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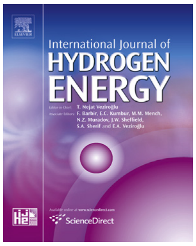

Production of bio-hydrogen by liquid processing of xylitol on Pt/Al_2O_3 catalysts: Effect of the metal loading

H.A. Duarte, M.E. Sad, C.R. Apesteguía*

Catalysis Science and Engineering Research Group (GICIC), INCAPE, UNL-CONICET, Predio CCT Conicet, Paraje El Pozo, 3000 Santa Fe, Argentina

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ABSTRACT

The aqueous-phase reforming of xylitol to produce bio-hydrogen was studied on Pt/Al_2O_3 catalysts containing 0.30, 0.57, 1.50 and 2.77%wt Pt by varying the weight hourly space velocity (WHSV) between 0.6 and 2.4 h^{-1}. At a constant WHSV value, the gaseous/liquid products ratio depended on the amount of surface Pt concentration on the sample (Pt_s). The xylitol conversion to gaseous products increased with Pt_s while xylitol conversion to liquid products did not change significantly. At a constant xylitol conversion, the H_2 selectivity increased with Pt_s. The H_2 yield increased continuously with both contact time and Pt_s. The H_2 productivity (Pr, mmol H_2/h g_{cat}) increased with both WHSV and Pt_s; indeed, the maximum Pr value obtained when using 1% xylitol in the feed (28 mmol H_2/g_{cat} h) was obtained on Pt(2.77)/Al_2O_3 catalysts at WHSV = 2.4 h^{-1}. The effect of the xylitol concentration on H_2 productivity was also investigated. At a constant space velocity, the H_2 selectivity and productivity decreased with increasing xylitol concentration in the feed.

Introduction

The production of bio-hydrogen via biomass-derived compounds is currently a subject of industrial and economical importance because hydrogen is not only an alternative energy source but also one of the key reactants to produce chemicals from conversion of natural renewable resources [1,2]. Although the high-water content of biomass turns it unsuitable for steam reforming processes, the liquid-phase reforming of biomass appears as a promising technology to produce bio-hydrogen. Pioneering work in aqueous-phase reforming (APR) with specific aim of hydrogen production from polyols was carried out by Dumesic and co-workers [3]. The APR process allows to generate hydrogen in a single reactor at low temperatures (473–543 K), compared with conventional reforming, which favors the water-gas shift reaction producing only traces of carbon monoxide. Operation at low temperatures also reduces energy costs of water vaporization and allows processing feedstocks sensitive to thermal decomposition. The APR of polyols to produce hydrogen was initially studied using shorter substrates such as ethylene glycol and glycerol [4–8]. Then, several papers have investigated the APR of larger substrates such as glucose

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* *Corresponding author*. INCAPE, Predio CCT Conicet, Paraje El Pozo, 3000 Santa Fe, Argentina.
E-mail address: capesteg@fiq.unl.edu.ar (C.R. Apesteguía).
URL: http://www.fiq.unl.edu.ar/gicic

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[9,10] and sorbitol [11–15], a sugar alcohol obtained by hydrogenation of glucose. Recently, the APR of xylitol, a five-carbon sugar alcohol derived from xylose hydrogenation, has been studied [16–20]. Although the H_2 yield diminishes with the reactant size [3,21], the liquid processing of larger substrates is economical attractive because minimizes pretreatment costs.

The reaction pathway to produce hydrogen by APR of biomass-derived oxygenated hydrocarbons involves the cleavage of C–C, C–H and O–H bonds on metal sites forming adsorbed CO that consecutively reacts with water to yield H_2 and CO_2 via the forward water–gas shift (WGS) reaction. This reaction pathway is depicted in Fig. 1 for the conversion of xylitol and shows the initial reactant decarbonylation (reaction 1) followed by the WGS reaction (reaction 2) that account for the stoichiometry of H_2 and CO_2 formed (reaction 3):

$$C_5O_5H_{12} \rightarrow 5\ CO + 6\ H_2 \tag{1}$$

$$5\ CO + 5\ H_2O \rightarrow 5\ CO_2 + 5\ H_2 \tag{2}$$

$$C_5O_5H_{12} + 5\ H_2O \rightarrow 5\ CO_2 + 11\ H_2 \tag{3}$$

Nevertheless, the selective formation of H_2 via APR of polyols is challenged by undesired parallel/consecutive reactions proceeding via cleavage of C–O bonds that form liquid alkanes and oxygenates [22]. The development of highly active catalysts that selectively promote the desired reaction pathways is then required to obtain competing technologies for generating hydrogen from liquid processing of polyols.

Few studies have been published addressing the selective production of H_2 from APR of xylitol [15,17–19]. Xylitol is obtained by catalytic hydrogenation of xylose monomer which is the major building block for the hemicellulose xylan, one of the main constituents of wood [23]. The content of xylose in the xylan-rich portion of hemicellulose, present in plant cell walls and fiber, can reach 25–30% in some species of hardwood [24,25]. Thus, xylitol is the second most abundant polyol resulting from lignocellulosic industry and provides a potential route for the sustainable production of hydrogen from natural renewable resources. Among the catalysts employed in these papers (monometallic Pt-supported on carbon, TiO_2, and Al_2O_3 and bimetallic Pt–Re/TiO_2) Pt/Al_2O_3 showed superior performance regarding hydrogen productivity. Actually, the literature shows that Pt/Al_2O_3 catalysts have been widely employed for the APR of polyols, probably because Pt is more selective for H_2 production than other noble metals [26] and alumina does not contain strong surface acid sites for promoting the acid catalyzed dehydration of xylitol [27]. The development of competing technology for generating hydrogen from biomass requires the use of highly active, selective and cost-effective catalysts for achieving optimal H_2 productivity that is the key parameter to evaluate the economic feasibility of using bio-hydrogen as an energy vector. Due to the high cost and limited availability of Pt, it is significant to establish what is the Pt loading required to obtain active, selective and stable catalysts for achieving the highest H_2 productivity. The effect of Pt particle size on the activity of Pt-supported catalysts has been investigated for the aqueous-phase reforming of glycerol [6,28] and ethylene glycol [29]. However, no studies have been performed on the effect of Pt surface concentration on both the gaseous/liquid products ratio and the H_2 productivity for liquid processing of xylitol. Precisely, we investigate here the APR of xylitol on Pt/Al_2O_3 catalysts containing different amounts of platinum, between 0.30% and 2.77% Pt. Results show that the hydrogen productivity obtained by liquid processing of xylitol may be regulated by the platinum surface concentration on the catalyst. At a given space velocity, the H_2 productivity increases continuously with the Pt surface concentration but reaches a plateau at about 40 μmol Pt/g that in our case corresponded to a Pt/Al_2O_3 catalysts containing 1.50% Pt.

Experimental

Catalyst preparation and characterization

Pt/Al_2O_3 catalysts with 0.30, 0.57, 1.50 and 2.77%wt Pt were prepared by incipient wetness impregnation. A high-purity γ-Al_2O_3 powder (Cyanamid Ketjen CK300) of 220 m^2/g BET specific surface area and 0.49 cm^3/g pore volume was impregnated at 303 K with a solution of tetraamine platinum nitrate, $Pt(NH_3)_4(NO_3)_2$ (Aldrich, 99.99%). After impregnation,

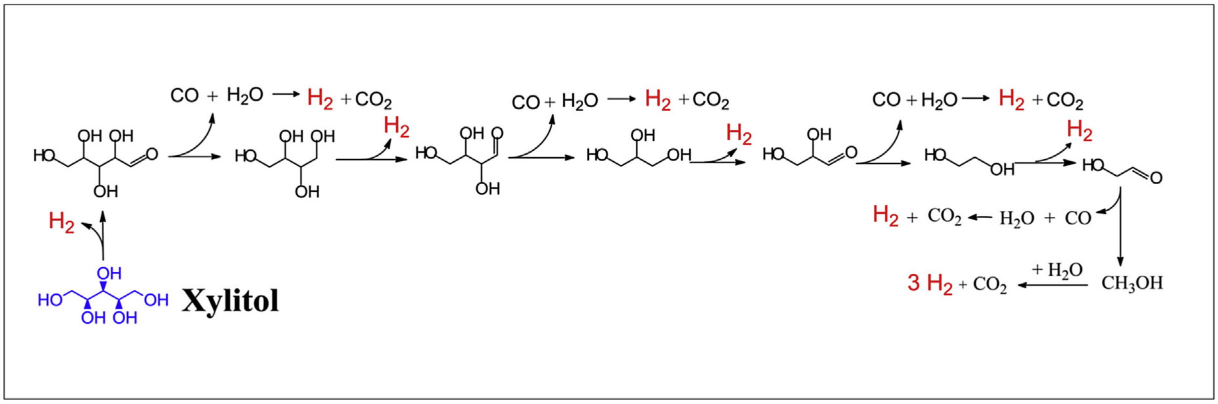

Fig. 1 – Scheme of the production of H_2 by the APR of xylitol.