Title: SYNTHETIC METHODS FOR LIQUID HYDROCARBONS FROM SYNGAS OVER ALUMINA-SILICA BASED CATALYSTS AND PREPARATION METHODS THEREOF

Abstract: The present invention relates to an alumina-silica support having a double-layered, bimodal pore structure with different pore sizes in which alumina is dispersed on silica surface, a catalyst using the support and a method for preparing liquid hydrocarbons in high yield by Fischer-Tropsch reaction of a syngas (CO/H2/CO2) in the presence of the catalyst.
Description
SYNTHETIC METHODS FOR LIQUID HYDROCARBONS FROM SYNGAS OVER ALUMINA-SILICA BASED CATALYSTS AND PREPARATION METHODS THEREOF

Technical Field
[1] The present invention relates to an alumina-silica support having a double-layered, bimodal pore structure with different pore sizes in which alumina is dispersed on silica surface, a catalyst using the support and a method for preparing liquid hydrocarbons in high yield by Fischer-Tropsch reaction of a syngas (CO/H₂/CO₂) in the presence of the catalyst.

[2] Background Art
[3] Recently, with the rapid increase of the international oil price, the method of producing synthetic petroleum products from synthesis gases resulting from the gasification of natural gas, coal or biomass is becoming more and more important. In this situation, the preparation of liquid hydrocarbons by the gas-to-liquid (GTL) process can solve various problems as outlined below because the final product is in the liquid form.

(1) The liquid product is easy to handle and can be transported across a long distance.
(2) The existing facilities can be utilized without the need of special transport, shipping and storing facilities. (3) High-price, clean products can be sold immediately after production. (4) Economical utilization of stranded/remote gases, or the medium-to-small scale gas resource distant from the demand site, becomes possible, without special transport facilities as in the case of LNG, if the reserve amounts to 1 trillion cubic feet.

[5] Since the Fischer-Tropsch (hereinafter referred to as F-T) was first developed in the 1920s, the GTL process has been refined and adjusted continuously. The GTL technology based on the F-T synthesis not only improves the environmental problem at the gas field, but also enables the production of clean synthetic fuels through processing of the flared gas. Further, the GTL products, which are clean liquid fuels with little sulfur, may provide a better market value than the conventional petroleum products produced by refining a crude oil. For instance, in 2004, Europe, Japan, etc., reduced the sulfur content in the diesel oil for cars from 500 ppm to 50 ppm and they are expected to further lower to below 10 ppm in the near future.

[6] The F-T synthetic oil is a fuel that can effectively cope with the recently reinforced...
environmental regulations from developed countries, along with the recent regulations of the Kyoto Protocol. According to Sasol's LCA study, the with little sulfur and aromatic compounds, the GTL synthetic fuel gives off less exhaust gas and nitrogen oxides and is capable of reducing the atmospheric acidification by more than 40%. Further, the emission of particulate matters (PM) can be reduced by more than 40% and the utilization of F-T synthetic oil in cars is expected to reduce the emission of greenhouse gas by at least 12% through increased thermal efficiency.

The F-T synthesis, the core process in the GTL technique, originates from the preparation of synthetic fuel from syngas by coal gasification invented by German chemists Fischer and Tropsch in 1923. The GTL process consists of the three major sub-processes of (1) reforming of natural gas, (2) F-T synthesis of syngas and (3) reforming of product. The F-T reaction which is performed at a reaction temperature of 200 to 350 °C and a pressure of 10 to 30 atm using iron and cobalt as catalyst can be described by the following four key reactions.

(a) Chain growth in F-T synthesis

CO + 2H₂ → -CH₂ - + H₂O Δ H(227 °C) = -165 kJ/mol

(b) Methanation

CO + 3H₂ → CH₄ + H₂O Δ H(227 °C) = -215 kJ/mol

(c) Water gas shift reaction

CO + H₂O ↔ CO₂ + H₂ Δ H(227 °C) = -40 kJ/mol

(d) Boudouard reaction

2CO ↔ C + CO₂ Δ H(227 °C) = -134 kJ/mol

The mechanism by which the main product, or the straight-chain hydrocarbons, is produced is mainly explained by the Schulz-Flory polymerization kinetic scheme. In the F-T process, more than 60% of the primary product has a boiling point higher than that of diesel oil. Thus, diesel oil can be produced by the following hydrocracking process and the wax component can be transformed into a high-quality lubricant base oil through the dewaxing process.

In general, the current reforming process of atmospheric residue or vacuum residue used in the refinery plant is a reliable one thanks to improvement of catalysts and processing techniques. However, for the F-T synthetic oil, further development of an adequate hydrocarbon reforming process is required, because there is a big difference in compositions and physical properties from the source material used in the refinery plant. Examples of the processes for treating the primary product of the F-T reaction include hydrocracking, dewaxing, isomerization, allylation, and so forth. The major products of the F-T reaction include naphtha/gasoline, middle distillates with a high cetane number, sulfur- and aromatic-free liquid hydrocarbons, α-olefins, oxygenates, waxes, and so forth.
For the F-T reaction, mainly iron- and cobalt-based catalysts are used. The iron-based catalysts were preferred in the past for F-T reaction. But, recently, cobalt catalysts are predominant in order to increase the production of liquid fuel or wax and to improve conversion. Iron-based catalysts are characterized in that they are the most inexpensive F-T reaction catalysts producing less methane at high temperature and having high selectivity for olefins and the product can be utilized as source material in chemical industry as light olefin or α-olefin, as well as fuel. In addition, a lot of byproducts, including alcohols, aldehydes, ketones, etc., are produced in addition to hydrocarbons. Furthermore, the iron-based catalyst mainly used in the low-temperature F-T reaction for wax production by Sasol comprises Cu and K components as cocatalyst and is produced by the precipitation using SiO₂ as binder. The Sasol's high-temperature F-T catalyst is prepared by melting magnetite, K, alumina, MgO, etc.

Disclosure of Invention

Technical Problem

Cobalt-based catalysts are more expensive than Fe catalysts. But, they have higher activity, longer lifetime and higher yield of liquid paraffin-based hydrocarbon production with less CO₂ generation. However, they can be used only at low temperature because the excessive CH₄ is produced at high temperature. Further, with the usage of expensive cobalt, the catalysts are prepared by dispersing on a stable support with a large surface area, such as alumina, silica, titania, etc. A small amount of a precious metal cocatalyst such as Pt, Ru, Re, etc., is added as cocatalyst.

At present, there are four types of F-T synthesis reactors: circulating fluidized bed reactor, fluidized bed reactor, multitubular fixed bed reactor and slurry-phase reactor. The reactor should be adequately selected considering the syngas composition and the final product, because they have different reaction characteristics. The F-T process parameters are determined by the final product. Typically, the high-temperature F-T process for producing gasoline and olefin is carried out in the fluidized bed reactor and the low-temperature F-T process for producing wax and lubricant base oil is carried out in the multitubular fixed bed reactor (MTFBR) or in the slurry-phase reactor. Mostly, linear-chain paraffins are produced by the F-T synthesis reaction, but CₙH₂₀ compounds having double bonds, α-olefins or alcohols are obtained as the byproduct from side reactions.

Typically, in order to disperse the highly expensive active components, cobalt or other activation substance is introduced to a support having a large surface area, such as alumina, silica, titania, etc., to prepare a catalyst. In the F-T reaction, a catalyst
prepared by dispersing cobalt on a single-component or multi-component support is commercially utilized. However, if the particle size of cobalt included in the support is similar, the activity of the F-T reaction much from the usage of one support to another [Applied Catalysis A 161 (1997) 59]. On the contrary, the activity of the F-T reaction is greatly affected by the dispersion and particle size of cobalt [Journal of American Chemical Society, 128 (2006) 3956]. Accordingly, a lot of attempts are being made to improve the FTS activity and stability by modifying the surface property of the supports by pretreating them with different metal components.

[24] For instance, when cobalt-supported alumina is used, the surface properties of γ-alumina may be transformed into, for example, that of boehmite because of the water produced during the reaction. As a result, the catalyst may become inactivated or thermal stability may be reduced due to the increased oxidation rate of the cobalt component support. In order to overcome this problem, there is a method of improving the stability of the catalyst by pretreating the surface of alumina using a silicon precursor [WO 2007/009680 A1].

[25] The other method of improving the activity of the F-T catalyst, there is a method of improving the stability of the catalyst by increasing the transfer rate of the compounds having a high boiling point produced during the F-T reaction, by preparing a silica-alumina catalyst having a bimodal pore structure is reported [US 2005/0107479 A1; Applied Catalysis A 292 (2005) 252]. However, the aforementioned methods are associated with the complicated processes of forming a support with a bimodal pore structure using a polymer substrate or physically mixing two alumina-silica gels prepared so as to have different pore sizes and then supporting cobalt or other active component.

[26] In case silica is used as a support, the decrease in reduction to cobalt metal and consequent reduction of activity is observed due to the strong interaction between cobalt and the support, as compared with the alumina support. It was reported that pretreating of the silica surface with zirconium or other metal is effective in overcoming this problem [EP 0167215 A2; Journal of Catalysis 185 (1999) 120].

[27] The aforesaid F-T catalysts show various specific surface areas, but the activity of the F-T reaction is known to be closely related with the particle size of the cobalt component, pore size distribution of the support and reducing tendency of the cobalt component. To improve these properties, a preparation method of the F-T catalyst by including the cobalt component through a well-known method on the support prepared through a complicated process is reported.

[28] Technical Solution
The present inventors have demonstrated to develop a support comprising silica and alumina and having a bimodal pore structure in order to solve the aforementioned problems in an economical and efficient way. As a result, they found that an alumina-silica support consisting of a predetermined proportion of Al₂O₃ and SiO₂ having double-layered, bimodal pore structure of the larger and smaller pores in which alumina is dispersed on silica. This is formed as alumina with smaller pores is dispersed mainly on silica surface forming a double layer, thereby reducing the distribution of larger pores, provides much better heat- and matter-transfer performance than the conventional unimodal support with single-sized pores. Further, as the silica surface is pre-treated by the alumina component, such chemical properties as dispersion of the activate component, electronic state, reducing property, etc., are improved, while comparing with two supports with different pore sizes are physically mixed, for a better production yield of liquid hydrocarbons attained through the F-T reaction.

Also, they discovered that a catalyst prepared using the support, particularly a catalyst including cobalt as active component, offers improved one-pass yield of carbon monoxide and hydrogen and long-term stability when used in the F-T reaction.

Accordingly, the objective of the present invention is to provide an alumina-silica support comprising SiO₂ and Al₂O₃, having a predetermined specific surface area and having smaller and larger pores. This enables the catalyst to attain a high syngas conversion with minimized byproducts and a good long-term stability for a catalyst using the same and a preparation method of liquid hydrocarbons from a syngas using the same.

Advantageous Effects

As described above, the porous alumina-silica support of the present invention having a double-layered, bimodal pore structure, in which alumina is uniformly dispersed on silica surface. This leads to superior heat- and matter-transfer performance and, thus, an F-T reaction catalyst prepared using the same provides superior one-pass yield of the reactant carbon monoxide and the support is applicable to the preparation of catalysts for the competitive design and development of a GTL process with improved long-term stability and reduced cost for removing unreacted materials.

Brief Description of the Drawings

Figure 1 shows carbon monoxide conversion and catalyst stability with time for the Fischer-Tropsch reaction performed using the catalysts prepared in Examples 1, 4, 7 and 8 and Comparative Examples 1 to 4.

Figure 2 shows specific surface area and pore size distribution of the catalysts.
prepared in Examples 4 and 8 and Comparative Example 2.

Figure 3(a) is the electron micrograph of the 20 wt% alumina-silica support prepared in Example 1 and Figure 3(b) is the electron micrograph of the 0.5 wt% Ru/20 wt% Co/20 wt% Zr/20 wt% alumina-silica catalyst prepared in Example 8.

Figure 4(a) shows the surface EDS (energy-dispersive X-ray spectroscopy) analysis result of the 20 wt% alumina-silica support prepared in Example 1 and Figure 4(b) shows the surface EDS analysis result of the 0.5 wt% Ru/20 wt% Co/20 wt% Zr/20 wt% alumina-silica catalyst prepared in Example 8.

Mode for the Invention

The present invention is characterized by a double-layered alumina-silica support comprising 1 to 80 wt% of Al$_2$O$_3$ and 20 to 99 wt% of SiO$_2$, alumina particles being dispersed on silica surface, and having a bimodal pore structure with pores of a relatively smaller size PSi and pores of a larger size PS$_2$. The pore sizes PSi and PS$_2$ being in the range:

\[ 2 \text{ nm} \leq \text{PS}_i \leq 4 \text{ nm}; \text{ and} \]

\[ 4 \text{ nm} < \text{PS}_2 \leq 20 \text{ nm}. \]

The present invention is also characterized by a preparation method of an alumina-silica support having a bimodal pore structure with pores of a smaller size PSi and pores of a larger size PS$_2$. The pore sizes PSi and PS$_2$ are being in the above range, comprising the steps of adding an aluminum alkoxide solution dissolved in an alcohol based solvent, silica gel slurry, organic carboxylic acid having a $pK_a$ value of 3.5 to 5 and water and heating at 80 to 130 °C to prepare boehmite sol-silica gel; and baking the boehmite sol-silica gel at 200 to 700 °C to prepare an alumina-silica support.

Hereunder is given a detailed description of the present invention.

Conventionally, in the F-T reaction for preparing liquid hydrocarbons from a syngas, a cobalt component or other active component is dispersed on a support having a large surface area, such as alumina, silica, titania, etc. In case only the cobalt component is added, the dispersion and reducing property of the active component decreases, resulting in decrease of catalytic activity or accelerated inactivation of the catalyst. To overcome this problem, attempts are being made to improve the activity and stability of the Fischer-Tropsch synthesis (FTS) by modifying the properties of the support through pre-treatment of the support with another component.

As for the alumina support, the water produced during the reaction may cause the change of the surface property of the γ-alumina to that of boehmite. Therefore, various methods of pretreatment with another component have been introduced to improve thermal stability of alumina. When silica is used as a support, a stronger bonding
between cobalt and the support than an alumina support is used results in the reduced reducing tendency to cobalt metal and consequently decreases the activity. To overcome this, a method is proposed to pretreat the silica surface with zirconium.

The support of the present invention comprises the components $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$, thereby solving the problems occurring when only one of the alumina and silica components are used. In addition, the bimodal pore structure attained by dispersing alumina on silica surface provides improved transfer of reaction heat and matters during the reaction as well as improving dispersion of cobalt in the process of including the active component cobalt in the support, thereby increasing FTS reaction activity. Specifically, the support has a specific surface area ranging from 150 to 400 m$^2$/g and has a bimodal pore structure with pores of a smaller size $\text{PS}_1$ ($2\text{ nm} \leq \text{PS}_1 \leq 4$ nm) and pores of a larger size $\text{PS}_2$ ($4\text{ nm} < \text{PS}_2 \leq 20$ nm). The proportion of the specific surface area $\text{Si}$ of the smaller pores to the specific surface area $\text{S}_2$ of the larger pores, or $\text{Si}/\text{S}_2$, is maintained at 0.05 to 0.5. Since the distribution of the larger pores is relatively larger, the compounds having a high boiling point may be produced during the reaction are transferred efficiently, thereby inhibiting the inactivation of the catalyst.

The support prepared in accordance with the present invention has a bimodal pore structure in which alumina is uniformly dispersed on silica pore surface. This is accomplished as only the smaller alumina pores are formed on silica pore surface as the alumina particles are uniformly dispersed as double layer, while the formation of relatively larger pores that may be formed between alumina particles is suppressed. The smaller pores are mainly due to the pores of alumina itself, while the larger pores are those of silica. Especially, the relatively larger distribution of larger pores than that of smaller pores provides superior heat- and matter-transfer performance and increased FTS reactivity due to the improved dispersion of cobalt or other active components. Various supports are known to consist of these properties. However, no support is known yet having a double-layered, bimodal pore structure in which each component is independently separated as in the present invention. Such a separated layer structure and a bimodal pore structure provides improved dispersion of cobalt or other active components and makes the control of the distribution of larger pores easier. The resultant support having a superior matter-transfer performance provides improved long-term stability of catalyst and one-pass conversion when applied to a catalyst for FTS reaction.

Typically, a catalyst prepared by baking with the metal oxides such as silica, alumina, etc., has a unimodal pore distribution with single-sized pores. In contrast, the catalyst of the present invention has a bimodal pore structure with two different pore sizes.
If the pore size of the smaller pores is smaller than 2 nm, the production of by-products such as carbon dioxide may increase because of insufficient heat- and matter-transfer performance. If the pores with a pore size larger than 100 nm exist in large amount, conversion may decrease due to the decrease of the specific surface area of the catalyst. In the present catalyst invention, the proportion of the specific surface area Si of the smaller pores of the pores size 2 to 4 nm and the specific surface area S2 of the larger pores of the pores size 4 to 10 nm, or Si/S2, is maintained at 0.05 to 0.5. The larger pores are mainly formed by silica and the smaller pores are formed by alumina. If the proportion of the specific surface area Si/S2 is smaller than 0.05, the effect resulting from the bimodal pore structure decreases and, thus, FTS reactivity also decreases. If the specific surface area Si/S2 exceeds 0.5, the silica pores are clogged by alumina, which causes the decrease of the specific surface area of the alumina-silica support, which further decreases the dispersion of cobalt or other active components and, thereby, decreases the FTS reactivity. The modification of the alumina component during the reaction, further decreases the FTS reactivity. Hence, the aforesaid range is preferred.

The support of the present invention comprises 1 to 80 wt% of Al2O3 and 20 to 99 wt% of SiO2. If the SiO2 content exceeds 99 wt%, the silica support characteristics becomes dominant, and compounds of cobalt silicate are formed easily during the pre-treatment process because of strong interaction with the main active component cobalt, thereby reduces the F-T reactivity. If the content is below 20 wt%, the alumina support property becomes dominant, and causes the decrease of thermal stability and oxidation of the cobalt component may occur easily due to the deformation of the support by the water produced during the reaction. The specific surface area of the support of the present invention is maintained in the range from 150 to 400 m2/g. If the specific surface area is smaller than 150 m2/g, the dispersion of cobalt decreases and, thus, FTS reactivity may also decreases. If it exceeds 400 m2/g, the formation of smaller pores with pore size PSi by alumina becomes dominant, so that the pores may be clogged during the process of including cobalt or other active components, resulting in the decrease of dispersion and, consequently, decrease of FTS reactivity. Hence, the aforesaid range is preferred.

Hereunder is given a detailed description of the preparation method of the alumina-silica support in accordance with the present invention.

An aluminum alkoxide solution dissolved in an alcohol based organic solvent, a silica gel slurry, an organic carboxylic acid having a pKₐ value of 3.5 to 5 and water are added and heated at 80 to 130 ºC to prepare boehmite sol-silica gel.

First, an aluminum alkoxide is dissolved in an alcohol based organic solvent to prepare an aluminum alkoxide solution.
For the alcohol based organic solvent, one having 1 to 4 carbon atoms, having a boiling point no higher than 150 °C and easy to dry is used. For example, the alcohol based organic solvent may be selected from methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol and 2-methylpropanol. Preferably, the alcohol is used in 5 to 200 mols per 1 mol of the aluminum alkoxide. If it is used less than 5 mols, it is difficult to dissolve the aluminum alkoxide with the alcohol solvent. The content in excess of 200 mols is unfavorable for the reaction efficiency and also economically.

Subsequently, to the 1 mol of the aluminum alkoxide solution, a silica gel slurry, 0.01 to 1 mol of an organic carboxylic acid having a $pK_a$ value of 3.5 to 5 and 2 to 12 mols of water are added and heating is performed to prepare boehmite sol-silica gel. Then, hydrolysis occurs rapidly and a white, amorphous aluminum hydroxide precipitate is formed in the alcohol solvent, which is peptized by the organic acid to form nano-sized boehmite sol.

The boehmite sol is an important factor affecting the crystal size and crystallinity, depending on the kind of an acid, amount of use and reaction temperature. In the present invention, a weak organic carboxylic acid having a $pK_a$ value of 3.5 to 5, for example, one selected from formic acid, acetic acid and propionic acid is used. The organic carboxylic acid is used in 0.01 to 1 mol, more preferably in the range 0.01 to 0.5 mol per 1 mol of the aluminum alkoxide. If less than 0.01 mol used the intended effect is not attained. If excess of the acid is used, the crystal size of boehmite decreases and the sol becomes transparent. As the amount of the acid increases, the aluminum hydroxide formed by the hydrolysis of the aluminum alkoxide is peptized quickly, resulting in more crystalline nuclei of boehmite and, consequently forms smaller size crystals. Accordingly, the crystal size of boehmite can be easily controlled with the input amount of the acid. Thus the physical properties of boehmite like specific surface area, porosity, etc. can be controlled easily. However, if the acid is used in excess of 1 mol, the organic carboxylic acid may form bonding with aluminum to form aluminum tricarboxylate. In addition, the use of an organic acid is advantageous over the use of an inorganic acid, because it is easily removable at relatively low drying temperature and the resultant boehmite does not undergo changes in structure or crystal phase.

The amount of the water used for the hydrolysis is maintained at minimum. It is used in 2 to 12 mols per 1 mol of the aluminum alkoxide. If it is used less than 2 mols, hydrolysis does not occur sufficiently. In excess of 12 mols used, the process of separation and recollection becomes complicated.

The silica gel is obtained by mixing silica with a solvent. The solvent may be an organic solvent commonly used in the art. In the present invention, isopropyl alcohol is used. Preferably, the solvent is used in 1 to 100 wt% per 1 wt% of silica. If it is used
less than 1 wt%, it is difficult to effectively carry out the precipitation of alumina because of inadequate dispersion of the silica. The use of the solvent in excess of 100 wt% is unfavorable in reaction efficiency and economy.

The reaction is performed at 80 to 130 °C for 1 to 48 hours. If the reaction temperature is below 80 °C, crystal growth of boehmite becomes slow, thereby resulting in the formation of impurities such as gibbsite and if it exceeds 130 °C, the boehmite crystal may become too large.

Such prepared boehmite sol-silica gel is baked at 200 to 700 °C to prepare the alumina-silica support. If the baking temperature is below 200 °C, the crystal growth of alumina is retarded and if it exceeds 700 °C, specific surface area decreases abruptly due to the change of the alumina phase. Thus, the aforesaid range is preferable in preparing the alumina-silica support by synthesizing alumina in silica-dispersed slurry phase.

The resultant support has a double layer structure with alumina dispersed on silica surface and a bimodal pore structure with both smaller and larger pores.

The present invention is characterized by a catalyst prepared using the alumina-silica support. With pores of two different sizes, the support provides superior heat- and matter-transfer performance to the conventional support having single-sized pores and thus provides better catalytic activity.

The present invention is particularly preferable for the catalyst used in the Fischer-Tropsch reaction. The active component of the catalyst may be one commonly used in the art and is not particularly limited. Specifically, at least one of the transition metal selected from cobalt (Co), zirconia (Zr), ruthenium (Ru), rhenium (Re) and platinum (Pt) may be used. The metals are used in the form of precursors, such as nitrate salt, acetate salt, chloride salt, etc.

Preferably, cobalt (Co) is used as main component and zirconia (Zr) is supported or such precious metal component as ruthenium (Ru), rhenium (Re), platinum (Pt), etc. is added to improve dispersion and the reducing property of the main component cobalt (Co) prior to supporting cobalt. The improvement of the reducibility of the active component cobalt leads to long-term performance of the catalyst improved as oxidation by the water produced during the F-T reaction is prevented. Here, the zirconia (Zr) used for the pre-treatment is 1 to 50 wt% per 100 wt% of the support. If the content of zirconia is less than 1 wt%, the effect on the dispersion of the active component cobalt is slight. If it exceeds 50 wt%, the specific surface area of the support decreases abruptly and, thereby, the dispersion of the active component cobalt decreases. The additional component added in addition to the active component is used in 0.005 to 1 wt% per 100 wt% of the support. If the content is less than 0.005 wt%, the effect of the addition is not significant. If it exceeds 1 wt%, the catalyst man-
ufacture cost increases and the selectivity for methane increases.

The proportion of the support to the active component is in the range 60-95:5-40 wt%. If the content of the active component is less than 5 wt%, the yield of liquid hydrocarbons decreases because of insufficient F-T reactivity. If it exceeds 40 wt%, the catalyst manufacture cost is too high as compared with the improvement of F-T reactivity.

The catalyst is prepared by the method commonly used in the art. Specifically, it is prepared by direct supporting, co-precipitation, etc., followed by baking. The baking is performed at 100 to 700 °C, preferably at 150 to 600 °C. If the baking temperature is below 100 °C, the solvent and the precursor component may remain in the catalyst and cause the side reactions. If it exceeds 700 °C, the particle size of the active component increases by sintering, which may result in the decrease of the dispersion of cobalt or other active component can lead to the decrease of the specific surface area of the support. Hence, it is preferable to maintain the aforesaid conditions.

The present invention is also characterized by a preparation method of liquid hydrocarbons from a syngas by the Fischer-Tropsch reaction in the presence of the catalyst. In the present invention, the F-T reaction is performed using the catalyst in a fixed bed, a fluidized bed or a slurry reactor, in the temperature range of from 200 to 700 °C, after reducing under hydrogen atmosphere. Using the reduced F-T reaction catalyst, F-T reaction is performed under a standard condition, specifically at a temperature of 300 to 500 °C, at a pressure of 30 to 60 kg/cm² and at a space velocity of 1000 to 10000 h⁻¹ although not limited thereto.

Such prepared catalyst provides an F-T reaction conversion of 25 to 99 mol% and a selectivity for hydrocarbons with five carbon atoms or more, specifically naphtha, diesel, middle distillate, heavy oil, wax, etc., of 25 to 86 mol%.

Hereinafter, the present invention is described in detail through examples. However, the following examples do not limit the present invention.

Example 1

A silica gel slurry was prepared by mixing 20 g of silica having a specific surface area of 300 m²/g and a pore size of 15 nm with 100 g of isopropyl alcohol (2-propanol). After mixing aluminum isopropoxide with the silica gel slurry, acetic acid and water were slowly added. Amorphous aluminum hydroxide was obtained by hydrolysis. The molar proportion of the reactants aluminum isopropoxide, 2-propanol, acetic acid and water was maintained at 1 : 25 : 0.035 : 3 and the content of the aluminum isopropoxide (based on alumina) was maintained at 20 wt% per 100 wt% of the silica gel slurry (based on silica). Subsequently, the silica gel slurry and the
amorphous aluminum hydroxide were heated for 20 hours at 85 °C under reflux to prepare boehmite sol-silica gel, which was baked at 500 °C for over 5 hours to prepare a 20 wt% alumina-silica support.

Approximately 5.092 g of cobalt nitrate (Co(NO$_3$)$_2$6H$_2$O) dissolved in 60 mL of deionized water was mixed with 5 g of the prepared 20 wt% alumina-silica support and stirring was performed at room temperature for over 5 hours. After the stirring, vacuum drying was performed at 70 °C using a rotary evaporator. Then, a 20 wt% Co/20 wt% Al$_2$O$_3$SiO$_2$ catalyst was prepared by drying in an oven of 100 °C for over 12 hours and baking at 400 °C for 5 hours under air atmosphere. The prepared catalyst had a specific surface area of 228 m$^2$/g and a bimodal pore structure having smaller pores with a pore size of 2 to 4 nm and larger pores with a pore size of 4 to 10 nm, the proportion of the specific surface area Si of the smaller pores to the specific surface area S$_2$ of the smaller pores, or Si/S$_2$, being 0.111.

Approximately, 0.3 g of the prepared 20 wt% Co/20 wt% Al$_2$O$_3$-SiO$_2$ catalyst was loaded in a 1/2-inch SUS-316 fixed bed reactor and reduced for 12 hours under hydrogen atmosphere (5 vol% H$_2$/He) at 400 °C prior to performing reaction. Subsequently, the reactants carbon monoxide, hydrogen, carbon dioxide and argon (internal standard) were supplied to the reactor at a fixed molar proportion of 28.4 : 57.3 : 9.3 : 5 under the condition of: reaction temperature = 220 °C; reaction pressure = 20 kg/cm$^2$; and space velocity = 2000 L/kg cat/hr. The contents of the product of the Fischer-Tropsch reaction are summarized in Table 1. The steady-state condition was obtained after around 60 hour operation and the averaged values for 10 hours at the steady-state were taken.

Reference Example

An alumina support was prepared in the same manner as in Example 1, except for excluding the silica gel slurry. The prepared alumina support had a specific surface area of 455 m$^2$/g.

Example 2

An alumina-silica support was prepared in the same manner as in Example 1, except for supporting zirconium before supporting cobalt on the alumina-silica support as active component. About 0.981 g of a zirconium precursor (ZrCl$_2$O8H$_2$O) was dissolved in 60 mL of deionized water and supported on 5 g of the 20 wt% alumina-silica support. Subsequently, 5.092 g (20 wt% per the support based on metal weight) of cobalt nitrate (Co(NO$_3$)$_2$6H$_2$O) was dissolved in 60 mL of deionized water and mixed with 5 g of the prepared 20 wt% alumina-silica support and stirring was
performed at room temperature for over 5 hours. After the stirring, vacuum drying was performed at 70 °C using a rotary evaporator. Then, a 20 wt% Co/5 wt% Zr/20 wt% Al 2O 3 -SiO 2 catalyst was prepared by drying in an oven of 100 °C for over 12 hours and baking at 400 °C for 5 hours under air atmosphere. The prepared catalyst had a specific surface area of 214 m²/g and a bimodal pore structure of smaller pores with a pore size of 2 to 4 nm and larger pores with a pore size of 4 to 10 nm, the proportion of the specific surface area Si of the smaller pores to the specific surface area S 2 of the smaller pores, or Si/S 2 , being 0.122. Fischer-Tropsch reaction was performed using the prepared catalyst.

[83] The contents of the product of the Fischer-Tropsch reaction are summarized in Table 1. The steady-state condition was obtained after around 60 hour operation and the averaged values for 10 hours at the steady-state were taken.

[84] Example 3

[85] A 20 wt% Co/20 wt% Zr/20 wt% Al 2O 3 -SiO 2 catalyst was prepared in the same manner as in Example 2, except for using 3.925 g (20 wt% per the support based on metal weight) of a zirconium precursor (ZrCl 4 O8H 2 O). Fischer-Tropsch reaction was performed using the prepared catalyst.

[86] The contents of the product of the Fischer-Tropsch reaction are summarized in Table 1. The steady-state condition was obtained after around 60 hour operation and the averaged values for 10 hours at the steady-state were taken.

[87] Example 4

[89] An alumina-silica support was prepared in the same manner as in Example 2, except for, after supporting the cobalt component, drying in an oven of 100 °C for over 12 hours. Subsequently, a 0.5 wt% Ru/20 wt% Co/5 wt% Zr/20 wt% Al 2O 3 -SiO 2 catalyst was prepared by supporting 0.065 g (0.5 wt% per the support based on metal weight) of a ruthenium precursor (RuCl 3 H 2 O) and then baking at 400 °C for 5 hours under air atmosphere. The prepared catalyst had a specific surface area of 204 m²/g and a bimodal pore structure of smaller pores with a pore size of 2 to 4 nm and larger pores with a pore size of 4 to 10 nm, the proportion of the specific surface area Si of the smaller pores to the specific surface area S 2 of the smaller pores, or Si/S 2 , being 0.135. Fischer-Tropsch reaction was performed using the prepared catalyst.

[90] The contents of the product of the Fischer-Tropsch reaction are summarized in Table 1. The steady-state condition was obtained after around 60 hour operation and the averaged values for 10 hours at the steady-state were taken.

[91] Example 5

[93]
An alumina-silica support was prepared in the same manner as in Example 2, except for, after supporting the cobalt component, drying in an oven of 100 °C for over 12 hours. Subsequently, a 0.5 wt% Ru/20 wt% Co/5 wt% Zr/20 wt% Al₂O₃-SiO₂ catalyst was prepared by supporting 0.078 g (0.5 wt% per the support based on metal weight) of a ruthenium precursor (Ru(NO)(NO₃)₂) and then baking at 400 °C for 5 hours under air atmosphere. The prepared catalyst had a specific surface area of 204 m²/g and a bimodal pore structure of smaller pores with a pore size of 2 to 4 nm and larger pores with a pore size of 4 to 10 nm, the proportion of the specific surface area Si of the smaller pores to the specific surface area S₂ of the smaller pores, or Si/S₂, being 0.135. Fischer-Tropsch reaction was performed using the prepared catalyst.

The contents of the product of the Fischer-Tropsch reaction are summarized in Table 1. The steady-state condition was obtained after around 60 hour operation and the averaged values for 10 hours at the steady-state were taken.

Example 6

A catalyst consisting 0.5 wt% Ru/20 wt% Co/10 wt% Zr/20 wt% Al₂O₃-SiO₂ was prepared in the same manner as in Example 4, except for using 1.963 g (10 wt% per the support based on metal weight) of a zirconium precursor (ZrCl₂O₈H₂O). Fischer-Tropsch reaction was performed using the prepared catalyst.

The contents of the product of the Fischer-Tropsch reaction are summarized in Table 1. The steady-state condition was obtained after around 60 hour operation and the averaged values for 10 hours at the steady-state were taken.

Example 7

A catalyst consisting 0.5 wt% Ru/20 wt% Co/15 wt% Zr/20 wt% Al₂O₃-SiO₂ catalyst was prepared in the same manner as in Example 4, except for using 2.944 g (15 wt% per the support based on metal weight) of a zirconium precursor (ZrCl₂O₈H₂O). Fischer-Tropsch reaction was performed using the prepared catalyst.

The contents of the product of the Fischer-Tropsch reaction are summarized in Table 1. The steady-state condition was obtained after around 60 hour operation and the averaged values for 10 hours at the steady-state were taken.

Example 8

A catalyst consisting 0.5 wt% Ru/20 wt% Co/20 wt% Zr/20 wt% Al₂O₃-SiO₂ catalyst was prepared in the same manner as in Example 4, except for using 3.925 g (20 wt% per the support based on metal weight) of a zirconium precursor (ZrCl₂O₈H₂O). The prepared catalyst had a specific surface area of 172 m²/g and a bimodal pore structure of smaller pores with a pore size of 2 to 4 nm and larger pores with a pore size of 4 to
10 nm, the proportion of the specific surface area $S_i$ of the smaller pores to the specific surface area $S_2$ of the smaller pores, or $S_i/S_2$, being 0.414. Fischer-Tropsch reaction was performed using the prepared catalyst.

The contents of the product of the Fischer-Tropsch reaction are summarized in Table 1. The steady-state condition was obtained after around 60 hour operation and the averaged values for 10 hours at the steady-state were taken.

Example 9

A catalyst consisting 0.5 wt% Ru/20 wt% Co/5 wt% Zr/10 wt% $\text{Al}_2\text{O}_3$-$\text{SiO}_2$ catalyst was prepared in the same manner as in Example 4, except for maintaining the content of the aluminum isopropoxide (based on alumina) at 10 wt% per 100 wt% of the silica gel slurry (based on silica). Fischer-Tropsch reaction was performed using the prepared catalyst.

The contents of the product of the Fischer-Tropsch reaction are summarized in Table 1. The steady-state condition was obtained after around 60 hour operation and the averaged values for 10 hours at the steady-state were taken.

Example 10

A catalyst consisting 0.5 wt% Ru/20 wt% Co/5 wt% Zr/30 wt% $\text{Al}_2\text{O}_3$-$\text{SiO}_2$ catalyst was prepared in the same manner as in Example 4, except for maintaining the content of the aluminum isopropoxide (based on alumina) at 30 wt% per 100 wt% of the silica gel slurry (based on silica). The prepared catalyst had a specific surface area of 218 m$^2$/g and a bimodal pore structure of smaller pores with a pore size of 2 to 4 nm and larger pores with a pore size of 4 to 10 nm, the proportion of the specific surface area $S_i$ of the smaller pores to the specific surface area $S_2$ of the smaller pores, or $S_i/S_2$, being 0.212. Fischer-Tropsch reaction was performed using the prepared catalyst.

The contents of the product of the Fischer-Tropsch reaction are summarized in Table 1. The steady-state condition was obtained after around 60 hour operation and the averaged values for 10 hours at the steady-state were taken.

Example 11

An alumina-silica support was prepared in the same manner as in Example 8, except for, after supporting 3.819 g (15 wt% based on metal weight) of the cobalt nitrate salt precursor (Co(NO$_3$)$_2$.6H$_2$O), drying in an oven of 100 °C for over 12 hours. Subsequently, a 0.5 wt% Ru/15 wt% Co/20 wt% Zr/20 wt% $\text{Al}_2\text{O}_3$-$\text{SiO}_2$ catalyst was prepared by supporting a 0.5 wt% of a ruthenium precursor (RuCl$_3$.3H$_2$O) per 100 wt% of the support and baking. The prepared catalyst was reduced with hydrogen at 400 °C for 12 hours and introduced to a slurry reactor after sealing. 300 mL of squalane was
added as solvent in the slurry reactor. After adding 5 g of the catalyst, another reduction was performed at 220 °C for over 12 hours. The reactants carbon monoxide, hydrogen, carbon dioxide and argon (internal standard) were supplied to the reactor at a fixed molar proportion of 28.4 : 57.3 : 9.3 : 5 under the condition of: reaction temperature = 220 °C; reaction pressure = 20 kg/cm²; space velocity = 2000 L/kg cat/hr; and stirring rate = 200 rpm.

The contents of the product of the Fischer-Tropsch reaction are summarized in Table 1. The steady-state condition was obtained after around 30 h operation and the averaged values for 10 hours at the steady-state were taken.

A catalyst was prepared and Fischer-Tropsch was performed in the same manner as in Example 9, except for increasing the temperature to 240 °C. The contents of the product of the Fischer-Tropsch reaction are summarized in Table 1. The steady-state condition was obtained after around 30 h operation and the averaged values for 10 hours at the steady-state were taken.

The support with 20 wt% alumina-silica was prepared in the same manner as in Example 1, except for maintaining the molar proportion of the reactants aluminum isopropoxide, 2-propanol, acetic acid and water was maintained at 1 : 25 : 0.5 : 6 and maintaining the content of the aluminum isopropoxide (based on alumina) at 20 wt% per 100 wt% of the silica gel slurry (based on silica). The prepared alumina support had a specific surface area of 350 m²/g. A 20 wt% Co/20 wt% Al₂O₃-SiO₂ catalyst was prepared using the 20 wt% alumina-silica support.

The prepared catalyst had a specific surface area of 194 m²/g and a bimodal pore structure of smaller pores with a pore size of 2 to 4 nm and larger pores with a pore size of 4 to 10 nm. The proportion of the specific surface area Si of the smaller pores to the specific surface area S₂ of the smaller pores, or Si/S₂, is 0.905. Fischer-Tropsch reaction was performed using the prepared catalyst.

The contents of the product of the Fischer-Tropsch reaction are summarized in Table 1. The steady-state condition was obtained after around 30 h operation and the averaged values for 10 hours at the steady-state were taken.

A 0.5 wt% Ru/20 wt% Co/5 wt% Zr/SiO₂ catalyst was prepared in the same manner as in Example 4, except for using silica gel alone as a support, i.e., excluding alumina.
Fischer-Tropsch reaction was performed using the prepared catalyst. 

The contents of the product of the Fischer-Tropsch reaction are summarized in Table 1. The steady-state condition was obtained after around 60 hour operation and the averaged values for 10 hours at the steady-state were taken.

Comparative Example 2

A 20 wt% Co/Al$_2$O$_3$ catalyst was prepared in the same manner as in Example 1, except for using alumina having a specific surface area or 455 m$^2$/g alone as a support. Fischer-Tropsch reaction was performed using the prepared catalyst.

The contents of the product of the Fischer-Tropsch reaction are summarized in Table 1. The steady-state condition was obtained after around 60 hour operation and the averaged values for 10 hours at the steady-state were taken.

Comparative Example 3

A 0.5 wt% Ru/20 wt% Co/5 wt% Zr/Al$_2$O$_3$ catalyst was prepared in the same manner as in Example 4, except for using alumina having a specific surface area or 455 m$^2$/g alone as a support. Fischer-Tropsch reaction was performed using the prepared catalyst.

The contents of the product of the Fischer-Tropsch reaction are summarized in Table 1. The steady-state condition was obtained after around 60 hour operation and the averaged values for 10 hours at the steady-state were taken.

Comparative Example 4

An alumina-silica support was prepared in the same manner as in Example 4, by the previously known alumina synthesis method. 10 g of silica gel having a specific surface area of 300 m$^2$/g and a pore size of 15 nm was mixed with 400 mL of deionized water to prepare the slurry of silica gel. A boehmite-silica gel support was prepared in a three-neck flask reactor maintained at 70 °C by co-precipitation, using 15.02 g of aluminum silicate (Al(NO$_3$)$_3$·$\text{9H}_2\text{O}$) as alumina precursor and 14.94 g of sodium carbonate (Na$_2$CO$_3$) as precipitant. The content of aluminum silicate (based on alumina) was maintained at 20 wt% per 100 wt% of the silica gel slurry (based on silica). The cake obtained after filtering and washing was baked at 500 °C for over 5 hours to prepare an alumina-silica support. Subsequently, a 0.5 wt% Ru/20 wt% Co/5 wt% Zr/20 wt% A12O3-SiO2 catalyst was prepared in the same manner as in Example 4. The prepared catalyst had a specific surface area of 135 m$^2$/g. Fischer-Tropsch reaction was performed using the prepared catalyst.

The contents of the product of the Fischer-Tropsch reaction are summarized in Table 1. The steady-state condition was obtained after around 60 hour operation and the
averaged values for 10 hours at the steady-state were taken.

Table 1

<table>
<thead>
<tr>
<th></th>
<th>CO conversion (carbon mol%)</th>
<th>Carbon selectivity (carbon mol%)</th>
<th>Yield of hydrocarbons C₅ or more (carbon mol%)</th>
<th>BET surface area (m²/g)</th>
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<tr>
<td>Ex. 1</td>
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</tr>
</tbody>
</table>

1) Yield of target compounds
2) Specific surface area of prepared catalysts

As shown in Table 1, the alumina-silica supports prepared in accordance with the present invention had a bimodal pore structure with larger and smaller pores. As such, when F-T reaction was performed using the supports of the present invention, the catalytic stability and one-pass yield of carbon monoxide improved as compared with the conventional F-T reaction catalysts (Comparative Examples 1 to 4).
[149] Although the same alumina-silica support was used in Comparative Example 4 as that of the present invention, specific surface area was smaller and a bimodal pore structure was not attained due to the difference in preparation method. As a result, CO conversion was smaller and reaction efficiency decreased significantly due to the accelerated inactivation of the catalyst as the pores were clogged by the compounds having a high boiling point produced during the reaction.

[150] When ruthenium was added to improve the long-term stability of the catalyst by improving the reducing property of the active component cobalt and preventing re-oxidation by the water produced during the reaction, different F-T reactivity was observed with different ruthenium precursors (Examples 4 and 5). The F-T catalytic activity was superior when the nitrate precursors was used than when the chloride salt was used. When ruthenium was not used, the inactivation of the catalyst was accelerated (Examples 2 and 3). And, the addition of zirconium, which is known to improve the dispersion of the major active component cobalt and provide a reduction state of cobalt metal suitable for the F-T reaction, showed difference in catalytic activity and stability depending on the content (Examples 6, 7 and 8). The stability of the F-T catalyst improved when the zirconium content was at least 20 wt%.

[151] In addition, the alumina content during the preparation of the alumina-silica support also affected the F-T reactivity (Examples 4, 9 and 10).

[152] Figure 1 shows carbon monoxide conversion and catalyst stability with time passage for the Fischer-Tropsch reaction performed using the catalysts prepared in Examples 1, 4, 7 and 8 and Comparative Examples 1 to 4. And, Figure 2 shows specific surface area and pore distribution of the catalysts prepared in Examples 4 and 8 and Comparative Example 2. The superiority of the Examples over the Comparative Examples can be ascertained.

[153] Figure 3(a) is the electron micrograph of the 20 wt% alumina-silica support prepared in Example 1 and Figure 3(b) is the electron micrograph of the 0.5 wt% Ru/20 wt% Co/20 wt% Zr/20 wt% alumina-silica catalyst prepared in Example 8. As can be seen from the electron micrographs, alumina is uniformly dispersed on silica surface in the form of spherical nanoparticles. Especially, Figure 3(b) shows nano-sized particles are more uniformly dispersed on silica surface through several pre-treatment processes.

[154] Figure 4 shows the surface elementary components of the catalysts provided by the present invention. Figure 4(a) shows the surface EDS analysis result of the 20 wt% alumina-silica support prepared in Example 1. In the figure, Zr was a Pt coating material for SEM analysis. Al content was 13% and Si content was 87%. When converted into Al₂O₃ and SiO₂, the contents are 21% and 79%, respectively. Figure 4(b) shows the surface EDS analysis result of the 0.5 wt% Ru/20 wt% Co/20 wt% Zr/20 wt% alumina-silica catalyst prepared in Example 8. Zr was a Pt coating material for
SEM analysis, too.

[155] It will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the spirit or scope of the invention. Other embodiments of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims.

[157] [158]
Claims

[1] A double-layered alumina-silica support comprising 1 to 80 wt% of Al₂O₃ and 20 to 99 wt% of SiO₂, alumina particles are being dispersed on silica surface, and having a bimodal pore structure with pores of a relatively smaller size PSi and pores of a larger size PS₂, the pore sizes PSi and PS₂ being in the range:
2 nm ≤ PS₁ ≤ 4 nm; and
4 nm < PS₂ ≤ 20 nm.

[2] The alumina-silica support as claimed in claim 1, wherein the support has a total specific surface area of 150 to 400 m²/g.

[3] The alumina-silica support as claimed in claim 1, wherein the proportion of the specific surface area S_i of the smaller pores having a pore size of 2 to 4 nm to the specific surface area S₂ of the larger pores having a pore size of 4 to 20 nm, or Si/S₂, is maintained at 0.05 to 0.5.

[4] The alumina-silica support as claimed in any of claims 1 to 3, which is used for the preparation of liquid hydrocarbons from a syngas by the Fischer-Tropsch reaction.

[5] A preparation method of an alumina-silica support shows a bimodal pore structure with pores of a smaller size PSi and pores of a larger size PS₂, the pore sizes PSi and PS₂ being in the range:
2 nm ≤ PS₁ ≤ 4 nm; and
4 nm < PS₂ ≤ 20 nm,
This comprises the steps of:
adding an aluminum alkoxide solution dissolved in alcohol, silica gel slurry, organic carboxylic acid having a pKₐ value of 3.5 to 5 and water and heating at 80 to 130 °C to prepare boehmite sol-silica gel; and
baking the boehmite sol-silica gel at 200 to 700 °C to prepare an alumina-silica support.

[6] The preparation method as claimed in claim 5,
wherein 0.01 to 1 mol of an organic carboxylic acid having a pKₐ value of 3.5 to 5 and 2 to 12 mols of water is used per 1 mol of the aluminum alkoxide.

[7] The preparation method as claimed in claim 5, wherein the proportion of the silica gel slurry (based on the solid content) to the aluminum alkoxide (based on alumina) is 20-99 wt% : 1-80 wt%.

[8] The preparation method as claimed in claim 5, wherein, in the support, the proportion of the specific surface area S_i of the smaller pores having a pore size of 2 to 4 nm to the specific surface area S₂ of the larger pores having a pore size of 4 to 20 nm, or Si/S₂, is maintained at 0.05 to 0.5.
[9] A catalyst using the alumina-silica support as claimed in any of claims 1 to 3.

[10] The catalyst as claimed in claim 9, wherein at least one transition metal selected from cobalt (Co), zirconia (Zr), ruthenium (Ru), rhenium (Re) and platinum (Pt) is supported.

[11] The catalyst as claimed in claim 9, wherein the support is comprised in the amount of 60 to 95 wt%.

[12] A preparation method of liquid hydrocarbons from a syngas by the Fischer-Tropsch using a catalyst in which cobalt (Co) is supported as active component on any alumina-silica support as claimed in claims 1 to 3.

[13] The preparation method of liquid hydrocarbons from a syngas as claimed in claim 12, wherein, in addition to the active component, at least one transition metal selected from cobalt (Co), zirconia (Zr), ruthenium (Ru), rhenium (Re) and platinum (Pt) is further supported.

[14] The preparation method of liquid hydrocarbons from a syngas as claimed in claim 12, wherein the support is used in 60 to 95 wt%.
【도면】

【도 1】
【도 2】

![Graph showing pore diameter distribution](image)

- Example 4
- Example 8
- Comp. 2

Pore Diameter (angstrom)

dw/d(log(D)) porevolum
[도 3]

(a)

(b)
(a)

(b)