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Research Paper

Whisker carbon formation in catalytic steam reforming of biomass gasification gas

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ABSTRACT

Whisker carbon formation in the steam reforming of biomass gasification gas was studied in a laboratory scale reactor using two commercial nickel catalysts, precious metal catalyst and inert materials. The synthetic feed gas contained ethylene, tar model compounds and H_2S as impurities. Whisker carbon was formed below the reaction temperature of 700 °C on an calcium-doped nickel catalyst and below 850 °C on an undoped nickel catalyst when the feed gas contained no sulfur. With the addition of more than 50 ppmv of H_2S in the feed gas, the whisker carbon formation was inhibited. Thermodynamic calculations were carried out to estimate the upper limit temperature for the whisker carbon formation but the calculations did not correlate well with the experimental results. One of the probable explanations for this was the high concentration of unsaturated C_{2+} hydrocarbons in the feed gas.

1. Introduction

The gasification of forest residues and other woody biomass produces useful gasification gas. Typically, this gas contains CO, CO_2, H_2, H_2O, N_2, H_2S, NH_3, CH_4, C_2H_4 and tars [1]. The gasification gas can be conditioned to synthesis gas and used in numerous processes for heat, power, Ni/Ca and chemical production [2,3]. One alternative for upgrading biomass gasification gas to CO and H_2 is through catalytic steam reforming of hydrocarbon residues at approximately 800–1000 °C [2]. However, impurities such as tar and H_2S in the biomass gasification gas, and the formation of carbonaceous deposits through side reactions can be hazardous to the steam reforming catalysts and to process operation.

Nickel catalysts are traditionally applied in steam reforming of hydrocarbons as they are robust, well-known and comparatively inexpensive [3–5]. The downside of the nickel catalysts is the enhanced production of coke through the side reactions. In the steam reforming of biomass gasification gas two types of carbon may form: whisker and pyrolytic carbon [5]. Generally speaking, the formation of pyrolytic carbon is enhanced by increasing temperature to over 600 °C whereas whisker carbon is typically formed at 500–600 °C [4]. However, exact temperature ranges are difficult to define as other process conditions (such as feed gas composition, impurities, pressure and catalyst) also affect the carbon formation. Therefore, in steady state operation of the reformer at 800–1000 °C the formation of pyrolytic carbon is more of a concern but during start-ups, shut-downs and process disturbances when the temperature in the catalyst bed may drop below the design values, the risk for whisker carbon formation can be high.

The whisker carbon is formed from methane decomposition (R1), C_{2+} hydrocarbon decomposition (R2) or from CO by Boudouard reaction (R3). Whisker carbon formation begins by the diffusion of adsorbed carbon through the nickel crystal. The carbon atoms form a graphitic fibre that lifts the nickel particle off of the catalyst surface. The whisker can also destroy the structure of the support material which leads to the breakdown of the entire catalyst particle [6]. Both the broken catalyst particles and the whisker carbon itself increase the pressure drop in the reformer and can cause clogging in the equipment. Whisker carbon formation is enhanced by the presence of C_{2+} hydrocarbons, especially ethylene and tars [5]. On the other hand, steam reforming (R4) and carbon gasification (R5) reactions reduce the carbon formation by removing the carbon atoms from nickel surface.

$$CH_4 \leftrightarrow C + 2H_2 \qquad \text{(R1)}$$

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Nomenclature

CHN	elemental analysis
EXP	experiment
FTIR	Fourier transform infrared spectroscopy
GC	gas chromatography
MS	mass spectrometer
SiC	silicon carbide
S/C	steam-to-carbon molar ratio
TPO	temperature-programmed oxidation
T_R	temperature inside the reactor

$$C_nH_m \rightarrow nC + 0.5mH_2 \tag{R2}$$

$$2CO \leftrightarrow C + CO_2 \tag{R3}$$

$$C_nH_m + nH_2O \leftrightarrow nCO + (n + 0.5m)H_2 \tag{R4}$$

$$C + H_2O \leftrightarrow CO + H_2 \tag{R5}$$

The probability for whisker carbon formation from natural gas on nickel catalyst can be estimated by thermodynamic calculations. This can be done by using the principle of equilibrated gas [5] or calculating the chemical equilibrium. The predictability of whisker formation by simple calculation method would be advantageous considering industrial operation. However, the biomass gasification gas also contains plenty of C_{2+} hydrocarbons which complicate the estimation as the carbon formation is kinetically controlled and the rate of formation depends on the type of the hydrocarbon [4,5]. Especially difficult are unsaturated hydrocarbons, such as ethylene and tars, which begin to form carbon rapidly compared to methane or saturated hydrocarbons.

Gasification gas from woody biomass also contains H_2S in quantities usually around 100 ppmv [1,7]. H_2S has a inhibiting effect on steam reforming, gasification and carbon formation reactions on the nickel catalyst when it adsorbs on the active nickel sites and thereby prevents these reactions from taking place. As the methane steam reforming reaction requires a smaller ensemble of active sites than the carbon formation reaction, it is possible to inhibit carbon formation with adsorbed sulfur so that steam reforming activity is not entirely lost (Fig. 1) [5,8]. Industrially this method has been utilized in sulfur passivated reforming, i.e. SPARG, process [5]. Therefore, it could be possible to avoid whisker formation in the case of biomass gasification gas when the H_2S content is high, despite the concomitant high concentration of ethylene and tars.

The primary goal of this study was to investigate whisker carbon formation on nickel catalyst in a process utilising biomass gasification gas, and compare the experimental results to the data obtained by thermodynamic calculations. Also, the effect of H_2S on whisker carbon formation was studied in order to estimate how much H_2S coke-free operation would require.

2. Experimental

2.1. Reactor set-up

The catalysts were tested in a pressurized packed bed reactor which was presented in an earlier study [9]. It was considered advantageous if more than one catalyst could be tested at the same time. The emphasis was therefore on the comparison of carbon formation and not on the individual steam reforming activities of the catalysts. A quartz glass sample holder with removable inner walls was designed and manufactured specifically for this purpose (Fig. 2). The sample holder was 2.5 cm high, inner diameter 2 cm, and it was divided in four sectors that could hold up to four catalyst samples at a time. It was placed inside the tubular reactor and sealed on the rim with quartz wool to prevent any bypass flow.

2.2. Experimental methods

The variable conditions (reactor temperature T_R, and H_2S and H_2O concentrations) are summarised in Table 1. All experiments were carried out at 4 bar(a). The run time was 35 min, expect for experiment 2 which was 30 min. The short run time was chosen to limit the carbon growth. With longer run time, carbon would have grown outside sample holder sectors and collecting a representative sample of would have been impossible. In sulfur-free experiments steady-state was typically reached after the first 10 min. The gas composition was continuously monitored to verify stable operation.

Before each experiment the fresh catalysts were reduced for 15 min at 800 °C with 1 dm^3/min gas flow containing 50 vol% H_2 in N_2. After that, the reactor was purged with nitrogen and cooled down to the experiment temperature. The reaction gases were fed to the reactor only after the set point temperature had stabilized. The temperature inside the reactor was monitored by a K-type thermocouple which was

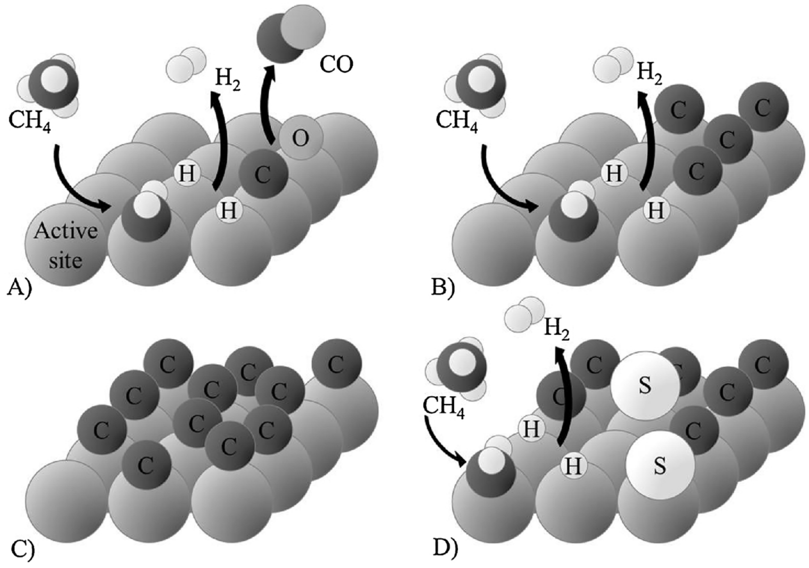

Fig. 1. Simplified schematic depiction of methane reforming, carbon formation and effect of sulfur on nickel catalyst. (A) Methane reforming steps on active sites. (B) Carbon accumulation due to insufficient amount of oxygen on surface. (C) Adjacent carbon atoms nucleate. (D) Sulphur inhibits carbon nucleation while reforming reactions can still take place.