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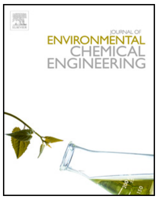

Effect of CO_2 co-feeding on the conversion of syngas derived from waste to liquid fuel over a bi-functional Co/H-ZSM-5 catalyst

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ABSTRACT

A bi-functional Co-HZSM-5 catalyst was synthesised by the Incipient Wetness Impregnation (IWI) of cobalt onto H-ZSM-5 and effect of CO_2-co-feeding on the performance of the catalyst during Fischer Tropsch (F-T) was investigated. Physico-chemical property of the catalyst was checked with N_2 physisorption (for BET surface area), Transmission Electron Microscopy and Scanning Electron Microscopy equipped with EDS. Effect of CO_2 co-feeding was investigated at Gas Hourly Space Velocity (GHSV):1200 ml h^{-1} g^{-1}; pressure: 15 bar, temperature: 250 °C; and H_2/CO ratio: 2.5; with a syngas mixture containing 5% CO_2. Pre-calibrated GCs were used to analyse the reaction products. The BET surface area, the pore volume and the pore size of the catalyst were 292 m^2/g, 0.18 cm^3/g and 2.83 nm, respectively. TEM images showed that cobalt particles were well dispersed within the support. In the presence of CO_2 co-feeding, CO conversion was 73% and CO conversion was 53% without CO_2 co-feeding. In addition, the co-fed CO_2 was converted to hydrocarbons and a CO_2 conversion of 63% was obtained. The selectivity of the catalyst to methane was 53%, 34% to C2, <4% to C4-C5 and <10% to C6+ in the presence of CO_2 co-feeding. Co-feeding CO_2 also affected the selectivity of the catalyst to olefin as well. Selectivity of the catalyst to C_3 decreased from 43% to 35% while C4 increased from 25% to 32% during CO_2 co-feeding. However, selectivity of the catalyst to C6+ olefin hydrocarbon increased from 9% to 15% during CO_2 co-feeding.

1. Introduction

Management of waste has been a crucial and delegated responsibility, undertaken on behalf of the industry, public authorities by waste management specialists. Waste accumulation has been known to create various problems to the environment and to the human health. These problems are aggravated when waste accumulates at incorrect landsite [1]. However to solve environmental problems and ensure a healthy living, waste management is very essential. Therefore the need for environmentally acceptable waste disposal methods and/or beneficiation has become a priority in developing countries like South Africa.

One way to beneficiate solid waste materials is to gasify them to syngas (major components are CO and H_2). Syngas gas can be used to produce a variety of chemicals and liquid fuels. Liquid fuels can be made from syngas *via* four basic processes: (i) Higher alcohol synthesis, (ii) Fischer-Tropsch (F-T) synthesis, (iii) Methanol-to-Gasoline (MTG) synthesis, and (iv) Methanol-to-Olefins (MTO) synthesis [2]. Higher alcohol synthesis focuses on ethanol production, and has enjoyed much attention, but still offers a low productivity and poor selectivity. Fischer-Tropsch synthesis is a surface-catalyzed polymerization reaction that involves conversion of synthesis gas (CO and H_2) derived from coal, natural gas, heavy oil or biomass into hydrocarbons consisting of paraffins, olefins, alcohols and aldehydes Fischer-Tropsch (F-T) synthesis produces a wide range of mainly linear paraffinic hydrocarbons, and the product distribution depends on the type of catalyst, the process conditions and reactor configuration [2]. After F-T reaction, the obtained long-chain linear paraffins are cracked further into short-chain hydrocarbons in fluidized-bed catalytic cracking (FCC) units to maximize the realization of the desired product fractions [3]. Cobalt (Co) and Iron (Fe) are the two most metal catalysts employed in the commercial F-T synthesis [4,5]. These metal catalysts can catalyze F-T synthesis at temperatures below 523 K, also known as the Low-Temperature Fischer-Tropsch (LTFT) [3,4]. Co-based catalyst is more preferred at LTFT to Fe-based catalyst while Fe-based catalyst is preferred at high-Temperature Fischer-Tropsch (HTFT) [6]. In addition, Co-based catalysts have high

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selectivity to C5+ linear paraffin hydrocarbons (HCs) and low selectivity to methanation and water gas shift (WGS) reactions, making them preferable catalysts for low temperature F-T synthesis to produce long chain linear hydrocarbons [7].

During the gasification of biomass waste, such as corn cob, wood biomass, to mention a few, 5–12% CO_2 is produced. Separation of the CO_2 from the gasification products to obtain the syngas required for F-T synthesis requires additional equipment, translating into additional costs. The CO_2 could be co-fed with the syngas stream during F-T synthesis, thereby by-passing the gas cleaning stage. However, CO_2 co-feeding could have beneficial or detrimental effect on the F-T process, especially on the reactivity of the catalyst. Therefore, effect of CO_2 co-feeding on the performance of F-T catalyst especially Co-based catalyst needs to be understood. Against this background, effect of CO_2 co-feeding on the performance of a bi-functional Co/H-ZSM-5 catalyst during F-T synthesis was investigated in this study. The bi-functional catalyst, Co/H-ZSM-5, combined F-T synthesis and hydrocracking together in the same catalyst. The catalyst was synthesized *via* the Incipient Wetness Impregnation (IWI) method and the performance of the catalyst was tested using a fixed-bed reactor that was operated as a plug flow reactor (PFR) under steady-state and isothermal condition. The IWI method was chosen to ensure moderate Co particle loading and good dispersion within the support. The H-ZSM-5 zeolite was used as the support because of its high acidity and good hydrocracking activity.

2. Materials and methods

2.1. Materials

Cobalt (II) nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$) salt, which was used as the source of Cobalt (Co) metal, was purchased from Sigma-Aldrich (Pty) South Africa. Ammonium form of Zeolite Socony-Mobil-5 (ZSM-5), from which the H-form of Socony-Mobil-5 (H-ZSM-5) that served as the support for the catalyst was obtained, was purchased from Zeolyst (USA). Two syngas cylinders (one with a mixture of $H_{2,}$ CO and N_2 and the other with a mixture of $H_{2,}$ CO, CO_2) were purchased from Afrox (Pty) South Africa to mimic the syngas composition expected from the gasification of biomass. Nitrogen (N_2, 99.99% purity) and Argon (Ar, 99.9% purity) used as purge gas and carrier gas (for the GC), respectively, hydrogen and air were purchased from Afrox (Pty) South Africa. All these materials were used as-supplied without any further pre-treatment.

2.2. Methods

The catalyst was synthesized using Incipient Wetness Impregnation (IWI) with Cobalt nitrate solution as the precursor for cobalt using modified technique reported by [4,5]. The solution was impregnated onto the H-ZSM-5 support; the H-form of ammonium ZSM-5 zeolite obtained after the calcination of the ammonium form ZSM-5 at 550 °C for 5 h. Cobalt supported on silica catalyst (Co/SiO_2) was prepared and evaluated at the same conditions as the Co/HZSM-5 catayst for comparison. Scheme of the catalyst preparation is depicted in Fig. 1.

The techniques employed for the characterization of the catalyst were: (i) N_2 physisorption at 77 K to determine the BET surface area, pore volume and average pore size of the synthesized catalyst; (ii) transmission electron microscopy (TEM) that produces 2-D images to understand the dispersion and the particle size of the dispersed Co particles; (iii) scanning electron microscopy equipped with energy-dispersive X-ray (SEM/EDX) that produces 3-D images to understand the morphology and elemental composition of the catalyst; (iv) X-ray diffraction (XRD) to provide information about the crystallinity and phase of the catalysts; (v) Thermogravimetric analysis (TGA) to understand the thermal stability of the prepared catalyst; and (vi) H_2-Temperature Programmed Reduction (TPR) to obtain the temperature at which the prepared catalyst will be completely reducible from in-active oxide of the metal to active metal phase.

The Nitrogen physisorption experiment was carried using on about 0.2 g of the catalyst sample on a BET set-up (model: Micromeritics TriStar 3000 V6.05 A). The samples were degassed at 150 °C before nitrogen adsorption experiment was conducted. Transmission Electron Microscopy analysis was performed using JEOL 100S FEI (from Field Electron and Ion (FEI) Corporate USA). About 0.1 mg of the support sample and the catalyst sample were ultra-sonicated in methanol for 5 min, before placing a drop of the solution in a copper grid. The Cu-grid with the solution on it was ventilated and then fed into the TEM chamber for the analysis. X-

Fig. 1. Scheme for the synthesis of the Co/H-ZSM-5 catalyst. The same procedure was followed for the preparation of the Co/SiO_2 catalyst, except the step that involves the conversion of ammonium form-ZSM-5 to H-ZSM-5.