



Characterization of the mechanism of gasification of a powder river basin coal with a composite catalyst for producing desired syngases and liquids

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ABSTRACT

The objective of this research was to examine the mechanisms of FeCO_3 , Na_2CO_3 , and $\text{FeCO}_3\text{-Na}_2\text{CO}_3$ based catalytic coal gasification of a low-sulfur sub-bituminous Wyodak coal from the Powder River Basin (PRB) of Wyoming. X-ray diffraction (XRD), Mössbauer spectroscopy, scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), gas chromatography (GC-MS) and nuclear magnetic resonance spectroscopy (NMR) were used to perform the analyses. Use of composite catalysts for coal gasification overcomes some of the limitations of the standalone use of Na or Fe catalysts. The XRD results are consistent with interactive mechanisms or the formation of Na-Fe oxides as the catalytic pathway. Mössbauer spectroscopy indicated the presence of metallic iron and cementite in the char at different stages. The Fe catalysts were better at tar decomposition than the Na catalysts, as indicated by GC-MS analyses. NMR spectra confirmed that tar compositions vary with the catalytic mechanism. FTIR analysis confirmed the presence of high yields of aromatic components and long aliphatic chains in the tar. Composite Fe-Na catalysts provide a method to tailor the amounts and composition of product generated during gasification.

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1. Introduction

Upcoming strict CO_2 emissions regulations [1–5] by the Environmental Protection Agency (EPA) will no longer be achievable by traditional means of coal combustion. The “Standards of Performance for Greenhouse Gas Emissions from New Stationary Sources: Electrical Generation Units” [6] proposed rule sets limits in the range of $950\text{--}1200\text{ lb}_m\text{ CO}_2/\text{MWh}$ for new stationary combustion turbines depending on the heat input rating. Therefore, increasing dependence on different energy sources has drawn attention to clean coal technologies, such as coal-to-liquids processing, due to its potential for lower environmental impacts and higher efficiencies than direct coal combustion [7]. Coal-to-liquids processing can be achieved through direct coal liquefaction (DCL) or indirect liquefaction (ICL). The core of the ICL process is gasification. Coal

gasification is an energy intensive process that requires high temperatures; however, the use of catalysts is one of the most effective methods to improve its efficiency, reduce the operational temperature, and manipulate the selectivity of the product syngas, which is the feed for ICL. Furthermore, process oriented life-cycle analyses (LCA) of the emissions generated by a 381 MW IGCC unit over a 30 year life of the plant, indicates total emissions of CO_2 on order of $5.34 \times 10^7\text{ Mt}$, whereas at the same conditions, direct coal combustion may generate $\sim 24\%$ more CO_2 compared to gasification without any CO_2 capture technology, and at least 37% when CO_2 capture technologies are in place [8].

Catalysts play a major role in the efficiency enhancement of many industrial chemical processes in the energy and fossil fuel processing industries, including coal utilization and petrochemical processing and refining, in which over 80% of the processes are catalytic. Examples include fluid catalytic cracking, naphtha reforming, isomerization, Fischer–Tropsch synthesis, coal gasification, coal tar hydrogenation, and many others [9–13]. Catalysts are also widely used in the pollution remediation industry, where their

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consumption ranges from automotive exhaust treatment to NO_x reduction from coal-fired furnaces [14,15].

Given the complexity of current chemical processes, single component catalysts cannot satisfy some high performance requirements, such as high activity, selectivity, and stability against deactivation [16]. Recent advances in catalytic technology suggest that composite catalysts not only overcome the disadvantages of their individual components, but also synergize their effects by improving reaction rates more than the sum of their individual components rates [16]. Composite catalysts are widely used in sulfur recovery units, the fuel cell industry, naphtha reforming in petrochemical refining, etc. [13,16,17]. There are many kinds of composite catalysts, including simple physical mixtures, crystallite composites obtained by intergrowth, in situ combinations, matrix materials, host-guest composites, hybrid composites that comprise a matrix material, and hierarchical porous composites [16–18]. Some of the catalytic performance enhancements observed with the use of composite catalysts include support effects, stabilization of active components, formation of new compounds that act as stabilizers, dual-function effects in elementary reactions, adjustment of acid and base properties, redox performance control, surface bonding state control, adsorption/desorption and diffusion enhancement, and improved migration or transference of active species [16,19–21].

Proper use of composite catalysts has great potential in terms of improving the efficiency of many industrial applications. In particular, Na–Fe composite catalysts have demonstrated high effectiveness in applications such as coal combustion, NO_x reduction, and enhancement of carbon conversion rates in coal gasification [15,22]. Traditionally, the process of reducing nitrogen oxides from coal-fired boilers has been accomplished through the use of selective catalytic reduction (SCR), which typically employs NH₃ as a reducing agent in a reactor upstream of electrostatic precipitators and scrubbers. However, recent findings have demonstrated that the addition of Na–Fe composite catalysts to the char prior to combustion inhibits NO emissions [15]. Use of such catalysts could reduce many associated costs and simplify this pollution remediation operation.

Suzuki et al. [22,23] studied the effects of Na–Fe composite catalysts on coal gasification of Yallourn char using NaHFe(CO)₄, while Song and Kim [22,23] investigated the same catalysts by mixing Na₂CO₃ and FeSO₄ and impregnating them onto an Alaskan subbituminous coal. In both cases, a synergistic effect was observed in conversion rates.

Additional applications of sodium–iron (Na–Fe) composite catalysts include the hydrogenation of carbon dioxide and Fischer–Tropsch synthesis. However, in the latter application, the effect of these catalysts has been varied, proving to be negative when residual Na from the material preparation participates in the reaction [10,24,25].

An additional benefit of Na–Fe composite catalysts for coal gasification observed by our research group is the remediation of coal tar. Coal tar has been classified as all volatile organics from coal that condense at room temperature, generally with a molecular weight greater than benzene [26] and is highly undesirable due to the negative process effects associated with its condensation and deposition. Reported tar tolerance limits in gaseous fuels vary widely for different machines: 50–500 mg/m³ for compressors, 50–100 mg/m³ for internal combustion systems, and 5 mg/m³ for direct-fired industrial gas turbines [27]. Without the use of catalysts, significant steam reforming of tars occurs only above 900 °C [24]. Catalytic steam and dry reforming reactions are a promising way to remove the tar components from the syngas at lower temperatures [24]. Other studies have revealed that Fe-based catalytic coal gasification can substantially reduce overall tar yield [28,29] and reduce the proportion of tar acids, though in hematite (Fe₂O₃)

catalyzed coal gasification, a complete tar breakdown still required temperatures above 900 °C [28,30].

Changes in selectivity (H₂ and CO yield augmentation), conversion rate enhancement, activation energy decrease, tar reduction, and general improvements of the overall efficiency of the process are some of the advantages of composite Na–Fe catalysts. These are directly correlated to additional process advantages, such as decreased gasification temperatures with associated increase of the gasifier service life. Further research on these catalysts is crucial to the advancement of carbon gasification technologies [22,23,31]. The mechanism of the Na–Fe couple acting as catalytic agents has not been studied in depth at this point. Our previous study found that the combined catalysts had advantages over the individual sodium or iron catalysts; this synergistic mechanism could include the presence of sodium iron oxides acting as intermediates or final products, increased Fe mobilization, or a combination of these effects [31]. The previous work raised questions about the mechanism that governs Na–Fe interactions with coal and how are they different from the standalone catalytic activity. This current study focused on the answers to these questions and the description of the catalytic products formed in the coal char. Therefore, the main objective of this work was to determine the mechanisms through which Na interacts with Fe to improve the performance of their individual catalytic capabilities.

2. Experiments

2.1. Materials

2.1.1. Catalyst preparation

Iron carbonate was prepared from 10% (w/v) aqueous solutions with equimolar amounts of FeSO₄·7H₂O (99.81% Matheson, Coleman & Bell) and Na₂CO₃ (99.81% FMC Inc.). The resulting precipitate (siderite, or FeCO₃) was filtered, washed with Na carbonate and distilled water, dried at 92 °C, and calcined in air at 250 °C to produce a brown powder. The FeCO₃ was sieved to retain 125 μm particles and stored in air tight, dark colored containers to prevent structural and moisture content changes. Aqueous Na₂CO₃ 10% (w/w) solutions were prepared with Na₂CO₃ (99.81% FMC Inc.).

2.1.2. Catalyst loading

FeCO₃, Na₂CO₃, and FeCO₃–Na₂CO₃ were used as catalysts for coal gasification. The mixtures of pulverized PRB (200 mesh) coal and catalysts were prepared by adding FeCO₃, Na₂CO₃, or FeCO₃–Na₂CO₃ to obtain the following weight ratios of catalyst to dry ash free (DAF) basis coal: 0%–Fe + 4%–Na, 1%–Fe + 3%–Na, 2%–Fe + 2%–Na, 3%–Fe + 1%–Na, and 4%–Fe + 0%–Na. Proper quantities of the Na₂CO₃ solution and/or FeCO₃ were mixed with the coal, slurried with water, and finally dried at 90 °C for 72 h prior to gasification.

2.2. Char and tar collection

The tests were conducted at local atmospheric pressure, about 75 kPa in our laboratory. FeCO₃–Na₂CO₃ catalysts and coal mixtures were pyrolyzed and gasified in N₂ and H₂O–N₂ mixtures. 5.0 g DAF coal were used for each gasification test. Pyrolysis was performed by flowing 4.1 ml/min of N₂ while heating the sample at a constant rate of 20 °C/min to the gasification temperature of 800 °C. The apparatus used for the catalytic coal gasification includes a set of calibrating gases, mass flow controllers, heaters, water pump, packed bed reactor, furnace, tar collection section and gas chromatograph. The tests were conducted at local atmospheric pressure, about 75 kPa in our laboratory. FeCO₃–Na₂CO₃ catalysts and coal mixtures were pyrolyzed and gasified in N₂ and H₂O–N₂ mixtures. 5.0 g DAF coal was used for each gasification test.

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