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Aqueous phase reforming of polyols from glucose degradation by reaction over Pt/alumina catalysts modified by Ni or Co

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ARTICLE INFO

Article history:

Received 13 March 2017
 Received in revised form
 6 June 2017
 Accepted 11 June 2017
 Available online xxx

Keywords:

Aqueous phase reforming
 Polyols
 Nickel
 Cobalt
 Platinum
 Urea matrix combustion method

ABSTRACT

A comparison of Pt-M/Al₂O₃ catalysts (M = Ni, Co, none) for the aqueous phase reforming (APR) of different polyols that can be obtained from glucose degradation was made. A standard monometallic Pt/Al₂O₃ catalyst was prepared by incipient wetness impregnation (IWI) of platinum on an alumina support. The bimetallic catalysts had Ni or Co promoters incorporated by the urea matrix combustion method (UCM) and Pt by IWI technique (PtNi and PtCo catalysts).

The catalysts were characterized by ICP/MS analysis, CO/chemisorption, TPR, XPS, SEM-EPMA and XRD. The catalytic activity was assessed with the tests of APR of an aqueous solution of 10 %wt of ethylene glycol (EG), glycerol (Gly) or sorbitol (Sorb), in a tubular fixed bed reactor at 498 K, 2.2 MPa, WHSV = 2.3–2.5 h⁻¹, 3 cm³min⁻¹ He carrier. Monitored variables were: conversion to carbon product in the gas phase, hydrogen and methane yield, selectivities, TOF and coke content on the spent catalysts.

PtNi and PtCo catalysts had better hydrogen yield and stability during the experiments than the un-promoted Pt catalyst, (H₂ yield = 24.4, 21.2 and 15% for PtNi, 17.9 and 15.1 for PtCo and 13.7, 10.8 and 7.5% for Pt after 8 h on stream in APR of EG, Gly or Sorb solution, respectively). Especially PtNi showed excellent yield and selectivity to hydrogen and a good stability, steadily generating hydrogen for long times. Co addition mainly helped in keeping low levels of coke and a low selectivity to methane.

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Introduction

It has been implicated that the burning of fossil fuels has a major impact on increasing concentrations of CO₂ in the atmosphere. Energy derived from biomass releases carbon with a carbon-energy ratio similar to that of coal. However,

biomass has already absorbed an equal amount of carbon from the atmosphere before its emission, so that the net carbon emissions of biomass fuels are zero during their life cycle [1]. The production of hydrogen from bio-renewable sources could result promising to minimize environmental problems associated with the combustion of fossil fuels [2].

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<http://dx.doi.org/10.1016/j.ijhydene.2017.06.100>

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Three main types of processes exist for production of hydrogen and fuels from biomass: gasification to produce syngas, thermo-chemical liquefaction and/or pyrolysis for bio-oils production [3], and acid [4] or enzymatic hydrolysis of lignocellulose [5] for production of sugars that are then refined to produce hydrogen, alkanes, alcohols or aromatic hydrocarbons [6].

Gasification of biomass produces renewable hydrogen, is an efficient clean way for large-scale hydrogen production, and has less dependence on fossil energy sources. Steam reforming of natural gas and gasification of biomass could become the dominant technologies by the end of the 21st century [7].

Catalytic conversion of biomass-derived polyols has recently attracted attention [7]. The conversion of polyols into H_2 can be performed either in gas phase (gas phase reforming, GPR) [8] or liquid phase.

Hydrolysis of biomass can generate different starting compounds for hydrogen production, as shown in Fig. 1 for the case of glucose. These final product alcohols can be transformed into hydrogen over an appropriate catalyst.

Due to the good water solubility of the involved reactants the liquid phase reforming is usually carried out in an aqueous phase (aqueous phase reforming, APR) [9]. Due to the high thermal sensitivity of the reactants, APR is performed at lower temperatures than gas phase reforming [10–12], which is a great advantage.

Advantages of APR cannot be over emphasized: i) the process eliminates the need to vaporize both water and the oxygenated hydrocarbon, which reduces the energy requirements for producing hydrogen; ii) The oxygenated compounds of interest are nonflammable and non-toxic, allowing them to be stored and handled safely; iii) liquid phase reforming shows higher H_2/CO selectivity ratios due to the more favorable conditions for the water-gas-shift thermodynamics, iv) Pressures used during the process (typically 1.5–5.0 MPa) are those where the hydrogen-rich effluent can be effectively purified using pressure-swing adsorption or membrane technologies, and the carbon dioxide can also be effectively separated for either sequestration or use as a chemical; v) APR occurs at low temperatures that minimize undesirable decomposition reactions; vi) production of H_2 from carbohydrates may be accomplished in a single-step, low-temperature process, in contrast to the multi-reactor steam reforming system required for producing hydrogen from hydrocarbons [12].

Catalysts for APR are metallic (normally noble metals of the transition metals group) and can have high loadings of the active metal. Dumesic et al. [12] found that the rate of ethylene glycol reforming decreases in the following order: Pt, Ni > Ru > Rh, Pd > Ir.

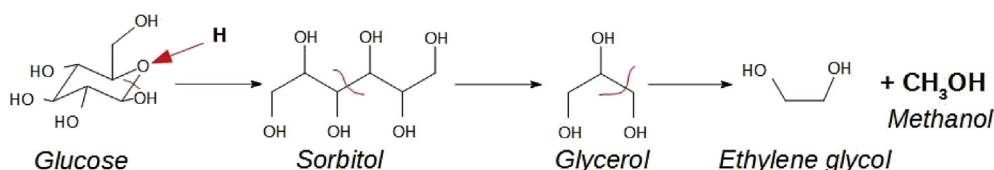


Fig. 1 – Polyols products of Glucose degradation.

APR involves a complex network of elementary reaction steps. In this sense Dumesic et al. [12] have suggested that active catalysts for APR reactions should possess high catalytic activity for the water-gas shift (WGS) reaction and sufficiently high catalytic activity for cleavage of C–C bonds. On this basis, Pt-based catalysts have been identified as promising. Due to their low cost and good catalytic activity, Ni-based catalysts are also attractive despite their undesired activity for producing alkanes. Dumesic et al. [13] have suggested in other reports that alloying Pt with Ni, Co or Fe improves the activity for H_2 production by lowering the *d*-band center, which causes a decrease in the heats of CO and hydrogen adsorption, thereby increasing the fraction of the surface available for the reaction of ethylene glycol.

An analysis of the state-of-the-art catalysts (e.g. Pt/ Al_2O_3) and process conditions shows that catalysis with high noble metal content (e.g. > 3%) [14–17] and highly diluted feedstocks (e.g. 1%) are commonly used [18,19]. In this sense it could be advantageous to use combinations of metals that yield similar activity levels but contain a lower amount of expensive noble metals. Reacting feedstocks of higher concentration could also lead to higher reaction rates and lower requirements for reactor vessel size.

In order to study these aspects the effect of Ni and Co addition on the catalytic activity and selectivity of alumina supported Pt catalysts of low noble metal content is studied in this work. The focus will be put on increasing the hydrogen yield and the stability of the catalyst. The catalysts will be tested in the APR of different polyols coming from glucose degradation: ethylene glycol, glycerol and sorbitol. Feedstocks of low dilution (10 %wt) were used.

Experimental

Catalysts preparation

Three metal supported catalysts were prepared by using a commercial gamma alumina support (Sasol Alumina Spheres 2.5/210). A monometallic Pt/ Al_2O_3 catalyst, with 1% wt Pt was prepared with tetra amine platinum nitrate ($Pt(NH_4)_4(NO_3)_2$, Sigma-Aldrich) aqueous solution by the incipient wetness impregnation technique (IWI), followed by drying, 12 h in a stove at 373 K and finally calcining in an air stream, 3 h at 723 K. This catalyst was named Pt-IWI.

For the modified bimetallic catalysts a combination of two methods was used. Either Ni or Co were added to the alumina support by means of the urea matrix combustion method (UCM) or solution combustion method [20–22] while Pt was added by incipient wetness impregnation (IWI). The necessary amounts of cobalt nitrate or nickel nitrate (in order to obtain

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