Aqueous phase reforming of xylitol and sorbitol: Comparison and influence of substrate structure

Alexey V. Kirilin\textsuperscript{a,b}, Anton V. Tokarev\textsuperscript{a}, Leonid M. Kustov\textsuperscript{b}, Tapio Salmi\textsuperscript{a}, J.-P. Mikkola\textsuperscript{a,c}, Dmitriy Yu. Murzin\textsuperscript{a,*}

\textsuperscript{a} Laboratory of Industrial Chemistry and Reaction Engineering, Process Chemistry Centre, Åbo Akademi University, Biskopsgatan 8, FI-20500 Åbo-Turku, Finland
\textsuperscript{b} Zelinsky Institute of Organic Chemistry, Leninsky Pros. 47, 199991 Moscow, Russia
\textsuperscript{c} Department of Chemistry, Technical Chemistry, Chemical Biological Centre, Umeå University, SE-901 87 Umeå, Sweden

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\textbf{ABSTRACT}

The behavior of abundant polyol stemming from hemicelluloses, xylitol, was investigated in the aqueous phase reforming (APR) over supported Pt/Al\textsubscript{2}O\textsubscript{3}. The data obtained in the case of xylitol was compared to aqueous phase reforming of sorbitol under the same operating conditions. The effect of weight hour space velocity on the performance of a catalytic system as well as on selectivity toward hydrogen and alkanes was studied. The catalyst showed stable performance with insignificant deactivation over 160 h time-on-stream. The selectivity toward H\textsubscript{2} diminished from 86 to 70\% within 120 h. The regeneration of the catalytic system in a H\textsubscript{2} flow allowed to recover the catalyst activity and to improve selectivity toward H\textsubscript{2} to 75\%. It was found that both polyols demonstrated similar behavior in the APR in the whole range of space velocities studied. The selectivity toward H\textsubscript{2} went through a maximum in the case of xylitol and sorbitol when changing a space velocity. This behavior was attributed to a number of side reactions which involved hydrogen thus leading to its consumption. Additionally, the yields of target APR product, hydrogen, were higher in the case of xylitol compared to sorbitol due to the longer carbon chain in the latter substrate. The plausible reaction network based on the hypothesis that APR process proceeds through the terminal position of polyol was proposed to explain similarity in the gas and liquid product composition in the APR of xylitol and sorbitol. The reaction scheme describing formation of the main gas and liquid products via various pathways was proposed and discussed. The results obtained and explanations provided are in perfect agreement with the results obtained for other feedstocks in the literature.

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1. Introduction

Due to constantly increasing world energy demand, along with unstable prices for fossil fuels and their finiteness, conversion and processing of biomass and biomass-derived feedstocks is of high significance. Aqueous phase reforming (APR) first introduced by Dumesic and co-workers in 2002 [1], attracted a lot of attention, illustrating a promising technology for sustainable production of both hydrogen and liquid hydrocarbons [2 and references cited therein]. The process was successfully applied to convert polyols such as ethylene glycol (EG), glycerol (Gly) or sorbitol to hydrogen and hydrocarbons [1,3,4]. The process opens new horizons in terms of efficient and selective hydrogen production from renewables. Under the same experimental conditions, the water-gas shift (WGS) reaction takes place resulting in only trace amounts of carbon monoxide. The APR reaction of polyols is usually performed at 225 \degree C and 29.3 bar in the inert atmosphere. However, a modification of this process called aqueous phase dehydration/hydrogenation can be performed either under flow of hydrogen obtained from external source or in situ via APR of the feed [5].

Intensive studies have been conducted in the APR of ethylene glycol and glycerol wherein mainly supported Pt-based catalysts were examined [6–15] as well as other transition metals such as Ni, Pd, Rh, Ir [6] and Co [16].

Sorbitol also was investigated and revealed much more complicated process chemistry of APR (or APD/H) than ethylene glycol or glycerol comprising many chemical reactions and intermediates [5,17]. Surprisingly, the second most abundant polyol, xylitol, stemming from lignocellulosic processing industry as a product of xylose hydrogenation has attracted little attention; however, studies on formation of hydrocarbons from sugar alcohols, including xylitol are of high importance. To our best knowledge there is only one article in the open literature devoted to this problem [18]. In the