

Hydrogen Production via Steam Gasification of Petroleum Coke.

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Introduction

An alternative new cost effective way of producing hydrogen could be the steam gasification at low temperature [1] of the larger coke deposits available in the North of Alberta. This approach could be one way to produce hydrogen from the upgrader facilities that later can be used for hydroconversion reactions. This alternative for hydrogen production at the upgrading sites is of great interest for both installed and future upgraders. This method may also mitigate the potential environmental issue associated with the large coke deposits in the province. Additionally, the large coke production from the upgraders could be used, as a starting material for the production of hydrogen via steam gasification [1]. The hydrogen resulting from the gasification of this heavy coke could be added to enhance the fractions of the synthetic crude via hydrotreating or, in the long term, pipeline-blended with other gases, and/or added to liquid products for separation and use at another destination.

Materials and Methods

A sample of petroleum coke drum was obtained from SUNCOR, milled, sieved to a range of particle sizes between 120 and 180 microns. The coke was modified via thermal or chemical treatment in order to enhance the metal sorption. The thermal treatment was carried out in a mixture of oxygen 3 % (v/v) in helium 97 % (v/v) for 15 minutes. Then, the system was heated up to 350 °C at 8 °C/min and maintained at that temperature for a given time.. The chemical treatment was performed with HNO₃ solution (20 % v/v) for 15 hrs [2]. The active phases for steam gasification of petroleum coke have been described in the literature and consist of combinations of alkali and earth alkali metals [1]. The novelty of this catalysis is the fact that the support (pet coke) is also a reactant. The coke catalyst was prepared by a wet-impregnation method adapting the procedure reported by Pereira et al. [1d]: briefly, a sample of activated powdered coke was impregnated with a water/isopropanol solution (4:1) of equimolar amounts of Ca(NO₃)₂ and KNO₃, and dried at 100 °C overnight. The characterization of activated coke and catalyst were performed by FTIR, N₂ and CO₂ surface area using a CHEMBET-3000 instrument from Quantachrome Instruments and Tristar 3000 from Micromeritics. The reactivity tests, which involve running steam at temperatures between 600 and 650 °C, were carried out on an SDT TA Instruments thermobalance coupled with a quadrupole mass spectrometer (QMS) from Omnistar/Thermostar GSD 301

Results and Discussion

Initially, the coke was activated by thermal and chemical treatment. From thermal, the composition of the gases as function of temperature followed by MS indicated that around 200 °C, oxygen is consumed with a simultaneous production of CO and CO₂ mainly. The water concentration increased when the temperature reached 300 °C, which is indicative of complete

combustion [5]. By using this procedure, different coke samples were prepared with varying temperatures and times of reaction. From the chemical treatment, an evolution of NO_x gases indicates that the decomposition reaction of catalyst precursors took place. The main characteristics of the two sample of coke prepared using both methodologies are presented in Table 1.

Table 1 Characterization of cokes prepared thermal oxidation.

Sample	Treatment	Time (h)	N ₂ S.A. (m ² /g)	CO ₂ S.A. (m ² /g)	N ₂ /CO ₂
Coke (120-180 microns)	none		4.6	85	0.05
Coke-T	Thermal	3	1.3	107	0.01
Coke C	Chemical	15	2.1	151	0.01

Thermal: coke 6 g, T: 350 °C, He/O₂: 97/3; Chemical: coke: 5g, T: 90 °C, HNO₃: 20 % (v/v), 10 mL

The surface area measured by N₂ uptake decreased while the surface area measured with CO₂ increased after either thermal or chemical treatment (Table 1). The dependence of surface area on adsorbate may be an indication of an increase in the microporosity for those materials under these treatments. FTIR was used to determine the presence of oxygenate functional groups on the surface, after such treatments. They are characterized by carboxylic acid, ketones, aldehydes, phenols and others. Preliminary steam gasification experiments were carried out with a coke support activated thermally for 3 h at 350 °C and impregnated with a solution of KNO₃ and Ca(NO₃)₂ ratio 1:1. By using TGA coupled with a MS and with optimized temperature program, it was observed that the presence of those metals modified the thermal behaviour of the sample, increasing the weight loss. The qualitative analysis of the obtained products reveals that H₂, CO₂, CH₄ (from coke dealkylation) are the main products. Without a catalyst, the H₂ production starts after 700 °C. While the incorporation of active metal leads the H₂ production below 600 °C.

Significance: This work shows the potential application of coke material as support-catalyst-reactant for H₂ production to be used for different application at the upgraders' facilities with a mitigation of the potential environmental issue associated coke deposits.

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