Attrition Resistant Iron-Based Fischer-Tropsch Catalysts

Final Report

Work Performed Under
Grant No: DE-FG22-96PC96217

for
U.S. Department of Energy
Federal Energy Technology Center
Pittsburgh, PA 15236

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October 1999

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ABSTRACT

Fischer-Tropsch (FT) synthesis to convert syngas (CO + H_2) derived from natural gas or coal to liquid fuels and wax is a well-established technology. For low H_2 to CO ratio syngas produced from CO_2 reforming of natural gas or from gasification of coal, the use of Fe catalysts is attractive because of their high water gas shift activity in addition to their high FT activity. Fe catalysts are also attractive due to their low cost and low methane selectivity. Because of the highly exothermic nature of the FT reaction, there has been a recent move away from fixed-bed reactors toward the development of slurry bubble column reactors (SBCRs) that employ 30 to 90 μm catalyst particles suspended in a waxy liquid for efficient heat removal. However, the use of Fe FT catalysts in an SBCR has been problematic due to severe catalyst attrition resulting in fines that plug the filter employed to separate the catalyst from the waxy product. Fe catalysts can undergo attrition in SBCRs not only due to vigorous movement and collisions but also due to phase changes that occur during activation and reaction.

The objectives of this research were to develop a better understanding of the parameters affecting attrition of Fe F-T catalysts suitable for use in SBCRs and to incorporate this understanding into the design of novel Fe catalysts having superior attrition resistance.

A Ruhrchemie iron catalyst of composition 100Fe/5Cu/4.2K/25SiO_2 was obtained and tested for FT activity in a 1 cm i.d. high pressure fixed bed micro-reactor system. This catalyst will serve as a baseline catalyst for this work from which improvements in attrition resistance and activity will be sought. The effect of silica addition via coprecipitation and as a binder to a doubly promoted FT iron catalysts (100/Fe/5 Cu/4.2K) was studied. The catalysts were prepared

by coprecipitation, followed by binder addition and spray drying at 250°C in a 1 m diameter, 2 m tall spray dryer. The binder silica content was varied from 0 to 20 wt %. A catalyst with 12 wt % binder silica was found to have the highest attrition resistance. The FT activity and selectivity of this catalyst are better than a Ruhrchemie catalyst at 250 °C and 1.48 MPa. F-T reaction studies over 100 hours in a fixed-bed reactor showed that this catalyst maintained around 95% CO conversion with a methane selectivity of less than 7 wt % and a C_5^+selectivity of greater than 73 wt %. The effect of adding precipitated silica from 0 to 20 % pbw (containing 12 wt % binder silica) was also studied. Addition of precipitated silica was found to be detrimental to attrition resistance and resulted in increased methane and reduced wax formation. Based on the experience gained, a proprietary HPR-43 catalyst has been successfully spray dried in 500-g quantity. This catalyst showed 95% CO conversion over 125 h of testing at 250 °C, 1.48 MPa, and 2 NL/g-cat/h and had less than 4% methane selectivity. Its attrition resistance was one of the highest among the catalysts tested.

ACKNOWLEDGMENTS

This study was sponsored by the U.S. Department of Energy (DOE) under Grant No: DE-FG-22-96PC96217. The authors would like to acknowledge with gratitude the guidance provided by the DOE Contracting Officer's Representative, Dr. Richard E. Tischer. The authors also acknowledge the guidance of United Catalysts Inc., and Energy International.

CONTENTS

Section Page

LIST OF TABLES

LIST OF FIGURES

Attrition Resistant Iron-Based Fischer-Tropsch Catalysts

1.0 INTRODUCTION

Fischer-Tropsch synthesis (FTS) is a set of reactions by which CO and H_2 (syn gas) are converted into a wide variety of hydrocarbons. This synthesis provides the best means currently available for the conversion of coal into synthetic transportation fuels. While over the near to mid term this indirect coal liquefaction route is not likely to be competitive with cheap oil on a global basis, there are a number of commercial activities in this area. SASTECH is making commercially synthetic fuels and chemicals by FTS from coal, China plans to make town gas via this route, and Williams Company is constructing a pilot plant to determining the economics of underground coal gasification, while Shell is using FTS commercially to convert natural gas to high value products. Improvements and innovation in FTS is strategically very important to the U.S. because of its vast coal reserves and because it represents the best way to make high quality liquid products from coal.

Since the gasification of coal gives syn gas relatively lean in hydrogen ($H_2/CO \cong 0.5\text{-}0.7$), the use of a catalyst which converts the oxygen of the CO to CO_2 rather than H_2O is preferable. This is achieved by using catalysts which, in addition to being active for FTS, are also active for the water gas shift reaction (WGS):

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

Fe is the preferred catalyst since it is one of the more active FTS catalysts, active for the WGS reaction, and relatively inexpensive.

Because FTS is so exothermic, one of the major problems in control of the reaction is heat removal. Recent work by industry (Gulf, Statoil, Exxon, SASOL/ SASTECH, Rentech, and others), DOE, and universities has concentrated on the use of slurry-phase reactors, especially slurry bubble column reactor (SBCRs), which are able to be controlled more easily because of the liquid phase present. Such reactors have relatively simple designs and low initial costs while still permitting high catalyst and reactor productivity.

Obviously, much recent work related to slurry-phase FTS based on coal-derived syn gas has focused on using Fe catalysts. Unfortunately, the use of Fe catalysts in SBCRs have been found to present a number of problems. Because of the difficulty in reducing highly dispersed Fe and its lower FTS activity than Co (which does not posses much WGS activity) or Ru (which is too expensive to use by itself), bulk Fe catalysts have had to be used in order to have sufficient active surface area per catalyst weight. The Fe catalysts used in SBCRs have been usually prepared by precipitation, one of the typical methods of preparation of Fe catalysts for use in fixed bed reactors.

The problems encountered in using precipitated iron catalysts are mainly due to two major characteristics: (a) their low density and (b) their attrition properties. Since SBCRs are used to produce high alpha (α) FTS products, there is a need to easily and inexpensively separate the catalyst from the liquid products. The apparent density of typical precipitated Fe catalysts is estimated to be very close (near 0.7 g/cm^3) to that of Fischer-Tropsch wax (about 0.68 g/cm^3) at reaction conditions (Donnelly, 1989). While this is beneficial for keeping the catalyst slurried, catalyst separation from the products can be difficult since the catalyst does not settle well.

Although internal/external filtration systems can be incorporated with slurry reactors, plugging of the filters by Fe catalyst particles is encountered. This is due to the low attrition resistance of the Fe catalyst and the significant breakage of the Fe particles. Fe catalysts are subject to both chemical as well as physical attrition in a SBCR. Chemical attrition can be caused due to phase changes that any Fe catalyst goes through ($Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow$ Fe metal$\rightarrow$Fe carbides) potentially causing internal stresses within the particle and resulting in weakening, spalling or cracking. Physical attrition can result due to collisions between catalyst particles and with reactor wall. Catalyst particles of irregular shapes and non-uniform sizes produced by conventional methods are subject to greater physical attrition. Recently, there has been an in-depth development of precipitated Fe catalysts for use in the slurry phase at the University of Kentucky (O'Brian et al., 1995). However, none of the catalysts produced by this route appears to offer much improvement in attrition resistance.

1.1 Use of Fe Catalysts in SBCRs

Recent work by industry (Gulf, Statoil, Exxon, SASOL/SASTECH, Rentech, and others), DOE, and universities has concentrated on the use of slurry-phase reactors, especially SBCRs. The advantages of the SBCRs are (i) the ability to use low H_2/CO ratio synthesis gas, (ii) the ability of the liquid phase to efficiently withdraw the heat of reaction and thereby control reaction temperature, (iii) high catalyst and reactor productivity, (iv) favorable conditions for catalyst regeneration, and (v) simple construction and low investment cost.

Much recent work related to slurry-phase FTS based on coal-derived syngas has focused on using Fe catalysts. The major problem encountered in the use of Fe catalysts in SBCRs is their tendency to undergo attrition which can result in fouling/plugging of downstream filter and equipment and make the separation of the catalyst from the oil/wax product very difficult if not impossible.

To date, the only group reporting any success in solving this problem is SASTECH. They have patented a wax-catalyst separation system for use external to the reactor. However, it appears that this may be only part of the solution and that catalyst "pretreatment" also plays an important role. Unfortunately, not only are all of the details proprietary, they are owned by a foreign company. Also, even if some combination of improved catalyst and external separation system is successful, the need for a separate separation system beyond in-system filters creates added cost for this process.

1.2 Catalyst Attrition

The factors which affect attrition dynamics include the properties of the catalyst particles, the reactor environment, and the types of breakage mechanics. Spherical particles are less likely to attrit than irregularly shaped particles. The size of the particle and the size distribution of the entire catalyst particle population also influence attrition. In general, larger particles are more easily attrited than smaller ones. However, there is no systematic relationship between particle size, size distribution, and friability. The porosity of the particle influences its friability. Also, pores filled with liquids are more likely to rupture due to changes in state of the liquid caused by temperature or pressure changes. Catalyst particle hardness provides a general measure of the particles ability to resist wear and its susceptibility to fracture (Lee et al., 1993).

In addition to the physical properties of the catalyst, the reaction environment can have a major impact on attrition by causing solid-state phase transformations in the catalyst. During activation of the polycrystalline precipitated Fe catalyst, iron oxide transforms from hematite to magnetite and finally into Fe^o and iron carbide phases. While the transformation from hematite to magnetite is extremely rapid, the magnetite-to-carbide transition is much slower (Shroff et al., 1995). Because of the multiplicity of phases, grain boundaries phase growth kinetics, significant stresses can be introduced into the Fe particle leading to breakage.

1.3 Fe Catalyst Preparation

The preparation of the early precipitated iron catalyst developed by Ruhrchemie and used in the fixed-bed reactors at SASOL as well as the more recent work carried out on these catalyst to improve their performance has been reviewed extensively (Dry 1981, Anderson 1984, Lang, et al., 1995). The work done on precipitated iron catalysts intended specifically for liquid-phase synthesis has also been reviewed (Kolbel 1980). Basically, these iron catalysts are prepared by precipitation from a preheated solution of iron and copper nitrates (40 g Fe and 2 g Cu per liter) with sodium carbonate (Dry 1981). The addition of sodium carbonate is carried out with vigorous stirring for several minutes until the pH reaches 7-8. Sodium is removed by washing with hot distilled water in a filter press. The resulting precipitate is slurried in water and impregnated with a potassium waterglass solution to provide 25 g SiO_2 per 100 g Fe. SiO_2 is present as a structural promotor. The precipitated silica is adsorbed onto or reacted with the high area Fe_2O_3 and excess potassium removed by the addition of sufficient HNO_3 to give 0.5 g K_2O per 100 g Fe after filtration. The catalyst is filtered, extruded , and dried to less than 10 wt% water (Dry 1981). If no silica is added or if it is to be added in forms other than potassium waterglass, alkali addition to the precipitate is carried out using a dilute potassium carbonate solution. Precipitation with ammonia or ammonium carbonate solution may be preferable in order to eliminate the promoter effect of retained sodium carbonate, greater ease of filtration, and use of 40% less water is in the washing process (Kolbel 1980).

The structure of the catalyst is affected by the concentrations of the different solutions, the time of precipitation, and the control of temperature and pH during the precipitation process. Silica stabilizes the iron oxide by preventing crystal growth and results in higher surface area catalysts. The porosity of the catalyst is also dependent on the amount of shrinkage during the drying process. The pore volume can be increased more than two fold when the precipitate is re-slurried in acetone and then dried. However, the physical strength is an inverse function of the pore volume (Dry 1981). The non-uniform particle sizes and, especially, the irregular shapes of the catalyst particles produced by precipitation lead to high production of catalyst fines by abrasion. Although the addition of silica to catalysts produced by precipitation may improve their physical and mechanical properties, especially their hardness, it does not make them suitable for operation in a SBCR. Their low density (~0.7 g/cm^3) which is close to the density of FT wax (0.68 g/cm^3) makes it difficult to separate them from the wax following reaction although it helps to keep them slurried.

Supported metal catalysts on attrition resistant supports such as alumina or silica are commonly used in the refining and chemical industry. The attrition resistance of these supports is due in major part to their ability to be produced in a spheroidal shape, their refractory properties, and their strength. While supported Co catalysts have been found to be very effective for FTS and, in fact, are being used by Shell in their plant in Malaysia, supported Fe catalysts have been found to be less effective for FTS compared to precipitated ones (Dry 1981; Anderson 1984; Bukur, D.B., et al., 1990 a, b). This is due to an increased difficulty in reducing the Fe, the lower inherent activity of Fe, an interaction of promoters such as alkali with the support making higher concentrations of these promoters necessary, and the presence of small pores which can be clogged by wax during reaction thereby eliminating active Fe sites within the pores. Other tradition routes for preparing Fe catalysts appear even less attractive.

1.4 Spray Drying

Spray drying is a technique which is widely used to produce up to 60 mesh spheroidal materials starting from colloidal or uniform size powders (Stiles 1983). Spray dried catalysts are used in fluidized bed reactors because of their spheroidal shape, excellent hardness, abrasion resistance, and size uniformity. Spray drying consists of first producing a slurry of catalyst precursor dispersed in a solution of the oxide precursor which will form the hard phase of the catalyst. The oxide material must be in the form of discrete subcolloidal or very small colloidal particles preferably less than 0.5 nm. The slurry is then spray dried to form porous microspheres which are calcined to produce the micron-size particles.

1.5 Catalyst Pre-Treatment

Before synthesis, a catalyst precursor is subjected to a pretreatment, the purpose of which is to bring the catalyst into an active form for synthesis. The pretreatment of Fe is not as straight forward as that for Ru, Co or Ni. The pretreatment for iron FT catalysts is not clearly understood (Srivastava et al., 1990; Rao et al., 1992; Soled et al., 1990). Part of the confusion stems from the fact that the nature and composition of iron catalysts undergo changes during reaction. These changes depend on the temperature, time of exposure to the reactant feed, nature of the reactor system, composition of the feed and activation conditions (time and temperature). The common pretreatment conditions employed in the case of iron catalysts are H_2 reduction, CO reduction (and carbiding), or reduction in the reactant gas. Recent work at the Federal Energy Technology Center has focused on the effect of catalyst pretreatment on the catalysts synthesis behavior in stirred tank slurry reactor (Pennline et al., 1987; Zarochak and McDonald, 1987).

Several phases of iron are known to exist when iron-based catalysts are subjected to F-T synthesis conditions (Amelse et al., 1978, 1984; Blanchard et al., 1982; Dictor and Bell, 1986; Dwyer and Somorjai, 1978; Jung et al, 1982; Niemantsverdriet et al., 1980; Raupp and Delgas, 1979; Teichner et al., 1982; Zou et al., 1992; Jung and Thomson, 1992;1993; Sault, 1993; Sault and Datye, 1993; Butt, 1990; Bukur et al., 1995a; 1995b; O'Brien et al., 1995). These include metallic iron (α -Fe), iron oxides (hematite, α-Fe_2O_3; magnetite, Fe_3O_4 and Fe_xO), and iron carbides, of which at least five different forms are known to exist. These include O-carbides (carbides with carbon atoms in octahedral interstices, ϵ-Fe_2C, ϵ'-$Fe_{2.2}C$, and Fe_xC) and TP-