

https://dspace.org/

Microwave induced solid-state interactions for the synthesis of Fischer-Tropsch catalysts

Linganiso, Linda Zikhona

2010-04-13T09:05:24Z
http://hdl.handle.net/10539/7969

Downloaded from a DSpace repository. https://dspace.org/

CHAPTER ONE

1.1 HISTORY AND DEVELOPMENT

The catalytic conversion of carbon monoxide and hydrogen to hydrocarbons from synthesis gas (syngas) was first observed by Sabatier and Senderens in 1902 (Sabatier and Senderens, 1902). The reaction under taken was methanation reaction of synthesis gas over cobalt and nickel catalysts. The first patent for the synthesis of hydrocarbons from synthesis gas was issued to 'Badische Anilin und Soda Fabrik' (BASF). This was done in 1913. In 1925, the German researchers, Fischer and Tropsch established the technology for the production of liquid hydrocarbons from CO and H_2 using metal catalysts at high pressures of up to 300 bar (Fischer et al., 1925). The experiments were conducted at Frank Fischer's laboratory at the Kaiser Wilhelm Institute for coal research in Muelheim. German scientists were successful in synthesizing liquid hydrocarbons over an iron catalyst in the Kaiser Wilhelm Institute for coal research.

Before that time, in the early 1900's the Kaiser Wilhelm Institute at Muelheim (KWIK) was opened for coal research for the production of fuel from coal. As from that time industrial and academic research has been carried out with the thought of improving the FT process.

In 1935-1945, the FTS was operated commercially in Germany using cobalt catalyst (Anderson, 1984); the synthesis was carried out at atmospheric pressure in fixed bed reactors (Tramm, 1959). This was done by the Ruhrchemie, Brabag, Gewerkschaft Viktor and Rheinpreussen.

One of the important developments which occurred before the beginning of the Second World War was that Pichler discovered that the iron catalyst life span can be extended considerably by conducting the synthesis at 10-15 bar pressures.

The research continued at the Kaiser Wilhelm Institute which led to the discovery of the synthesis over iron catalysts. Many variations in experimental conditions, the type of catalyst used and the reactor type were investigated. The usage of iron catalysts was further improved in the United States of America (Storch et al., 1951).

One of the interesting observations made by Pichler (1953) was that ruthenium was an excellent catalyst for the production polymer-type n-alkanes at very high pressure. Ruthenium catalysts are the most active FT catalysts and can produce a high molecular weight wax at reaction temperatures as low as 150 ^{o}C. However, the application of ruthenium in industry and in academic studies is limited because of its high price and limited availability.

The next stage in FT history was the participation of South Africa in 1950's. In 1943, a merger was established between Ruhrchemie and Lurgi to develop fixed bed reactors for the synthesis. The venture was named Arbeitsegemeinschaft Rurhchemie-Lurgi, shortened to ARGE. ARGE was responsible for the development of reactors that were installed at SASOL in 1955. The first commercial plant, known as SASOL I was brought on stream in 1955. The SASOL plant in Sasolburg had a capacity of 700 $\bullet 10^3$ t/a. The SASOL plant was using ARGE reactors to produce high yields of wax and diesel fuel. SASOL II and SASOL III were conceived at the time when world oil prices rose sharply in the wake of the Yom Kippur war in 1973. It was commissioned in 1980 (Thomas and Thomas, 1996).

Right now, SASOL uses two forms of FT operation with a merged capacity of 6000 $\bullet$ 10^3 t/a. The high-temperature (300-350 ^{o}C) FT process which uses iron-based catalysts is utilised for the production of gasoline and linear low molecular mass α-olefins. The low-temperature (200-240 ^{o}C) FT process with cobalt or iron-based catalysts is utilised in the production of high molecular weight linear waxes (Dry, 2002).

In 1992 the Mossgas, now PetroSA in Mossel Bay, South Africa commissioned the technology of synthesis gas conversion to hydrocarbons. They used natural gas-derived synthesis gas. The PetroSA plant in Mosel Bay has a capacity of 900 $\bullet 10^3$ t/a.

Shell operates its plant in Bintulu in Malaysia.

The Fischer-Tropsch synthesis has been used at an industrial level and today economically viable projects are being carried out e.g. three plants run by Sasol in South Africa and Shell FT process in Malysia (Eilers and Posthuma, 1997).

1.2 EFFECT OF CRYSTALLITE SIZE ON ACTIVITY AND SELECTIVITY OF FISCHER-TROPSCH CATALYSTS

Fischer-Tropsch synthesis occurs on the metallic surface, therefore it is crucial to design a catalyst with high surface area for dispersion of the active sites. High surface area of the metal is obtained at very small crystallite size. Fischer-Tropsch catalysts undergo a loss in activity due to loss of active surface area as the results of crystalline growth (sintering).

Fischer-Tropsch precursors are synthesized as α-Fe_2O_3 or ferrihydrite. During catalyst activation the α-Fe_2O_3 and/or ferrihydrite convert to the active phase (Fe_xC and/or Fe_3O_4). The loss in activity of cobalt catalyst (with small crystallite size) attributable to the presence of water (Fischer-Tropsch by product) was reported by Iglesia (1997). The diameter of cobalt particles was reported to be less than 5 nm. Fischer-Tropsch cobalt catalysts with diameter greater than 5 nm were found to display activity in Fischer-Tropsch synthesis. At larger crystallite size, the active surface area drops, but the increase in catalytic activity indicates that the catalytic activity depends on the structure (size) of the cobalt particles.

A study done by van Steen and the co-workers suggests that small crystallites of cobalt Fischer-Tropsch catalyst do form oxide at Fischer-Tropsch conditions (van Steen et al., 2005). In the case of iron-based Fischer-Tropsch catalyst, a comparable performance is expected to occur when the active phase is the iron carbide (Li et al., 2002). For the period of Fischer-Tropsch reaction, elevated water and carbon dioxide partial pressures might result in the transformation of the active small metallic crystallites or iron carbide crystallites to the inactive corresponding metal oxides.

There are a large number of different reactions taking place during Fischer-Tropsch synthesis; some take place on active sites of low coordination whereas others occur on high coordination sites (Schulz et al., 2002). This idea proposes that selectivity changes are expected to take place when testing catalysts with varying crystallite sizes.

In this study, the microwave method of catalyst pre-treatment and the conventional method were employed to effect a change in the catalytic activity and selectivity in Fischer-Tropsch synthesis using iron catalysts. After microwave pre-treatment of the iron catalyst, crystallite size increased due to microwave heating. The effect of crystalline size is discussed in details in chapter 6.

1.3 IRON CATALYST AND POTASSIUM AS A PROMOTER

Potassium has been used as a chemical promoter for iron catalysts to achieve a change in catalytic activity and selectivity in Fischer-Tropsch synthesis (McVicker et al. 1980, Dry 1981). Earlier studies suggested that potassium promotes CO chemisorption, facilitates CO dissociation while inhibiting hydrogen chemisorption (Bell et al., 1986) thus resulting in an increase of CO conversion via water gas shift reaction, formation of carbides and free surface carbon (Dry, 1981). This also results in lower FT rates and higher product molecular weight and greater olefin content (Anderson et al., 1951).

Although, potassium is known to improve the FTS activity and heavy product fraction, high potassium loading covers the surface of the iron catalyst, resulting in limited promotion effect and a decrease in FTS conversions (Davis et al., 2003).

The aim of the present research was to examine the microwave effect on potassium-containing iron catalysts.