



Precious metal catalysts in the clean-up of biomass gasification gas Part 1: Monometallic catalysts and their impact on gasification gas composition

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ARTICLE INFO

Article history:

Received 29 October 2010

Received in revised form 2 March 2011

Accepted 14 March 2011

Available online 19 April 2011

Keywords:

Gasification

Gas clean-up

Precious metal catalyst

Aromatic hydrocarbon decomposition

Liquid biofuels

ABSTRACT

The performance of Rh, Ru, Pt, and Pd on modified commercial zirconia support (m-ZrO₂) was compared to a benchmark Ni/m-ZrO₂ catalyst in the presence of H₂S in the clean-up of gasification gas from tar, methane, and ammonia. The aim was to produce ultra clean gas applicable for liquid biofuel production. In general, the activity towards the decomposition decreased in the order of aromatic hydrocarbons, ethylene > methane > ammonia. Hydrocarbon decomposition on m-ZrO₂ supported Rh, Ni, and Ru catalysts mainly occurred at 800–900 °C through reforming and/or dealkylation reactions. Aromatic hydrocarbon decomposition reactions proceeded on Pt/m-ZrO₂ and Pd/m-ZrO₂ via oxidation reactions at temperatures of 600–800 °C, while at 900 °C, the reforming and/or dealkylation reactions were dominating also on Pt/m-ZrO₂ and Pd/m-ZrO₂ catalysts. During longer test runs of ten hours at 800 °C, the activity of the Rh/m-ZrO₂ catalyst declined in the presence of 100 ppm H₂S due to the sulfur poisoning effects, coke formation, and the particle size growth. Although the performance of Rh/m-ZrO₂ declined, it still remained better than Ni/m-ZrO₂ both towards naphthalene and total aromatic hydrocarbon, while only Ni/m-ZrO₂ and Ru/m-ZrO₂ decomposed ammonia in the presence of sulfur. Nevertheless, the most promising catalyst for clean gas production was Rh/m-ZrO₂.

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1. Introduction

Liquid fuels produced via biomass gasification and subsequent Fischer–Tropsch (FT) synthesis are attractive biofuels for the transportation sector, e.g. due to the high greenhouse gas mitigation potential of this process route. In this process, the clean-up of the gasification gas prior to the FT synthesis step is a challenging task. The amount of tars, hydrocarbons, and other impurities need to be very low and the H₂/CO ratio in the gas should be near 2 for the FT conversion step [1]. Alternatively, biomass gasification gas can be utilized in heat and power production. It is also essential to remove tar and ammonia to prevent NO_x emissions in these energy applications [2].

Clean-up of the gasification gas in a separate catalytic hot gas purification unit is a promising decomposition method for both hydrocarbons and ammonia [3]. One challenge for the catalytic clean-up step is the remarkable amounts of H₂S (in the range of 100 to even 500 ppm depending on the feedstock) usually contained in biomass gasification gas [2]. For this reason, the sulfur tolerance of the catalyst is very important.

Various catalysts have been studied for catalytic hot gas clean-up. For example, dolomite has gained attention [e.g. 3,4], alkali metals have been reviewed by Sutton et al. [5], and nickel catalysts on various supports have extensively been investigated [e.g. 6–8, reviewed in 2]. Catalysts containing nickel are active, but easily poisoned by sulfur compounds below 900 °C and deactivated due to coke deposits [8–11]. Therefore, precious metals might be an attractive alternative to nickel to overcome deactivation.

The activity of precious metal catalysts on CeO₂/SiO₂ support in the gasification of cedar wood to synthesis gas [11] was found to decrease in the order of Rh > Pd > Pt > Ni = Ru at 550 °C. Rh/CeO₂/SiO₂ catalyst was also reported to exhibit a good performance in the gasification of cellulose in the temperature range of 550–650 °C as well as a better tolerance to sulfur and lower extend of carbon deposition when compared to Ni/CeO₂/SiO₂ [12,13]. In the presence of H₂S, Rh/CeO₂/SiO₂ also exhibited a higher, and a more stable, activity in the partial oxidation of tar (derived from the pyrolysis of cedar wood) compared to the Ni/CeO₂/SiO₂ catalyst [11]. On the other hand, Sutton et al. examined CO₂ reforming of gasification gas with CH₄ and C₃H₈ as model compounds. They compared Ni/Al₂O₃, Ru/Al₂O₃, and Pt/m-ZrO₂ catalysts and concluded that Ni/Al₂O₃ catalyst had the highest activity. [14].

Zirconia based supports are active in tar decomposition with a minor tendency to coking and deactivation by sulfur. The activity of zirconia based catalysts in ammonia conversion, however, is only

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moderate and the activity towards lower hydrocarbons in gasification gas clean-up is low [15–18]. Thus, after hot gas clean-up with zirconia based catalysts, the product gas quality is not sufficient for FT synthesis. On the other hand, our previous studies show that modified zirconia supported Rh catalyst is a good alternative for gas clean-up. This catalyst produces very low tar content in hot gas clean-up used in connection with air blown gasification, which is tailored for high efficiency power production in engine, turbine, or fuel cell applications [19].

In this work, we studied several precious metal catalysts using synthetic gasification gas, which resembles pressurized oxygen blown gasification thus aiming at producing ultra clean gas applicable for the production of liquid biofuel components. The composition of the end gas is impacted by the tendency of the precious metals to catalyze the multiple simultaneous reactions as well as by the thermal reactions proceeding particularly at hot gas clean-up at 800 °C and above. Thus, in this paper, we also analyze in detail the gas composition and evaluate the role of the catalytic metal in more detail to gain further insight on how to develop optimal catalysts for this challenging application.

2. Experimental

2.1. Catalyst preparation

A modified zirconia (MEL Chemicals) with a BET-surface area of $35 \text{ m}^2 \text{ g}^{-1}$ was used as the support (denoted by m-ZrO₂). Platinum, rhodium and palladium nitrates, ruthenium nitrosyl nitrate (Johnson Matthey), and nickel nitrate-hexa-hydrate (Aldrich Chem Co.) were chosen as precursors for the catalyst syntheses.

The catalysts were prepared in a vacuum by incipient wetness impregnation at room temperature, aged overnight, and dried in a rotary evaporator for 2 h. All the catalyst powders were calcined in air at 800 °C for 1 h (in an oven). The targeted metal loading was 0.5 wt.% for the precious metal catalysts [19,20] and 8 wt.% for the nickel catalyst (selected based on the wide literature on Ni catalysts [21]).

After calcination, water based slurries were prepared from the powders for the dip coating of cordierite monoliths. The monoliths (cell density 64 cpsi, cross sectional area $20 \cdot 20 \text{ mm}^2$ and length 100 mm) were dip coated and dried repeatedly until the desired coating amount was attained. Finally the catalysts were recalcined. The details of the catalyst preparation are proprietary information.

2.2. Catalyst testing

Activity evaluations were performed at atmospheric pressure in a fixed-bed quartz reactor packed with a monolith catalyst and placed inside a three-zone furnace. The experimental system is described in detail elsewhere [19]. The system is designed for catalyst screening purposes and the furnace has three heating zones: the first one is set at 180 °C lower than the middle zone, which is set to the actual set point temperature targeted to be reached at the center of the monolith, and finally the third zone is set at 180 °C lower temperature than the middle zone. Thus, the gas is intentionally introduced to the catalyst bed at lower temperature than the actual set point. This approach allows monitoring of the exothermic and/or endothermic reactions, which occur along the monolith catalysts. The observed changes in temperature are used as an indication of the reactions proceeding on the catalyst and thus provide valuable insight on the performance and reactivity of different metals or combinations thereof. Therefore, a quartz grid and a thermocouple pocket in the center of the reactor were used to measure the temperatures and thus facilitate a qualitative comparison of the reactions proceeding on the catalysts. When measuring the temperatures, a K-type thermo element with an outer diameter of 1 mm was moved downwards at 10 mm intervals inside the thermocouple pocket to detect the temperature profile along the

monolith. Unfortunately, it was not possible to measure the radial temperature profiles.

The gases (Table 1) were supplied by AGA Ltd and fed separately with Bronkhorst mass flow controllers. A mixture of 90 wt.% toluene (>99.5% purity, VWR International) and 10 wt.% naphthalene (>99% purity, VWR International) was used as the aromatic feed. Naphthalene was the model for higher aromatics whereas toluene represented the lighter aromatics. The liquid reactants were fed through HPLC pumps and vaporized before mixing into the gas stream. Oxygen was added to enable the oxidation reactions [16]. Hydrogen sulfide, H₂S, was added into the gas feed to model the sulfur impurities [22]. The gas composition employed for the experiments is listed in Table 1 and it resembles the gas obtained from gasification using oxygen as the gasification agent. To avoid condensation, all gas lines were heated to 200 °C. The feed gas flow rate was adjusted to $2 \text{ dm}^3 \text{ min}^{-1}$ (NTP) as the space velocity in the experiments was 3500 h^{-1} (refers to that within the monolith).

The precious metal catalysts on m-ZrO₂ and the m-ZrO₂ support were tested at a temperature range of 600–900 °C and Ni/m-ZrO₂ catalyst at 700–900 °C. After the activity measurements, the stability of the m-ZrO₂ supported Ni and Rh catalysts was also examined by measuring the activities at 800 °C for ten hours using the sulfur containing gas. In addition, a blank experiment on an uncoated monolith was performed to determine the significance of the thermal reactions. When addressing the data, the temperatures refer to the set point temperatures, because the measured temperatures varied depending on the catalysts.

The inlet and outlet gases were analyzed with a Gasmet FTIR gas analyzer, after which the condensable species were removed by a cold trap consisting of isopropanol and water in series in an ice bath. The flow rate and temperature of the dried gas were measured and the gas was directed to the on-line gas analyzers. Separate Sick Maihak type S710 on-line gas analyzers were used to measure the volumetric compositions of the dry gases CO, CO₂, CH₄, O₂, and H₂.

Separate sampling of higher hydrocarbons was performed by separating the FTIR temporarily from the gas line thus enabling the sampling procedure. Four sequential 40 cm³ gas washing bottles were used to absorb the compounds into isopropanol (<99.7% purity, VWR International). The first two bottles were held at an ambient temperature and the last two were placed in an ice bath. Approximately 10 dm³ of gas was drawn for each sample. The samples were analyzed with an HP 5890 gas chromatograph equipped with an HP Ultra 2 column and FID.

2.3. Catalyst characterization

The metal contents of the washcoats were analyzed by the X-ray fluorescence technique (XRF) with a Philips 1480 WDS spectrometer before the activity testing. Data were analyzed with the UNIQANT 4.34 program utilizing a DJ Kappa model to simultaneously calculate the composition and mass thickness of an unknown bulk or thin film sample [23].

The dispersions of metals on the surface of m-ZrO₂ were determined with the Coulter Omnisorp 100 CX. The H₂ (AGA 99.999% purity) chemisorption measurement was performed at 30 °C to minimize the H₂ spillover on the support [20,24]. The m-ZrO₂ supported Pt, Rh, Pd, and Ni catalysts (0.2 g) were reduced in situ at 500 °C for 3 h under flowing hydrogen. The Ru/m-ZrO₂ catalyst was reduced at 300 °C [25] to avoid the formation of volatile Ru compounds. After reduction, all samples were evacuated at 350 °C for 2 h before measuring the total H₂ chemisorption isotherms (15 steps between 0.6 kPa and 46.6 kPa). Thereafter, the samples were evacuated at 30 °C for 0.5 h, and a second, reversible isotherm of chemisorption was measured. Both isotherms were extrapolated to zero pressure, and their difference was used as a measure of strongly chemisorbed irreversible H₂.

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