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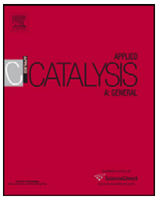

Cobalt based hybrid Fischer–Tropsch synthesis catalyst for improved selectivity of hydrocarbons in the JP-8 carbon number range from a synthesis gas obtained from the pyrolysis of the MixAlco process derived sludge

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ABSTRACT

The synthesis gas produced from the pyrolysis of the MixAlco process [5] (which converts wastes into fuels and chemicals) has the composition of ~45% H_2/35% CO together with up to about 20% CH_4. Recovery of the methane and application of steam reforming allows the adjustment of the H_2:CO ratio to about 1.9 optimum for cobalt performance in an enhanced Fischer–Tropsch synthesis (FTS) process. The performance of a new hybrid catalyst Co-SiO_2/Mo-Pd-Pt-HZSM-5 (with a metal–metal–acid functionality) was compared with that of a conventional Co-SiO_2 catalyst under the same thermodynamic condition of 10 atm and 250 °C. The specific surface areas of the two catalysts were characterized using the BET technique. The electron probe microanalyzer (with WDS and EDS capabilities) was then used to confirm the presence of the applied metals Co, Mo, Pd and Pt on the respective supports. The effect of pressure was then examined on the hybrid catalyst at the temperature of 250 °C and a higher pressure of 13.6 atm. At 10 atm and 250 °C, the conventional FTS catalyst produced fuels rich in hydrocarbons within the gasoline (C_4–C_{12}) carbon number range. Hydrocarbons with carbon numbers within the JP-8 (C_8–C_{17}) and to some extent diesel range (C_{15}–C_{25}) were also produced. At the same condition the Co-SiO_2-Mo-Pd-Pt/HZSM-5 catalyst increased the selectivity of JP-8 carbon number range hydrocarbons. When the hybrid catalyst Co-SiO_2/Mo-Pd-Pt-HZSM-5 was examined at 13.6 atm and 250 °C, a further increase in the selectivity of JP-8 carbon number range hydrocarbons and to some extent diesel was observed. The relative amounts of olefins and n-paraffins decreased with the distribution shifting towards the production of more isomers. A fixed bed continuous flow catalytic system was used.

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1. Introduction

With declining hydrocarbon petroleum deposits and increasing prices of petroleum fuels, there has been a renewed research interest in the search for alternative renewable sources of energy. One of the areas that has drawn interest is the catalytic conversion of syngas (H_2 and CO) to liquid transportation fuels. One of the key processes is the Fischer–Tropsch synthesis (FTS), which converts syngas into liquid hydrocarbons, primarily in the diesel range. The thermodynamic equilibrium conditions and the type of catalyst are the key factors determining hydrocarbon products distribution. A generic predictive model for the product distribution is the Anderson–Schulz–Flory probability model [1,2]. According to this model, at lower probabilities for molecular propagation (chain growth), the selectivity of lower hydrocarbons (C_1–C_4) is highest. At higher probabilities, the selectivity of diesel (C_{15}–C_{25}) and complex waxes increases dramatically. At medium chain growth probabilities, the selectivity of gasoline (C_4–C_{12}) and JP-8 (C_8–C_{17}) are medium with a value of ~48% reported for gasoline selectivity.

Sources of feedstocks used to produce syngas in FTS are: natural gas in gas-to-liquid (GTL), coal in coal-to-liquid (CTL) and biomass in biomass-to-liquid (BTL) conversion technologies [3]. Each source has its own merits and demerits which sometimes dictate syngas production, processing and composition adjustment technologies and catalyst selection. For example when the feedstock is biomass, ultimate analysis of the biomass may dictate the use of either gasification or pyrolysis. Also the low hydrogen production potential of biomass versus natural gas will require the use of iron

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Nomenclature

W_{cat}	weight of catalyst (g)
T	temperature (K)
P^*	atmospheric pressure (atm)
R	universal gas constant, 0.08205, (L atm/K/mol)
$\text{Feed}_{\text{ideal gas}}$	feed flow rate of ideal synthesis gas (standard lpm)
GHSV	gas hourly space velocity (min^{-1})
SLPM	standard liters per minute
$\dot{n}_{\text{ideal gas}}$	molar feed rate of ideal synthesis gas(mol/standard liter)
$\dot{Q}_{\text{ideal gas}}$	volumetric feed rate of ideal gas (standard 1pm)
$p_{\text{ideal gas}}$	feed partial pressure of ideal syngas (atm)
A_i	GCMS peak area of hydrocarbon with carbon number i

over cobalt since the former catalyzes the water-gas-shift (WGS) reaction which internally raises the H_2 partial pressure, thereby adjusting the H_2:CO ratio for good catalytic performance.

Recently, the FTS is at the center of efforts to produce drop-in fuels from biomass especially JP-8/jetfuels for the aviation industry [4]. This is because BTL catalytic conversion via the FTS process will not require modifications to the existing automotive infrastructure, thereby representing a huge saving in the initial capital investments.

The MixAlco process (which converts domestic wastes to chemicals and fuels) produces 8 tons of undigested material (in effluent sludge) per 40 tons of waste fed into the process. The pyrolysis of this sludge produces synthesis gas in the optimum concentration (v/v) of 45.3% H_2/34.5% CO [5]. 20.2% CH_4 is also produced in the pyrolysis process. Up to 95,160 g of syngas is generated per ton of sludge pyrolyzed. With an appropriate adsorbent, a pressure swing adsorption unit can separate H_2 and CO from the CH_4. To externally adjust the syngas composition to ∼1.90, the CH_4 can be converted to more H_2 and CO in a separate steam reforming of methane (SRM) step. Cobalt catalyst is known to increase the productivity of FTS process for higher hydrocarbons at low temperatures and will operate optimally if the H_2:CO ratio is between 1.71 and 2.00. The use of cobalt catalyst in FTS process for the production of liquid hydrocarbons from biomass feedstocks has not been given proper attention since iron has been the traditional catalyst [19,20].

The main goal of this work was to design and test a new hybrid cobalt-based FTS catalyst (Co-SiO_2/Mo-Pd-Pt-HZSM-5) with an enhanced capability of increasing the selectivity of hydrocarbons in the JP-8 and/or diesel carbon number ranges over normal Co-SiO_2 catalyst. This is possible at lower temperatures and pressures since the thermodynamics of the process favors oligomerization/polymerization together with isomerization as secondary reactions. Our proposition is that this can be achieved by bringing the catalytic FTS process to established technologies such as pyrolysis, pressure swing adsorption and steam reforming of methane for high methane producing thermo-chemical conversion processes as shown in Fig. 1.1. If applied to the MixAlco process increases its fuel production capacity thereby revitalizing the use of cobalt (in FTS process) over iron in BTL conversion processes.

2. Experimental

2.1. Description and layout of experimental setup

The feed synthesis gas was derived from the pyrolysis of sludge obtained as the by-product of the MixAlco process. This syngas was originally produced with an approximate H_2:CO ratio of 1.3. Three gas tanks (one with pure air, another with pure hydrogen and a third containing a 65 mol% H_2/35 mol% CO syngas mixture after adjustment of composition via steam reforming of methane) were connected to a catalyst bed via a pressure regulator (Air Gas, College Station, Texas), a mass flow controller (Alicat Scientific, Tucson, Arizona) and a pressure gauge (McMasters Carr, Aurora, Ohio) respectively. The catalyst was heated in a horizontal tube furnace (ThermoScientific, Ashville, North Carolina). The products of the process were then passed through another pressure gauge, a cooling trap and then a back pressure regulator (H. Lorimer Corp., Longview, Texas). While the uncondensed gases exited to be analyzed every hour, the liquid hydrocarbon products were condensed in a condenser maintained at the pressure of the system by the back pressure regulator. The schematic of the process is diagrammed in Fig. 2.1.

2.2. Catalyst selection

The conventional Fischer–Tropsch catalyst for the hydrogenation of CO was cobalt supported on silica. Cobalt catalysts tend to produce more higher molecular weight hydrocarbons [8]. Water is known to kinetically inhibit iron-based Fischer–Tropsch synthesis, whereas the rate of the Fischer–Tropsch synthesis over cobalt-based catalysts is mainly independent of water vapor partial pressure. Water causes re-oxidation of the catalyst leading to sintering and fouling.

Generally speaking, supports are expected to disperse the active phase, resulting in an increase in the available metal surface area of the catalyst. Supports stabilize the active phase thereby minimizing loss of active surface area and maintain overall catalyst thermal and mechanical strengths. Support pores and matrix provide a medium for mass and heat transfers for catalysts subjected to diffusion limitations. Catalyst-support interactions can facilitate or inhibit the reduction of the precursors to their active form [8]. Too high an interaction can inhibit reduction, while a loosely bound precursor on the support can lead to catalyst loss to attrition. The nano-particles under those scenarios eventually sinter and agglomerate leading to deactivation. SiO_2 was selected because its interaction with the metal is small enough to promote reduction but high enough to limit sintering and agglomeration. Metal-support interactions have been shown to decrease in the order $Al_2O_3 > TiO_2 > SiO_2$ for the acidic base metal supports [18]. Selection of SiO_2 therefore minimized high support-metal interaction, thereby decreasing the chance for the formation of irreducible forms of cobalt oxide which might sinter and agglomerate [7,9].

The second catalyst supported platinum, palladium and molybdenum on an acid form of ZSM-5 (HZSM-5). Palladium has been reported to have a stabilizing effect by binding active metals to the support although it also plays a key role in reforming/secondary reactions such as isomerization and cyclization [10,11]. Platinum and molybdenum have strong dehydrogenation/hydrogenation capabilities with molybdenum being able to further hydrogenate carbon monoxide, thereby increasing CO conversion [12]. Platinum can dehydrogenate alkanes into alkenes (via the hydrogenation of created carbonium ions) in the metal–acid dehydrogenation/hydrogenation reactions involving metal and acidic sites of Mo-Pd-Pt/HZSM-5 [13]. Mo catalyzes the hydrogenation of the carbonium ions on the acid sites and the subsequent oligomerization of these ions into oligomers. Favored thermodynamically, the effect of these secondary reactions is to increase the selectivity of hydrocarbons in the JP-8 carbon number range. Current roles of secondary reactions in hybrid catalysts involving ZSM-5 are to increase selectivity of hydrocarbons in the gasoline carbon number range. Given that the Co-SiO_2 catalyst has been extensively researched, it was used in this work only as a control (and not for comparison) for the investigation of the hybrid catalyst.