



# Hydrocarbon fuel synthesis from sorbitol over bifunctional catalysts: Association of tungstated titania with platinum, palladium or iridium

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## ABSTRACT

To selectively transform sorbitol into hydrocarbons in aqueous phase, new bifunctional catalytic systems are designed by associating a hydrogenating metallic catalyst (M/ZrO<sub>2</sub>, M = Pt, Ir or Pd) and a dehydrating acidic catalyst (TiO<sub>2</sub>-WO<sub>x</sub>) in a mechanical mixture. Zirconium oxide was chosen as support because it has virtually no dehydration activity and gives a good stability to the metal in water. This stability is evaluated through several characterizations before and after contact with the aqueous reaction medium. It is proposed that stability in water is driven by two parameters. The support stability is a key parameter for the overall catalyst stability, and the metal–support interaction determines the sintering extent. The nature of the metal has also an important influence on the activity and selectivity of the bifunctional M/ZrO<sub>2</sub> + TiO<sub>2</sub>-WO<sub>x</sub> system for sorbitol transformation. Pd and Ir are slightly active and mainly transform sorbitol into isosorbide, whereas Pt is selective for long-chain alkane production. The mass ratio between metallic and acidic catalysts in the mechanical mixture also modifies the yield structure, with a Pt/ZrO<sub>2</sub>:TiO<sub>2</sub>-WO<sub>x</sub> 20:80 ratio for optimal liquid hydrocarbons production.

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## 1. Introduction

To face the increasing demand for fuels, the exploitation of non-conventional supplies is necessary. One interesting alternative to oil for liquid fuels production is the use of lignocellulosic biomass as a carbon source [1–3]. Biomass is a cheap, renewable and well-distributed resource. However, it contains around 50 wt% oxygen instead of 5 wt% for conventional fuels. Deoxygenating ex-biomass compounds is thus required to obtain fuels but remains a challenge. One way of reducing the oxygen content is the elimination of alcohol groups of hydrogenated sugars (i.e. polyols) in aqueous phase over bifunctional metal/acid catalysts [4–7]. Sorbitol is an interesting example of polyol because it can be easily produced from glucose by catalytic hydrogenation [8,9] or directly from cellulose

[10–12] and is a potential source of hexane, a liquid alkane [13,14]. Several catalytic systems have been described in the literature for sorbitol transformation [5,7,15–17].

Successive dehydration (on acidic sites) and hydrogenation reactions (on metallic sites) are a way to hydrodeoxygenate sorbitol into alkanes [18]. However, due to numerous intermediates and various side reactions (decarbonylation, water gas shift and decarboxylation on metallic sites, retro-aldol condensation on basic sites), the formation of products different from alkanes is also observed: CO<sub>2</sub>, polyols, pyranic derivatives, furanic derivatives, ketones, carboxylic acids and alcohols [16,19,20]. A general reaction scheme illustrating this complex reaction network is presented in Fig. 1. We previously studied several bifunctional catalytic systems, notably Pt/ZrO<sub>2</sub> catalyst associated with various tungstated oxides [21–23]. Tungstated titania (TiO<sub>2</sub>-WO<sub>x</sub>) with 14.7 wt% tungsten content was identified as a very active acidic phase for sorbitol transformation into C6 hydrocarbons. In the present paper, we emphasize the role of the metallic sites in sorbitol transformation. New heterogeneous catalytic systems are designed by changing the type of metal used in the metallic phase or the metal/acid phase balance. The aim is to identify an optimal metallic phase, i.e. active for sorbitol transformation, selective for hydrogenating

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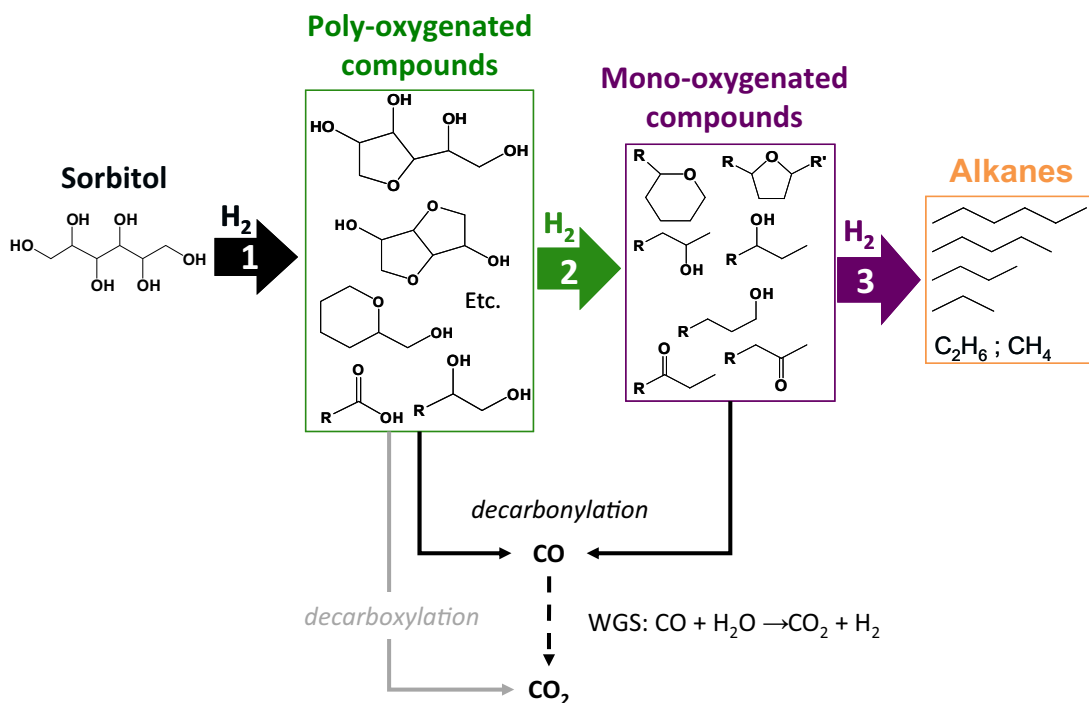


Fig. 1. Sorbitol transformation: general scheme (WGS: water gas shift reaction).

Adapted from Ref. [22].

the dehydration products formed on the acidic sites and stable under hydrothermal conditions. The selectivity criterion is crucial because the metallic sites can act as hydrogenation catalysts of C=O or C=C bonds formed during the dehydration reactions or as decarbonylation/decarboxylation catalysts, leading to C–C bond breaking (Fig. 1) [22,24,25]. The latter reaction is undesirable because it leads to a decrease in the carbon chain length.

In this work, mechanical mixtures are prepared in order to separate the metallic phase, supported on an inert solid (ZrO<sub>2</sub>), and the acidic phase (TiO<sub>2</sub>–WO<sub>x</sub>), which guarantees that the acidic sites remain unchanged when the metallic phase varies (the possible leaching/redeposition of metal on the acid phase is assumed to be insignificant). The preparation of the metallic catalysts and their stability in hydrothermal conditions are first presented. Their performances during sorbitol transformation are then depicted.

The lack of stability of several acid or bifunctional catalysts in APR or APD/H conditions has been recently reported: amorphization of H-Y zeolites [26], hydration of  $\gamma$ -alumina into boehmite [27] or of silica–alumina into kaolinite [21]. The deactivation of the support is supposed to be correlated with modifications in the metallic phases. The sintering of Pt when supported on  $\gamma$ -alumina [28,29] or on silica–alumina [21] was observed and attributed to support instability. Thus, the support of metal catalyst has to be stable in hydrothermal conditions. According to the literature, carbon supports (activated carbon, carbon black, carbon nanotubes and nanofibers), titania and zirconia are good candidates [30–33]. In this study, monoclinic zirconia has been selected since it is a mesoporous oxide, allowing a good diffusion of the reactant and products, and it can be considered as non-acidic for the considered reaction.

Among the available hydrogenating metals, platinum has been chosen as a reference. Palladium and iridium have been selected for their high activity in gas-phase olefin hydrogenation reactions [34]. Moreover, palladium is known for its low hydrogenolysis activity and Ir for its mono-cleaving behavior in gas-phase hydrogenolysis reaction (i.e. the selective cleavage of one C–C bond at the end of

the carbon chain) [34]. Pd has been recently studied for aqueous-phase hydrogenation of oxygenated compounds and showed an enhanced activity for acetaldehyde, furfural and furfuryl alcohol hydrogenation. Its activity in xylitol C–C cleavage was very low, which is interesting for our application [35].

The screening of the bifunctional catalytic system for sorbitol transformation was realized as follows:

- (i) In the first step, different metallic catalysts were associated with the TiO<sub>2</sub>–WO<sub>x</sub> acidic phase in a similar ratio and tested. The best couple was selected.
- (ii) In the second step, the influence of the metal/acid phase ratio was studied for the previously selected couple.

## 2. Experimental

### 2.1. Catalyst preparation

Tungstated titania was prepared by ionic exchange. TiO<sub>2</sub> rutile (IFPEN, from literature method [36]) was used as support. Fifty milliliters of H<sub>2</sub>WO<sub>4</sub> in 30% (v/v) H<sub>2</sub>O<sub>2</sub> solution (0.25 mol L<sup>-1</sup>) were added to 10 g of support dispersed in 75 mL of water and stirred overnight. The solution was centrifuged (30 min, 8000 rpm). The recovered solid was dried (80 °C, 18 h) and then calcined for 3 h at 600 °C. The TiO<sub>2</sub>–WO<sub>x</sub> solid was crushed and sieved (grain size 150–355  $\mu$ m). Platinum, palladium or iridium were deposited on zirconia extrudates (MEL Chemicals) by incipient wetness impregnation using aqueous solution of H<sub>2</sub>PtCl<sub>6</sub> (Alfa Aesar), H<sub>2</sub>PdCl<sub>4</sub> (prepared from PdCl<sub>2</sub>; Johnson Matthey) or H<sub>2</sub>IrCl<sub>6</sub> (Strem Chemicals), respectively. The amount of loaded metal was calculated to be equal to 125  $\mu$ mol g<sup>-1</sup>, i.e. 2.1 wt% for Pt, 2.1 wt% for Ir and 1.0 wt% for Pd. The impregnated catalysts were dried at 120 °C for 5 h and then calcined at 520 °C for 2 h (Pt and Ir) or at 400 °C for 3 h (Pd) under airflow. The catalysts were tested as extrudates in the hydrothermal stability test or milled and sieved to 150–355  $\mu$ m for the sorbitol transformation test. The bifunctional catalytic systems

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