GALAXY INTERNATIONAL INTERDISCIPLINARY RESEARCH JOURNAL (GIIRJ)
ISSN (E): 2347-6915
Vol. 13, Issue 3 March (2025)

GENERAL INFORMATION ABOUT THE PROCESS OF SYNTHESIS OF LOW MOLECULAR HYDROCARBONS BASED ON THE FISHER-TROPISH SYNTHESIS

Egamnazarova Fazilat Dustqobilovna
Assistant Teacher at Karshi State Technical University

ABSTRACT

Ruthenium, nickel, cobalt and iron are transition metals that have proven to be active in Fischer-Tropsch synthesis. They are located in subgroups eight to ten. Ruthenium has a very high FT activity.

Keywords: Olefins, hydrocarbon, selectivity, ruthenium, nickel, cobalt, Iron, copper, potassium, silicon, dioxide, boudouard, catalytic cracking.

INTRODUCTION

Lower olefins are the basic carbon-based building blocks, usually referring to ethylene, propylene and butylene, which are widely used in the chemical industry and are traditionally produced by thermal or catalytic cracking of a range of hydrocarbon feedstocks such as naphtha and gas oil [1]. Olefins with C_2 to C_4 are traditionally produced from steam cracking of naphtha. The need for alternative routes to produce these basic commodity chemicals through non-petroleum-based processes has fueled research during past oil crises. Currently, due to high oil prices, environmental regulations and strategies to achieve independence from oil imports, there has been renewed interest in producing lower olefins from alternative feedstocks such as coal, syngas, natural gas or biomass [2]. Literature reviews show that studies on the effect of Fe crystal size have been conducted on unpromoted carbon and γ-Al_2O_3 supported catalysts. Under the following conditions (1 bar, 275 °C va H_2 CO = 3), The small size of Fe particles (<1.6 nm) leads to low cycle frequencies, low methane selectivity and high olefin to paraffin (O/P) ratios for CO hydrogenation. A subsequent study found similar trends for methane selectivity and TOF with increasing iron (carbide) particle size. However, they observed higher O/P ratios for catalysts with larger Fe particles. The discrepancy in the results is due to the different test conditions used in the study. (1 bar, 200 °C and $H_2/CO = 2$). Both studies showed that carbonaceous catalysts were more selective towards olefins than samples prepared with γ-Al_2O_3 as a support[3]. Short-chain olefins (C_2-C_4) form the basis of many plastics that have become an integral part of our world today, and the olefin-based polymer industry accounts for approximately 20% of the annual production value of the chemical industry in Uzbekistan. [4]. Olefins are traditionally produced from crude oil by steam cracking. Therefore, there is great interest in developing alternative routes for the production of olefins. In 2017, 152 million tonnes of ethylene and 102 million tonnes of propylene were produced.[5] Based on the carbon balance, 800 million tonnes of CO_2 could be used to synthesize olefins.[6] One way to convert CO_2 emissions into short-chain olefins, in combination with sustainably produced hydrogen from plastic pyrolysis or CO_2-containing synthesis gas, is through Fischer–Tropsch synthesis (FTS), a polymerization reaction that can produce a wide range of products depending on the catalyst selected. In the classical FTS process, CO is hydrogenated with H_2 over iron and cobalt catalysts to produce CH_2 fragments, which are then assembled into hydrocarbon chains. Since CO_2 is not directly converted to Fischer–Tropsch products, if CO_2 emissions are to be recycled, the reverse gas shift reaction of water to CO must first occur. This combination of endothermic equilibrium and strongly exothermic FTS can be carried out in two separate or combined reactor units.[7] Due to the opposing reaction enthalpies, direct thermal integration is a significant advantage of combining the two reactions in a single reactor. In addition, equilibrium shifts can be achieved, as CO is converted to valuable products through a series of irreversible sequential reactions during FTS. As a result, a catalyst system that catalyzes both the shift reaction and the FTS is required. Iron meets these requirements.[8] Many academic studies describe the use of iron catalysts in AGVs.[9-11] Apart from solid catalysts, the focus here is on supported systems. In particular, carbon-based iron catalysts are of increasing interest in this context.[12-14] In general, carbon materials are characterized by their chemical inertness and easily tunable structure. This leads to a uniform distribution of metal components on the carbon surface.[15,16] Regarding FTS, C-supported iron systems are characterized by easier redox reactions compared to conventionally used inorganic support materials such as SiO_2 and Al_2O_3. The metal-support interaction is less pronounced. This facilitates the conversion of iron oxide species into FT-active carbides. Carbidization of elemental iron is also promoted.[17,18] In addition, carbon-iron systems have excellent sintering resistance, as demonstrated by the use of carbon nanotubes (CNTs).[19,20] Iron catalysts are versatile FTS catalysts at different operating temperatures, allowing the production of a wide range of products. A paraffin-rich, high molecular weight product can be synthesized at temperatures below 240 °C, while an olefin-rich, short-chain product can be synthesized at temperatures above 300 °C [21]. Iron catalysts for Fischer–Tropsch synthesis can be categorized according to the production method, such as soaking, melting, and soaking catalysts [22]. Precipitated catalysts made of iron, copper, potassium, and silica have surface areas ranging from 100 to 400 m_2 g-1; the surface area is strongly dependent on the composition [22].

Ruthenium, nickel, cobalt, and iron have proven to be active in the Fischer–Tropsch synthesis. They are found in subgroups eight to ten.[23–25] Ruthenium has a very high FT activity. It is highly selective for the formation of long-chain hydrocarbons at temperatures below 150 °C. However, operating pressures of over 100 bar are required. Furthermore, ruthenium is 30,000 times more expensive than iron and is one of the rarest non-radioactive elements on Earth. As a result, ruthenium is excluded from large-scale use as a Fischer–Tropsch catalyst.[24] Nickel is relatively abundant and has a low cost. However, the use of nickel mainly results in the formation of methane.[25] The production of linear alpha-olefins (α-olefins) is a practical way to increase the economic potential of the Fischer–Tropsch synthesis (FTS) due to their importance as chemical intermediates. Our study focused on the optimization of Na-promoted Fe1Zn1.2Ox catalysts for the selective conversion of syngas to linear α-olefins via FTS at 340 C and 2.0 MPa..

Stoichiometry of reactions

FTS is a very complex reaction system, giving a variety of products. The reactions in the FTS process vary depending on the catalyst and the operating conditions used. The main general reactions in FTS are the following equations [26]:

Formation of linear paraffins

$(2n + 1)H_2 + nCO = CnH_2n+2 + nH_2O$ (1.1)
$(n + 1)H_2 + 2nCO = CnH^2n+2 + nCO_2$ (1.2)

Olefins
$2nH_2 + nCO = CnH_2n + nH_2O$ (1.3)
$nH_2 + 2nCO = CnH_2n + nCO_2$ (1.4)

Formation of alcohols and aldehydes:
$2nH_2 + nCO = CnH_2n+1OH + (n - 1)H_2O$ (1.5)

$(2n + 1)H2 + (n + 1)CO = CnH2n+1CHO + nH2O$ (1.6)
Water Gas Shift (WGS) Reaction:
$H_2O + CO = CO_2 + H_2$ (1.7)

Methane formation and the Boudouard reaction (main side reaction):
$3H_2 + CO = CH_4 + H_2O$ (1.8)
$2CO = CO_2 + C$ (1.9)
The product distribution in FTS depends largely on the type of catalyst chosen and the process conditions.[8] The main reactions produce unsaturated (olefin):
$n\,CO + 2n\,H_2 \rightarrow CnH_2n + n\,H_2O$ (Olefine) (2)
Transition metals from groups 8–10 are generally suitable as catalysts for CO hydrogenation in decreasing order of activity.: Ru > Fe > Ni > Co > Rh > Pd > Pt.[27].
Iron catalysts are versatile FTS catalysts with a wide range of operating temperatures, allowing for the production of a wide range of products. A paraffin-rich, high molecular weight product can be synthesized at temperatures below 240 °C, while an olefin-rich, short-chain product can be synthesized at temperatures above 300 °C [28]. Iron catalysts for Fischer–Tropsch synthesis can be classified according to the production method, such as soaking, melting, and evaporation catalysts [29]. Precipitated catalysts made of iron, copper, potassium, and silica have surface areas ranging from 100 to 400 m2 g^{-1}; the surface area is strongly dependent on the composition [29]. Soaked catalysts are mainly used in low-temperature applications (200 to 240 °C) [11, 15]. Solution catalysts with less than 10 m2 g^{-1} have the lowest surface areas of iron catalysts [30]. They have no pore volume in their raw state and are therefore not formed except during shrinkage [31]. They are used for high temperature applications (300 to 350 °C) [32] and therefore in fluidized cases [33]. Iron sintered catalysts have been developed for the production of short chain olefins and consist of a mixture of iron, copper and potassium oxides [34]. Zinc oxide is also added to limit the chain length and increase the proportion of olefins [35]. The surface area (70 to 100 m2 g^{-1}) as well as the total pore volume11 lie under the precipitation catalysts; the synthesized catalysts have not yet been used on an industrial scale [36]. For iron catalysts, metallic iron is not considered the active component of the FTS, but rather iron carbides have been assigned this role [37]. The carbides are formed during the activation step, which is called formation. However,

hematite Fe_2O_3 [153], magnetite Fe_3O_4 [38] or metallic α-iron-carbide mixtures [39] have also been reported in the literature as possible active components. It is known that iron catalysts can be used as a C source with CO_2 and are still a subject of research [40]. Riedel et al. showed that the product distribution and olefin composition remain the same for C sources CO and CO_2, but the yield of organic components decreases slightly for CO_2/CO ratios greater than 1:1 [41]. The addition of metal oxides Al_2O_3, TiO_2 Cr_2O_3, MgO, MnO and CaO increases the high metal surface area and overall mechanical stability; they act as structural promoters [42]. Copper is mainly used as a reduction promoter in iron catalysts, but it helps to increase the WGS activity [43]. When using copper, the development of secondary reactions due to the increased readout capacity should also be taken into account [44]. Alkali metals such as potassium reduce the binding energy of hydrogen to iron [45]. This means that less hydrogen is available on the surface for hydrogenation reactions and the olefin content in the product increases [46]. Fe catalysts are prone to coking, sintering and, for example, sulfur poisoning [47]. In technical applications (LTFT), a service life of up to six months is the norm for iron catalysts [48].

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