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Catalytic membrane reactor for the production of biofuels

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ABSTRACT

The H_2-distributed feeding concept using Pd/Ag-based membranes and an Ru-based catalyst in a Packed Bed Membrane Reactor (H_2-PBMR) for the synthesis of biofuels via the so-called Fischer–Tropsch Synthesis has been demonstrated. The most successful approach resulted when H_2-poor syngas (H_2/CO = 1) typically obtained from the gasification of biomass was fed directly through the reaction chamber, i.e., to the catalyst bed, whereas the H_2 needed to reach the proper stoichiometry for the FTS (H_2/CO = 2) was admitted, and properly distributed, into the catalyst bed through the Pd/Ag-based membrane by flowing H_2/He mixtures at the retentate side of the membrane. Under the optimum reaction conditions, the CO conversion measured with the H_2-distributed feeding concept is lower than that obtained in a conventional Packed Bed Reactor with H_2/CO = 2 (37.9 vs 50.7%), but significantly higher than that obtained in a conventional reactor with H_2/CO = 1 (14.1%). Remarkably, the productivity towards high-molecular hydrocarbons increases by almost 70% and the methane production decreases by one order of magnitude when using the H_2-distributed feeding concept in a Packed Bed Membrane Reactor.

1. Introduction

The Fischer–Tropsch Synthesis (FTS) is a well-established technology for the production of synthetic fuels and chemicals from syngas obtained from natural gas or coal [1]. The overall process comprises the transformation of natural gas or coal into syngas, a mixture of H_2 and CO with different stoichiometries, depending on the source and reaction conditions, which is further transformed into hydrocarbons in the presence of a catalyst via the FTS. These processes are known as coal to liquids (CTL) or gas to liquid (GTL processes). In recent times, the possibility of obtaining syngas via biomass gasification has encouraged the interest in the FTS as a route for obtaining second-generation biofuels via the so-called BTL (biomass to liquid) process [2,3]. Industrial FTS plants are based on Fe- or Co-based catalysts producing mainly short olefins and gasoline or paraffinic waxes, respectively [4]. The scale of the CTL and

GTL plants is a key factor in the economy of the overall processes. In fact, in order to be competitive, modern GTL plants are very large. For instance, it is reported that Shell's Pearl GTL plant in Qatar has the capacity of producing up to 260,000 barrels of GTL products and natural gas liquids per day treating 1.6 billion cubic feet per day of gas. However, it is highly unlikely that biomass could supply syngas at similar high rates as natural gas. As a consequence, it is expected that the scale of BTL plants have to be significantly smaller than that of CTL or GTL plants. Thus, in order to be competitive, it is necessary to increase the per-pass production of HC from syngas by developing more efficient processes and improving the catalysts to produce the desired hydrocarbon fraction. It is well known that Ru-based catalysts exhibit remarkably higher intrinsic activities than Fe or Co catalysts [4]. Moreover, they can operate in the presence of high partial pressures of water (the main co-product of the FTS reaction) and other oxygenate-containing atmospheres that have triggered the interest in Ru-based catalysts for FTS [5–9].

The FTS results in the formation of a pool of heteroatom-free linear paraffinic hydrocarbons ranging from CH_4 to waxes of 50 plus carbon atoms. The high molecular weight hydrocarbons are reformed downstream into the desired product family, mostly diesel or jet fuel fractions. Hydrocarbon formation in the FT reaction

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is very similar to polymerization kinetics in which hydrocarbons are formed by the addition of monomers of activated C_1 groups to the end of an absorbed growing hydrocarbon chain [10]. Due to this polymerization kinetics, there will always be a range of hydrocarbon products C_{1+} whose selectivity can be described by the Anderson, Schulz, Flory (ASF) distribution. The chain growth possibility, the α value (which ranges between 0 and 1) is commonly used to describe the product distribution of the FTS. The higher the α value, the higher the fraction of high molecular weight products.

The FTS product distribution can be controlled, at least to some extent, by the adequate use of the catalyst and reaction conditions (pressure, temperature, H_2/CO ratio and Gas Hourly Space Velocity, GHSV) [10]. The use of membrane reactors offers the possibility of increasing process intensification, while increasing the reaction conversion and the selectivity towards the desired product fraction. However, studies about catalytic membrane reactors for the FTS are scarce, especially experimental studies. Most of these studies are based on H_2O-separation membranes in order to shift the equilibrium ($H_2 + CO \rightarrow -CH_2- + H_2O$) to the formation of hydrocarbons. However, the results obtained show no benefits as compared to those reported in a Packed Bed Reactor (PBR), mostly because the membranes did not show sufficient selectivity for water removal under FTS conditions [11].

Membranes as reactant distributor along the reactor axis have been proposed to control the activity and product selectivity, since they depend significantly on the H_2/CO ratio. Thus, the concept of distributed feeding of H_2 can be used to enhance the selectivity to long-chain products, since the H_2/CO ratio remains constant along the reactor axis [12]. Leonard et al. [13,14] and Guillou et al. [15] presented a conceptual study on distributed feeding of H_2 along the reactor axis. The membrane was either inert (γ-Al_2O_3 on α-Al_2O_3) or coated with a ZSM-5 zeolite layer. The distribution of H_2 into a CO feed stream lead to low H_2/CO-ratios in the catalytic bed and as a consequence to lower conversions along with higher C_{10+} hydrocarbon yield and lower methane selectivity. In addition, low H_2/CO ratios could result in a higher formation of coke and/or high molecular weight hydrocarbons that remain adsorbed on the catalyst surface thus deactivating the catalyst. The application of the ZSM-5 membrane also altered the product distribution by secondary reactions at the acidic sites of the zeolite, resulting in higher yields of short-chain hydrocarbons. These results show a promising alternative to convert biomass-derived H_2-poor syngas into valuable hydrocarbons.

Recently, some works have modeled the use of membrane reactors for the FTS. Rahimpour et al. proposed a 1D heterogeneous model of the FTS reactor using Fe-based catalysts in which a fixed bed reactor is combined with a membrane-assisted fluidized bed reactor. The results obtained by the model showed an enhancement in the gasoline yield, a main decrease in CO_2 formation and a favorable temperature profile compared with a conventional fixed bed reactor [16].

More recently, Ghareghashi et al. [17] reported a simulation of the use of two consecutive reactors: a catalytic fixed bed reactor for the oxidative coupling of methane (OCM) and a fixed bed membrane FTS reactor using a Pd/Ag based H_2 perm-selective membrane and an Fe-based catalyst. The study concluded that the concept of a membrane FTS reactor together with OCM feed is an interesting method for increasing C_{5+} and decreasing undesired products such as CO_2 and methane.

In addition, Nouryzadeh et al. modeled the H_2 and gasoline production in a heat exchanger reactor [18] called Thermally Coupled Recuperative Reactor which is composed of two concentric tubular fixed bed reactors. In this interesting concept, the exothermic reaction (FTS) generates heat that is transferred to the endothermic side (outer side) where the dehydrogenation of cyclohexane to produce H_2 takes place. The H_2 produced is fed along the FTS reactor through a Pd/Ag perm-selective membrane. According to the model results, this configuration offered some important improvements compared with the conventional FTS, thus increasing the gasoline yield.

In summary, some experimental results and especially some recent modeling studies indicate that the use of the so-called H_2-distributed feeding concept in FTS by using membrane reactors could have a beneficial effect enhancing the selectivity towards high molecular weight hydrocarbons while decreasing the selectivity to undesired methane and/or CO_2. Moreover, the use of Pd/Ag membranes have recently received great interest due to their unique properties for the separation of H_2, high permeability and selectivity to H_2 [19,20]. These improved properties could help to implement the use of H_2-distributed feeding concept in a membrane reactor applied to the FTS.

To the best of our knowledge, there are no experimental works about the use of the H_2-distributed feeding concept with membrane reactors for FTS using Pd/Ag membranes.

In this paper, we show the beneficial effect of using Pd/Ag membranes for H_2-distributed feeding in a Packed Bed Membrane Reactor (PBMR) compared to a conventional Packed Bed Reactor (PBR) for FTS with a Ru-based catalyst. H_2-poor syngas ($H_2/CO = 1$), which is the typical value of the syngas obtained by gasification of biomass [21], was fed to the reaction chamber (inner side of the membrane) and the H_2 needed to reach the desired FTS stoichiometry ($H_2/CO = 2$) was admitted (and properly distributed) into the reaction chamber through the Pd/Ag-based membrane resulting in an enhancement of the productivity of high molecular weight hydrocarbons. The experimental study is supported by model simulations.

2. Experimental

2.1. Preparation of the B-Ru/TiO2 catalyst

B-doped Ru/TiO_2 (3 wt% Ru; B:Ru 1:1 at), RuB1Ti was used as the FTS catalyst. The catalyst was prepared by sequential impregnation of TiO_2 (P25) with water solutions of $RuNO(NO_3)_3$ and HBO_3. A solution of the Ru precursor was added to TiO_2 by incipient wetness impregnation with a 0.09-M aqueous solution of Ru precursor and dried overnight. The solid recovered was calcined in static air at $450\,^{\circ}C$ ($10\,^{\circ}C\,min^{-1}$) for 3 h. The resulting solid (Ru/TiO_2) was impregnated with aqueous solution with the adequate amount of H_3BO_3 to obtain a B/Ru atomic ratio of 1, dried at room temperature and calcined again in static air at $450\,^{\circ}C$ ($10\,^{\circ}C\,min^{-1}$) for 3 h.

2.2. Catalyst characterization

X-ray diffractograms were collected on a Seifert 3000 powder diffractometer operating with Cu Kα radiation ($\lambda = 0.15418\,nm$) generated at 40 kV and 40 mA. Scans were recorded at $0.02\,^{\circ}s^{-1}$ for 2θ values between 10° and 90°. H_2 temperature-programmed reduction (H_2-TPR) analysis of the catalyst was carried out with a Micromeritics instrument using a U-shaped quartz reactor. Prior to the reduction experiment, the catalyst was flushed with a He stream at 373 K for 30 min and then cooled down to room temperature. TPR profiles were obtained by heating the sample under a 10% H_2/Ar flow ($50\,mL\,min^{-1}$) from 303 to 1173 K ($10\,K\,min^{-1}$).

2.3. Preparation of Pd/Ag-supported membranes

A 15-cm long alumina tube with an outside pore size of 100 nm and 10/7 mm o.d/i.d. was used as membrane support (provided by Rauschert Kloster Veilsdorf), both ends were glazed leaving 60 mm of porous part in the middle of the membrane. A thin Pd–Ag layer ($\approx 4\,\mu m$ thick and silver content of $\sim$23–27%) was deposited on the