



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/ZrO₂ + TiO₂-WO_x. 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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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].

Several catalytic systems have been studied for the catalytic transformation of sorbitol. Metallic catalysts such as Pt/Al₂O₃ lead to hydrogen and CO₂ production [20,23], whereas acid catalysts such as supported phosphopolytungstic acid [24] or TiO₂-WO_x [25] produce isosorbide. Bifunctional catalytic systems containing an hydrogenating metallic phase (Pt, Pd, Ni, Ru, Ir) and a dehydrating acid phase (SiO₂-Al₂O₃ [9,21], Nb₂O₅ and derivatives [26], ZrO₂-PO_x [27], ZrO₂-WO_x, TiO₂-WO_x [28]) are preferred to form hydrocarbons. We recently demonstrated that an original mixture of Pt/ZrO₂ + TiO₂-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

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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

TiO₂–WO_x (14 wt.% W) was prepared from rutile TiO₂ (IFPEN) by ion exchange with a H₂WO₄/H₂O₂ aqueous solution. 2.2 wt.% Pt/ZrO₂ was prepared by wet impregnation of ZrO₂ (MEL Chemicals) using an H₂PtCl₆ aqueous solution. Both catalysts were mixed to form a bifunctional catalytic system with the mass ratio Pt/ZrO₂:TiO₂–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 was 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 μm particle size, 4 g of TiO₂–WO_x and 1 g of Pt/ZrO₂) was mixed with SiC (VWR, 500 μm particle size) in order to get a 12 cm³ 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 °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 °C min^{−1} to the required temperature (200–240 °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 °C, 22 bar; 220 °C, 28 bar; 240 °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 h^{−1} to 4 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

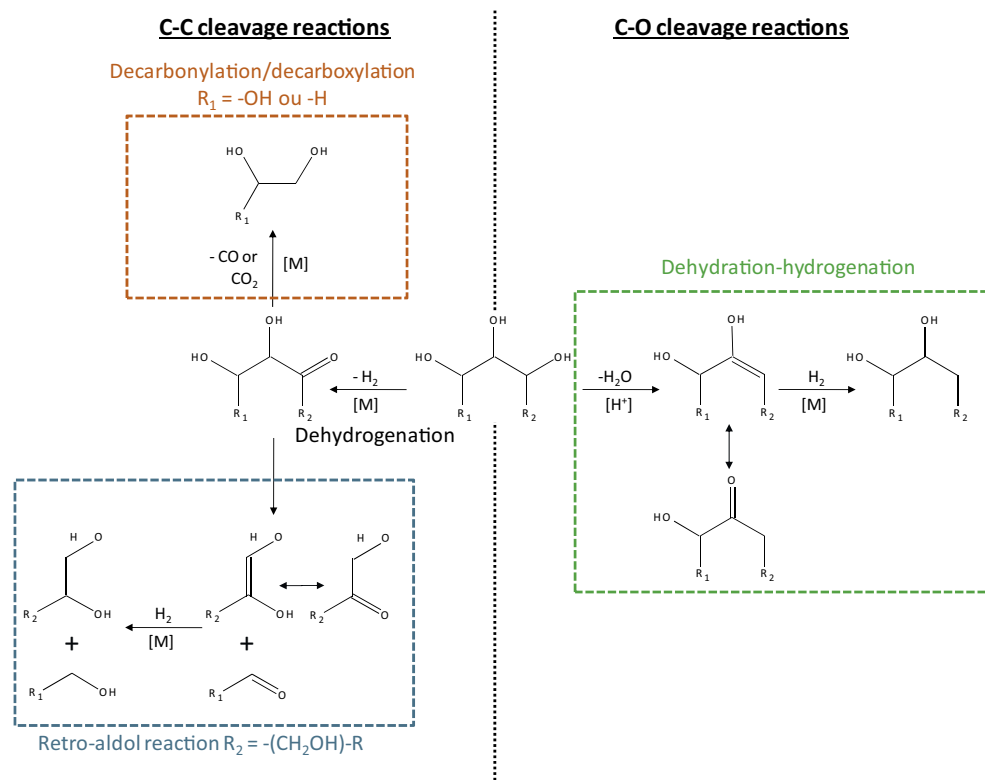


Fig. 1. Reactions involved in polyols transformation over a bifunctional catalyst.

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