Steam Reforming of Fast Pyrolysis-Derived Aqueous Phase Oxygenates over Co, Ni, and Rh Metals Supported on MgAl_2O_4

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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 CH₄ over Co remained relatively stable at approximately 80% and 1.2%, respectively. By contrast, the Rh and Ni catalysts CH₄ selectivity's were approximately 7-8%. The low selectivity to CH₄ 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.

Keywords: biomass, steam reforming, aqueous phase, oxygenates, rhodium, nickel, cobalt

1.0 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 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 H₂ 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 H₂ 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 as Pt, Pd, Ir, Ru, and Rh [11, 19-23]. Several reports

of metal alloys commonly employing Ni have been also been reported [12, 24-27, 28 , 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], CeO₂-ZrO₂ [35, 36], K-La-ZrO₂ [37], CeO₂-Al₂O₃ [12], MgAl₂O₄ [10, 38-40], and graphitized activated carbon [41] have been evaluated. MgAl₂O₄ 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 MgAl₂O₄ 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 MgAl₂O₄ 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 hours and calcined under static air at 500°C for 3 hours.

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 hours 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 $10^\circ\text{C} / \text{min}$.

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) camera 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 $2\theta=10^\circ$ 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-Scherrer relation $d=0.89\lambda/B\cos\theta$, where λ is the wavelength of Cu K α 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 determined from the peaks located at $2\theta=41^\circ$ for Rh, $2\theta=52^\circ$ for Ni, and $2\theta=51^\circ$ for Co, respectively.

For all measurements, replicate tests were routinely conducted to obtain accurate results.

2.3 Reactivity Measurements

Catalytic activity measurements of steam reforming reactions were performed using a 3/8 in. OD fixed-bed Monel reactor. The catalyst diluted with α -Al₂O₃ (20:1 weight ratio of Al₂O₃ to catalyst) was loaded into the reactor. A K-type thermocouple was placed into the reactor to measure the catalyst bed temperature. Prior to the test, all catalysts were reduced at 850°C under a 10%H₂/N₂ gas mixture for 2 hours. The catalysts were tested at atmospheric pressure in the

temperature range of 460-850°C, over a range of gas hour space velocities (cc/hr/cc). N₂ was introduced into the system using a Brooks Mass Flow controller (5890 E series) and served as both a carrier gas (typically ~20% in the feed) and an internal standard reference. Liquid feed was introduced using a HPLC pump (Chrom Tech series 1500) through a 1/16 in. stainless steel tubing into a vaporizer where the temperature was set at 250°C. Liquid products were trapped into a 1 liter condenser cooled by a circulating ethylene glycol chiller with a temperature set at -2 °C. Flow rates of dry gas products in the effluent gases were monitored by a digital flow meter (DryCal). Gas products were separated using MS-5A and PPU columns and analyzed online by means of an Agilent Micro GC (Agilent 3000A series) equipped with a TCD detector. To check the carbon balance, some liquid samples were analyzed by HPLC and GC-MS. HPLC analysis was conducted using a Waters high performance liquid chromatography (HPLC) equipped with a Waters 2414 refractive index detector. A Bio-Rad Aminex HPX-87H ion exclusion column (300 mm × 7.8 mm) was used for analytes separation. Sulfuric acid (0.005 M) was used as eluent at a flow rate of 0.55 mL/min). Carbon conversion and selectivities are calculated using the following equations:

$$\% \text{ Conversion} = \frac{\text{moles of C in-moles of C, out}}{\text{moles of C, in}} \times 100 \quad (1)$$

$$\% \text{ CH}_4 \text{ selectivity} = \frac{\text{moles of CH}_4}{\text{moles of total C in gas product}} \times 100 \quad (2)$$

Steam reforming of bio-oil can be described by the following reaction:

This reaction is accompanied by the water-gas-shift (WGS) reaction:

Thus, the overall process can be represented by the following reaction:

According to Equation (5) the stoichiometric H_2 is calculated and then H_2 yield is determined as follows:

$$\% \text{H}_2 \text{ Yield} = \frac{\text{Actual H}_2 \text{ Composition}}{\text{Stoichiometric H}_2 \text{ Composition}} \times 100 \quad (6)$$

Thermodynamic equilibrium product selectivity at different reaction conditions and reactant composition was calculated by Gibbs free energy minimization using the ChemCAD software package.

3. Results and Discussion

3.1 Comparative evaluation of MgAl_2O_4 supported transition metal catalysts

A variety of catalytically relevant transition metals supported on MgAl_2O_4 were evaluated for steam reforming of a complex model feed simulating the aqueous fraction of fast pyrolysis bio-oil. As shown in Table 1 the feed comprised a mixture of oxygenates with varying functional groups and included acids, polyols, cycloalkanes, and phenolic compounds. The complex mixture used in this work was approximated based on the work of Vispute and Huber [5] and Elliott and Baker [7]. The mixture was not an exact replicate of any specific stream but meant to be representative of an aqueous phase produced by the addition of water to whole bio-oil or the aqueous phase separated after “mild-upgrading”. “Mild-upgrading” refers to the hydrotreatment

of the bio-oil performed at relatively lower temperature (150-275°C) in order to stabilize the bio-oil so that higher temperature (350-400°C) hydrotreatment may be employed for further oxygen content reduction. Rh (5 wt%), Pt (5 wt%), Ru (5 wt%), Ir (5 wt%), Ni (15 wt%), and Co (15 wt%) supported on MgAl₂O₄ were evaluated when operating at 500°C, 1 atm, and 30,000 hr⁻¹. For comparison purposes, a commercial naphtha reforming catalyst (Haldor Topsoe RKNR) was also evaluated at 500 °C and 1 atm. However, due to lower activity, the commercial catalyst was tested at a GHSV of 3,000 hr⁻¹. Primary gaseous products detected were H₂, CO, CO₂, and CH₄.

In Figure 1 it can be seen that the Rh catalyst was the most active and achieved complete conversion under these conditions. Both the Ni and Co catalysts were more active than the Pt, Ru, and Ir noble metals, with approximately 85 and 75% conversion, respectively. However, it should be noted that higher metal loadings were utilized for the base metals (15 wt%) compared to the noble metals (5 wt%) and that these activity results were not normalized on a per active metal site basis because the feed contains a mixture of species. The commercial Ni-based catalyst evaluated at 10X lower GHSV proved significantly less active than the 15 wt% Ni catalyst prepared for this study, which can be largely explained by its relatively low surface area of 17 m²/g. By comparison the MgAl₄O₄ supported catalysts had surface areas between 120 and 135 m²/g. A blank test, in which the reactor was loaded with only α -alumina diluent, exhibited little activity.

Total carbon data performed on spent catalysts and reported in Figure 1 demonstrates coke deposition was significantly less on the both the Rh and Co catalysts as compared to Ni. While Ni is well known to be more prone to coking as compared to other noble metals for steam reforming reactions[15, 20, 44], the relatively low amount of carbon found on the spent Co catalyst was unanticipated. Taken together, these results provides promise for Rh and also the

more economic Co metal as potentially suitable catalysts for steam reforming the oxygenated feed thus warranting further study.

3.2 Effect of Temperature on Stability

The effect of temperature on stability for the 5 wt% Rh/MgAl₂O₄ catalyst was evaluated when steam reforming the complex feed mixture (Table 1). Due to its relative resistance to carbon formation observed when screening various catalysts, the Rh catalyst was chosen for catalytic stability evaluation when operating at 500°C, 700°C, and 800°C. For a rigorous stability comparison, the gas hour space velocity (GHSV) was varied at each temperature such that initial conversions were the same, at approximately 70%. Figure 2(a) shows carbon conversion as a function of accumulated moles of carbon fed (used as a basis for comparison in lieu of time-on-stream due to the different GHSV's utilized). When operating at 800°C, the conversion remained relatively constant at approximately 74% throughout the entire test duration. At 700°C conversion sharply decreases from 65% to 29% (from 28 to 140 mol C fed/g cat) and the pressure significantly increased as well. At 500°C conversion exhibited a slow but gradual decrease from 67% to 61% (from 10 to 72 mol C fed/g cat), but no pressure increase was observed.

Total carbon analysis of the spent Rh catalysts tested at various temperatures (Table 2), revealed a relatively high amount of coke present on the spent catalyst after operating at 700°C (0.07 wt% C/hr). However, after evaluation at either 500°C (0.02 wt% C/hr) or 800°C (0.01 wt% C/hr), significantly less carbon was detected. Thus, at 700°C the greatest extent of carbon deposition was found, which may explain the fastest increase of the reactor pressure during the experiment (Figure 2(b)). A separate blank test conducted at 700°C showed no pressure increase, thus indicating coke formation occurred primarily on the catalyst surface. By operating

at 800 °C formation of carbon deposits on the catalyst surface was minimal and plugging of the reactor was due to carbon deposits found in the reactor entrance, obtained from thermal degradation of the reactants.

TPO-DTGA measurements of the spent catalysts were carried out to identify the carbon species deposited on the catalyst surface. Figure 3 shows the change of the DTGA profile as a function of the heating temperature for the three spent catalysts. For the catalyst tested at 500°C the DTGA profile shows that coke is removed at a lower temperature (440°C) versus the 700°C sample (665°C). For the 800°C sample only a very small amount of weight loss was observed. The difference in temperature of the carbon oxidation between the 500°C and 700°C profiles suggest that different types of carbon were formed on the catalyst surface with the higher temperature catalyst having “harder” or more graphitic-like carbon, which may be another reason to explain difference in catalytic performance and reactor pressure drop (Figure 2).

TEM micrographs for the spent catalysts presented in Figures 4(a-c) also reveal distinct differences in carbon deposition. Only a small amount of carbon was observed for the catalyst tested at 800°C, which is in agreement with its DTGA profile and catalytic performance. This reconfirms that the reactor pressure increase at 800°C was mainly caused by the formation of thermal decomposition and coking deposits in the reactor bed but not on the catalytic active sites. For the two catalysts tested at 500°C and 700°C graphitic carbon sheets were observed. The accumulation of carbon on the catalyst surfaces likely covers the metallic active sites, which explains the progressive loss of the catalytic activity. However, the structure of the graphite sheets is different. For the catalyst tested at 500°C, highly disordered graphite sheets were observed and appear to be more amorphous films covering both the Rh particles and the support. For the catalyst tested at 700°C well-ordered graphite sheets with multiple layers (4-5 layers) are

formed on the catalyst surface thus revealing a more dense packing than those observed for the catalyst tested at 500°C. This is in agreement with the study by Llorca et al. reporting the extent and degree of ordering of carbon deposits formed during the steam reforming reaction strongly depend on the reaction temperature [45].

Rh particle size distributions of the catalysts tested at 500, 700 and 800°C obtained from the TEM micrographs are shown in Figures 3(d-f). It was found that the spent Rh particles after operating at either 500°C or 700°C have similar average particle size of 2.6-2.8 nm. Rh particle size distributions for the freshly reduced catalysts (all three catalysts were reduced at 850 °C prior to evaluation) are also in the 2.6- 2.8 nm range thus indicating metal sintering to be minimal. The catalyst after operating at 800°C on average exhibited slightly larger particles with the average Rh particle sizes in the range of 2.6-3.0 nm, thus indicating only a small degree of metal sintering.

The results of this temperature investigation suggest that an operating temperature of around 500°C would be more suitable than operating at higher temperatures (700-800°C) due to comparable less coke formation. This is analogous to the petroleum industry where heavier components found in naphtha are first steam reformed in a pre-reformer at around 500°C followed by higher temperature reformation of the lighter hydrocarbons. In the case of steam reforming oxygenates a similar concept could be utilized where steam reforming oxygenates would be performed in a medium temperature range (500°C) followed by steam reformation of the residual methane and other light components at higher temperatures. Preferably the catalyst in the pre-reformer would be selective towards H₂ thus reducing load on the high temperature reformer.

3.3 Catalytic performance comparison of Rh, Ni, and Co

The Rh, Ni, and Co supported MgAl_2O_4 catalysts were further evaluated for catalytic performance. Figure 5 illustrates conversion and selectivity comparisons as a function of GHSV. The GHSV was varied by changing the flow rates of N_2 and liquid feed, while keeping the N_2 mole fraction constant at each GHSV. For the Rh catalyst, complete conversion was achieved at $30,000 \text{ hr}^{-1}$ and the less active Ni and Co catalysts reached complete conversion at approximately $10,000 \text{ hr}^{-1}$. The Rh and Ni catalysts produce equilibrium amounts of CH_4 with a selectivity of approximately 22% when at complete conversion. Conversely, the CH_4 selectivity over Co is significantly less than equilibrium, at approximately 5% when complete conversion is achieved. This suggests that CH_4 is formed predominantly as a secondary product over Co. Moreover, these results demonstrate Co to be the significantly more selective to H_2 compared to either Rh or Ni. H_2 yield for all three catalysts is shown in Figure 5(d) when operating under conditions that provide complete conversion.

3.4 Stability Comparison between Rh, Ni, and Co

Stability tests were carried out at 500°C with the multi-component feed mixture (Table 1) and results are shown in Figure 6. Stability for the three catalysts was compared by varying the GHSV such that initial conversion was approximately the same for each catalyst, and then running the duration of the test for approximately the same amount of carbon fed. The Rh, Ni, and Co catalysts were tested for approximately 64, 79, and 123 hours' time-on-stream, respectively. For the Rh catalyst, the feed conversion shows a gradual decrease from approximately 86 to 73% (at 32 mol C fed/g cat). CH_4 selectivity was relatively stable at approximately 7.6%. The Ni catalyst conversion peaked after an initial induction period at approximately 78%, followed by a slight decrease to 76% (at 32 mol C fed/g cat). CH_4

selectivity slowly increased throughout the entire test duration, increasing from approximately 7% to 12%. The Co catalyst's conversion and CH₄ selectivity were both quite stable during the entire test duration at approximately 80% and 1.2%, respectively. Among the three catalysts investigated the Co catalyst demonstrated the best combination of stability and selectivity towards H₂ formation.

Total carbon analysis on the spent catalysts showed carbon formation on the Rh, Co, and Ni catalysts to be 0.01, 0.023, and 0.18 wt. C%/hr, respectively (Table 3). These results show that Rh and Co had higher resistance to coke formation than Ni. This in agreement with literature reports for Rh [22] and Co [24, 41].

HRTEM micrographs for the three spent catalysts are shown in Figures 7(a-c). Deposition of carbon on the catalyst surfaces was observed for all the spent catalysts, however morphology of the carbon deposits appear different. Carbon on the Rh catalyst appears to be more of an amorphous film and contains highly-bent graphitic sheets covering both the support and metal particles. Most of the support particles were completely encapsulated in a thick carbon layer. The coking resulted in less accessible Rh centers that are available to reactant molecules before the formation of this layer, thus causing the Rh catalyst to deactivate. Both the spent Ni and Co catalysts show a similar level of surface coverage that consists of bundles of filamentous or whisker-like carbon fibers [46] with relatively uniform diameters (~16 nm for the Ni catalyst and ~20 nm for the Co catalyst, respectively). Formation of carbon fibers have been widely reported by other researchers in the non-oxidative activation of methane [46-49] and the steam reforming of hydrocarbons [50, 51]. In these reports the mechanism of carbon filament growth suggested to be linked to CH₄ cracking and CO disproportionation. In the case of this study, most of the carbon fibers are tangled together to form a winding material and can be followed even for a few

hundred nanometers without any signs of discontinuities around the support particles. Numerous nanosize catalyst particles are observed inside the carbon network. Compared to the spent Ni catalyst, the spent Co catalyst shows a lower degree of coking.

XRD characterizations were also performed on the fresh and spent Ni and Co catalysts and these results are shown in Figures 8 (a-b). Note that Rh^0 was not observed in either the fresh or spent catalyst due to the relatively small metal particle size (~ 3 nm) as indicated by HRTEM. Hence, Rh XRD patterns are not included here. XRD results show there was no phase structure changes after reaction for either metal or support. Table 3 summarizes the BET surface area and the XRD metal particle sizes of the catalysts before and after the stability test. Metal particle sizes obtained via XRD for the spent Ni and Co catalyst are in good accordance with the TEM analysis. Sintering of the metal clusters during the reforming reaction at 500°C was negligible.

4. Conclusions

In this study we have examined the feasibility of steam reforming an aqueous phase oxygenated mixture obtained from fast pyrolysis bio-oil. 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, and a commercial naphtha reforming catalyst was also tested for comparison purpose. When operating at 500°C and 1 atm the Rh catalyst was found to be the most active and coke resistant. The Ni and Co catalysts were more active than the other noble metal catalysts evaluated (Pt, Ru, Ir). However the Ni catalyst produced significantly more coke than Co. Interestingly, Co was also found to be the most selective towards H_2 production and thus exhibited the lowest selectivity toward CH_4 formation. Lower than equilibrium concentration of CH_4 was observed over Co,

whereas equilibrium levels of CH_4 were observed over both the Rh and Ni catalyst at full conversion, suggesting that CH_4 is a secondary product over Co.

The Rh catalyst was evaluated for stability as a function of reaction temperature (500, 700, and 800°C). Operating at 500°C provided the best balance of maintaining stable conversion and minimizing carbon formation. Severe catalyst deactivation was observed when operating at 700°C as evidenced by loss in activity and a relative large amount of coke deposits on the catalyst surface. When operating at 800°C thermal pyrolysis occurred inducing plugging of the reactor with relatively little carbon observed on the catalyst surface. These results indicate a moderate temperature range (e.g., ~ 500°C range) is desired for optimum stability. This concept is analogous to the petroleum industries use of a pre-reformer operated at approximately 500°C first steam reforming the heavier naphtha components, followed by a high temperature methane reforming operated in the 600-850°C temperature range.

Long-term stability comparisons between Rh, Ni, and Co reveal the Co catalyst to be the most stable and selective toward H_2 production. Comparing under similar starting conversions, the Co catalyst conversion and CH_4 selectivity remained relatively stable at approximately 80% and 1.2%, respectively. However, some deposition of carbon on the Co surface was observed. High resolution TEM on the spent catalysts revealed graphitic carbon formation on the Rh catalyst, and filamentous carbon formation on both Ni and Co catalysts. However, graphitic carbon was more pronounced on the Ni catalyst as compared to the Co.

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Table Captions

Table 1. Composition of complex mixture simulating the aqueous fraction of fast pyrolysis bio-oil (S/C=3.5 mol).

Table 2. Total carbon analysis for the spent 5 wt% Rh/MgAl₂O₄ catalysts after stability evaluation as a function of temperature (Figure 1).

Table 3. BET surface area and XRD metal particle size for the three catalysts before and after stability evaluation (Figure 6). Fresh catalysts were all reduced at 850°C in 10%H₂/Ar for 2 hours.

Figure Captions

Figure 1. Catalyst comparison for the steam reforming of complex aqueous phase mixture (Table 1) comparing activity and coke formation. Testing conditions: Temperature = 500°C, P = 1 atm, GHSV = 30,000 hr⁻¹; GHSV = 3,000 hr⁻¹ for commercial naphtha reforming catalyst RKNR (Haldor Topsoe).

Figure 2. Effect of temperature on (a) conversion, and (b) reactor pressure when steam reforming the complex aqueous phase mixture (Table 1) over 5 wt% Rh/MgAl₂O₄. The GHSV was varied in order to obtain similar starting conversions: GHSV = 120,000 hr⁻¹ (500°C), GHSV = 1,110,000 hr⁻¹ (700°C), and GHSV = 3,900,000 hr⁻¹ (800°C).

Figure 3. TPO-DTGA profile for the spent 5 wt% Rh/MgAl₂O₄ catalysts after the reactivity measurements performed at 500°C, 700°C, and 800°C.

Figure 4. HRTEM images of the spent 5 wt% Rh/MgAl₂O₄ catalysts after steam reforming the feed mixture (Table 1) at (a) 500°C, (b) 700°C, and (c) 800°C, and corresponding Rh particle size distributions shown in (d) through (e) obtained by HRTEM analysis for a few hundred particles.

Figure 5. Conversion and selectivity as a function of GHSV when steam reforming the complex feed mixture (Table 1) while operating at 500°C over (a) 5 wt% Rh/MgAl₂O₄, (b) 15 wt% Ni/MgAl₂O₄, and (c) 15 wt% Co/MgAl₂O₄.

Figure 6. Activity and CH₄ selectivity comparison as a function of accumulated moles of carbon fed when steam reforming the complex feed mixture (Table 1) over 5 wt% Rh/MgAl₂O₄, 15 wt% Ni/MgAl₂O₄, and 15 wt % Co/MgAl₂O₄. GHSV was varied in order to obtain similar starting conversions: GHSV = 90,000 hr⁻¹ (Rh), GHSV = 47,000 hr⁻¹ (Ni), and GHSV = 31,000 hr⁻¹ (Co). The Rh, Ni, and Co catalysts were tested for approximately 64, 79, and 123 hours' time-on-stream, respectively.

Figure 7. HRTEM micrographs of the spent catalysts after stability evaluation at 500°C (Figure 6) for (a) 5 wt% Rh/MgAl₂O₄, (b) 15 wt% Ni/MgAl₂O₄, and (c) 15 wt% Co/MgAl₂O₄.

Figure 8. Comparison of XRD patterns before and after stability evaluation at 500°C (Figure 6) for (a) 15 wt% Ni/MgAl₂O₄, and (b) 15 wt% Co/MgAl₂O₄.

Table 1. Composition of complex aqueous phase mixture simulating the aqueous fraction of fast pyrolysis bio-oil (S/C=3.5 mol).

Chemical name	Structure	Composition, wt. %
Acetic acid		6.3
Phenol		6.0
Ethylene glycol		4.9
Propylene glycol		4.7
Tetrahydrofuran alcohol		1.3
1,4-butanediol		1.3
γ -butyrolactone		1.3
Formic acid		0.9
Water	H ₂ O	73

Table 2. Total carbon analysis for the spent 5 wt% Rh/MgAl₂O₄ catalysts after stability evaluation as a function of temperature (Figure 1).

Temperature °C	Total Carbon Analysis wt% C/hr
500	0.02
700	0.07
800	0.01

Table 3. BET surface area and XRD metal particle size for the three catalysts before and after stability evaluation (Figure 6). Fresh catalysts were all reduced at 850°C in 10%H₂/Ar for 2 hours.

Catalyst	BET surface area m ² /g		XRD particle size nm		Total Carbon Analysis wt.% C/hr
	Fresh	Spent	Fresh	Spent	Spent
5 wt % Rh/MgAl ₂ O ₄	144.6	-	2.2	-	0.01
15 wt % Co/MgAl ₂ O ₄	128.4	101.3	10.6	11.2	0.02
15 wt % Ni/MgAl ₂ O ₄	107.0	97.1	9.7	10.4	0.18

Figure 1. Catalyst comparison for the steam reforming of complex aqueous phase mixture (Table 1) comparing activity and coke formation. Testing conditions: Temperature = 500°C, P = 1 atm, GHSV = 30,000 hr⁻¹; GHSV = 3,000 hr⁻¹ for commercial naptha reforming catalyst RKNR (Haldor Topsoe).

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Figure 5. Conversion and selectivity as a function of GHSV when steam reforming the complex feed mixture (Table 1) while operating at 500°C over (a) 5 wt% Rh/MgAl₂O₄, (b) 15 wt% Ni/MgAl₂O₄, and (c) 15 wt% Co/MgAl₂O₄, and (d) H₂ yield comparison between the three catalysts.

Figure 6. Activity and CH₄ selectivity comparison as a function of accumulated moles of carbon fed when steam reforming the complex fed mixture (Table 1) over 5 wt% Rh/MgAl₂O₄, 15 wt% Ni/MgAl₂O₄, and 15 wt % Co/MgAl₂O₄. GHSV was varied in order to obtain similar starting conversions: GHSV = 90,000 hr⁻¹ (Rh), GHSV = 47,000 hr⁻¹ (Ni), and GHSV = 31,000 hr⁻¹ (Co). The Rh, Ni, and Co catalysts were tested for approximately 64, 79, and 123 hours' time-on-stream, respectively.

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GRAPHICAL ABSTRACT

Steam Reforming Aqueous Fraction of Bio-oil: Rh, Ni, Co metals supported on MgAl_2O_4