One-pot tandem processing of glycerol stream to 1,2-propanediol with methanol reforming as hydrogen donor reaction

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ABSTRACT

1,2-propanediol is formed efficiently using bio-glycerol feedstock via hydro-deoxygenation reaction with H_2 formed *in-situ* by a novel reaction cycle. The new catalytic route presented here includes the reformation of methanol, remained unreacted after transesterification, for the production of the active H_2 which is consumed in the tandem reaction of glycerol hydrogenolysis. The overall process proceeds in liquid phase over Pt or Cu based catalysts at 220–250 °C and 3.5 MPa initial N_2 pressure for 1 and 4 h reaction time. The test over Pt/SiO_2 catalyst resulted in 1,2-propanediol yield of 21.4%. The yield to the desired product in the presence of Al_2O_3 supported Pt is further limited due to the high extent of the over-hydrogenolysis reactions to propanols, which are promoted by the catalyst acidity. Cu:Zn:Al catalysts showed promising performance in the combined reaction cycle. The Cu bulk catalyst (with 49 wt% Cu) synthesized by the oxalate gel co-precipitation route exhibits ~35% yield to 1,2-propanediol at the standard reaction conditions. Further increase to 1,2-propanediol yield (up to ~45%) was achieved by tuning the reaction conditions. Experiments with labeled $^{13}CH_3OH$ shed light into the H_2 formation origin and proved that ~70% of the total H_2 is indeed produced from the reformation of methanol.

1. Introduction

Production of value added-chemicals via catalytic conversion of biomass derived and renewable sources has attracted much consideration [1]. Glycerol, one of the top 12 building block chemicals and largely available from the biodiesel production process, can serve as a feedstock for the production of valuable chemical products [2–5]. One of the most attractive routes of upgrading glycerol is the formation of 1,2-propanediol (propylene glycol). Propylene glycol, a major commodity chemical currently produced by hydration of the fossil derived propylene oxide, could alternatively be formed using glycerol as a starting material [6]. Glycerol can be converted to propylene glycol over a metal catalyst and H_2 via hydrogenolysis (or hydrodeoxygenation) reaction [7–17] under H_2 pressures up to 10 MPa [18]. As glycerol hydrogenolysis reaction involves C–O bond cleavage and simultaneous hydrogen addition, most of the previous related studies have been carried out under hydrogen pressure

providing H_2 from an external source. In spite of these several research efforts, the need to provide H_2 presents one of the main drawbacks of the new glycerol hydrogenolysis technology. These drawbacks are mainly related with the fact that currently H_2 is mainly formed using fossil feedstocks and on the other hand with its properties like flammability and diffusivity.

The concept *of in-situ* hydrogen formation and consecutive consumption overrides the above mentioned problems [19,20]. Within this concept two different approaches have been explored: the hydrogenolysis of glycerol with H_2 produced *in-situ* via reforming part of glycerol (APR – aqueous phase reforming) and H_2 formed by transfer reactions (CTH – catalytic transfer hydrogenation) using 2-propanol or formic acid as donor molecules. The first study was reported in a communication paper from Prof. Jacobs group in 2008 [19]. Glycerol hydrogenolysis was carried out at APR conditions over a Pt/NaY catalyst for propylene glycol formation in the absence of added hydrogen resulting in a 54.6% propylene glycol yield (64% selectivity at 85.4% glycerol conversion) at 230 °C and 15 h reaction time. The above groups have also patented the process of glycerol conversion to 1,2-propanediol in absence of added H_2 [21]. Some other groups have also investigated the possibility of coupling glycerol APR with hydrogenolyis [20–25]. Recently, Barbelli et al. [25] investigated the promotion of Pt with Sn and tested a series of bimetallic catalysts at 2 h batch tests under both H_2 and

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N_2 pressure. The best catalytic results were achieved in the presence of the Pt-Sn (Sn/Pt = 0.2) leading to a glycerol conversion to liquid products equal to 54% with 59% propylene glycol selectivity (31.8% yield) at 200 °C and 0.4 MPa pressure. The authors attribute the positive effect of Sn to the existence of Sn^{n+} "acid Lewis sites" which would facilitate the reactant adsorption and C–O cleavage.

On the other hand, the formation of hydrogen via CTH reactions as alternative of using a part of glycerol itself, have been firstly reported in a communication paper by Musolino et al. [26]. The authors exploited the selective transfer of glycerol to propylene glycol over a Pd/Fe_2O_3 catalyst using 2-propanol or ethanol as H_2 sources. They observed that at 180 °C after 24 h glycerol was fully converted to a mixture of propylene glycol and ethylene glycol (94 and 6% selectivity respectively). The combination of CTH with glycerol hydrogenolysis was also studied by Gandarias et al. [27–29]. In their most recent publication [29] the glycerol hydrogenolysis reaction was examined over a $Ni-Cu/Al_2O_3$ catalyst using formic acid as a hydrogen donor molecule. A glycerol conversion of 90% along with 82% propylene glycol selectivity (73.8% yield) was obtained by increasing the catalyst weight after 24 h reaction time at 220 °C and 4.5 MPa N_2. A reaction mechanism involving the formation of an alkoxide and proposing competitive adsorption between glycerol and propylene glycol was also proposed.

In spite of the significant progress that have been made as above described, there are still some drawbacks related with both APR and CTH methods. In the case of glycerol APR, even though the glycerol hydrogenolysis reaction is an exothermic one ($\Delta H_{513\,K} = -103$ kJ/mol) [30], the strong endothermic ($\Delta H_{523\,K} = 349$ kJ/mol) character of the APR may render the overall process energetically non efficient. In addition, in most of the reported studies concerning glycerol APR as a hydrogen source, the requirement of noble metal catalysts-Pt and Ru based-is essential as the reaction involves C–C bond scission of glycerol [19–22,25]. On the other hand, when H_2 is formed via CTH reactions and although this process allowed higher yields, the addition of a H_2 donor molecule in the reaction mixture (such as 2-propanol or formic acid) is necessary [26–29].

The catalytic system presented for the first time herein (Scheme 1) is the subject of a patent application [31]. It provides proof of concept for the utilization of the glycerol stream, avoiding separation steps after transesterification (e.g. methanol recovery), to run the hydrogenolysis reaction without external addition of H_2 gas. After the final separation step and the removal of the FFAs and the catalyst, the stream which contains glycerol, methanol and water (bio-glycerol) is used as a feedstock and upgraded according to the new concept. It should be underlined that the present route can be directly applied to heterogeneous catalyzed transesterification units where the crude glycerol stream does not contain impurities (catalyst and soaps). The H_2 needed is *in-situ* formed via methanol reformation in liquid phase over the same catalyst as in hydrogenolysis and under identical conditions. The proposed scheme offers certain advantages in terms of process intensification and energy savings conforming to the need for sustainable green processes. It is conducted in liquid phase eliminating the need of heat of vaporization for the oxygenate feedstocks. In addition, the carbon footprint of the process is further lowered because of the use of a single reactor, where the endothermic aqueous phase methanol reforming (APR) and the exothermic glycerol hydrogenolysis are coupled. But most importantly, the one-pot tandem processing of by-product stream reduces drastically the number of steps necessary for the production of propylene glycol, improving thus the efficiency of the process.

The present work explores the potentiality of 1,2-propanediol production from glycerol using methanol APR as the H_2 donor reaction. Within this context the synthesis, characterization and evaluation of Pt and Cu catalysts in the methanol

reforming-glycerol hydrogenolysis reaction cycle under inert atmosphere are investigated. In addition, issues like competitive adsorption of methanol and glycerol on the catalytic surface and quantification of the H_2 formation route using labeled methanol ($^{13}CH_3OH$) are also examined.

2. Experimental

2.1. Catalyst preparation

2.1.1. Pt-based catalysts:

Supported (5 wt% Pt) catalysts were prepared using the wet impregnation method. SiO_2 (Saint-Gobain, Norpro, $S_{BET} = 106$ m^2 g^{-1}) and γ-Al_2O_3 (Saint-Gobain, Norpro, $S_{BET} = 211$ m^2 g^{-1}) were used as the support materials. Pt was loaded on the supports using $H_2PtCl_6 \cdot 6H_2O$ as the metal precursor. After solvent removal under vacuum using a rotary evaporator, drying (110 °C) overnight, the solid is treated in flowing air (450 °C) for 3 h and reduced in flowing mixture of hydrogen/nitrogen (250 °C) for 2 h.

2.1.2. Cu bulk catalysts:

The bulk Cu:Zn:Al catalysts were synthesized using the co-precipitation and the gel-coprecipitation of oxalate precursor methods. The metal precursors used were nitrate salts of each component while the atomic composition of the metals was Cu:Zn:Al = 0.34:0.33:0.33 and 0.59:0.31:0.1. The procedure for the samples synthesized via the conventional carbonate co-precipitation method was as follows: the required quantities of the metal nitrates were dissolved in 150 ml distilled water each, to form transparent aqueous metal nitrate solutions. Another 200 ml of distilled water was stirred continuously on a hot plate magnetic stirrer at a constant temperature at 60 °C and pH 6–7. The metals solution was added in a stepwise manner. Precipitation was achieved via drop wise addition of Na_2CO_3 aqueous solution under continuous stirring and a constant pH of 6–7. After aging for 1 h at room temperature, the precipitate was filtered and washed thoroughly with distilled water for three times. The resulting solid was dried overnight at 120 °C and calcined in synthetic air at 350 °C for 4 h (heating ramp 2 °C/min). For the oxalate gel co-precipitation method an alcoholic solution of 20% excess of oxalic acid was injected rapidly into a mixed alcoholic solution of copper nitrate, zinc nitrate, aluminum nitrate at room temperature and vigorous stirring. The ethanol was separated from the gel-like precipitates at 70 °C using a rotary evaporator. The solid dried at 120 °C overnight and calcined at 150 °C for 1 h, 200 °C for 1 h, 300 °C for 1 h and 360 °C for 4 h with a heating ramp 10 °C/min. All Cu:Zn:Al catalysts were finally reduced at 420 °C for 2 h in flowing mixture of hydrogen/nitrogen. These samples will be referred to as CZA-1-X and CZA-2-Y, where 1 stands for lower loading and 2 for higher loading Cu samples and X or Y: coprec. or oxalate respectively for the synthesis method. For comparison reasons a commercial Cu:Zn:Al-Cu-com. (Alfa-Aesar HiFUELTM R120, Low Temperature Water Gas Shift Copper-based) was also tested.

2.2. Catalyst characterization

Surface areas of the samples were determined by N_2 adsorption at −196 °C, using the multipoint BET analysis method, with an Autosorb-1 Quantachrome flow apparatus. Prior to the measurements, the samples were dehydrated in vacuum at 250 °C overnight.

X-ray diffraction (XRD) patterns were obtained using a Siemens D500 diffractometer, with Cu-Kα radiation.

Inductive coupled plasma-atomic emission spectroscopy (ICP-AES) was used for the determination of the chemical composition