Toward hydrogen production from aqueous phase reforming of polyols on Pt/Al$_2$O$_3$ catalyst

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ABSTRACT

In aqueous phase processing of bio-oil, hydrogen (H$_2$) is produced in three steps: extraction with water, mild hydrogenation of the aqueous fraction and reforming in the aqueous phase. Polyols are the familiar hydrogenation products of the unsaturated oxygenates present in the bio-oil aqueous fraction. In this work, we decided on studying the aqueous phase reforming of two such polyols, viz. 1,2-propanediol and 1,4-butanediol. Activity trials were performed in a fixed-bed reactor using Pt/Al$_2$O$_3$ catalyst. Reactions conditions selected for these studies were like so: temperature, 433–493 K, pressure, 0.9–2.67 MPa, polyol concentration, 5–15 wt%, and weight hourly space velocity, 0.08–0.68 1/h. A chemical control regime prevailed at these conditions. The dependency of polyol conversion and H$_2$ yield on the aforesaid reaction variables was studied. The turnover frequency (TOF$_{H2}$) was measured and it was found that the activation energy for H$_2$ production from 1,2-propanediol and 1,4-butanediol was 82.7 and 70.1 kJ/mol.

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Introduction

Aqueous phase processing is a promising scheme for manufacturing hydrogen (H$_2$) from bio-oil. Extraction of bio-oil with water, mild hydrogenation of its aqueous fraction and reforming in the aqueous phase are the three key stages of this process [1]. Reforming in liquid water, also known as aqueous phase reforming (APR), is performed at low temperature (423–523 K) and high pressure to maintain liquid phase conditions in the reformer [2,3]. The APR process is energy-efficient, and it results in improved H$_2$ production, according to Cortright et al. [2]. Further benefits of this process are suppression of undesirable side-reactions and progression of water-gas shift reaction at low temperature. Thus, one-step

production of H$_2$ (and CO$_2$) with low levels of CO is viable [4,5]. Interestingly, Vispute and Huber [1] and Pan et al. [6] selectively produced H$_2$ from APR of bio-oil over Pt-based catalyst; by now, these are the only investigations on catalytic reforming of bio-oil in liquid water.

A significant number of APR studies are available in the literature for H$_2$ production from model oxygenated hydrocarbons in bio-oil such as alcohols (e.g., methanol [2,7–9], ethanol [4,9,10] and propanol [11]), polyols (e.g., ethylene glycol [2,4,5,7,11–19] and glycerol [2,14,20–24]) and sugars (e.g., glucose [2,25,26], sorbitol [2,14,27,28] and xylitol [28,29]). In this work, we decided on studying APR of 1,2-propanediol (or propylene glycol, PG) and 1,4-butanediol (BD). They represent the hydroxylated aliphatic C$_3$ and C$_4$ diols present in bio-oil. They are the familiar hydrogenation products of the

unsaturated oxygenates present in the bio-oil aqueous fraction such as hydroxyacetone [1,30] and levoglucosan [1,31]. Interestingly, PG is an intermediate formed during APR of glycerol [2,23,24,32—35] and sorbitol [36], whereas BD is formed as an intermediate in APR of xylitol [28,37], sorbitol [36] and glycerol [38]. Previously, Kim et al. [16] and Barbelli et al. [39] studied APR of 1,3-propanediol to compare H_2 production efficiency with ethylene glycol and glycerol over Pt-based catalysts. This is the only information available on APR of PG available, whereas there is no information available in the literature on APR of BD.

In this work, we investigated the APR process in a fixed-bed reactor over the ranges in temperature, 433—493 K, system pressure, 0.9—2.67 MPa, PG and BD concentrations, 5—15 wt% and WHSV, 0.08—0.68 1/h. We opted for Pt/Al_2O_3 catalyst because it is renowned for selectively producing H_2 from bio-oil [1,6], its model compounds [17,18,40] and other polyols such as ethylene glycol and glycerol [2].

Experimental

Materials

1,2-propanediol and 1,4-butanediol, used during experimentation, were purchased from S. D. Fine Chemicals Pvt. Ltd., Mumbai. Both chemicals were 99% pure. Cylinders containing air, H_2 and nitrogen (purity 99.995%) were bought from Industrial Oxygen Company Ltd., Mumbai. Gas mixtures containing H_2, nitrogen (N_2), carbon oxides (CO and CO_2), methane (CH_4), ethylene (C_2H_4), ethane (C_2H_6) and propane (C_3H_8) were procured from Chemtron Science Laboratory Pvt. Ltd., Mumbai, and used for calibration. A commercial 0.5% Pt/Al_2O_3 catalyst (2.7—3.3 mm pellets) was obtained from Johnson Matthey Chemicals India Pvt. Ltd., India. It was crushed and sieved before use.

Experimental setup

In all experiments, a tubular up-flow reactor (material SS316, inner diameter 19 mm, height 200 mm, Autoclave Engineers, USA) was employed. It was purchased from Chemito Technologies Pvt. Ltd., Mumbai. Together with this setup, a control panel, an electric furnace (Applied Test Systems, Inc., USA), back-pressure regulator (LowFlow, Jordan Valve, USA), high pressure liquid chromatography (HPLC) pump (Scientific Systems, Inc., USA), gas chromatograph (Chemito GC 8610) unit and a data acquisition system (Proficy HMI/SCADA − iFIX 4.0, GE India) were provided. A temperature controller (West, Germany), whose accuracy was ±1 K, was used for maintaining the desired temperature. To measure pressure, a pressure transducer (0—10 MPa) was used; the uncertainty in its measurement was ±0.01 MPa. The H_2 and N_2 flow rates were controlled by mass flow controllers (5800 Series, Brooks Instrument, USA) with an accuracy of ±1 cm^3/min.

Experimental procedure

In every experiment, a fixed amount of the unused catalyst (particle diameter < 63 μm) was sandwiched between two beds of quartz wool inside the reactor. Then the reactor was mounted in the furnace. In the beginning, the catalyst was reduced at 623 K for 2 h in the presence of pure H_2 flowing at 50 cm^3/min. After reduction, the reactor was cooled and the system was purged with flowing N_2. An aqueous polyol (PG or BD) solution was introduced from a reservoir at a predetermined flow rate by using the HPLC pump and contacted with the catalyst. The system was then pressurized with pure N_2 to the desired pressure. The system pressure was controlled by the back-pressure regulator. The pressure drop in the system was less than 0.05 MPa. After the reactor was entirely filled with the liquid solution, it was heated to the reaction temperature. The temperature and pressure at reaction conditions were estimated using Aspen Plus® simulation to ensure operation in the liquid-phase. Accordingly, the total system pressure (P_{Sys}) was maintained at a value higher than the saturation vapor pressure of the feed solution at the reaction temperature by 0.3 MPa. By this way, the P_{Sys}/P_{H2O} ratio was maintained at a value higher than unity and liquid-phase operation was ensured [41]. In APR, the temperature and pressure are interrelated due to changes in solubility of the products, viz. H_2 and CO_2 in water. Since P_{Sys} was maintained higher than the bubble point pressure of feed solution by 0.3 MPa, the vaporization of water and variations in solubility of H_2 and CO_2 were neglected. The effluent stream leaving the reactor was passed through a condenser, gas—liquid separator and back-pressure regulator. The gases in the off-gas stream from the separator, which could not be condensed, were analyzed by GC with the help of a valve injection system. Moreover, the liquid products were regularly collected and analyzed by HPLC. Since a steady state condition was achieved within 4 h, the results reported here are after 4 h of time-on-stream.

Unless stated otherwise, a fixed amount of catalyst was used in every experiment (4 g). An initial polyol concentration of 10 wt% (equivalent to steam/carbon ratio of 12.2 for PG and 11 for BD) was used in all experiments unless specified. As usual, the weight hourly space velocity (WHSV, 1/h) was expressed as the ratio of the mass of polyol fed per unit mass of the catalyst per hour. The liquid flow rate was varied between 0.05 and 0.45 cm^3/min, which corresponds to WHSV of 0.08—0.68 1/h. A N_2 flow rate of 30 cm^3/min was used in all experiments unless mentioned otherwise. The volume change due to reaction was neglected because we worked with dilute feed solutions. It was assumed that the catalyst was not deactivated by quartz wool. On the whole, we performed 44 experiments. To corroborate the correctness of our measurements, we replicated few experiments and discovered that the error was ±3%. In the experiments at 493 K, where no catalyst was used, it was found that the H_2 yield was negligible for both the polyols viz., PG and BD.

Product analysis

Using N_2 as the carrier for GC, H_2 in the product gas was detected with a HayeSep DB column. Contrarily, H_2 was used as a carrier during the analysis of CH_4, CO and CO_2. The product gas contained low levels of CO. This was affirmed