



Support effects in the aqueous phase reforming of glycerol over supported platinum catalysts

Aysegul Ciftci^a, Baoxiang Peng^b, Andreas Jentys^b, Johannes A. Lercher^b, Emiel J.M. Hensen^{a,*}

^a Schuit Institute of Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

^b Department of Chemistry and Catalysis Research Center, Technische Universität München, Lichtenbergstr. 4, 85747 Garching, Germany

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ABSTRACT

Aqueous phase glycerol reforming was studied for a set of Pt catalysts supported on γ -Al₂O₃, SiO₂ and amorphous silica–alumina (ASA) with varying alumina concentrations. The main products at 225 °C under 29 bar N₂ pressure for a feed of 20 wt.% glycerol are H₂, CO₂ and C₁–C₃ alkanes, 1,2-propanediol, hydroxyacetone and C₁–C₃ monoalcohols are the products in the liquid phase. Boehmite formation is observed for the γ -Al₂O₃ and ASA supported catalysts. The higher the Al concentration of ASA, the higher the amount of boehmite. Especially at low Al concentrations, the presence of boehmite is limited and silica leaches from the ASA support under reaction conditions. The increased surface acidity as a result of the presence of boehmite leads to increased hydroxyacetone formation (glycerol dehydration) and 1,2-propanediol (hydroxyacetone hydrogenation) formation. The activity of boehmite supported Pt for hydrodeoxygenation and reforming reactions is higher than that of γ -Al₂O₃ and SiO₂ supported Pt.

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1. Introduction

Biomass is considered as a sustainable replacement of finite petroleum reserves for the production of fuels and chemicals. In general, there is a mismatch between the composition of the biomass derived feedstocks and the desired fuel components and chemicals, especially in terms of the O/C ratio. Therefore, active and selective catalysts to upgrade such products streams need to be developed. Glycerol is a by-product of bio-diesel production and considered to play a central role in future biorefineries [1,2]. Next to ethylene glycol, it is also often used as a model compound for the conversion of polyols derived from lignocellulose. Aqueous phase reforming (APR) converts such feedstocks to H₂, whereas hydrodeoxygenation reactions produce oxygenated chemicals, in case of glycerol propanediols. Processing of glycerol and related feedstocks in the aqueous phase is attractive because of the limited volatility of the reactants and higher energy efficiency [3]. Another advantage of this approach is that product H₂ only contains very small concentrations of CO, which is useful when producing fuels for electrochemical devices.

Liquid phase processing of polyols has been the subject of a large number of recent studies [3–18]. The selectivity will depend on the rates of C–C bond and C–O bond hydrogenolysis reactions [4,5,12–17]. From glycerol, diols are either obtained by consecutive

dehydration and hydrogenation reactions or by dehydrogenation and direct bond cleavage of intermediates, while preserving the carbon–carbon bonds. The former reaction sequence requires two types of active sites, namely acid ones for the dehydration and metal sites for hydrogenation. The latter reaction is preferred in the presence of H₂. Carbon–carbon bond cleavage, which eventually will lead to H₂ and CO₂, takes place over metallic sites. Recently, the group of Lercher has shown that diols and triols are mainly converted due to dehydration, whereas mono-alcohols convert via dehydrogenation followed by decarbonylation (C–C bond cleavage) [18].

In general, supported Pt catalysts have been most frequently used for APR. Besides carbon, also Al₂O₃ and SiO₂ have been employed as carrier material for Pt nanoparticles. For instance, Pt/Al₂O₃ was found to give the highest H₂ selectivity in APR of ethylene glycol [9]. However, Luo et al. found evidence that γ -Al₂O₃ undergoes a phase transformation under APR reaction conditions [7]. In line with this, Ravenelle et al. [19] showed that under aqueous phase reforming conditions γ -Al₂O₃ is transformed into a hydrated boehmite phase with significant changes in surface area and acidity. The authors also noted that the supported metal particles decreased the rate of the transformation of γ -Al₂O₃ to boehmite. The use of silica as support has been associated with lower H₂ selectivity compared to Pt/Al₂O₃ in APR of ethylene glycol [11]. Also, the use of amorphous silica–alumina (ASA) supports has been described for catalysts for the APR process. Gandarias et al. investigated the role of acid sites of Pt/ASA in glycerol hydrogenolysis to obtain 1,2-propanediol [20]. Dehydration of glycerol to

* Corresponding author. Tel.: +31 402475178; fax: +31 402455054.

E-mail address: e.j.m.hensen@tue.nl (E.J.M. Hensen).