Catalysis Today xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Steam reforming of fast pyrolysis-derived aqueous phase oxygenates over Co, Ni, and Rh metals supported on $MgAl_2O_4$

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ARTICLE INFO

Article history:
Received 1 August 2015
Received in revised form
20 November 2015
Accepted 30 November 2015
Available online xxx

Keywords:
Biomass
Steam reforming
Aqueous phase
Oxygenates
Rhodium
Nickel
Cobalt

ABSTRACT

In this study we examine the feasibility of steam reforming the mixed oxygenate aqueous fraction derived from fast pyrolysis bio-oils. Catalysts selective towards hydrogen formation and resistant to carbon formation utilizing feeds with relatively low steam-to-carbon (S/C) ratios are desired. Rh (5 wt%), Pt (5 wt%), Ru (5 wt%), Ir (5 wt%), Ni (15 wt%), and Co (15 wt%) metals supported on $MgAl_2O_4$ were evaluated for catalytic performance at 500 °C and 1 atm using a complex feed mixture comprising acids, polyols, cycloalkanes, and phenolic compounds. The Rh catalyst was found to be the most active and resistant to carbon formation. The Ni and Co catalysts were found to be more active than the other noble metal catalysts investigated (Pt, Ru, and Ir). However, Ni was found to form significantly more carbon (coke) on the catalyst surface than Co. Evaluating the effect of temperature on stability for the Rh catalyst we found that catalyst stability was best when operated at 500 °C as compared to the higher temperatures investigated (700 °C, 800 °C). When operating at 700 °C, significantly more graphitic carbon was observed on the spent catalyst surface. Operating at 800 °C resulted in significant carbon deposition, resulting in reactor plugging as a result of thermal decomposition of the reactants. Thus, a concept analogous to the petroleum industries' use of a pre-reformer, operated at approximately 500 °C for steam reforming of the heavier naphtha components, followed by a high temperature methane reformer operated in the 600–850 °C temperature range, could be applied in the case of steam reforming biomass derived oxygenates. Additional stability evaluations performed over the Rh, Ni, and Co catalysts at 500 °C and 1 atm, under similar initial conversions, reveal the Co catalyst to be the most stable and selective towards H_2 production. However, deposition of carbon on the surface was observed. High resolution TEM on the spent catalysts revealed the formation of graphitic carbon on the Rh catalyst, and filamentous carbon formation on both the Ni and Co catalysts, albeit less pronounced on Co. Conversion and selectivity to CH_4 over Co remained relatively stable at approximately 80% and 1.2%, respectively. By contrast, the Rh and Ni catalysts CH_4 selectivity's were approximately 7–8%. The low selectivity to CH_4 and enhanced resistance to coke formation suggests the Co catalyst may be a desirable economic alternative for the steam reforming of biomass-derived oxygenates compared to the more conventional Ni and Rh-type steam reforming catalysts.

1. Introduction

Increasing energy demand worldwide and environmental concerns have driven the development of new technologies to obtain clean energy from renewable resources. Biomass has received much attention as a renewable feedstock for the production of hydrogen, liquid fuels, and chemicals [1,2]. Direct liquefaction thermochemical processes such as fast pyrolysis, catalytic fast pyrolysis, and hydrothermal liquefaction have been the subject of significant research [3,4]. Fast pyrolysis bio-oils can be separated into aqueous and organic phases by the addition of water or a solvent or hydrotreating, whereby oxygen is removed from the organic compounds, increasing the hydrophobicity and inducing a phase separation [3]. Other liquefaction technologies, such as hydrothermal liquefaction and some permutations of catalytic pyrolysis, directly yield biphasic, gravity separable aqueous and organic layers. The organic phase can be converted to suitable liquid fuels through processes such as hydrotreating, while the aqueous phase

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http://dx.doi.org/10.1016/j.cattod.2015.11.046
0920-5861/

Please cite this article in press as: R. Xing, et al., Steam reforming of fast pyrolysis-derived aqueous phase oxygenates over Co, Ni, and Rh metals supported on $MgAl_2O_4$, Catal. Today (2016), http://dx.doi.org/10.1016/j.cattod.2015.11.046

is currently considered as a waste stream. Depending on the severity and extent of the hydrotreating, the aqueous phase may contain a considerable amount of biogenic carbon. Effective utilization of the aqueous phase oxygenates is highly desirable from an overall economic perspective.

Conventional (i.e., non-catalytic) fast pyrolysis (FP) produces bio-oil with about 25 wt% water present in the bio-oil [3]. The whole bio-oil (including the dissolved water) is usually sent for hydrotreating to stabilize the bio-oil properties. Alternatively, water can be added to bio-oil to induce a phase separation containing many light oxygenates in the aqueous phase [5] while the organic phase would be sent to hydrotreating. Another method to remove the light oxygenates could be to separate an aqueous phase during hydrotreating. Due to the thermal instability of FP bio-oil, hydrotreating must be done step-wise with increasing temperature in each step. Lower temperature (150–275 °C) hydrotreating of FP bio-oil is necessary to stabilize the bio-oil so that higher temperature (350–400 °C) hydrotreating may be performed to reduce more refractory oxygenates such as phenolics [6]. An aqueous phase is formed after the lower temperature hydrotreating of FP bio-oil [7]. Separating the aqueous phase after "mid-hydrotreatment" may have significant advantages. For example, many low molecular weight oxygenates such as organic acids are apparently stable during lower temperature hydrotreating [7]. Currently, these low molecular weight compounds are reduced in the higher temperature hydrotreating step to produce low value light alkanes. Separation of the aqueous phase from the bio-oil for separate processing of the light oxygenates would facilitate lower overall H_2 consumption during upgrading and allow for separate processing of the aqueous stream oxygenates via, for example, steam reforming.

Steam reforming the aqueous phase light oxygenated organics is one processing route that is desirable because it produces H_2 required for the upgrading of the organic phase to hydrocarbon fuel. The oxygenated organic compounds found in biomass-derived aqueous phases vary widely but typically include acids, alcohols, aldehydes, ketones, furans, and aromatics [3,5]. A steam reforming catalyst that is resistant to deactivation by coking and selective to hydrogen production for a variety of feeds is highly desirable. Studies consisting of single oxygenated model compound systems have been frequently investigated to produce hydrogen via the steam reforming process [8–12]. There are a few reports on reforming multi-component mixtures [13], whole bio-oils [9,14] or water separated bio-oils [14–17]. Relatively high operating temperatures (600–850 °C) and steam-to-carbon (S/C) ratios are often employed in order to maintain catalytic stability [14,16]. Catalysts investigated include base metals such as Ni, Fe, and Cu [14,18] as well as noble metals such Pt, Pd, Ir, Ru, and Rh [11,19–23]. Several reports of metal alloys commonly employing Ni have been also been reported [12,24–29]. Ni-based catalysts are well established for steam reforming of various hydrocarbons; however deactivation due to coke deposits can be problematic depending on the feed and conditions utilized. On the other hand, supported noble metals have been reported to reform small oxygenates such as ethanol, acetic acid, glycerol, and phenol with increased reactivity and resistance to coke formation [11,19,23,30,31]. Various catalyst supports have been evaluated and include MgO [32–34], CeO_2–ZrO_2 [35,36], K–La–ZrO_2 [37], CeO_2–Al_2O_3 [12], $MgAl_2O_4$ [10,38–40], and graphitized activated carbon [41] have been evaluated. $MgAl_2O_4$ is a widely employed support for steam reforming due to its relatively low cost, high thermal stability, and basic properties which help mitigate coking. Our recent work has demonstrated that small Ir (∼1 nm) and Rh (∼2 nm) metal particles can be maintained on a $MgAl_2O_4$ support even after operating at very high temperatures (850 °C) [42,43].

In this study we evaluate steam reforming of a complex oxygenated feed mixture representative of an aqueous fraction derived from fast pyrolysis bio-oil [5]. Several metals (Rh, Pt, Ru, Ir, Ni, and Co) supported on $MgAl_2O_4$ were evaluated for catalytic performance. The effect of operating temperature on stability was also evaluated. Long term stability for the Rh, Ni, and Co catalysts was compared. Characterizations of spent catalysts were carried out using combined HRTEM, TGA-TPO, XRD, and total carbon analysis techniques in order to rationalize catalytic deactivation mechanism.

2. Experimental

2.1. Catalyst preparation

Rh (5 wt%), Ni (15 wt%), and Co (15 wt%) supported on $MgAl_2O_4$ were prepared by incipient wetness impregnation of $MgAl_2O_4$ (Sasol Puralox 30/140) calcined at 500 °C with solutions of corresponding metal nitrate dissolved in de-ionized water. After the impregnation, the catalysts were dried at 120 °C for 8 h and calcined under static air at 500 °C for 3 h.

2.2. Catalyst characterization

BET surface area, pore size, and pore volume of the catalysts were measured by nitrogen adsorption at 77 K with an automatic adsorption meter (Micromeritics Tristar 3000). The samples were treated at 150 °C for 12 h under vacuum before the adsorption measurement. Surface areas were determined from adsorption values at five relative pressure values (P/P_0) ranging from 0.05 to 0.2 using the BET method.

H_2 temperature-programmed reduction (H_2-TPR) experiments were performed on an automated catalyst characterization unit (Micromeritics Autochem 2910) equipped with a TCD detector. Typically, 0.1 g catalyst was first loaded into a U-type quartz tube, then a gas stream containing 5%H_2/Ar was flown through the sample. The temperature was increased from 20 °C up to 900 °C at a ramping rate of 10 °C/min.

The amount of solid carbon deposited on the spent catalysts was measured by a Shimadzu Total Carbon Analyzer (TOC-5000A with a SSM-5000A Solid Sample Module). TPO–TGA experiments were conducted with a Netzsch 409C Thermogravimetric Analyser. A 1%O_2/Ar gas mixture was flown through the sample starting from 40 °C and heating up to 900 °C with a ramping rate of 10 °C per min. Replicate tests were routinely conducted and results for the repeated data sets were all within 10%.

High Resolution Transmission Electron Microscopy (HRTEM) measurements were performed with a FEI Titan 80–300 operated at 300 KV. All images were digitally recorded using a charge-coupled device (CCD) cameral and were analyzed using Gatan Digital Micrograph. TEM images were collected from at least three different locations on the grid. The TEM sample preparation includes the mounting of powder samples onto copper grids covered with lacey carbon support films and immediate loading them into the TEM airlock to minimize an exposure to atmospheric air.

X-ray powder diffraction patterns were recorded using a Rigaku diffractometer with copper anode (wavelength = 0.15405 nm) and a scanning rate of 0.008° per second between $2\theta = 10°$ and 80°. The diffraction patterns were analyzed using PDXL-2 software and the Powder Diffraction File database. Particle sizes of the samples were determined from the XRD patterns using the Debye–Sherrer relation $d = 0.89\lambda/B\cos\theta$, where λ is the wavelength of Cu Kα radiation, B is the calibrated half-width of the peak in radians, and θ is the diffraction angle of a crystal face. The particle sizes were deter-

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