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# New insights into the mechanism of sorbitol transformation over an original bifunctional catalytic system

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## Abstract

Sorbitol can be selectively transformed into liquid alkanes over a bifunctional catalytic system Pt/ZrO<sub>2</sub> + TiO<sub>2</sub>-WO<sub>x</sub>. In this paper, we investigated the reaction mechanism by carefully analyzing the numerous products issued from sorbitol and by studying the reactivity of some identified intermediates (1-hexanol 2-hexanol, 2-hexanone, 2,5-dimethyltetrahydrofuran, 1,2-hexanediol and 1,2,6-hexanetriol). This led us to propose that C—C cleavage reactions occur on terminal C—C bonds and mainly consist of dehydrogenation—decarbonylation reactions. The limiting steps of the sorbitol transformation are the isosorbide and mono-oxygenated intermediate transformations, especially the hydrogenation of ketones. It is also assessed that diols or triols with *n* carbon atoms are mainly converted in compounds with *n* – 1 carbon atoms. Short compounds (1 to 3 carbon atoms) are obtained via a dehydrogenation-retro-aldol reaction pathway and not from isosorbide conversion.

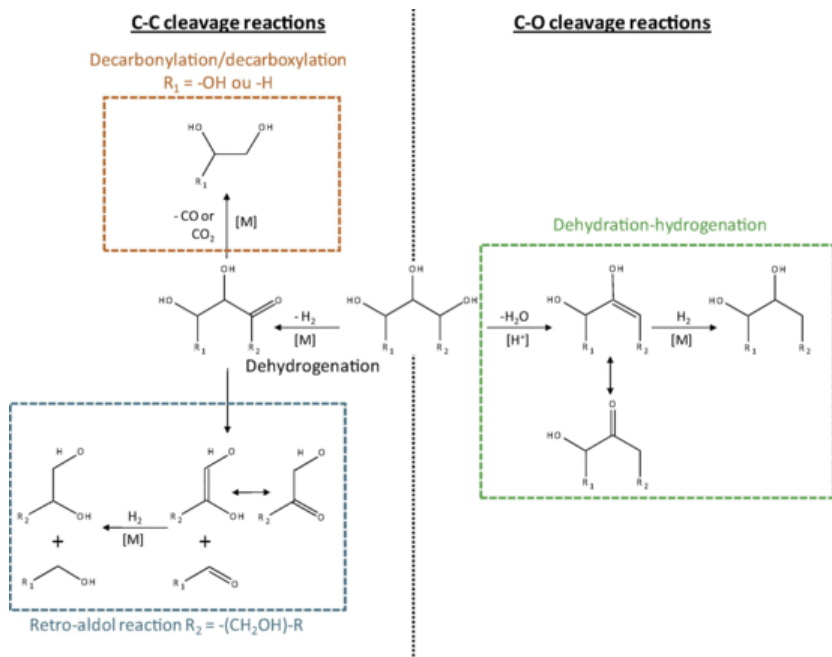
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**Keywords:** Alkanes production; Biofuels; Biomass; Polyol; Pt; TiO<sub>2</sub>-WO<sub>x</sub>

## 1 Introduction

The biomass conversion into fuels and chemicals is becoming a research topic of importance in today's context of fossil fuel depletion and increasing energy consumption [1]. Biomass is composed of three main components: cellulose and hemicellulose, polymers of hexoses and pentoses, and lignin, a macromolecule containing phenolic groups [2]. Cellulose and hemicellulose can be hydrolyzed into the corresponding sugar monomers [3]. However, the resilient nature of crystalline cellulose requires harsh hydrolysis conditions which lead to glucose degradation. Thus, the chemical trapping of glucose into valuable chemicals before its degradation in reaction media increases the yield of the hydrolysis process [4]. The production of sorbitol from cellulose by hydrolysis and hydrogenation is proposed as a viable pathway for biomass conversion [5]. It can be achieved using a bifunctional catalytic system [6,7]. Sorbitol can be converted into hydrocarbons over bifunctional solid catalysts, with or without hydrogen supply [8]. Hydrocarbons separate from the aqueous reaction medium and are more easily integrated into the existing fuels than ethanol [9,10]. The selective transformation of sorbitol into hexane is however a challenge since multiple reactions occur in aqueous medium.

We recently reviewed the reaction of polyols conversion in aqueous medium and underlined the lack of reaction studies on sorbitol transformation [8]. Polyols transformation reactions are generally classified in C—C and C—O cleavage reactions. The former can take place at the end of the carbon chain over aldehyde or carboxylic acid group (decarbonylation and decarboxylation) [11–14] or in the middle of the carbon chain (retro-aldol reaction) [15] along with dehydrogenation, hydrogenation, and water—gas shift (WGS) reactions. The latter consists in dehydration—hydrogenation reactions over alcohol groups [16–19]. These reactions are represented in Fig. 1. They occur successively or simultaneously, leading to a complex mixture of reactants, intermediates and products. In the case of sorbitol, hundreds of products have been detected [20,21] and according to a recent kinetic model, more than 4000 reactions can be involved in the sorbitol reaction pathway [22].



**Fig. 1** Reactions involved in polyols transformation over a bifunctional catalyst.

Several catalytic systems have been studied for the catalytic transformation of sorbitol. Metallic catalysts such as Pt/ $Al_2O_3$  lead to hydrogen and  $CO_2$  production [20,23], whereas acid catalysts such as supported phosphopolytungstic acid [24] or  $TiO_2-WO_x$  [25] produce isosorbide. Bifunctional catalytic systems containing an hydrogenating metallic phase (Pt, Pd, Ni, Ru, Ir) and a dehydrating acid phase ( $SiO_2-Al_2O_3$  [9,21],  $Nb_2O_5$  and derivatives [26],  $ZrO_2-PO_x$  [27],  $ZrO_2-WO_x$ ,  $TiO_2-WO_x$  [28]) are preferred to form hydrocarbons. We recently demonstrated that an original mixture of Pt/ $ZrO_2$  +  $TiO_2-WO_x$  with a mass ratio 20:80 produces selectively C5–C6 hydrocarbons from sorbitol, with hydrogen supply [25,28]. In this paper, we propose a focus on the reaction mechanisms involved in sorbitol transformation over this original bifunctional catalytic system using the following strategy. First, we extracted preliminary information on the C—C cleavage reactions from a careful examination of the carbon distribution in the various products. Then, we identified the limiting steps during successive deoxygenation reactions by observing the oxygen distribution in sorbitol transformation products. Finally, we explored the reactivity of some intermediates.

## 2 Experimental part

### 2.1 Catalyst preparation

$TiO_2-WO_x$  (14 wt.% W) was prepared from rutile  $TiO_2$  (IFPEN) by ion exchange with a  $H_2WO_4/H_2O_2$  aqueous solution. 2.2 wt.% Pt/ $ZrO_2$  was prepared by wet impregnation of  $ZrO_2$  (MEL Chemicals) using a  $H_2PtCl_6$  aqueous solution. Both catalysts were mixed to form a bifunctional catalytic system with the mass ratio Pt/ $ZrO_2$ : $TiO_2-WO_x$  (20:80). More details were given in a previous work [8].

### 2.2 Catalytic tests

The transformation of sorbitol and of several organic compounds (1-hexanol, 2-hexanol, 2-hexanone, 2,5-dimethyltetrahydrofuran, 1,2-hexanediol, 1,2,6-hexanetriol) in aqueous solution were performed in a fixed-bed reactor. The concentrations of reactants in the feed flow were 10 wt.% for sorbitol, 0.5 wt.% for mono-oxygenated compounds, 2.5 wt.% for the di-oxygenated compound and 5 wt.% for the tri-oxygenated compound. These concentrations are the maximum ones according to the solubility of each compound.

The test unit was described in details in a previous article [29]. The aqueous solution containing the reactant was placed into the feed pot under argon bubbling in order to remove dissolved oxygen. Nitrogen and hydrogen were co-fed using Brooks gas flow regulators. The catalytic bed was loaded in a stainless steel tubular flow reactor placed into a tubular furnace. The liquid feed was introduced into the reactor (up-flow) using a JASCO PU980 HPLC pump. The liquid–gas mixture was recovered in a high-

pressure separator cooled by water circulation. The liquid effluents were collected in vials at the exit of the separator to be further analyzed. After the separator, the gaseous effluent flowed through a back pressure regulator and then through a gas bulb. A drum-type gas meter measured the gas flow after the separator. 5 g of fresh catalyst (150–355  $\mu\text{m}$  particle size, 4 g of  $\text{TiO}_2\text{-WO}_x$  and 1 g of  $\text{Pt/ZrO}_2$ ) were mixed with SiC (VWR, 500  $\mu\text{m}$  particle size) in order to get a 12  $\text{cm}^3$  catalytic bed and then loaded between two layers of SiC in the tubular reactor. Prior to reaction, the fresh catalyst was reduced under hydrogen flow at 450  $^\circ\text{C}$  for 2 h. After cooling down the reactor to room temperature and stripping with nitrogen flow, degassed water was introduced into the reactor. When liquid was detected in the separator, the reactor was pressurized to the required pressure (22–37 bar), and then heated at 3  $^\circ\text{C min}^{-1}$  to the required temperature (200–240  $^\circ\text{C}$ ). When the required temperature and pressure were achieved, the aqueous solution containing the reactant was co-fed with hydrogen, with a hydrogen/organic compound molar ratio equal to 25.

The temperature and pressure were set to maintain the aqueous medium in liquid state: 200  $^\circ\text{C}$ , 22 bar; 220  $^\circ\text{C}$ , 28 bar; 240  $^\circ\text{C}$ , 37 bar for the sorbitol transformation test. The weight hourly space velocity (WHSV = (mass flow rate of feed solution)/(mass of catalyst)) was based on the aqueous solution of sorbitol and varied from 2  $\text{h}^{-1}$  to 4  $\text{h}^{-1}$ . The values of WHSV were determined by the limitations of the experimental setup, namely by the lower flow limit of the HPLC pump and the upper flow limit of the gas-liquid separator. The catalytic transformation of intermediate organic compounds was studied at one set of operating conditions: 240  $^\circ\text{C}$ , 37 bar, WHSV feed = 2  $\text{h}^{-1}$ . The intermediate compounds were introduced successively over the same catalytic bed. Samples were taken when the system reached equilibrium.

$\text{CO}_2$  in the gaseous effluent was analyzed by GC-TCD using a Varian Porapak-Q column. Gaseous hydrocarbons and organic compounds in the aqueous phase were analyzed by GC-FID using an Agilent PONA column. Sorbitol, 1,4-anhydrosorbitol, isosorbide, and 1,2,6-hexanetriol in the liquid effluent were analyzed by HPLC-RI using a Phenomenex Rezex RCM- $\text{Ca}^{2+}$  column. Carbon in the aqueous phase was measured by TOC analysis on a Bioritech 1010 apparatus.

Analytical results are presented as molar yield, as follows:

$$Y_i = \frac{C_i}{C_{\text{sorbitol}}}$$

With  $Y_i$ : molar production of the compound  $i$  ( $\text{mol mol}^{-1}$ );  $c_i$ : concentration of  $i$  detected in the effluent ( $\text{mol mL}^{-1}$ );  $C_{\text{sorbitol}}$ : sorbitol concentration in the feed solution ( $\text{mol mL}^{-1}$ ).

The ratio between the number of C—C cleavages and the number of  $\text{CO}_2$  moles ( $R_{\text{CO}_2}$ ) and the ratio between the number of C—C cleavages and the number of C1 moles ( $R_{\text{C1}}$ ) are defined as follows:

$$R_{\text{CO}_2} = \frac{\sum Y_{\text{C5}} + \sum Y_{\text{C4}} \times 2 + \sum Y_{\text{C3}} \times 3 + \sum Y_{\text{C2}} \times 4 + \sum Y_{\text{C1}} \times 5}{Y_{\text{CO}_2}}$$

$$R_{\text{C1}} = \frac{\sum C_5 + \sum Y_{\text{C4}} \times 2 + \sum Y_{\text{C3}} \times 3 + \sum Y_{\text{C2}} \times 4}{Y_{\text{C1}}}$$

## 3 Results

### 3.1 Products of sorbitol transformation

The products of sorbitol transformation over an original bifunctional catalytic system,  $\text{Pt/ZrO}_2 + \text{TiO}_2\text{-WO}_x$ , with an optimized metal/acid mass ratio (20:80) were described in a previous study [25]. The results are reminded in Table 1, expressed as molar yields. At low temperature, 200  $^\circ\text{C}$ , sorbitol is not totally converted, indicating that the reaction rate is low. 1,4-anhydrosorbitol and isosorbide (obtained by dehydration of the sorbitol) are the main products, with a higher yield for 1,4-anhydrosorbitol. Hydrocarbons,  $\text{CO}_2$  and various oxygenated compounds are observed at low yields. At 220  $^\circ\text{C}$ , sorbitol is completely converted and isosorbide yield is high. At 240  $^\circ\text{C}$ , isosorbide yield becomes very low and oxygenated compounds and hydrocarbons yields increase together with  $\text{CO}_2$ 's one. At 240  $^\circ\text{C}$ , when the WHSV increases from 2  $\text{h}^{-1}$  to 4  $\text{h}^{-1}$ , the isosorbide yield increases whereas  $\text{CO}_2$  and hydrocarbons yields decrease.

**Table 1** Products of sorbitol transformation over  $\text{Pt/ZrO}_2 + \text{TiO}_2\text{-WO}_x$ .

		Operating conditions			
		200 $^\circ\text{C}$ 22 bar	220 $^\circ\text{C}$ 29 bar	240 $^\circ\text{C}$ 37 bar	240 $^\circ\text{C}$ 37 bar <sup>a</sup>
Aqueous products		Molar yield ( $\text{mol mol}_{\text{sorbitol}}^{-1}$ ) <sup>b</sup>			
Polyols	Sorbitol	0.085	0	0	0
	Anhydrosorbitol	0.212	0.085	0	Traces

	Isosorbide	0.062	0.338	0.014	0.033
	1,2,6-Hexanetriol	Traces	0	0	0
	1,2,4-Butanetriol	Traces	Traces	0	Traces
Alcohols	Methanol	Traces	0.009	0.017	0.013
	Ethanol	0.005	0.012	0.043	0.014
	1-Propanol	Traces	0.011	0.037	0.012
	2-Propanol	Traces	Traces	Traces	Traces
	1-Butanol	Traces	0.007	0.024	0.007
	2-Butanol	Traces	Traces	Traces	Traces
	1-Pentanol	0.013	0.040	0.056	0.051
	2-Pentanol	Traces	Traces	Traces	Traces
	1-Hexanol	0.008	0.018	0.036	0.021
	2-Hexanol	Traces	Traces	Traces	0
	3-Hexanol	Traces	Traces	Traces	Traces
	2-Methylpentanol	Traces	Traces	Traces	Traces
	2-Methylcyclopentanol	Traces	Traces	Traces	Traces
Total alcohols		0.042	0.111	0.227	0.123
Ketones	Acetone	Traces	0.012	0.007	0.011
	Butanone	Traces	0.019	0.007	0.014
	2-Pentanone	Traces	0.022	0.010	0.017
	3-Pentanone	0.006	0.040	0.018	0.034
	2-Hexanone	0.012	0.039	0.025	0.031
	3-Hexanone	0.012	0.052	0.052	0.052
	2-Methylcyclopentanone	Traces	0.016	0.004	0.021
Total ketones		0.0453	0.2009	0.1244	0.1810
Heterocycles	Tetrahydrofuran	Traces	Traces	0.007	Traces
	2-Methyltetrahydrofuran	Traces	Traces	0.008	0.006
	2-Methylfuran	0	0	Traces	0
	2,4-Dimethyltetrahydrofuran	Traces	Traces	Traces	Traces
	2,5-Dimethylfuran	0	0	0	Traces
	2,5-Dimethyltetrahydrofuran	Traces	Traces	Traces	Traces
	5-Methyltetrahydrofuran-2-Methanol	0	0	Traces	Traces

	2,4-Dimethylbutyrolactone	0	0	Traces	0
	Tetrahydropyran-2-methanol	Traces	Traces	Traces	Traces
	2-Methyltetrahydropyran	Traces	0.007	0.012	0.007
Total heterocycles		0.007	0.016	0.034	0.018
Carboxylic acids	Formic acid	0	0	0.012	0
	Acetic acid	0	0	Traces	0.009
	Propanoic acid	Traces	0.007	0.010	Traces
	Butanoic acid	0	Traces	0	0.004
	Pentanoic acid	Traces	0.007	0	0.007
	Hexanoic acid	Traces	0.006	0	0.008
Total carboxylic acids		0.003	0.022	0.025	0.029
Diols	Ethylene glycol	Traces	Traces	0	0
	1,2-Propanediol	Traces	0.001	Traces	Traces
	1,2-Butanediol	Traces	0	Traces	Traces
	2,3-Butanediol	0	0	Traces	Traces
	1,2-Pentanediol	Traces	Traces	0	Traces
	1,2-Hexanediol	Traces	Traces	0	0
Diones	2,3-Pentanedione	Traces	Traces	0	Traces
	3,4-Hexanedione	Traces	Traces	Traces	Traces
Total di-oxygenated		0.011	0.010	0.002	0.008
		200 °C	220 °C	240 °C	240 °C
	Operating conditions	22 bar	29 bar	37 bar	37 bar <sup>a</sup>
	Gaseous products	Molar yield (mol mol <sub>sorbitol</sub> <sup>-1</sup> )			
<i>n</i> -Alkanes	Methane	Traces	0.015	0.028	0.018
	Ethane	Traces	0.016	0.039	0.025
	Propane	Traces	0.016	0.035	0.019
	<i>N</i> -butane	0.008	0.030	0.047	0.032
	<i>n</i> -Pentane	0.008	0.030	0.062	0.039
	<i>n</i> -Hexane	0.016	0.042	0.069	0.058
Other hydrocarbons	Iso-butane	0	Traces	Traces	Traces

	Trans-2-butene	0	Traces	0	Traces
	Cis-2-butene	0	Traces	Traces	Traces
	Cyclopentane	Traces	Traces	Traces	0.006
	1-Pentene	Traces	Traces	Traces	Traces
	Trans-2-pentene	Traces	Traces	Traces	Traces
	Cis-2-pentene	0	Traces	Traces	Traces
	1-Methylcyclopentane	Traces	Traces	0.007	0.008
	1-Methylcyclopentane	Traces	Traces	Traces	Traces
	2-Hexene	Traces	Traces	Traces	Traces
	Cyclohexane	Traces	Traces	Traces	Traces
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	Total hydrocarbons	0.050	0.162	0.295	0.218
	CO <sub>2</sub>	0.064	0.293	0.613	0.277

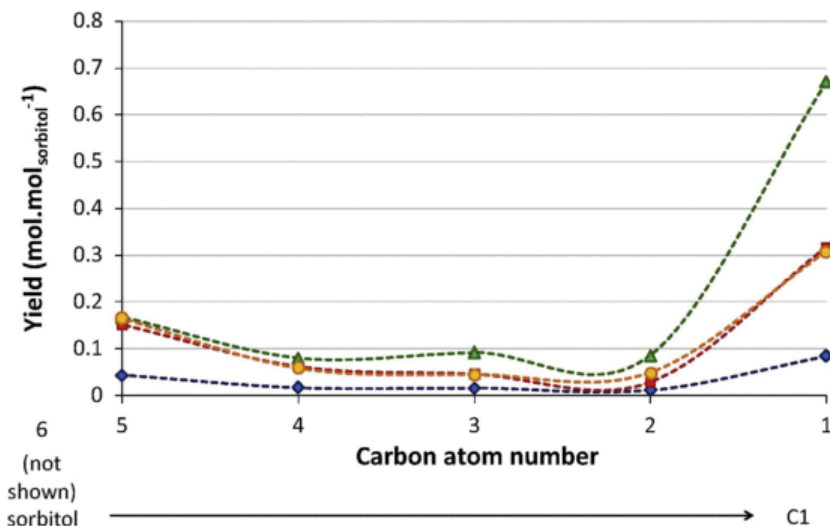
<sup>a</sup> WHSV = 4 h<sup>-1</sup>.

<sup>b</sup> Traces: the compound is detected but its amount is lower than 0.005 mol mol<sup>-1</sup>.

These observations indicate that sorbitol transformation produces first 1,4-anhydrosorbitol, then isosorbide, and finally oxygenated compounds, hydrocarbons, and CO<sub>2</sub>. The aim of this paper **is** to bring some new insights into this complex reaction scheme.

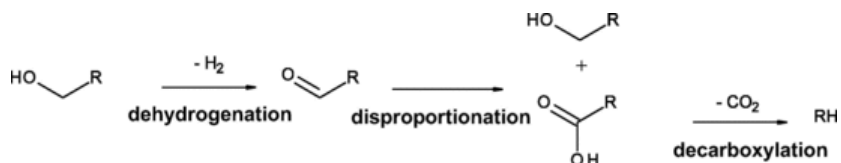
### 3.2 C—C cleavages

To study the mechanisms of the C—C bond cleavage, the carbon distribution in sorbitol transformation products is used. Fig. 2 depicts the C1—C5 compounds production as a function of the number of carbon atoms. Whatever the operating conditions, the major compounds are those with one carbon atom, indicating that the C—C cleavage takes place at the end of the carbon chain. The presence of C2, C3, **and** C4 compounds is a sign of multiple end-chain C—C cleavage. Middle-chain cleavages are also possible, but they must be minor given the low amount of C2—C3—C4 compounds compared to the amount of C1 compounds. The number of C—C cleavages increases with the temperature, between 200 °C and 240 °C (endothermic reactions). It is well known that C—C hydrogenolysis reactions have an activation energy much higher than hydrogenation reactions. Thus, the temperature increase logically favors the reaction with the highest activation energy, *i.e.* the C—C cleavage. The number of C—C cleavages also increases when the WHSV decreases from 4 h<sup>-1</sup> to 2 h<sup>-1</sup>.



**Fig. 2** Distribution of the products of C—C cleavages during sorbitol transformation over Pt/ZrO<sub>2</sub> + TiO<sub>2</sub>-WO<sub>x</sub> as a function of the carbon atom number at various operating conditions: 200 °C, 22 bar, WHSV = 2 h<sup>-1</sup> (◇, blue); 220 °C, 28 bar, WHSV = 2 h<sup>-1</sup> (□, red); 240 °C, 37 bar, WHSV = 2 h<sup>-1</sup> (△, green) and 240 °C, 37 bar, WHSV = 4 h<sup>-1</sup> (○, yellow). C1 refers to methane, methanol and formic acid (formaldehyde was not detected). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Two mechanisms are proposed in the literature to explain terminal C—C bond cleavage during polyols transformation: decarbonylation and decarboxylation. The decarbonylation reaction is a bond cleavage between a carbon atom from an aldehyde group and the adjacent carbon. It is a metal-catalyzed reaction. The CO eliminated from the molecule is adsorbed on the metallic surface and can be removed as a CO molecule or as CO<sub>2</sub>, if the water-gas shift reaction (WGS) occurs: CO + H<sub>2</sub>O → CO<sub>2</sub> + H<sub>2</sub>. The decarboxylation occurs on a carboxylic acid, **that which** might be formed by the disproportionation of two aldehydes compounds, following the Tischenko [30] or the Cannizzaro [31,32] mechanism. The bond between the carbon of the carboxylic group and the adjacent carbon is cleaved and a CO<sub>2</sub> molecule is eliminated (Fig. 3).

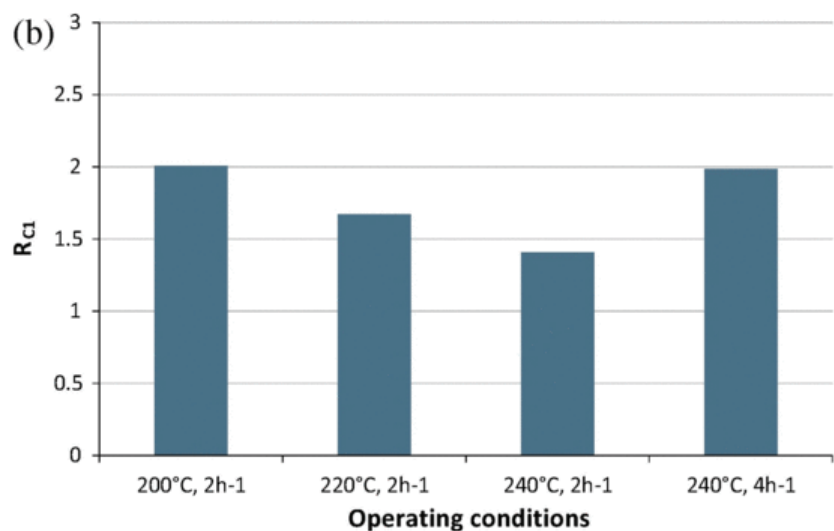
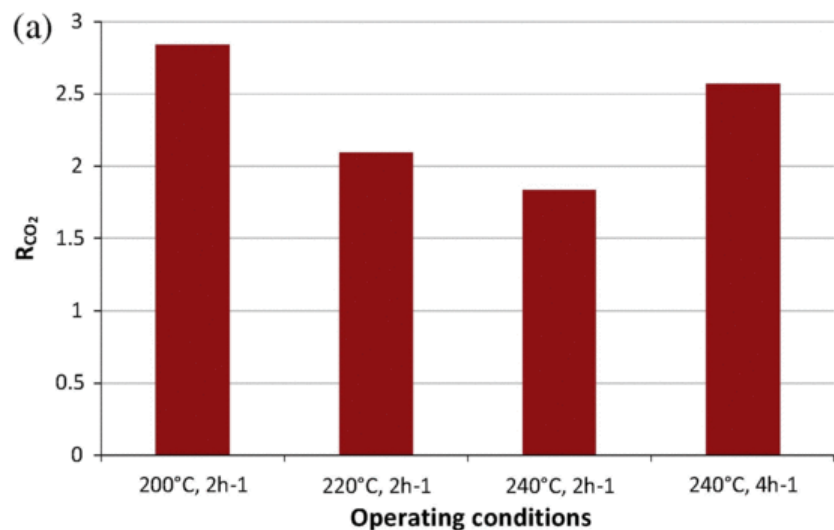


**Fig. 3** Mechanism of dehydrogenation-disproportionation-decarboxylation of a terminal alcohol.

In the presence of platinum-based bifunctional catalysts, CO formation is not reported in **the** literature whatever the catalyst or the operating conditions [9,21,26–29]. However, the decarbonylation mechanism can occur and be followed by the WGS reaction: Pt is known as an efficient catalyst for WGS, and the aqueous medium shifts the reaction equilibrium to the production of CO<sub>2</sub> and H<sub>2</sub>.

To determine the predominant mechanism in C—C cleavage reactions, we calculated the  $R_{CO_2}$  ratio between the number of C—C cleavages (based on the hypothesis of terminal and successive cleavages) and the number of CO<sub>2</sub> molecules when starting from sorbitol (Fig. 4a). If the  $R_{CO_2}$  ratio is equal to 1, this would evidence that CO<sub>2</sub> is the **one only** product of C—C cleavage. If the  $R_{CO_2}$  ratio is higher than 1, CO<sub>2</sub> is not the only product of C—C cleavage. At all studied conditions, this ratio is higher than 1, evidencing that the decarbonylation-WGS mechanism is not the only one implied in the C—C cleavage reactions. However, if we consider that the C1 compounds are by-products of terminal C—C cleavage as well as CO<sub>2</sub>, a new  $R_{C1}$  ratio can be calculated. Thus, by taking exclusively the C2 to C5 compounds into account in the cleavage number calculation and by including the C1 compounds in the denominator, the  $R_{C1}$  ratio comes closer to 1 (Fig. 4b). This indicates that methanol, formic acid and methane (C1 compounds) are also produced during the terminal C—C cleavage, for example, by hydrogenation, hydroxylation or methanation of adsorbed CO. The transformation of CO<sub>2</sub> into methane during the aqueous phase reforming of sorbitol over a Ni-Pd/Al<sub>2</sub>O<sub>3</sub> catalyst was recently evidenced [33].





**Fig. 4** Ratio of C—C cleavage number over the amount of  $CO_2$  ( $R_{CO_2}$ ) (a) and over the amount of C1 compounds ( $R_{C1}$ ) (b).

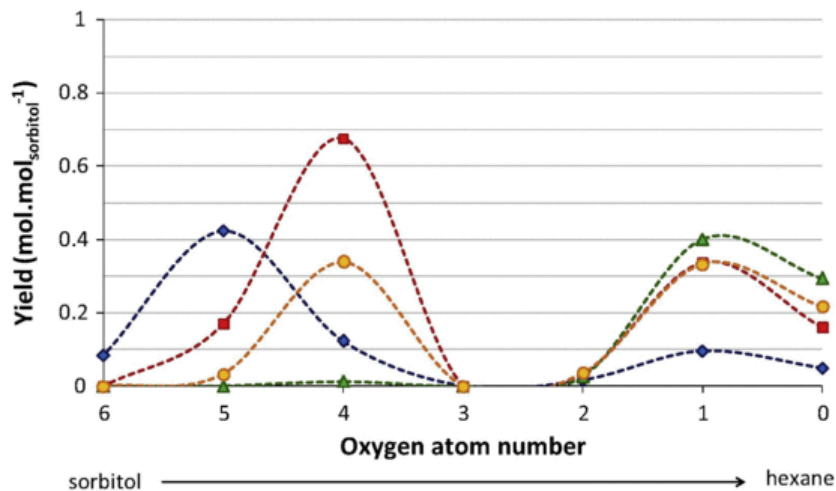
To conclude on this part, the distribution of C1 to C5 products shows that the C—C bond cleavage mainly occurs via successive terminal C—C bond breakings producing  $CO_2$  and eventually other C1 compounds. It is not possible at this stage to conclude on the C—C cleavage mechanism. It is suggested in the literature that decarbonylation and decarboxylation can be present as competitive mechanisms for the aldehydes transformation [14].

### 3.3 C—O cleavages

During polyols transformation, C—O cleavages occur by dehydration reactions, leading to the elimination of a mole of water and the formation of an unsaturated compound (alkene, ketone or heterocycle) which can be hydrogenated on a metallic site in the presence of hydrogen. By this way, the six alcohol groups of the sorbitol molecule can be theoretically removed successively: Sorbitol is first cyclodehydrated into 1,4-anhydrosorbitol and then isosorbide, afterward dehydrated-hydrogenated into triols, diols (or other di-oxygenated compounds), mono-alcohols (or ketones, furanic and pyranic derivatives) and finally alkanes. The product distribution as a function of oxygen atom number is thus a good indicator of the global “deoxygenation” of sorbitol into

hydrocarbons. Here, we call  $O_n$  the compounds containing  $n$  oxygen atoms.

Fig. 5 represents yields of products observed during sorbitol transformation as a function of their oxygen atom number (non-converted sorbitol is also represented). Oxygen eliminated as  $H_2O$ ,  $CO_2$  or  $CO$  is not represented, which explains variations in total amounts of oxygen from a condition to another. At 200 °C, the main compounds are the  $O_6$ — $O_5$ — $O_4$ , but some mono-oxygenated compounds ( $O_1$ ) and hydrocarbons ( $O_0$ ) are also present. When the temperature increases to 220 °C, the  $O_6$  and  $O_5$  yields decrease drastically whereas the yields in  $O_4$ ,  $O_1$  and  $O_0$  increase. At 240 °C, the mono-oxygenated compounds ( $O_1$ ) and the hydrocarbons ( $O_0$ ) represent almost all the reaction products. When the spatial velocity increases from  $2\text{ h}^{-1}$  to  $4\text{ h}^{-1}$ , the  $O_4$  and  $O_5$  yields increase again. These results show a fast deoxygenation of sorbitol into mono-oxygenated compounds, particularly at 240 °C,  $WHSV = 2\text{ h}^{-1}$ . The predominance of  $O_4$  and  $O_1$  species suggests that the  $O_6 \rightarrow O_5$  and  $O_3 \rightarrow O_2 \rightarrow O_1$  steps are fast and not critical for the kinetics of the overall transformation of sorbitol into hydrocarbons, whereas the conversion of mono-oxygenated compounds ( $O_1$ ) into hydrocarbons is one of the limiting steps of the reaction.



**Fig. 5** Distribution of the products of C—O cleavages during sorbitol transformation over  $Pt/ZrO_2 + TiO_2-WO_x$  as a function of the oxygen atom number at various operating conditions: 200 °C, 22 bar,  $WHSV = 2\text{ h}^{-1}$  ( $\diamond$ , blue); 220 °C, 28 bar,  $WHSV = 2\text{ h}^{-1}$  ( $\square$ , red); 240 °C, 37 bar,  $WHSV = 2\text{ h}^{-1}$  ( $\triangle$ , green) and 240 °C, 37 bar,  $WHSV = 4\text{ h}^{-1}$  ( $\circ$ , yellow).  $CO_2$  and  $H_2O$  are not represented. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

### 3.4 Reactivity of intermediates

To understand the reaction mechanisms of this particular step of mono-oxygenated compounds into hydrocarbons, catalytic tests were performed by replacing the sorbitol feed with identified mono-oxygenated intermediates in aqueous solution. The chosen model compounds are six-carbon atoms molecules: a primary alcohol (1-hexanol), a secondary alcohol (2-hexanol), a ketone (2-hexanone) and a furanic derivative (2,5-dimethyltetrahydrofuran). In sorbitol transformation effluent (Table 1), 1-hexanol and 1-pentanol are the major alcohols and secondary alcohols are present as minor products, whatever the operating conditions. 2- and 3-hexanones are also major products in the aqueous phase.

Two model  $O_2$  and  $O_3$  intermediates were also studied: a diol (1,2-hexanediol) and a triol (1,2,6-hexanetriol). Diols and triols are present as traces in sorbitol transformation effluents, only at low temperature (200–220 °C). Among them, 1,2-hexanediol and 1,2,6-hexanetriol are the main products. The reactivity of intermediates was studied at 240 °C,  $WHSV = 2\text{ h}^{-1}$ .

Even if isosorbide and 1,4-anhydrosorbitol were identified as true intermediates of the sorbitol transformation, their transformation is not studied in the present paper in order to focus on the reactivity of less oxygenated compounds.

#### 3.4.1 Mono-oxygenated intermediates

**3.4.1.1 Secondary alcohol: 2-hexanol** The 2-hexanol is totally transformed into  $n$ -hexane during the test (Table 2, entry 1). This evidences that the dehydration—hydrogenation of secondary alcohols is fast and does not lead to any secondary reaction such as  $n$ -hexane cracking. The cyclodehydration of 2-hexanol is theoretically possible but was not observed.

**Table 2** Products observed during the transformation of various intermediates compounds over  $Pt/ZrO_2 + TiO_2-WO_x$ .

Reactant	Conversion (%)	Products (yield, $\text{mol mol}_{\text{reactant}}^{-1}$ )

			2,5-diMeTHF	2-Hexanone	2-Hexanol	1-Hexanol	1-Pentanol	<i>n</i> - <i>n</i> -C6	<i>n</i> - <i>n</i> -C5	<i>n</i> - <i>n</i> -C4	CO <sub>2</sub>
1.	2-Hexanol	100	–	–	0	0	0	1.00	0	0	0
2.	1-Hexanol	100	–	–	–	0	0	0.31	0.69	0	0.45
3.	2-Hexanone	43	–	0.57	Traces	0	0	0.40	0	0	0
4.	2,5-diMeTHF	58	0.42	Traces	Traces	0	0	0.55	0	0	0
5.	1,2-hexanediol	100	0	0	0	traces	traces	0.21	0.51	0.20	0.68
6.	1,2,6-Hexanetriol	100	0	0	0	0.06	0.18	0.14	0.34	0.22	0.62

Traces: the compound is detected but its amount is lower than 0.05 mol mol<sup>-1</sup>.

Operating conditions: 240 °C, 37 bar, WHSV = 2 h<sup>-1</sup>.

**3.4.1.2 Primary alcohol: 1-hexanol** The transformation of 1-hexanol over Pt/ZrO<sub>2</sub> + TiO<sub>2</sub>-WO<sub>x</sub> leads to the total conversion of the reactant into *n*-hexane (product of a dehydration–hydrogenation reaction), *n*-pentane and CO<sub>2</sub> (products of dehydrogenation–decarbonylation-WGS reaction) (Table 2, entry 2). The molar ratio between *n*-hexane and *n*-pentane is 0.44, which means that in the studied conditions, the dehydration–hydrogenation reaction is disfavored over the dehydrogenation–decarbonylation one.

The CO<sub>2</sub> amount should be equal to the *n*-pentane amount. However, it is lower than expected (–30%). Since no other product of C—C cleavage is observed (CH<sub>4</sub>, CH<sub>3</sub>OH or CH<sub>3</sub>COOH), this result is attributed to CO<sub>2</sub> dissolution in the aqueous phase, not measured, and to the experimental error. CO is not analyzed.

**3.4.1.3 Ketone: 2-hexanone** The 2-hexanone transformation is much slower than alcohols one. The conversion only reaches 40% (Table 2, entry 3). This could be due to a negative effect of water on reaction kinetics, as already observed during butanone hydrogenation over Pt/Al<sub>2</sub>O<sub>3</sub> in liquid phase, and explained by a competitive adsorption of water on catalytic sites [34]. The main product is *n*-hexane, suggesting that the mechanism consists in a hydrogenation step producing 2-hexanol and then successive dehydration and hydrogenation steps leading to *n*-hexane (Fig. 6). The first hydrogenation is the slowest step since 2-hexanol is observed only as a trace in the effluent.

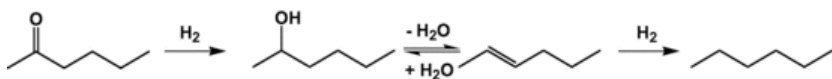


Fig. 6 Reaction scheme of 2-hexanone conversion into *n*-hexane over a bifunctional catalyst.

**3.4.1.4 Furanic derivative: 2,5-dimethyltetrahydrofuran** The 2,5-dimethyltetrahydrofuran (2,5-diMeTHF) transformation is also slow, with only 60% conversion (Table 2, entry 4). The major product is the *n*-hexane, but 2-hexanone and 2-hexanol are also detected as traces. The proposed mechanism consists of a hydrogenating C—O—C cleavage step producing 2-hexanol followed by the dehydration–hydrogenation steps giving *n*-hexane, as already discussed (Fig. 7). The very low yield of 2-hexanol indicates that the limiting step is the C—O—C cleavage. A few amount of 2-hexanone is also observed. It is proposed that 2-hexanone is formed by C—O cleavage of the heterocycle, in parallel to the 2-hexanol formation (Fig. 7).

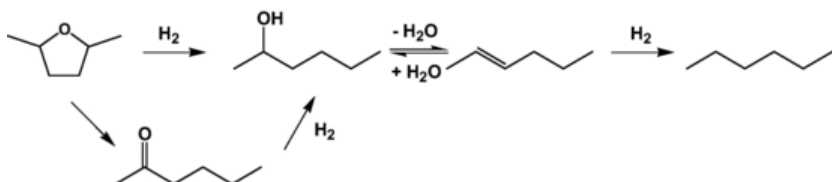


Fig. 7 Reaction scheme of 2,5-dimethyltetrahydrofuran conversion into *n*-hexane over a bifunctional catalyst.

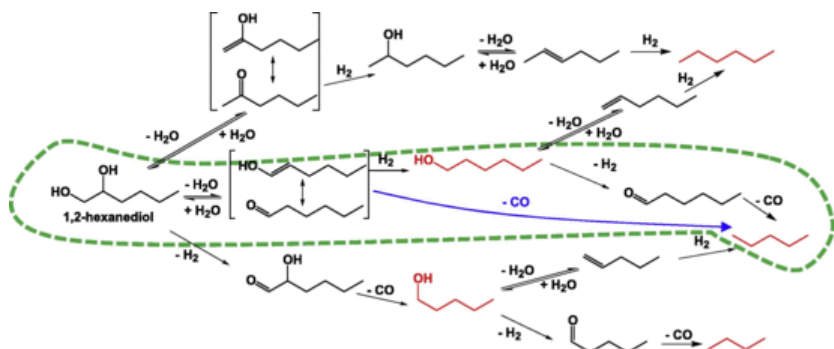
## 3.4.2 Other intermediates

**3.4.2.1 Diol: 1,2-hexanediol** 1,2-hexanediol conversion is total in the studied conditions (Table 2, entry 5). Numerous products are formed: primary alcohols (1-hexanol or 1-pentanol) and alkanes (*n*-hexane, *n*-pentane, *n*-butane). No cyclic product is observed. CO<sub>2</sub> is detected in concentrations lower than expected, as already discussed (see Section 3.4.1.2). Alkanes are the main products of the reaction, with a hexane/pentane molar ratio of 0.4.

Secondary alcohols are not detected. Most probably, they are formed and dehydrated–hydrogenated very quickly. Alcohol group in position 1 is thus the most difficult to dehydrate during the diol transformation.

The reaction scheme built from products analysis is complex (Fig. 8): 1,2-hexanediol can undergo two dehydration–hydrogenation reactions and gives *n*-hexane, or one dehydrogenation–decarbonylation plus one dehydration–hydrogenation to give *n*-pentane, or two

dehydrogenation-decarboxylation reactions producing *n*-butane.



**Fig. 8** Reaction scheme of 1,2-hexanediol transformation over Pt/ZrO<sub>2</sub> + TiO<sub>2</sub>-WO<sub>x</sub>.

1-Hexanol and *n*-pentane are the most represented alcohol and alkane products respectively, indicating that the major pathway consists in the dehydration-hydrogenation of the secondary alcohol group followed by the dehydrogenation-decarboxylation of the resulting primary alcohol (surrounded in green on Fig. 8). Alkene issued from the first dehydration reaction can also produce an aldehyde by tautomerization, which can be directly decarbonylated. This mechanism is a viable alternative to the hydrogenation-dehydrogenation-decarboxylation pathway, leading to a scheme where 1-hexanol is not an intermediate. However, this alcohol is detected in the reaction mixture, meaning that this alternative pathway is not the major one.

**3.4.2.2 Triol: 1,2,6-hexanetriol** The products observed during 1,2,6-hexanetriol transformation over Pt/ZrO<sub>2</sub> + TiO<sub>2</sub>-WO<sub>x</sub> are similar to products of 1,2-hexanediol transformation: 1-hexanol, 1-pentanol, *n*-hexane, *n*-pentane and *n*-butane (Table 2, entry 6). Thus, the involved reactions could be the same. However, the 1-pentanol concentration is higher than 1-hexanol one, contrarily to 1,2-diol transformation. Dealing with alkanes, *n*-hexane/*n*-pentane molar ratios are similar (0.42) for both experiments, whereas *n*-pentane/*n*-butane molar ratio is lower (1.5) when starting from the triol.

Minor products (less than 0.05 mol for 1 mol of converted 1,2,6-hexanetriol) are also detected (Table 3). Various compounds are identified: di-oxygenated products (tetrahydropyran-2-methanol), mono-oxygenated (3-methylcyclopentanone, 2-methyltetrahydropyran, 1-butanol, methanol), methane, cycloalkane (cyclohexane and methylcyclopentane) and carboxylic acids (hexanoic, pentanoic, propanoic).

**Table 3** Minor products observed during the transformation of 1,2,6-hexanetriol over Pt/ZrO<sub>2</sub> + TiO<sub>2</sub>-WO<sub>x</sub>.

Category	Compound	Yield* (mol mol <sub>hexanetriol</sub> <sup>-1</sup> )
Heterocycle	Tetrahydropyran-2-methanol	0.018
	2-methyltetrahydropyran	0.001
	tetrahydropyran	0.043
Ketone	3-Methylcyclopentanone	0.017
Alcohols	1-Butanol	0.019
	methanol**	0.009
Cycloalkanes	Cyclohexane	0.003
	Methylcyclopentane	0.002
Alkane	Methane	0.001
Acids	Hexanoic acid	0.007
	Pentanoic acid	0.017
	Propionic acid	0.006

Operating conditions: 240 °C, 37 bar, WHSV = 2 h<sup>-1</sup>.

\* The yields are given as indications. The amount of each compound is too low for a proper quantification.

\*\* Methanol may come from the cleaning procedure of the GC-FID.

The reaction pathway proposed from these analyses is given in Fig. 9. Hexanetriol is first transformed into di-oxygenated compounds by dehydrogenation-decarbonylation reactions, leading to pentanediols, or by dehydration-hydrogenation, leading to hexanediol or tetrahydropyran-2-methanol. The latter can undergo dehydration-hydrogenation and form methyl-tetrahydropyran, or decarbonylation, leading to tetrahydropyran.



Fig. 9 Reaction scheme of 1,2,6-hexanetriol transformation over Pt/ZrO<sub>2</sub> + TiO<sub>2</sub>-WO<sub>x</sub>.

The di-oxygenated compounds are transformed into primary or secondary alcohols containing 4 to 6 carbon atoms following mechanisms described for the 1,2-hexanediol reactivity. The pyranic derivatives are transformed in alcohols as described for 2,5-dimethyltetrahydrofuran.

Finally, the mono-alcohols intermediates can give alkanes by dehydration-hydrogenation or by dehydrogenation-decarboxylation, as discussed earlier.

The production of propane from 1-butanol is not drawn for the catalytic system Pt/ZrO<sub>2</sub> + TiO<sub>2</sub>-WO<sub>x</sub>, since no propane was identified in the products (grey zone on Fig. 9). Moreover, the butanol concentration in the effluent is very low, indicating that the 1-butanol formation pathway is minor and thus that the first step of 1,2,6-hexanetriol transformation is preferentially a dehydration reaction.

Some carboxylic acids are detected in the hexanetriol transformation effluent, contrary to what was observed in the case of hexanediol. They can be produced during the first steps of the reaction; they contain several oxygenated groups which are then eliminated. They can also be formed from aldehydes because the mechanism complexity leads to an increased competition on metal sites for decarbonylation, which favors the aldehydes disproportionation into alcohols and carboxylic acids on Lewis acid sites (Tischenko reaction) or basic sites (Cannizzaro reaction). The second hypothesis is presented in Fig. 9.

One can note that methanol and methane were detected in 1,2,6-hexanetriol transformation products. These C1 compounds are assumed to be formed from CO or CO<sub>2</sub> by reduction or methanation reactions, as suggested in part 3.2.

## 4 Discussion

The careful analysis of sorbitol transformation products leads to several assessments concerning the mechanisms involved in this reaction. The study of the products distribution as a function of their carbon atom number shows that C—C cleavages occur mainly at the end of the carbon chain and gives mainly CO<sub>2</sub> by decarbonylation and decarboxylation reactions, but also other C1 compounds such as methane, methanol and formic acid. C—C cleavages in the middle of the carbon chain with retro-aldol reactions occur too but are minor.

The oxygen distribution revealed that the successive deoxygenation reactions have different reaction rates. Isosorbide and mono-oxygenated conversions were identified as the slowest reactions.

Some mono-oxygenated compounds were transformed independently over the same catalytic system. Secondary alcohols produce only alkanes whereas primary alcohols with *n* carbon atoms produce alkanes with *n* and *n* - 1 carbon atoms and CO<sub>2</sub>. In the latter case two mechanisms are in competition: dehydration-hydrogenation, giving the *n* carbon atoms alkane, and dehydrogenation-decarbonylation-water-gas-shift, giving the *n* - 1 carbon atoms alkane and CO<sub>2</sub>.

For 1-hexanol the preferred mechanism is the dehydrogenation-decarbonylation mechanism. The study of non-saturated mono-oxygenated compounds, 2-hexanone and 2,5-dimethyltetrahydrofuran, led us to propose the following order in terms of increasing reactivity:  $C-O-C \sim C=O < C-OH$ .

1,2-Hexanediol and 1,2,6-hexanetriol were examined as model compounds for diol and triol. The first reaction is always the C—O cleavage by dehydration-hydrogenation. Then, the mono-oxygenated intermediates can undergo dehydration-hydrogenation or dehydrogenation-decarbonylation, leading to hydrocarbons and eventually CO<sub>2</sub>.

For 1,2-hexanediol, the preferred pathway is the dehydration-hydrogenation of the secondary alcohol group followed by the dehydrogenation-decarbonylation of the resulting primary alcohol. Other pathways such as double dehydration-hydrogenation reaction are also present but minor. The distance between acid and metallic sites on the catalyst could disfavor the double dehydration-hydrogenation pathway.

1,2,6-Hexanetriol reactivity is more complex and difficult to rationalize without some additional experiments. However, it was evidenced that the preferred pathway for 1,2,6-hexanetriol conversion would be one C—C cleavage, probably a decarbonylation reaction, and two dehydration-hydrogenation reactions, leading preferentially to alkanes with 5 carbon atoms. It is assumed that this trend can be extended to any polyol with at least one terminal alcohol: the preferred product will be the  $n - 1$  carbon atom alkane.

1,4-Anhydrosorbitol and isosorbide are assumed to be the main first intermediates of sorbitol transformation. The nature of the O3 intermediate is always under discussion. Li and Huber proposed that 1,2,6-hexanetriol is formed from isosorbide over a Pt/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst [21]. The O3 compounds are difficult to observe in the reaction medium because their transformation into di-oxygenated and then mono-oxygenated compounds is fast, as stated in part 3.3.

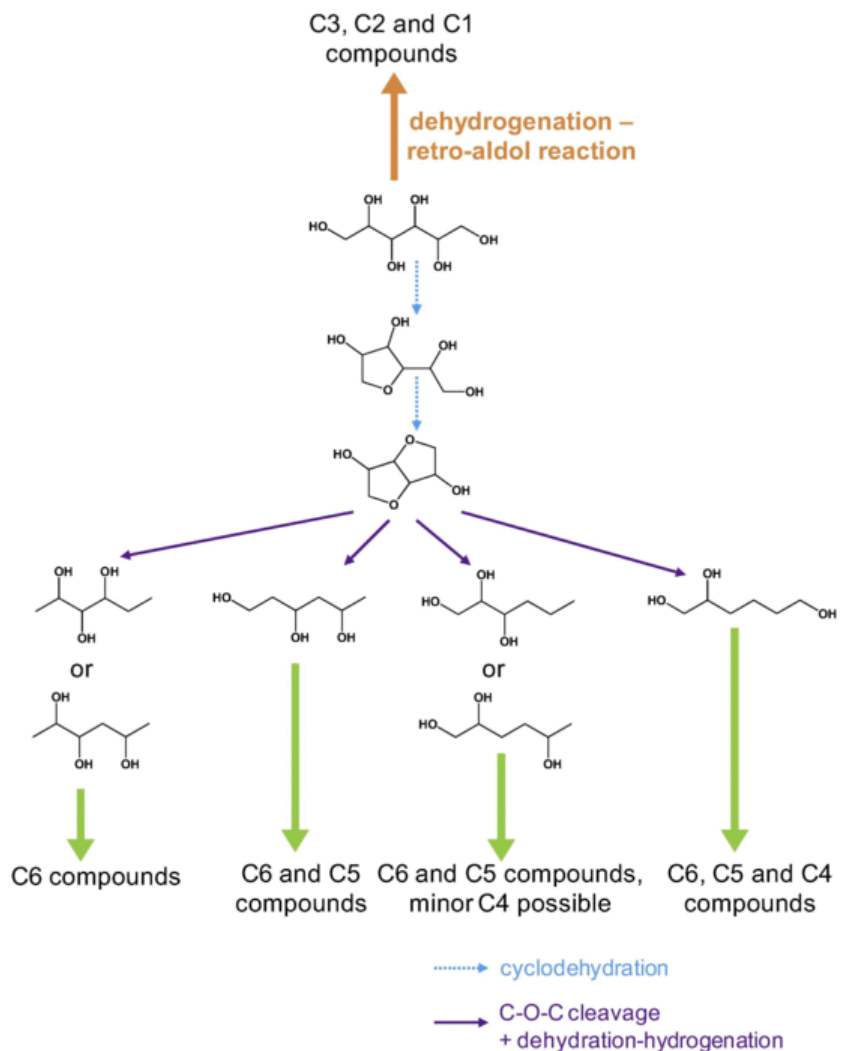
During the sorbitol transformation with our catalytic system, whatever the operating conditions, the *n*-hexane/*n*-pentane molar ratio is always higher than 1, whereas during 1,2,6-hexanetriol transformation the ratio is equal to 0.4. Obviously, 1,2,6-hexanetriol is not the only O3 intermediate contrary to the hypothesis made for the Pt/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst.

The mechanism should involve O3 intermediates able to give better C6 selectivity and *n*-hexane/*n*-pentane molar ratio higher than the one obtained with 1,2,6-hexanetriol. This is the case of intermediates without terminal alcohol group like 2,3,5-hexanetriol and 2,3,4-hexanetriol. Their selectivity is explained by the impossibility to break a C—C bond by decarboxylation.

Compounds containing one or two terminal alcohols (1,2,3-hexanetriol, 1,2,4-hexanetriol, 1,2,5-hexanetriol and 1,2,6-hexanetriol, respectively) will probably give worse C6 selectivity. Following this pattern, the 1,2,6-hexanetriol represents the worst case for C6 selectivity.

It was also shown that 1,2,6-hexanetriol, containing two primary alcohol groups and one secondary group, led mainly to C4 to C6 alkanes and not to propane. If this result is extrapolated to isosorbide, containing potentially two primary alcohol groups and two secondary ones, isosorbide transformation likely gives preferentially C4 to C6 hydrocarbons with similar mechanisms. Hence, it is suggested that C1 to C3 compounds are formed by minor reaction pathways including C—C cleavages in the middle of the carbon chain. In the literature, the retro-aldol condensation reaction is suggested to be the main pathway for the formation of short compounds from dehydrogenated sorbitol during aqueous phase process over Pt/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> [22].

A general reaction scheme is represented in Fig. 10. Sorbitol transformation occurs in two sequences: first, the sorbitol (C6, O6) is deoxygenated into isosorbide (C6, O4) with two cyclodehydration reactions, then the isosorbide is transformed into mono-oxygenates (C4—6, O1) and hydrocarbons (C4—6, O0) via dehydration-hydrogenation, dehydrogenation-decarbonylation and dehydrogenation-disproportionation-decarboxylation reactions.



**Fig. 10** General reaction scheme for sorbitol transformation over  $\text{Pt/ZrO}_2 + \text{TiO}_2\text{-WO}_x$ .

According to our study, the selectivity in C6 compounds from sorbitol transformation depends on three main parameters:

- (i) the selectivity towards middle-chain C—C cleavage during the early steps of sorbitol transformation;
- (ii) the nature of triol formed as intermediate;
- (iii) the  $C_n - 1$  selectivity when a  $C_n$  diol or triol is transformed.

C—C cleavage reactions in the middle of the carbon chain are mainly retro-aldol reactions usually involving basic catalytic sites. Tuning acido-basicity of the catalyst could improve C6 selectivity. Identification of (C6, O3) intermediates will probably need theoretical research. The  $C_n - 1$  selectivity comes from the preferred dehydrogenation—decarbonylation reaction following a dehydration—hydrogenation reaction. The  $C_n$  selectivity could be favored by different ways: get the acid sites closer to the metallic sites on the catalyst surface could avoid any diffusion issue favoring dehydrogenation rather than dehydration. For example, platinum particles could be formulated at the surface of the acid

TiO<sub>2</sub>-WO<sub>x</sub> phase rather than on an inert support. Increasing the hydrogen concentration around the catalytic site could disfavor dehydrogenation reactions and favor hydrogenation, for example by increasing the hydrogen pressure in the aqueous phase. Indeed, Moreno et al. [22] observed a positive effect of the pressure increase on the products chain length during sorbitol aqueous phase process over Pt/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>. Identifying and blocking decarbonylation metallic sites could also be an interesting progress.

## 5 Conclusion

The detailed study of the products distribution of sorbitol transformation over Pt/ZrO<sub>2</sub> + TiO<sub>2</sub>-WO<sub>x</sub> and reactions of model compounds bring important elements for understanding the reaction mechanism. We demonstrated that C—C cleavage reaction takes place at the end of the carbon chain, by decarbonylation or decarboxylation mechanisms. C—O cleavages occur with dehydration reactions, the slowest dehydrations being isosorbide transformation into tri-oxygenates and the mono-alcohols dehydration. The kinetic ranking of C—O cleavage reactions, from the fastest to the slowest, is C—OH > C=O ~ C—O—C.

During diols and triols transformation, the preferential pathway is the dehydration—hydrogenation of the secondary alcohol group followed by the dehydrogenation—decarbonylation of the primary alcohol group, leading to  $n - 1$  carbon atoms compounds from  $C_n$  diols or triols. The proximity of hydrogenation, dehydrogenation and decarbonylation catalytic sites on metal surface can be responsible for this selectivity orientation.

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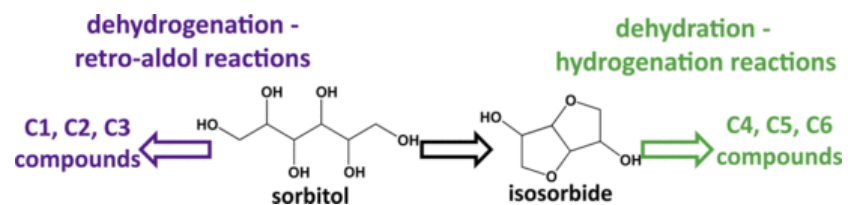
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### Graphical abstract



### Highlights

- The mixed (Pt/ZrO<sub>2</sub> + TiO<sub>2</sub>-WO<sub>x</sub>) solid **catalyses-catalyzes** sorbitol transformation into liquid alkanes.
- The limiting steps are the isosorbide and mono-oxygenated intermediate transformations.
- C—C bond cleavage mainly consists of dehydrogenation–decarbonylation reactions.
- The first reaction from 1,2-hexanediol and 1,2,6-hexanetriol is a C—O cleavage by dehydration–hydrogenation.

### Queries and Answers

**Query:** Please confirm that given name(s) and surname(s) have been identified correctly.

**Answer:** We confirm that names and surnames are correct

**Query:** Please check whether the designated corresponding author is correct, and amend if necessary.

**Answer:** The corresponding author is correct

**Query:** Please update Ref. [25].

**Answer:**

**[25]**

L. Vilcoq, A. Cabiac, C. Especel, S. Lacombe, D. Duprez, *Catal. Today*, 2014 (in press, corrected proof). DOI: 10.1016/j.cattod.2014.06.014

**Query:** Please check the layout of Table 1, and correct if necessary.

**Answer:** The layout is correct