fermentation of glucose (generally derived from**

corn or sugar cane [4]) and can be used as bio-fuel as well as feedstock to produce building block chemicals.

Biomass-derived polyols are characterized by a higher O/C ratio with respect to fossil-derived feedstocks, because, in their structure, every carbon atom is linked to a hydroxyl group. Therefore, deoxygenative technologies could face the need of the effective reduction of the oxygen content allowing the production of new high added value chemicals ready to be integrated into the modern market chain [26, 27].

In this context, the catalytic hydrogenolysis is an easily available technology, which is gaining increasing attention since it allows possible breaking of C-O, C-C, C-H and O-H bonds with the simultaneous addition of H₂. The process is typically ruled by dehydration, decarbonylation, retro-aldol condensation and/or hydrogenation reactions [28, 29]. Polyols hydrogenolysis is a long time studied reaction, often carried out in severe operating conditions and in presence of hydroxides as base, to drive the selectivity toward the desired products [6, 28, 30]. In particular, sorbitol hydrogenolysis was deeply investigated by using catalysts based on Ni, Ru, Cu, Pt metals [5, 28]. Since the pioneering work of I.T. Clark [31], nickel based catalysts have been widely investigated for their high intrinsic activity [28, 30, 32–35]. Progressively, the investigation was shifted toward ruthenium systems that were found to show high performance both in conversion and selectivity [28, 36–43]. Heterogeneous copper catalysts represent another interesting alternative to promote the conversion of polyols [44–46], being less active than Ni and Ru in reducing the C-C cleavage, so favouring C₄-C₆ products [47, 48]. Besides, also platinum was found very active in hydrogenolysis and hydrodeoxygenation of sorbitol [28, 42, 49–51].

Bimetallic catalytic systems play a crucial role since they address the selectivity towards a desired product, also starting from lignocellulosic biomasses (cellulose, hemicellulose, lignin) [52-65]. Generally, the introduction of a second metal has been found helpful to increase the performance [66-75]. Palladium based catalysts, for example, were found commonly less reactive towards hydrogenolysis of polyols [5, 28]. However, addition of iron to palladium, through the co-precipitation

technique, creates intimate interactions that generate a synergistic effect [76,77] enabling a remarkable reactivity in several important reactions for chemical industry [78-94]. In recent years, some of the authors investigated the hydrogenolysis of glycerol both in presence and in absence of added hydrogen by using the co-precipitated Pd/Fe₃O₄ catalyst under mild operating conditions. With the aim to extend the substrate scope, in this paper, we evaluate the performance and the reaction pattern of the co-precipitated Pd/Fe₃O₄ catalyst in the hydrogenolysis of sorbitol and lower polyols (such as xylitol, erythritol, butanediols, glycerol, 1,2-propanediol). Under the conditions adopted, C2-C3 alcohols were obtained in high selectivity with ethanol becoming the main product in liquid phase at higher reaction temperatures demonstrating also that the co-precipitated Pd/Fe₃O₄ system can be a suitable catalyst for the chemical valorisation of bio-derived polyols.

2. Experimental Section

2.1 Catalysts preparation

All chemicals were purchased and used without further purification.

The Pd/Fe₃O₄ catalyst was prepared through the co-precipitation technique, designed with a nominal palladium loading of 5 wt%. An aqueous solution of palladium nitrate and iron (III) nitrate nonahydrate was added dropwise into a 1M aqueous solution of Na₂CO₃. The obtained catalyst was filtered, washed and dried for 1 day under vacuum at 120°C. Before use, the catalyst was reduced at 200°C for 2 h under a hydrogen flow.

The Pd/C catalyst was acquired from a commercial source (Alfa Aesar) and used after reduction, under H₂ flow, at 200 °C for 2 h.

The main characteristics of the investigated Pd-based catalysts are reported in Table S1.

2.2 Catalysts Characterization.

XRD data were acquired at room temperature on a Philips X-Pert diffractometer by using the Ni β-filtered Cu Kα radiation ($\lambda=0.15418$ nm) in the 2θ range of 20–80° at a scan speed of 0.5°min⁻¹.

The particle size and the relative morphology of investigated catalysts were analysed by performing Transmission Electron Microscopy (TEM) measurements using a JEM-2100F (JEOL, Japan) operating at an acceleration voltage of 200 kV and directly interfaced with a computer controlled-CCD for real-time image processing. Particle size distributions were obtained by counting several hundred particles visible on the micrographs on each sample. From the size distribution, the average diameter was calculated by using the expression: $d_n = \sum n_i d_i / n_i$ where n_i is the number of particles of diameter d_i .

H₂-TPR measurements were performed using a conventional TPR apparatus. The dried samples (50mg) were heated at a linear rate of 10 °C min⁻¹ from 0 to 1000 °C in a 5vol % of H₂/Ar mixture at a flow rate of 20 cm³ min⁻¹. H₂ consumption was monitored with a thermal conductivity detector (TCD).

XPS measurements were performed on a JPS-9010MC photoelectron spectrometer using an Al Kα (1486.6 eV) radiation source. After the reduction treatment, samples were introduced into the XPS

chamber, avoiding exposure to air. All spectra were recorded at room temperature, and the binding energies (BE) were set taking the C 1s peak at 284.6 eV as reference.

2.3 Catalytic Tests.

Hydrogenolysis reactions were carried out in a 300 ml stainless steel autoclave at a stirring speed of 500 rpm. The reactor was purged three times with He (99.99%) and subsequently pressurized at the desired H₂ pressure and heated at the reaction temperature, monitored using a thermocouple fixed into the autoclave and connected to the reactor controller.

The range of operative conditions used for hydrogenolysis reactions was: 150-240°C, 5-20 bar initial H₂ pressure, 80 ml of 4 wt% C6-C3 polyol aqueous solutions and 500 mg of reduced catalyst. After 6-24 hours of reaction, the system was cooled and, when at room temperature, the pressure was released carefully and the liquid phase analyzed.

The reactant and products, in the liquid phase, were analyzed using an off-line Shimadzu HPLC equipped with an Aminex HPX-87-H column and a TOC analyzer Shimadzu, in order to confirm the carbon balance in the liquid phase. The gas phase products were analyzed with a GC (Agilent 7890A) equipped with a molecular sieve column (Supelco, Porapak Q column 80/100 mesh) and a capillary column (HP-PLOT/Q, internal diameter: 0,53mm; length: 30 m; film thickness: 40 μ) linked with the TCD detector and a capillary column (HP-AI, internal diameter: 0.53 mm; length: 50 m; film thickness: 15 μm) connected to a FID detector.

The conversion and product selectivity in the liquid phase were calculated on the basis of the following equations:

$$\text{Conversion [\%]} = \frac{\text{mol of reacted substrate}}{\text{mol of substrate feed}} \times 100$$

$$\text{Liquid phase selectivity [\%]} = \frac{\text{mol of specific product in liquid phase}}{\text{sum of mol of all products in liquid phase}} \times 100$$

The products yield was calculated on carbon basis and defined as:

$$\text{Product Yield [\%C]} = \frac{\text{mol of specific product} \times \text{C atoms in specific product}}{\text{mol of total C atoms in substrate}} \times 100$$

The carbon balance at the end of each reaction was confirmed by using a liquid Total Organic Carbon analyzer (Shimadzu TOC-VCSH). Through the comparison of the carbon balance evaluated by HPLC analysis and by TOC measurements it has been estimated a percentage of carbon loss in liquid phase lower than 5%. The total organic carbon of the gas phase, when calculated, was estimated as the difference between the TOC measurements before and after hydrogenolysis reactions. In all experiments, the analytical results of GC analysis showed a carbon balance in gas phase higher than 95%.

3. Results

3.1 Catalyst preparation and characterization

The Pd/Fe₃O₄ catalyst was prepared through the co-precipitation of palladium nitrate and iron (III) nitrate nonahydrate, simultaneously added dropwise into a 1 M aqueous solution of Na₂CO₃. The precipitated solid was filtered, washed with distilled water, calcinated overnight and reduced under a flow of molecular hydrogen at 200°C [81,84].

In the last decade, the co-precipitated Pd/Fe₃O₄ has been deeply analysed by several research groups, including that of authors, and a detailed description of its physico-chemical and structural properties was discussed in detail in different reports [76-95]. For clarity, the main peculiarities of the co-precipitated Pd/Fe₃O₄ catalyst are here concisely summarized. The catalyst is characterized by palladium nanoparticles ranging mainly between a diameter of 1-2 nm (as revealed by the high-resolution transmission electron microscopy, HR-TEM) well dispersed over the Fe₃O₄ surface (as shown by X-ray diffraction (XRD), Figure S1). H₂-TPR analysis of the Pd/Fe₃O₄ catalyst shows a profile having only an intense peak centred at about 80°C, in which reductions of either palladium [Pd(II) → Pd(0)] and iron [Fe(III) → Fe₃O₄] are involved, indicating that Pd nanoparticles are effective in promoting the reduction of hematite (Fe₂O₃) into magnetite (Fe₃O₄) (Figure S2). Extended x-ray absorption fine structure (EXAFS) characterization confirms formation of Pd–Fe bimetallic ensembles, having the Pd-Fe distance shorter (0.259 nm) than that of Pd-Pd atoms (0.266 nm) [78, 81, 83]. X-ray photoelectron spectroscopy (XPS) evidences that the Pd 3d_{5/2} binding energy is 0.5 eV higher than the binding energy of metallic Pd, denoting the presence of partial positively charged metal species (Pd^{δ+}) (Table S1) [81, 95, 96]. All these findings indicate the presence of Pd-Fe ensembles/alloy and that strong interactions between palladium nanoparticles and the iron oxide support are present on the Pd/Fe₃O₄ catalyst.

Figure 1 about here

3.2 Catalytic tests on the hydrogenolysis of sorbitol

The catalytic performance of the bimetallic Pd/Fe₃O₄ catalyst was compared with that of the commercial Pd/C and results are reported in Table 1 and Table S2.2.

Table 1 about here

The bimetallic Pd/Fe₃O₄ catalyst shows excellent performances affording an almost complete conversion at 180°C (91%) and a total conversion (100%) at 210°C. The distribution pattern of products, in liquid phase, was found to change within the temperature range investigated. Indeed, at lower temperatures (150° and 180°C) the main reaction products are xylitol (Xyl) and glycerol (Gly), followed by lesser amounts of erythritol (Ery) and ethylene glycol (EG). When the temperature increases, xylitol and glycerol are gradually converted into smaller polyols such as butanediols (BDOs = 1,2-butandiol + 1,4-butandiol + 2,3-butandiol), 1,2-propanediol (1,2-PDO), propanols (POs = 1-propanol + 2-propanol), ethylene glycol (EG) and ethanol (EtOH). It is worth noting that, as the reaction proceeds toward products having lower molecular weight, the quantity of ethanol progressively increases, so that it becomes the main product, in liquid phase, at 240°C (63.5% mol-based selectivity, 25.4% carbon-based yield).

On the contrary, the commercial Pd/C exhibits a significant lower activity. Indeed, at 210°C the sorbitol conversion is less than 30% and the maximum is 60% at 240°C, the highest temperature investigated. The selectivity pattern, on increasing the temperature, follows a similar trend as that reported for the Pd/Fe₃O₄ catalyst; furthermore, a much lower ethanol yield is always registered (12.0% carbon-based yield at 240°C - Table S2.2).

Furthermore, pure Fe₃O₄ was tested within the same temperature range and no appreciable sorbitol conversion was found.

The lack of significant reactivity using either Pd/C or pure Fe₃O₄, confirms that the marked activity shown by the bimetallic Pd/Fe₃O₄ catalyst has to be attributed to the strong interaction between palladium and iron, as consequence of the preparation method (co-precipitation) [76, 77] in analogy with other reports attaining to C3 and C2 polyols.

Gaseous products were also quantitatively analysed, pulling out the gas phase from the reaction vessel, cooled down at room temperature, after every experiment without accounting for the amount of molecular hydrogen, added as pure reactant (5 bar at 25°C) at the start of each reaction. The amount of gas products rises on increasing the reaction temperature (180-240°C), although its composition was found quite constant, being composed by mainly of carbon dioxide and only small amounts of alkanes (methane, ethane and propane). Gaseous compositions, detected at different temperatures, are depicted in Figure 2 (the detailed distribution of liquid and gas products - including carbon-based yield - is available in Table S2.1). It is worth to highlight that carbon monoxide was never detected in the gas phase, indicating that the Pd/Fe₃O₄ catalyst is also effective in promoting the water gas shift (WGS) reaction, as previously observed in the hydrogenolysis of glycerol and ethylene glycol, carried out under APR conditions [84].

Figure 2 about here

Considering the 240 °C value as a significant reaction temperature to maximize the ethanol production in liquid phase, sorbitol hydrogenolysis was also investigated at different reaction times (3, 6, 12 and 24 h). The sorbitol conversion was complete already after 3 h of reaction, although the ethanol selectivity in liquid phase increases as the reaction proceeds from 3 to 24 h (Figure 3, top). Results

obtained from investigations at different reaction times at 180 and 210 °C are reported in S.I (Sections 2.4 and 2.5)

The effect of the hydrogen pressure increase from 5 to 20 bar was also investigated. At 240°C the conversion of sorbitol remains complete; however, the decrease of ethanol selectivity in liquid phase was ascertained (Figure 3, bottom). A similar effect was also observed at 180 and 210°C (Figure S4). The result suggests an inhibitory effect, on the hydrogenolysis reaction, of the hydrogen pressure, probably ascribed to a competitive adsorption of substrate and hydrogen on the catalyst surface [84-97].

3.2 Catalytic tests on the hydrogenolysis of C5-C3 polyols

In order to get a complete reactions pattern, the hydrogenolysis of C5-C3 polyols, over the Pd/Fe₃O₄ catalyst, was also investigated under the same operative conditions. The results obtained at 180 and 210 °C are reported in S.I. (Sections 2.7 and 2.8), whereas the results relative to 240 °C are detailed in Table 2 and Table S2.3.

Table 2 about here

The conversion of all C5-C3 polyols at 240 °C is very high ranging from 78.7 to 100% except for 2,3-butanediol (2,3-BDO) that, as expected, is a stable molecule and does not give any appreciable reactivity [98]. From the products distribution in liquid phase, it is quite clear that ethanol is mainly formed from xylitol, 1,4-BDO, 1,2-PDO and glycerol hydrogenolysis, demonstrating that, under the reaction conditions adopted, both C-O and C-C cleavages simultaneously occur.

Xylitol is mostly converted into C2 and C3 alcohols, respectively ethanol (64.1% mol-based selectivity, 25.6% carbon-based yield) and POs (16% mol-based selectivity, 8.6% carbon-based yield) and, in a lesser amount, di-alcohols, such as butanediols and 1,2-PDO.

Erythritol follows a similar pattern affording **C2 and C3 alcohols** in almost equal amount. However, di-alcohols are also obtained, being BDOs the most abundant products, confirming the efficiency of erythritol in BDOs manufacture [98].

Investigated BDOs show a different pattern in the hydrogenolysis reaction. 1,2-BDO produces preferentially 1-propanol (80% **mol-based selectivity, 49.4% carbon-based yield**) followed by a smaller amount of 1,2-PDO (18% **mol-based selectivity, 11.1% carbon-based yield**). On the contrary, 1,4-BDO breaks preferentially the C2-C3 bond leading to an ethanol **mol-based selectivity**, that slightly overcomes 90% (**67,5% carbon-based yield**). As previously mentioned, the 2,3-BDO does not give any reactivity.

C3 polyols reactivity, in analogy with our previous report [84], follows the order: glycerol (100%) > 1,2-PDO (78.7%) being both very selective in ethanol production.

4. Discussion

4.1 Understanding the C-O and C-C bond breaking: the reaction mechanism

Consistent with the catalytic results obtained from the hydrogenolysis of sorbitol and C5-C3 polyols, a global reaction pathway, promoted by the bimetallic co-precipitated Pd/Fe₃O₄ catalyst, is proposed in Figure 4.

Figure 4 about here

It is well accepted that the initial reaction step in the hydrogenolysis of polyols is the dehydrogenation of primary or secondary alcoholic group, leading to an aldehyde or a ketone [99-101]. In the light of observed reaction products, the hydrogenolysis of sorbitol follows, at the beginning, two main alternative ways: (i) the dehydrogenation/decarbonylation of terminal C-OH groups and (ii) the cleavage of internal C-C bonds via dehydration/retro-aldol reaction.

The first steps in sorbitol hydrogenolysis is sketched in Scheme 1. Three possible reaction routes have to be considered. In the case of an adsorption of a primary hydroxyl group on the catalyst surface, the dehydrogenation process allows at first formation of glucose (open chain). In the following reaction pathway leading to short the polyols chain, the terminal C–CO breaking enables xylitol production (Route A). On the other hand, if the internal C-C bond of glucose is cleaved by a retro-aldol mechanism erythritol and ethylene glycol are formed as reaction products (Route B).

Conversely, if a secondary hydroxyl group is dehydrogenated, the retro-aldol cleavage of C3-C4 bond affords two molecules of glycerol (Route C). Subsequently, consecutive reactions such as dehydrogenation/decarbonylation and dehydration/hydrogenation occur, leading, to final products including butanediols and C2-C3 alcohols, particularly ethanol.

The contribution of other reaction mechanisms, such as the dehydration of sorbitol into cyclic compounds (e.g. isosorbide and 1,4-sorbitan) was not found to be operating in the reaction network over the Pd/Fe₃O₄ catalyst.

Scheme 1 about here

Therefore, sorbitol appears to be simultaneously and consecutively subjected to two alternative patterns, as data at 150 °C, where the conversion degree is low but useful to appreciate the initial steps, demonstrate (Table 1). The dehydrogenation/decarbonylation of terminal C-OH groups produces xylitol (33 % mol-based selectivity), while the retro-aldol condensation operates on the internal chain either breaking the C3-C4 bond, that forms two molecules of glycerol (35% mol-based selectivity at 150°C) or, to a lesser extent, breaks the C2-C3 bond producing erythritol (7% mol-based selectivity) and ethylene glycol (8% mol-based selectivity).

Xylitol is, in turn, converted into erythritol through dehydrogenation/decarbonylation, or through retro-aldol condensation, affording glycerol and ethylene glycol. Production of butanediols probably

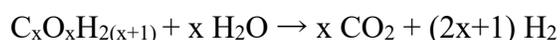
stems from erythritol rather than directly from xylitol. Indeed, erythritol, through the dehydration/hydrogenation, leads to BDOs in considerable amount, while, through retro-aldol condensation, ethylene glycol is obtained. Glycerol undergoes successive hydrogenolysis reactions leading, in liquid phase, prevalently to POs and ethanol.

Butanediols (BDOs) react through different hydrogenolysis patterns depending on the isomer considered. The 2,3-BDO does not give any appreciable conversion in the reactive conditions investigated. The 1,2-BDO, probably through dehydrogenation/decarbonylation, affords mainly 1-propanol **whereas** the 1,4-BDO through retro-aldol condensation breaks the C2-C3 bond producing ethanol, and leads, marginally, to POs through dehydrogenation/decarbonylation.

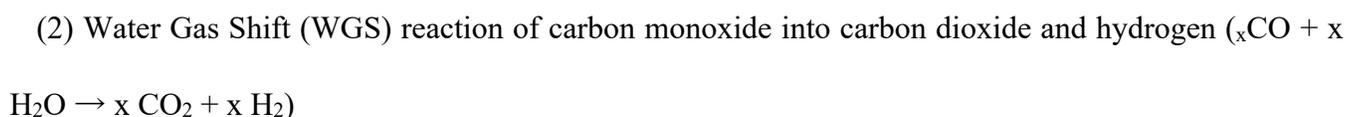
The glycerol detected during the hydrogenolysis of sorbitol, almost entirely, derives from the initial retro-aldol condensation of sorbitol and only in slight percentages, from xylitol and erythritol hydrogenolysis. Furthermore, glycerol dehydration/hydrogenation or dehydrogenation/decarbonylation affords 1,2-PDO and EG, respectively. 1,2-PDO then leads to POs or ethanol, after dehydration/hydrogenation or dehydration/decarbonylation, respectively. Finally, the hydrogenolysis of ethylene glycol could lead to ethanol or methanol.

It is worth noting that, at the beginning of the reaction, having 5 bar of H₂ pressure, the initial molar ratio of H₂/sorbitol is about 2,5. However, in order to perform the complex pattern of reactions observed (Figure 4) the amount of H₂ should be higher than that available on the vessel volume.

Nevertheless, it is useful to remember that H₂ can be also formed by APR of sorbitol itself (as well as from the other polyols formed through the hydrogenolysis process):



where the stoichiometry involves the sum of the two reactions:



As mentioned above, in section 3.2, the gas phase is composed, together with molecular H₂, by carbon dioxide and only traces of alkanes are detected (Table S2.1). Therefore, hydrogenation, leading to gaseous hydrocarbons is negligible with our catalyst. Moreover, the complete absence of carbon monoxide indicates that all the CO deriving from decarbonylation is converted into carbon dioxide through the water-gas-shift reaction promoted by the Pd/Fe₃O₄ catalyst.

Hydrogenolysis of sorbitol over Pd/C occurs with a similar reaction pathway as that observed on using the Pd/Fe₃O₄ catalyst. However, both sorbitol conversion and products distribution point to a slower reactivity. Indeed, at a lower temperature (150 °C) a very small amount of sorbitol seems to be converted entirely into glycerol, through retro-aldol condensation. This is then partially hydrogenolized into 1,2-PDO and EG. Conversely, upon increasing the temperature, starting from 180 °C formation of erythritol, partially converted to BDOs, also occurs. The lateral C-C cleavage of sorbitol into xylitol, seems to be absent. At temperatures above 200 °C, the cascade hydrogenolysis processes are more shifted towards C3-C2 diols and alcohols and, at 240 °C, ethanol is the prevalent product in liquid phase, although the amount is significantly lower than that obtained over the Pd/Fe₃O₄ catalyst. The lower activity of the Pd/C catalyst, if compared with that of Pd/Fe₃O₄, can be correlated to its lower ability to dehydrogenate sorbitol in analogy with a recent report on the use of simple primary and secondary alcohols as H-donor molecules for the transfer hydrogenolysis of benzyl phenyl ether [88].

5. Conclusions

The catalytic conversion of biomass-deriving sorbitol and C5-C3 polyols was investigated under mild hydrogenolysis conditions over the bimetallic Pd/Fe₃O₄ catalyst, exhibiting a higher performance compared to that of the Pd/C catalyst. The hydrogenolysis reactions of C5-C3 polyols with the Pd/Fe₃O₄ catalyst were also carried out in order to completely understand the main pathways occurring in the reaction.

The starting reactions were found to be the dehydrogenation/decarbonylation of the terminal C-COH group and the dehydrogenation followed by the retro-aldol reaction (internal C-C bond cleavage). At the beginning, the sorbitol carbon chain is preferentially shortened leading to xylitol and C3 or C4-C2 polyols. After the initial cleavage of sorbitol, a series of cascade reactions (such as -H₂/-CO, -H₂O/H₂, retro-aldol condensation and hydrogenation) occur, leading to production of shorter diols, alcohols and gaseous products. A similar cascade pattern of reactions leads to the preferential formation of ethanol, at the highest temperature investigated (240 °C).

With the exception of 2,3-butanediol, C2-C3 alcohols are the main reaction products obtained by the hydrogenolysis of the investigated substrates suggesting that the co-precipitated Pd/Fe₃O₄ catalyst can be a suitable catalyst for the production of ethanol from bio-derived C6-C3 polyols.

Finally, the gas phase analysis, in all experiments, shows the total absence of CO revealing the excellent performance of the Pd/Fe₃O₄ catalyst in promoting the water-gas-shift (WGS) reaction.

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