



Hydrogen production via steam reforming of bio-oil components over calcium aluminate supported nickel and noble metal catalysts

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ABSTRACT

Steam reforming of two representative bio-oil components, acetic acid and acetone, was investigated thermally and catalytically over nickel (5 wt%) and noble metal (0.5 wt% Rh or Ir) catalysts supported on calcium aluminates ($\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ and $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$). The thermal reactions (with or without water) were studied in the presence of inert quartz particles and showed that at 750 °C, acetone and to a lesser extent acetic acid undergo a series of homogeneous reactions forming CO, CO₂, CH₄ and H₂ in concentrations which depend on the organic, and the presence or absence of water. Characteristic of acetone thermal steam reforming is that high amounts of acetic acid are produced. The catalysts prepared were tested at three reaction temperatures 550–650–750 °C using steam/carbon = 3 and space velocities around 30 000 h⁻¹. The results showed that acetic acid is easily reformed over the catalysts to hydrogen rich gas with yield approaching that of equilibrium. Hydrogen yields depend on the metal type and loading and the ratio of CaO to Al₂O₃ of the support. The best performance in terms of highest hydrogen yield is achieved with the 5 wt% Ni/CaO·2Al₂O₃ catalyst, while the 0.5 wt% Rh/CaO·2Al₂O₃ catalyst presents the highest resistant to coking. These catalysts were tested in acetone reforming showing also very high activity, low coking deposition rate and slight superiority of the Rh catalyst in terms of hydrogen yield.

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1. Introduction

Hydrogen is an emerging new energy carrier with significant environmental impact as its combustion is clean of pollutants. It is anticipated that in medium to long term, hydrogen will be a key player in the global economy. Nowadays, a large amount of hydrogen that is commercially used for ammonia production and refining processes, is produced from fossil fuels such as natural gas, naphtha, heavy oil and coal via catalytic reforming and partial oxidation processes [1]. One of the limitations of current hydrogen generation is the depletion of these sources and the substantial amounts of CO₂ emitted to the atmosphere during the process steps associated with its production.

Biomass has been proposed as an alternative feedstock for hydrogen production not only because it is renewable but also because it is a CO₂ neutral energy supply. Hydrogen can be produced from biomass mainly via two thermochemical processes, the gasification [2,3] and the flash pyrolysis [4–6] followed by steam reforming of the pyrolysis oil. Fast pyrolysis of biomass

produces 60–75 wt% of liquid, 15–25 wt% of solid char, and 10–20 wt% of non condensable gases, depending on the feedstock used [7]. The pyrolysis oil, known as bio-oil, is a mixture of acids, alcohols, aldehydes, esters, ketones, sugars, phenols, guaiacols, syringols, furans, and multifunctional compounds [8]. With the addition of water, bio-oil, can be separated in two distinct fractions: a monomer-rich aqueous fraction (containing typically 20 wt% organics) and a hydrophobic fraction composed mainly of oligomers derived from lignin [9].

Steam reforming can be used to convert the entire bio-oil or each of the fractions of the oil to a hydrogen rich stream. Despite the fact that the hydrogen yields obtained from the whole oil are higher than when only the aqueous, carbohydrate-derived fraction is processed, the economics of the whole bio-oil reforming are less favorable [10]. On the other hand, the water-insoluble fraction can be used in high value applications producing phenolic resins and fuel additives [11]. An integrated approach in which the water insoluble fraction of the bio-oil is used for the production of high added value products and the water soluble one is steam reformed to hydrogen, presents certain advantages in terms of feasibility.

Our research activities in biomass utilization focus on the production of hydrogen via reforming of the aqueous fraction of bio-oil. Thermodynamic calculations of steam and autothermal

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reforming of particular model compounds of bio-oil, acetic acid, ethylene glycol and acetone, were performed in order to define the optimum conditions for maximizing hydrogen production [12,13]. It was found that the bio-oil oxygenates in the presence of steam are easily converted to hydrogen rich mixtures achieving maximum hydrogen yield (80–90%) at 625 °C without any coke formation for operation under atmospheric pressure and steam/carbon >1.

During the last decade, steam reforming of bio-oil components, has been persistently studied, focusing on acetic acid as one of the most representative compounds [14–28]. Chornet and coworkers [14,15] explored the mechanism of thermal decomposition and steam reforming reactions over commercial Ni reforming catalysts. The effect of different parameters like temperature, steam to carbon ratio and space velocity was investigated in the presence of commercial Ni [16] and Ni–Al coprecipitated catalysts [17,18]. The influence of the metal (Ni and noble metals) and the support type (Al_2O_3 , $\text{La}_2\text{O}_3/\text{Al}_2\text{O}_3$, $\text{MgO}/\text{Al}_2\text{O}_3$) on acetic acid reforming were investigated by Basagiannis and Verykios [19,20,21]. Steam reforming of model compounds and full bio-oil was investigated over Pt, Pd and Rh supported on ZrO_2 , Al_2O_3 and $\text{CeO}_2\text{–ZrO}_2$ [22,23]. Much less attention has been given to acetone steam reforming. It was mainly investigated as a by-product of acetic acid reforming in the presence of commercial nickel [16,22] and Pt/ ZrO_2 catalysts [24] and over Pd–Cu/ $\gamma\text{-Al}_2\text{O}_3$ catalyst under auto-thermal and endothermic steam reforming conditions of C3 organics [25].

A serious side effect of the reforming reactions is the formation of carbonaceous species, which deposit on the catalyst surface. Carbon deposits on the catalyst can be minimized by inhibiting the surface reactions leading to solid carbon formation via the presence of specific metals [22] and by the use of specially designed reactors [26]. The concept of sequential cracking and coke burn off was successfully studied by the group of Mirodatos and coworkers [27,28] as an alternative heat integrated process for bio-oil processing.

Earlier work on methane steam reforming, partial oxidation and dry reforming demonstrated the superior performance of Ni catalysts supported on various types of calcium aluminates [29–33]. These catalysts showed high hydrothermal stability, low coke productivity and high hydrogen yield. The molar ratio of CaO to Al_2O_3 and the catalyst preparation method has been reported as crucial factors that affect both the activity and the coke production rate in methane dry reforming and partial oxidation [30,34].

The aim of the present work is to investigate the thermal decomposition/reforming in the absence/presence of steam and the catalytic steam reforming of two representative bio-oil components, acetic acid and acetone. The influence of active metal (Ni and noble metals) and the type of calcium aluminate used as catalysts support on hydrogen yield and coke deposition is evaluated for acetic acid and acetone steam reforming.

2. Experimental

2.1. Catalyst preparation

The carriers employed, $x\text{CaO}\cdot y\text{Al}_2\text{O}_3$ with two different molar ratios $x/y = 1/2$ and $12/7$, were prepared by solid state reaction between CaCO_3 (J.T. Baker, Analyzed Reagent) and $\gamma\text{-Al}_2\text{O}_3$ (Catapal alumina) calcined at 1100 °C for 20 h. The particles formed were grounded and the fraction 108–180 μm was used for catalyst preparation. Details on their preparation can be found elsewhere [35]. The wet impregnation method was applied for the preparation of catalysts. The precursors used for Ni, Rh and Ir metals were $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, $\text{RhCl}_3\cdot 3\text{H}_2\text{O}$ and $\text{IrCl}_3\cdot 4\text{H}_2\text{O}$, respectively. The aqueous solutions of the precursors were mixed with

the support particles and stirred for 1 h at 70 °C. The solvent was removed via evaporation under mild vacuum conditions and the samples afterwards were dried overnight at 120 °C. The catalysts were calcined in air flow at 600 °C for 4 h and at 900 °C for 6 h. The nominal metal composition of the final catalysts was 5 wt% for Ni and 0.5 wt% for noble metals Rh and Ir. The catalysts were reduced at 750 °C in 25% H_2/He flow for 1 h before the reforming experiments.

The catalysts are referred to as $z\text{Me}/\text{Ca}2\text{Al}$ (where z is the metal wt% and Me is Ni, Rh or Ir) for samples supported on $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ and $z\text{Me}/12\text{Ca}7\text{Al}$ for those supported on $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$.

2.2. Catalyst-characterization

X-Ray diffraction (XRD) patterns were obtained using a Siemens D500 diffractometer, with Cu-K α radiation. The morphology of the synthesized materials was examined by scanning electron microscopy (SEM) on a JEOL 6300 microscope, coupled with energy-dispersive X-ray analysis (EDX; Oxford Link ISIS-2000) for local elemental composition determination. The surface area of the calcium aluminate catalysts was measured by N_2 adsorption at 77 K, using the multipoint BET analysis method with an Autosorb-1 Quantachrome flow apparatus. The samples were dehydrated in vacuum at 250 °C overnight, before surface area measurements.

NH_3 temperature-programmed desorption (TPD) was used to determine the acidic properties of the catalysts. The experiments were performed in a gas flow system using a U-tube reactor connected online with a quadrupole mass analyzer (Omnistar, Balzers). The catalysts (200 mg) were pretreated at 650 °C for 0.5 h and then cooled to 100 °C under He flow. The pretreated samples were saturated with 5% NH_3/He for 1 h at 100 °C, with subsequent flushing with helium at 100 °C for 1 h to remove the physisorbed ammonia. TPD analysis was carried out from 100 to 700 °C at a heating rate of 10 °C/min. Quantitative analysis of the desorbed ammonia was based on (m/z) 15.

The used catalysts were transferred to a CHN stoichiometric analyzer LECO 800, for the measurement of the carbon deposited on the catalyst.

2.3. Catalytic testing

The experiments were performed at atmospheric pressure in a laboratory unit equipped with a mass flow controlled system, a fixed bed quartz reactor and an online gas chromatograph. An HPLC pump (Gilson 350) was used for the feeding of the liquid reactants (a mixture of acetic acid or acetone and water) to the reactor through a preheater. The fixed bed quartz reactor was equipped with coaxial thermocouple for temperature monitoring. The external diameter of the reactor tube in the catalytic zone is 10 mm whereas the external diameter in the pre- and post-catalytic sections is 6 mm to minimize the extent of gas phase reactions. The reactor was heated electrically by a tubular furnace, with three independently controlled temperature zones. The temperature in the middle of the catalytic bed was measured with a coaxial thermocouple. The hot gases exiting the reactor were cooled to condense the liquid products and the unconverted reactants. The gas phase products were analyzed with an online gas chromatograph (Varian 3700) equipped with TCD. To separate the products, two columns were used: Porapak Q for CO_2 , C_2H_4 and C_2H_6 and MS 5A for H_2 , O_2 , N_2 , CO and CH_4 . The liquid products were analyzed offline in gas chromatograph (Varian 3300) equipped with FID using an HP-FFAP column.

The experiments were performed in a temperature range from 550 to 750 °C at atmospheric pressure. The duration of the runs in each temperature examined was 1 h. A steam to carbon molar ratio

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