



# Bio-hydrogen production by APR of C<sub>2</sub>-C<sub>6</sub> polyols on Pt/Al<sub>2</sub>O<sub>3</sub>: Dependence of H<sub>2</sub> productivity on metal content

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## ABSTRACT

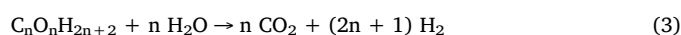
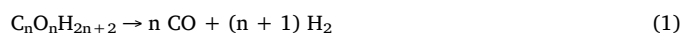
The effect of the platinum loading on the production of hydrogen by aqueous-phase reforming of ethylene glycol, glycerol, xylitol and sorbitol was studied on Pt/Al<sub>2</sub>O<sub>3</sub> catalysts containing 0.30, 0.57, 1.50 and 2.77 Pt%. Catalytic runs were performed at a space velocity of 1.2 h<sup>-1</sup>, 498 K, 29.3 bar and using a polyol(1.0%)/water feed. The total polyol conversion and the polyol conversion to gaseous products increased with surface Pt concentration (Pt<sub>s</sub>, μmol Pt/g<sub>cat</sub>). Similarly, the yield and the productivity to hydrogen (*Pr*, mol H<sub>2</sub>/g h) increased continuously with Pt<sub>s</sub> in all the cases, but the *Pr* values diminished with the polyol chain length. Coke formation depended on Pt<sub>s</sub> and the polyol size; the amount of carbon formed on the catalyst increased indeed with Pt<sub>s</sub> and diminished with the polyol chain length. The metal fraction was severely sintered during the APR reaction, irrespective of the reactant size. Nevertheless, the magnitude of the Pt dispersion drop was not dependent on the amount of platinum on Pt/Al<sub>2</sub>O<sub>3</sub> catalysts.

## 1. Introduction

Reforming of biomass-derived compounds in aqueous phase (APR) is a promising technology to produce bio-hydrogen, a renewable energetic carrier that is also used for producing valuable chemicals [1,2]. The APR process was introduced by Dumesic's group in 2002 aiming the production of hydrogen from polyols, sugars and sugar alcohols obtained from lignocellulosic biomass [3]. The process generates hydrogen with low amounts of CO in a single reactor at low temperatures (423 K–543 K) and moderate pressures (15–40 bar), which avoids the costs of water vaporization and favors the purification of the hydrogen effluent stream [4,5]. The production of bio-hydrogen was initially investigated for APR of polyols with shorter carbon chains such as ethylene glycol and glycerol [6–9]. Then, the APR of larger sugar alcohols (sorbitol, xylitol) and sugars (glucose) were also studied [10–14]. The conversion of biomass-derived oxygenated hydrocarbons to hydrogen is characterized by a complex chemistry, especially as the size of the substrate increases.

The direct reaction pathway to produce H<sub>2</sub> via APR of polyols involves the C–C as well as C–H and O–H bond scissions on the catalyst surface to form adsorbed CO that consecutively yields CO<sub>2</sub> and H<sub>2</sub> via the water-gas shift (WGS) reaction. As an example, Fig. 1 shows a simplified scheme accounting for the production of hydrogen via the APR of glycerol. For a polyol containing *n* carbon atoms (polyol P<sub>n</sub>) the APR reaction pathway involves the initial reactant decarbonylation

(reaction 1) followed by the WGS reaction (reaction 2). The formation stoichiometry of H<sub>2</sub> and CO<sub>2</sub> from polyol P<sub>n</sub> is represented by reaction 3:



Significant formation of byproducts may occur in the APR of polyols, in particular via parallel reactions involving cleavage of C–O bonds that leads to formation of side products such as alkanes and alcohols [11,15]. In the gas phase, formation of methane by hydrogenation of CO and CO<sub>2</sub> is also an undesired side reaction. Development of catalysts that selectively promote the C–C bond cleavage and water-gas shift reaction is therefore a requisite for efficiently generating H<sub>2</sub> from APR of polyols. Platinum supported on alumina or carbon has been widely employed for the APR reaction [3,9,10,13,16]. In this regard, previous studies have shown that Pt is more selective than other metals [17] and that the moderate acidity of alumina or carbon does not favor the undesired acid catalyzed dehydration of the substrate to liquid products [18]. Platinum is a high-priced metal of limited availability and is therefore important to determine the optimal Pt content required to achieve the highest H<sub>2</sub> productivity. However, very few studies addressing the relationship between the Pt loading and the

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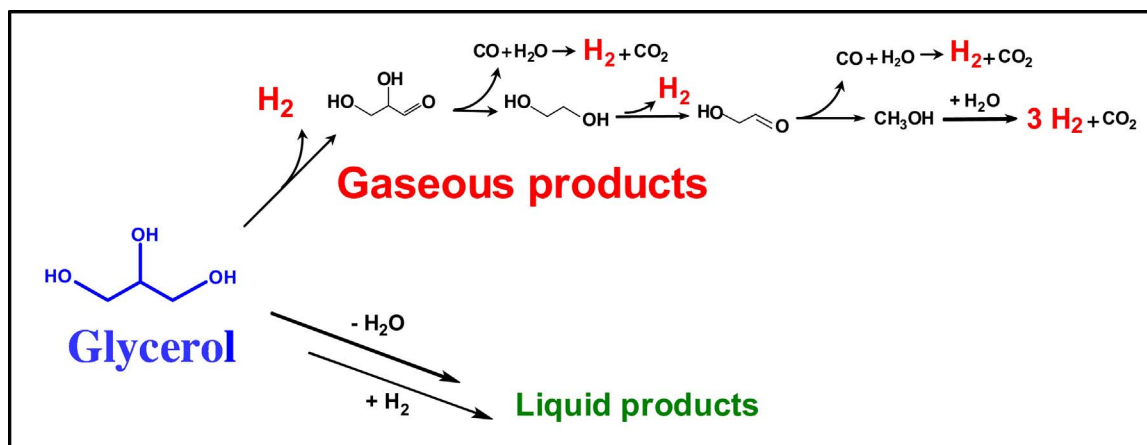


Fig. 1. Simplified scheme of H<sub>2</sub> production via APR of glycerol.

H<sub>2</sub> productivity for APR of polyols on Pt-supported catalysts have been reported. In particular, no reports were published so far on the effect of Pt content on the formation of coke and catalyst deactivation in aqueous phase reforming of polyols. The structure sensitivity of the APR of glycerol and ethylene glycol was investigated by varying the Pt particle size on platinum supported on alumina or carbon [8,19,20]. Recently, we used Pt/Al<sub>2</sub>O<sub>3</sub> catalysts containing different %Pt to investigate the effect of the Pt content on the production of H<sub>2</sub> for the APR of sorbitol [21]. Here, we have extended these studies on Pt/Al<sub>2</sub>O<sub>3</sub> catalysts to establish and compare the effect of Pt surface concentration on the catalyst activity, selectivity and stability for the APR of ethylene glycol (EG), glycerol (Gly), xylitol (Xyl) and sorbitol (Sorb). Results show that at a given space velocity, the H<sub>2</sub> yield and productivity as well as the amount of coke formed on the catalyst depend essentially on the Pt surface concentration and the polyol size.

## 2. Experimental

### 2.1. Catalyst preparation and characterization

Four Pt/Al<sub>2</sub>O<sub>3</sub> catalysts containing different Pt contents were prepared and are identified here as catalysts I (0.30 Pt%), II (0.57 Pt%), III (1.50 Pt%) and IV (2.77 Pt%). All the catalysts were prepared by incipient-wetness impregnation at 303 K of a high-purity  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powder (Cyanamid Ketjen CK300) with an aqueous solution of tetraamine platinum nitrate, Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> (Aldrich, 99.99%). The CK300 alumina had BET surface area of 220 m<sup>2</sup>/g, pore volume of 0.49 cm<sup>3</sup>/g and contains 50 ppm sulfur. The impregnated alumina was dried overnight at 353 K, then heated in air at 773 K for 3 h and finally reduced 2 h at 773 K in pure hydrogen.

Specific surface areas (S<sub>g</sub>, m<sup>2</sup>/g) were measured by N<sub>2</sub> physisorption at its boiling point using a Autosorb Quantochrome Instrument 1-C sorptometer and BET analysis methods. Prior to N<sub>2</sub> physisorption, the samples were outgassed for 1 h at 623 K. The Pt content of the samples were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES), using a Perkin-Elmer Optima 2100 unit. The Pt dispersion (D<sub>pt</sub>, surface Pt atoms/total Pt atoms) of the samples was determined by hydrogen chemisorption, using the double isotherm method as described in [22]. The volumetric adsorption experiments were performed in a conventional vacuum apparatus. Catalysts were reduced in H<sub>2</sub> at 673 K for 1 h and then outgassed 2 h at 673 K. After cooling to room temperature, a first isotherm was drawn for measuring the total H<sub>2</sub> uptake. Then, and after 1 h of evacuation at room temperature, a second isotherm was performed to determine the amount of weakly adsorbed hydrogen. The amount of irreversibly held hydrogen, (HC)<sub>i</sub>, was calculated as the difference between total and weakly adsorbed hydrogen. The pressure range was 0–7 kPa and

extrapolation to zero pressure was used as a measure of the H<sub>2</sub> uptake on the metal. A stoichiometric atomic ratio of H/Pt = 1 was used to determine the metal dispersion. Mean Pt crystallite sizes ( $\bar{d}_{pt}$ , nm) were determined from H<sub>2</sub> chemisorption data by using site densities of  $1.12 \times 10^{15}$  sites per cm<sup>2</sup> of metal [23].

Catalysts III and IV were analyzed by transmission electron microscopy (TEM) using a JEOL 100 CX II microscope with an acceleration voltage of 100 KV and magnification of 450,000x. A significant number of Pt particles was observed to obtain reliable particle size distribution histograms. The average volume/area diameter of Pt crystallites (d<sub>V/A</sub>, nm) was calculated from  $d_{V/A} = \frac{\sum n_i d_i^3}{\sum n_i d_i^2}$ , where n<sub>i</sub> is the number of Pt particles of size d<sub>i</sub>.

Powder X-ray diffraction patterns (XRD) were collected on a Shimadzu XD-D1 diffractometer using nickel filtered CuK $\alpha$  radiation. The acid properties of alumina support were determined by temperature-programmed desorption (TPD) of NH<sub>3</sub> preadsorbed at 373 K. Samples were pretreated in He at 773 K for 1.5 h and then exposed at 373 K to a flow of 1% NH<sub>3</sub>/He for 40 min. Weakly adsorbed NH<sub>3</sub> was removed by flushing with He at 373 K for 0.5 h and then the temperature was increased at 10 K/min. The NH<sub>3</sub> concentration in the effluent was analyzed by mass spectrometry (MS) in a Baltzers Omnistar unit.

The nature of surface acid sites on alumina was determined by Fourier infrared transform spectroscopy (FTIR) of adsorbed pyridine using a Shimadzu FTIR-8101 M spectrophotometer. Samples were ground to a fine powder and pressed into wafers (20–40 mg). The discs were mounted in a quartz sample holder and transferred to an inverted T-shaped Pyrex cell equipped with CaF<sub>2</sub> windows. Samples were initially outgassed in vacuum at 723 K during 2 h and then a background spectrum was recorded after being cooled down to room temperature. Spectra were recorded at room temperature, after admission of pyridine, and degassing at 373 K.

The amounts of carbon formed on the catalysts during the catalytic tests were measured by temperature-programmed oxidation (TPO). Samples (50 mg) were heated in a 2% O<sub>2</sub>/N<sub>2</sub> stream at 10 K/min from room temperature to 1073 K. The evolved CO<sub>2</sub> was converted to methane by means of a methanation catalyst (Ni/kieselghur) operating at 673 K and monitored using a flame ionization detector in an SRI 8610C gas chromatograph.

### 2.2. Catalytic tests

Catalytic tests for the APR of EG, Gly, Xyl and Sorb were carried out in a continuous packed-bed reactor at 498 K and 29.3 bar using aqueous solutions containing 1%wt polyol. Catalysts were sieved to retain particles with 0.35–0.42 mm diameter for catalytic measurements and reduced in hydrogen at 573 K for 1 h before reaction. The 1%wt polyol

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