# Aqueous phase reforming of xylitol and sorbitol over Pt/Al<sub>2</sub>O<sub>3</sub> catalysts: Effect of Pt content on hydrogen production

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## Introduction

Aqueous-phase reforming (APR) was proposed as a catalytic approach to produce  $H_2$  and/or alkanes from biomass-derived oxygenates [1]. In order to favor  $H_2$  production, the catalyst used must promote the cleavage of C-C, O-H, and C-H bonds in the oxygenated reactant (leading to  $H_2$ , CO and  $CO_2$ ), and facilitate the water-gas shift (WGS), as opposed to the cleavage of C-O bonds (leading to alkanes). Pt/Al<sub>2</sub>O<sub>3</sub> has been proved to be active and selective for APR due to its capability to break C-C bond and suitability to catalyze the WGS reaction. The APR process is very complex and many side reactions may also occurred over



# bifunctional catalysts as it is shown in Scheme 1 for xylitol APR. APR of ethylene glycol, glycerol and even sorbitol was widely studied [1] and few papers deals with C5 sugars, which are founded in lignocellulose biomass and are difficult to be used in biological fermentation process [2]. Even little work has been carried out so far to optimize the metal content in the catalysts. Therefore, we study in this work the effect of Pt loading when using Pt/Al<sub>2</sub>O<sub>3</sub> over the selective production of H<sub>2</sub> via APR reaction from xylitol and sorbitol.

#### **Materials and Methods**

Pt/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by incipient wetness impregnation using  $Pt(NH_3)_4(NO_3)_2$ , and reduced prior reaction. APR of aqueous xylitol and sorbitol solutions (1) wt%) were investigated at 225°C and 29.3 bar. Condensable products were collected and analyzed using HPLC (RI detector, Aminex HPX-87Ca column) whereas gaseous products were analyzed using a GC. Catalytic results reported here were taken after a stabilization period (about 100 min), these values remained invariant during 6 h on stream. Total conversion  $(X_T)$  accounts both the moles of C from the reactant converted into gaseous and liquid products, conversion to gaseous products ( $X_G$ ) accounts for the amount of polyol transformed into gaseous products containing carbon atoms of the fed, i.e. CO, CO<sub>2</sub> and CH<sub>4</sub>. Hydrogen yield ( $\eta_{H2}$ ) is defined as the moles of H<sub>2</sub> produces/total C atoms fed to reactor x 1/R x 100 where R is the  $H_2/CO_2$  reforming ratio of 11/5 and 13/6 for xylitol and sorbitol, respectively.

## **Results and Discussion**

According to Scheme 1, liquid and gas-products formation take place via two parallel mechanisms (the first one initially needs the assistance to the support to catalyze dehydration whereas the dehydrogenation for the second pathway is catalyzed by metal sites). According to this, the metal content would influence over the selective formation of gas-phase

products from xylitol in good agreement with the results reported in Table 1. Both total and to gas-phase products conversions decrease when WHSV increases as expected for all the catalysts. H<sub>2</sub> was the most abundant specie in gas phase follow by CO<sub>2</sub>; CO was detected in low concentration whereas only traces of methane were formed. 1.5% and 2.77% Pt/Al<sub>2</sub>O<sub>3</sub> formed the highest amount of gas-products ( $X_G=72$  and 66 % respectively at 0.6 h<sup>-1</sup>). All the

Table 1:APR of xylitol: Conversions vs Pt content and WHSV							
%	D <sub>Pt</sub>	WHSV=0.6 h <sup>-1</sup>		WHSV=1.2 h <sup>-1</sup>		WHSV=1.8 h <sup>-1</sup>	
Pt	%	XT	X <sub>G</sub>	XT	X <sub>G</sub>	XT	X <sub>G</sub>
0.30	63	83	30	42	15	36	13
0.55	53	89	42	55	21	37	16
1.50	59	100	72	60	30	40	17
2.77	48	90	66	65	37	45	18
[225°C, 29.3 bar, 1wt.% xylitol]							



catalysts resulted less active for sorbitol than xylitol APR. Figure 1 shows the hydrogen yield vs WHSV for different % Pt loading for both

xylitol and sorbitol APR reaction. Generally, when the Pt content increases, the  $\eta_{H2}$ increases. The highest  $\eta_{H2}$  for xylitol (54%) WHSV=0.6 h<sup>-1</sup>) was achieved using both 2.77 and 1.5% Pt and it was higher than those previously reported in literature [2]. The higher  $\eta_{H2}$  for sorbitol APR was 43 % when using 2.77% Pt. Our results

Figure 1: Hydrogen yield vs WHSV for xylitol and sorbitol APR

confirmed that the Pt content plays an important role over the initial selectivity of polyols to gas phase products since dehydrogenation is efficiently catalyzed by this metal. In addition, a further transformation of CO with excess of water to render even more H<sub>2</sub> and CO<sub>2</sub> is also promoted by these catalysts. However, when Pt content increases from 1.5 to 2.77 %, the improvement in  $\eta_{H2}$  is not so significant suggesting that it is not necessary to overloading the Al<sub>2</sub>O<sub>3</sub> to reach high hydrogen yields.

## Significance

We study the effect of metal loading when using Pt/Al<sub>2</sub>O<sub>3</sub> catalyst over H<sub>2</sub> production via xylitol and sorbitol APR. When Pt content increases, the selective formation of gas-phase products also increases. However, similar H<sub>2</sub> yield (54%) was achieved when using 1.5 or 2.77 % Pt/Al<sub>2</sub>O<sub>3</sub> for xylitol APR showing that there is not necessary to impregnate with an excess of Pt as usually reported in literature for APR reaction.

# References

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