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(71) Applicants
**Research Association for Petroleum Alternatives Development,**
**4—2 Uchikanda 1-chome,**
**Chiyoda-ku, Tokyo, Japan**
(72) Inventors
**Minotu Koikeda,**
**Yoshihiko Nishimoto,**
**Takashi Suzuki,**
**Koutaro Munemura,**
**Tetsuya Imai**
(74) Agents
**Boult, Wade and Tennant,**
**27 Furnival Street,**
**London EC4A 1PQ**

# (54) Fischer-Tropsch catalyst for the production of hydrocarbons from synthesis gas

(57) A catalyst suitable for use in the production of hydrocarbons from synthesis gas comprises an iron-containing Fischer-Tropsch catalyst, a zeolite and at least one of ruthenium, rhodium, platinum, palladium, iridium, cobalt or molybdenum. This catalyst gives a high CO conversion and hydrocarbons enriched with $C_5$+ gasoline fraction. A method of making the catalyst and a process for production of hydrocarbons using it are also provided.

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SPECIFICATION

## Fischer-Tropsch catalyst for the production of hydrocarbons from synthesis gas

This invention relates to a process for the production of hydrocarbons having a boiling point range of gasoline from mixed gases of carbon monoxide and hydrogen (which will hereinafter be referred to as "synthesis gas") and to a catalyst suitable for use in this conversion reaction.

The supply of petroleum at present is very unstable and it has been feared that a "valley" of energy will come in the last half of the 1980s to the 1990s due a deficiency of petroleum. It will therefore be desirable to practice economy in the consumption of petroleum in future and to use alternative energy sources to petroleum, such as coal, nuclear fuel and LNG. In particular, there has lately been keen interest in the development of $C_1$-chemistry to make up for the short supply of gasoline, kerosine and gas oil. The starting carbon compounds can be produced from other carbon sources than petroleum, e.g. coal and natural gas which can be found in abundance in the world.

Methods of producing hydrocarbons from coal can be classified mainly into two types; direct methods by liquefaction of coal and indirect methods through the use of synthesis gas. A number of studies have hitherto been made concerning these two methods. The liquefaction of coal is generally carried out by subjecting coal to hydrogenation under a high pressure in the presence of a solvent to obtain gaseous or liquid hydrocarbons, but this method is still under development and unfavourable economically and the quality of the products is inferior to petrolem at present. On the other hand, the indirect method, which has already been put to practical use by SASOL in South Africa, consists in converting a carbon source into hydrocarbons by making carbon monoxide and hydrogen in the presence of air, oxygen or steam and reacting in the presence of a Fischer-Tropsch catalyst. It is well known in the art that carbon sources such as coal, natural gas and asphalt which are hard to convert directly into gasoline, kerosene or gas oil are converted into mixed gases of carbon monoxide and hydrogen by established gasification techniques and that the resulting mixed gases are contacted in the presence of a suitable catalyst and converted into hydrocarbons. This has been conducted on a commercial basis, as set forth above.

For example, the Fischer-Tropsch process is known as a process for producing hydrocarbon mixtures from synthesis gas in the presence of a catalyst based on iron, cobalt, nickel, ruthenium, thorium and rhodium. However, the use of this catalyst results in reaction products of hydrocarbons including paraffins and olefins, distributed widely from methane to wax, and of various oxygen-containing compounds including alcohols and ethers and thus it is impossible to obtain selectively valuable products with a specified boiling point range. More particularly, the yield of the valuable gasoline fraction is not sufficient and the gasoline fraction is not usable as motor gasoline as it is and must be modified, for example, by catalytic reforming, since it contains a small amount of aromatic hydrocarbons or highly branched paraffins or olefins and has a low octane number.

Iron catalysts used on a commercial scale as a Fischer-Tropsch catalyst comprise a precipitated catalyst or a fused catalyst, to which copper or potassium is added to raise the selectivity thereof. These catalysts are effective for increasing waxes in the product, but do not serve to increase the yield of the gasoline fraction and the octane number. On the other hand, ruthenium catalysts are excellent in the formation of high molecular weight waxes, but give only a low conversion of carbon monoxide unless the reaction pressure is kept at more than 50 kg/cm$^2$ and they produce liquid hydrocarbons enriched with n-paraffins and a small gasoline fraction. In addition, rhodium is known as a noble metal effective for the Fischer-Tropsch synthesis, but it results in a product consisting predominantly of oxygen-containing compounds in spite of its high activity. Other noble metals such as platinum, palladium and iridium have scarcely any catalytic activity according to some reports. Nickel is a methanation catalyst rather than the Fischer-Tropsch catalyst, since it has a very high conversion activity of carbon monoxide, but the resulting hydrocarbon substantially consists of methane.

Also, a two-stage process is known wherein the synthesis gas is contacted with a carbon monoxide-reducing catalyst and the product is then contacted with a high silica zeolite catalyst of specified type in a same or different reactor, thus converting the synthesis gas into hydrocarbons containing mainly a gasoline fraction with high octane number. The carbon monoxide-reducing catalyst used therein is a methanol synthesis catalyst containing two or more of copper, zinc and chromium or an iron type Fischer-Tropsch synthesis catalyst consisting of precipated iron or fused iron. The two-stage conversion process consists in producing a gasoline fraction having a high octane number in a high yield by converting the synthesis gas into oxygen-containing compounds in the case of the methanol synthesis catalyst or converting the synthesis gas into hydrocarbons distributed widely from methane to waxes and oxygen-containing compounds in the case of the Fischer-Tropsch synthesis catalyst, and thereafter, contacting these products with a zeolite catalyst having a specified pore diameter.

Of late, processes for producing selectively hydrocarbons with a specified boiling point range from synthesis gas in one stage have been found. One of these consists in using a catalyst obtained by mixing mechanically the carbon monoxide reducing catalyst and a specified zeolite used in the two-stage process (U.S. Patent No. 4,086,262), and another consists in using a catalyst obtained by supporting a carbon monoxide reducing metal or metal oxide on a specified zeolite (U.S. Patent No. 4,157,338). In any process, the product is limited by the shape selectivity of a zeolite with specified pores as a component of the catalyst, so that products having a larger molecular size than the pore diameter are hardly formed and hydrocarbons having a smaller molecular size and boiling point range of gasoline or less can selectively be obtained. A one-stage process is a more economical process than a two-stage process because of its simplified process. However, the first one-stage process described above, using the mechanically mixed catalyst, is inferior to the two-stage process because of the catalytic defects that the conversion of carbon monoxide and the yield of gasoline are low and there is formed a large amount of methane which is useful only as a fuel gas. The other one-stage process, using the catalyst obtained by supporting a metal capable of exhibiting a Fischer-Tropsch activity on a particular zeolite, aims at subjecting the synthesis gas to a Fischer-Tropsch reaction by the metallic component in the catalytic composition to form a hydrocarbon mixture distributed from methane to waxes as an intermediate and then converting these hydrocarbons into hydrocarbons having a boiling point range of gasoline or less by the shape selectivity of a zeolite which is known to be effective for cracking waxes, e.g. ZSM-5 zeolite catalyst. The catalyst of this kind is prepared by impregnating ZSM-5 zeolite with iron or ruthenium as disclosed in Japanese Patent Application (OPI) No. 142502/1975. The former catalyst gives a relatively high conversion, but has the drawback that the conversion of carbon monoxide to carbon dioxide is increased resulting in decrease of the yield of the $C_{5+}$ gasoline fraction and the resulting hydrocarbons consist predominantly of methane. The latter catalyst gives a higher yield of $C_{5+}$ gasoline fraction than the former catalyst, but has the drawback that the activity rapidly deteriorates with the passage of time and a higher reaction pressure, e.g. more than 50 Kg/cm$^2$ is required in order to obtain $C_{5+}$ gasoline fraction effectively. This catalyst is not useful because it loses activity through heating at a temperature above 300°C in an oxidizing atmosphere and thus it cannot be regenerated.

According to the present invention there is provided a catalyst for the production of hydrocarbons from synthesis gas, which comprises an iron-containing Fischer-Tropsch catalyst, a zeolite and at least one of ruthenium, rhodium, platinum, palladium, iridium, cobalt and molybdenum. The invention also provides a process for the production of hydrocarbons from synthesis using the catalyst.

In more detail, the specified metal such as ruthenium according to the present invention is added to iron and intimately contacted therewith to suppress formation of methane, which is formed in large amounts by iron catalysts, to increase the yield of the gasoline fraction containing aromatic hydrocarbons and branched paraffins or olefins and to suppress formation of carbon dioxide as a byproduct leading to the loss of carbon. Furthermore, the conversion of carbon monoxide is held sufficiently high even at relatively low reaction pressures, e.g. 10 to 20 Kg/cm$^2$. Similar effects can be found when platinum, palladium and iridium that do not have Fischer-Tropsch activity are added. This shows that the effects of the catalyst according to the present invention are not just the sum of the effects of both the metallic components, but are the result of a synergistic effect. In this catalyst, the iron component is preferably contained in a proportion of from 5 to 80% by weight as iron oxide of the sum of the zeolite and iron oxide, and the specified metal component is preferably in a proportion of from 0.1 to 10% by weight of the sum of the zeolite and iron oxide.

It is not clear why such synthesis effects are derived by adding ruthenium or the other specified metal according to the present invention to the iron, but it will be understood from the above described results that the chemical combination of both the metals is important. Therefore, preparation of the catalyst according to the present invention should be carried out in such a manner that the chemical combination of the both proceeds sufficiently.

A process for the preparation of the catalyst and a conversion process using the same according to the present invention will now be illustrated.

The catalyst of the present invention is generally prepared by mixing intimately a zeolite, preferably a high silica zeolite and an iron-containing Fischer-Tropsch catalyst and then impregnating the mixture with a solution containing at least one metal salt selected from the group consisting of salts of ruthenium, rhodium, platinum, palladium, iridium, cobalt and molybdenum. The intimate mixing is preferably carried out by a gel mixing process or dry mixing process, which will hereinafter be illustrated in detail. The impregnated mixture can be used as a catalyst for the conversion reaction after drying, but it is preferable to calcine it at a temperature of 300—550°C for 1—20 hours so as to increase the selectivity of the catalyst. The zeolite used herein is generally a crystalline aluminosilicate in which silica and both bond to oxygen to hold a three-dimensional network structure, the ratio of oxygen atoms to the sum of aluminium atoms and silicon atoms is 2 and the negative electrovalence of $AlO_4$ tetrahedrons is used for the conversion reaction of hydrocarbons, e.g. cracking, isomerization or disproportionation. Generally, the zeolites used for the conversion reaction include erionite, offretite and ferrierite each having a pore diameter of about 5 Å, mordenite and X-zeolite or Y-zeolite of faujasite type each having a pore diameter of about 9 Å, and zeolites of ZSM-5 series having an intermediate pore diameter of 5—9 Å and an $SiO_2$ to $Al_2O_3$ ratio of at least 1, 2. Any suitable zeolites may be used for the present invention.

In addition, there can also be used other silicates which have a similar zeolite structure to that described above but whose aluminium in the aluminosilicate is partially or completely replaced by trivalent metals such as iron, chromium, vanadium, bismuth, lanthanum, cerium and titanium or by other suitable metals, and which are generally synthesized by a hydrothermal method starting from the corresponding compounds.

When using a zeolite having a pore diameter of about 5 Å, the resulting hydrocarbons are linear paraffins, olefins or light hydrocarbons of 5 of less carbon atoms, each having a molecular size of at most about 5 Å and, accordingly, such zeolite is suitable for obtaining lower olefins such as ethylene, propylene, butylene and the like, useful as petrochemical raw materials. In order to increase the yield of the gasoline fraction, however, these products should further be subjected to recycling or alkylation in known manner.

equilibrated with alkali metal cations, in particular, sodium, potassium or organo nitrogen cations. These zeolites occur often in nature, but can be provided by synthesis. They are characterized by a high adsorption capacity and sometimes are

When using a zeolite having a pore diameter of at least 9 Å, there are formed not only hydrocarbons of the gasoline fraction or less, but also the kerosene and gas oil fractions. Thus, such zeolites are used when it is required to produce jointly kerosene and gas oil.

A zeolite having a pore diameter of 5 to 9 Å is the most preferable zeolite for the purpose of obtaining a gasoline fraction in a high yield, typical of which are the ZSM series developed by Mobil Oil Corp., such as ZSM-5, ZSM-11, ZSM-12, ZSM-21, ZSM-35 and ZSM-38 with a silica to alumina ratio of at least 12. Also suitable are high silica zeolites consisting of silica-iron-alumina and giving an X-ray diffraction pattern similar to ZSM-5, developed by Shell Internationale Research. ZSM-5 type zeolites obtained by a different production process but having the same X-ray diffraction pattern as ZSM-5, and those in which a part or all of the aluminum is replaced by a trivalent metal. Preparation of the zeolite of this type is preferably carried out by subjecting a silica source, alumina source and alkali source to hydrothermal synthesis in the presence of at least one of organic amines, tetrapropylammonium salts, alcoholamines and diglycoamines and precursors thereof.

The iron-containing Fischer-Tropsch comprises precipitated iron or fused which is uniformly mixed with the above described zeolite. The precipitation iron is ordinarily prepared by adding a precipitant such as ammonia or sodium hydroxide to a solution of an iron salt such as ferric nitrate or ferrous chloride, washing the precipitate and calcining at a temperature of above 300°C. The fused iron is ordinarily prepared by adding a metal oxide as an accelerator to natural magnetite and fusing the mixture, or by fusing high purity cast iron, electrolytic iron or iron carbonyl while blowing oxygen against it to prepare artificial magnetite, to which a metal oxide as an accelerator is added, followed by fusing again. Mixing of the two components is generally carried out by a gel mixing process or dry mixing process. The gel mixing process comprises mixing and kneading previously prepared iron oxide hydrated gel with a zeolite powder or suspending a zeolite powder in a solution containing an iron salt such as iron nitrate, chloride, sulfate, carbonate or oxalate, adding an alkali such as aqueous ammonia thereto to precipitate iron oxide and thereby obtaining a uniform mixture of iron and zeolite. The dry mixing process is called "mechanically mixing process", which comprises mixing iron oxide and zeolite powder with grinding to obtain a uniform mixture. Optionally, the preparation of the iron catalyst can be carried out in the presence of copper or potassium in such an amount as used in the ordinary Fischer-Tropsch catalyst. Furthermore, alumina, silica, silica-alumina or their hydrates or natural clays or minerals can be added so as to increase the strength of the catalyst and to improve the moldability of the catalyst as far as the catalytic performance is not deteriorated.

Addition of ruthenium, rhodium, platinum, palladium, iridium, cobalt or molybdenum to the zeolite and iron is generally carried out in the form of salts. These metal salts are not particularly limited. However, ruthenium, rhodium, platinum, palladium and iridium are usually added as water-soluble halides or ammine complex salts that are readily available. Particularly, chlorides are preferably used, for example, ruthenium trichloride, rhodium trichloride, chloroplatinic acid, palladium chloride and ammonium hexachloroiridate. Organometal salts such as water-insoluble acetylacetonate salts can also be used. Cobalt is usually added as cobalt nitrate, cobalt chloride, cobalt bromide, cobale acetate, cobalt carbonate and cobalt sulfate. Molybdenum is preferably added as ammonium molybdate, but organo-salts such as acetylacetonate salt and tetrapropylmolybdenum can also used. Addition of ruthenium, rhodium, platinum, palladium, iridium, cobalt and molybdenum can be carried out to any of zeolite, iron or a mixture of zeolite and iron, but it is preferable to add it on iron or a mixture of zeolite and iron by impregnation. When ruthenium or other metals are impregnated and supported on a zeolite, grinding and mixing thereafter is required so as to bring the iron and ruthenium or other metal into close contact with each other.

A zeolite is generally synthesized in the form containing sodium, potassium or organonitrogen as cation and when using this zeolite for the conversion reaction according to the present invention, at least 50% by weight of the cation is preferably replaced by hydrogen ion, ammonium ion, alkaline earth irons or transition metal ions to increase the acidity. This may be done using the prior art ion exchange technique comprising treating the zeolite with an aqueous solution containing the cation to be exchanged. An organonitrogen cation can readily be exchanged with hydrogen ion by heating the zeolite at a temperature of 400 to 700°C to decompose and burn the organonitrogen cation. The proportion of iron and a zeolite in the catalyst is important and generally, the proportion of iron is 5 to 80% by weight as iron oxide of the sum of the zeolite and iron oxide. In addition, ruthenium, rhodium, platinum, palladium, iridium, cobalt and molybdenum are generally supported on the zeolite and iron oxide in a proportion of 0.1 to 10% by weight, preferably 0.3 to 5% by weight as metal of the sum of the zeolite and iron oxide. When such a metal is supported on the iron-containing composition, it is necessary to keep the iron in the form of an iron oxide and, accordingly, in the case of gel mixing a zeolite and iron, a hydrated iron oxide gel is adequately washed with water to remove anionic impurities from the iron salt used as the raw material, dried and calcined at a temperature of 250 to 550°C. After supporting the metal such as ruthenium, the resulting catalyst after dried can be used for a conversion reaction, but preferably, it is calcined at a temperature of 300 to 550°C for 1 to 20 hours for the purpose of increasing the selectivity of the catalyst.

The synthesis gas used a feed gas in the process of the present invention can suitably be prepared by subjecting a carbon source such as coal, natural gas, petroleum coke, shale oil, tar sand or residual oil from petroleum distillation to a prior art gasification technique, e.g. partial oxidation or steam reforming. A precursor of synthesis gas, i.e. a mixture of carbon monoxide and steam or mixture of carbon dioxide and hydrogen can also be used as the feed gas. Furthermore, a gaseous mixture containing unreacted gases, obtained by removing liquid hydrocarbons from a fluid discharged out of the reactor for the conversion reaction, can also be used as the feed gas. The mole ratio of hydrogen to carbon monoxide in the synthesis gas, depending upon the variety of a carbon source used as a starting material of gasification, is preferably 0.2 to 6.0 for the present conversion reaction. The conversion reaction according to the present invention is preferably carried out by contacting the synthesis gas with the catalyst at a temperature of 200 to 500°C, preferably 250 to 450°C under a pressure of 5 to 200 $Kg/cm^2$, preferably 10 to 50 $Kg/cm^2$ at a gas volume hourly space velocity (GHSV) of 250 to 10,000 volumes of gas at the standard temperature and pressure per volume of catalyst. The catalyst can be used in a fixed bed, fluidized bed or suspended bed. In a fixed bed or suspended bed, contacting is preferably carried out in the same contact time as the above described GHSV.

The present invention is illustrated by the following examples.

EXAMPLE 1

A high silica zeolite was prepared by the following procedures. Silica gel, sodium aluminate, caustic soda and water were mixed to give a mole ratio of $10Na_2O \cdot Al_2O_3 \cdot 46SiO_2 \cdot 1300H_2O$ to which diglycolamine ($NH_2CH_2CH_2OCH_2CH_2OH$) as an organic reagent was added in a quantity of 18 times the moles of alumina with mixing adequately, and the resultant mixture was charged in a 2000 ml stainless autoclave. When the temperature was gradually raised by means of an electric heater and the temperature reached 160°C, the mixture was heated under the spontaneous pressure for 3 days and then allowed to cool naturally. The hydrothermal reaction product was filtered by a glass filter, washed adequately with water until the pH of the washing water became about 8 and dried at 130°C for 3 hours. Analysis showed that the resulting fine powder contained 1.8% by weight of sodium and 10.0% by weight of diglycolamine and had a silica to alumina ratio of 27, and X-ray diffraction analysis showed that the product has a diffraction pattern similar to that of ZSM-5 zeolite.

Then, the high silica zeolite was subjected to the following ion exchange treatment to convert into an acid-type zeolite. 500 g of the zeolite was charged with 3000 ml of a 4N aqueous solution of ammonium chloride in a 5000 ml flask, heated gradually and boiled for 3 hours. After cooling, the zeolite was filtered, washed with water, mixed again with a fresh aqueous solution of ammonium chloride and subjected to the same treatment. This operation was carried out three times to exchange the most part of sodium in the zeolite with ammonium ion. After this ion exchange treatment, the zeolite was washed with water to remove the residual ammonium chloride, dried at 130°C for 3 hours and calcined at 550°C for 5 hours, whereby to convert the ammonium ion into hydrogen ion, to burn and remove the diglycolamine ion and to convert into hydrogen ion, and to decrease the quantity of the sodium in the zeolite to 0.01% by weight.

Mixing of the zeolite and iron was carried out by the following procedures. 150 g of the above described H-type high silica zeolite power was added to an aqueous solution containing 759.4 g of ferric nitrate in 2000 ml of water, to which 3N aqueous ammonia was added with adequate agitation until the pH of the solution became 9.0, thus precipitating the iron oxide. The resulting mixture of the zeolite and iron oxide hydrated gel was filtered, washed adequately with water until the washing water was free from nitrate ion, then dried at 130°C for 3 hours and calcined at 500°C for 3 hours in a muffle furnace. Chemical analysis showed that the thus resulting composition contained 50% by weight of the zeolite and 50% by weight of the iron oxide.

This composition was then impregnated in conventional manner with an aqueous solution of ruthenium trichloride in a quantity sufficient to give a ruthenium content of 1% by weight, dried at 130°C and calcined at 500°C for 3 hours to prepare a ruthenium-containing iron oxide-zeolite catalyst.

Using this catalyst, a synthesis gas conversion reaction was carried out in a microreactor of fixed bed and flow system under the following conditions. 4 ml of the catalyst was charged in the reactor and before the conversion reaction, it was reduced with hydrogen at a temperature of 450°C under a pressure of 20 $Kg/cm^2G$ for 8 hours and with a synthesis gas at a temperature of 325°C under 1 atm. for 8 hours. The synthesis gas is mixed gases of $H_2$ and CO with a molar $H_2/CO$ ratio of 2 and the reaction was effected under conditions: reaction temperature 320°C, reaction pressure 20 and

40 Kg/cm$^2$G, GHSV 1,000 h$^{-1}$. The reaction results are shown in Table 1.

The conversion of carbon monoxide in the synthesis gas was 78.1% under a reaction pressure of 40 Kg/cm$^2$G and 91.2% under a reaction pressure of 20 Kg/cm$^2$G. This catalyst gave a higher conversion efficiency under a lower pressure. The conversion into hydrocarbons reached about 80% while the unfavourable conversion into carbon dioxide was lower, i.e. about 20%. The resultant hydrocarbons were hydrocarbons of at most 10 carbon atoms up to the gasoline boiling point range, which contained a smaller proportion of methane than in the case of using the prior art Fischer-Tropsch synthesis catalyst and a larger proportion of $C_{5+}$ gasoline fraction, amounting to 49.2% under a reaction pressure of 20 Kg/cm$^2$G. According to detailed analysis, the composition of gasoline fraction contained 40% by weight of aromatics, 20% by weight of olefins and 40% be weight of paraffins and had an octane number of 91. This composition was a high quality fuel suitable for use as motor gasoline.

EXAMPLES 2 to 4

Using ruthenium-supported catalysts having an iron oxide content of 10, 30 and 70% by weight, prepared in an analogous manner to Example 1 except that iron oxide content, the conversion reactions of the synthesis gas were carried out to obtain results as shown in Table 1. The pretreatment of the catalyst and reaction conditions were the same as those of Example 1. The conversion efficiency of CO was increased with the increase of the iron oxide content and substantially constant when the iron oxide content was at least 50% by weight. In an iron oxide content of 10% by weight, the CO conversion was 55%, but the selectivity of CO into hydrocarbons was the highest, i.e. 86.4%. The resulting hydrocarbons contained only about 30% of unfavourable methane, which was not so increased even with the increase of the iron oxide content, and showed a high yield of $C_{5+}$ gasoline fraction as well as a high octane number, about 90.

EXAMPLE 5

Using a catalyst containing 50% by weight of iron oxide and 1% by weight of ruthenium prepared in an analogous manner to Example 1 except using a crystalline lanthanum silicate synthesized by the following procedure instead of the high silica zeolite with a silica to alumina mole ratio of 27, the conversion reaction of the synthesis gas was carried out to obtain results shown in Table 1.

The synthesis method of the crystalline lanthanum silicate is as follows: Water glass, lanthanum chloride, sodium chloride and water were mixed to give a mole ratio of

$$36NA_2O \cdot La_2O_3 \cdot 80SiO_2 \cdot 1600H_2O,$$

to which hydrochloric acid was added to adjust the pH of the solution to 9 and propylamine and propyl bromide as organic compounds were added in a quantity of 20 times the mole of $La_2O_3$ while mixing adequately, and the resultant mixture was charged in a 1000 ml stainless autoclave. This mixture was thermally treated at 160°C for 3 days with agitation, cooled, filtered, washed adequately with water until the pH of the washing water be about 8, dried at 110°C for 12 hours and then calcined at 550°C for 3 hours. The product had a crystal particle size of about 1 μm and a composition represented by a dehydrated form and omitting the organic compounds:

$$0.4Na_2O \cdot La_2O_3 \cdot 80SiO_2$$

which are substantially free from aluminium. According to the X-ray diffraction analysis, it was found that the product had a diffraction pattern substantially similar to that of the zeolite synthesized in Example 1 with a high intensity and thus the product was a crystalline lanthanum silicate. This zeolite was immersed in 1N hydrochloric acid at 80°C for 7 days, washed, filtered, dried at 110°C for 12 hours, and then combined with precipitated iron and ruthenium in a similar manner to Example 1 to prepare a catalyst. This catalyst gave a high CO conversion with decreased formation of $CO_2$ as well as a high yield of gasoline fraction containing much aromatic hydrocarbons and having a high octane number, i.e. 91. Thus, a high quality gasoline was obtained therefrom.

TABLE 1

| | Example 1 | | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|
| Catalyst Component (wt %) | | | | | | |
| Zeolite | | 50 | 90 | 70 | 30 | 50 |
| Iron as $Fe_2O_3$ | | 50 | 10 | 30 | 70 | 50 |
| Ru | | 1 | 1 | 1 | 1 | 1 |
| Reaction Condition | | | | | | |
| Temp. (°C) | 320 | 320 | 320 | 320 | 320 | 320 |
| Press. ($Kg/cm^2G$) | 20 | 40 | 20 | 20 | 20 | 20 |
| GHSV ($h^{-1}$) | 1,000 | 1,000 | 1,000 | 1,000 | 1,000 | 1,000 |
| CO Conversion (%) | 91.2 | 78.1 | 55.0 | 81.5 | 92.3 | 96.7 |
| Selectivity (%) | | | | | | |
| to $CO_2$ | 20.4 | 16.8 | 13.6 | 21.7 | 26.3 | 22.8 |
| to Hydrocarbons | 79.6 | 83.2 | 86.4 | 78.3 | 73.7 | 77.2 |
| Components of Hydrocarbons (wt %) | | | | | | |
| $C_1$ | 26.2 | 32.3 | 29.3 | 30.2 | 33.1 | 33.5 |
| $C_2$ | 7.7 | 9.6 | 6.3 | 6.9 | 10.5 | 11.2 |
| $C_3$ | 4.5 | 5.2 | 5.6 | 5.0 | 4.6 | 6.8 |
| $C_3^{=}$ | 0.7 | 0.7 | 0.3 | 0.6 | 0.6 | 0.3 |
| $C_4$ | 9.8 | 8.8 | 9.9 | 10.9 | 8.7 | 7.8 |
| $C_4^{=}$ | 1.9 | 2.2 | 0.5 | 1.0 | 1.5 | 0.7 |
| $C_{5+}$ Gasoline | 49.2 | 41.2 | 48.1 | 45.4 | 40.8 | 39.7 |
| $C_{5+}$ ON F-1 Clear* | 91 | 84 | 92 | 91 | 89 | 91 |

Note: * Octane Number according to Research Method, "Clear" = lead-free

EXAMPLES 6 and 7

To 2000 ml of an aqueous solution containing 759 g of ferric nitrate was added 5N aqueous ammonia to pH 9 and gelled. The resulting iron oxide hydrated gel was filtered, washed adequately with water until the nitrate iron was hardly detected in the washing water, dried at 130°C for 5 hours and then calcined at 500°C for 3 hours in a muffle furnace to form iron oxide.

*Example 6:* The thus obtained iron oxide powder was mixed adequately with the same H-type high silica zeolite powder as prepared in Example 1, while grinding the both, to which ruthenium trichloride in an amount corresponding to 1.0% by weight of ruthenium was then added. The mixture was allowed to stand for one day, subjected to evaporation, dried and calcined at 500°C for 3 hours to prepare a catalyst.

*Example 7:* The thus obtained iron oxide powder was impregnated with ruthenium trichloride in an amount corresponding to 1.0% by weight of ruthenium and then mixed adequately with the same H-type high silica zeolite while grinding the both to prepare another catalyst.

Using these two catalysts differing in preparation process, the conversion reactions of the synthesis gas were carried out in an analogous manner to Example 1, thus obtaining results as shown in

Table 2. Any catalysts gave a high CO conversion as well as a high selectivity. It is apparent from these results that even the mechanically mixed iron component and zeolite component give a markedly improved catalytic performance similar to the gel mixing of Example 1.

In this case, addition of ruthenium can be carried out to both the components coexistent, but addition to only the iron component is preferable for raising the selectivity to hydrocarbons and obtaining hydrocarbons enriched with $C_{5+}$ gasoline fraction and with a decreased quantity of methane. It is thus assumed that the improvement of the performance in this catalytic system is mainly due to modification of the iron-containing Fischer-Tropsch catalyst by the addition of the metallic component such as ruthenium.

EXAMPLES 8 to 10 (CONTROL)

Example 8 uses, as a catalyst, a composition comprising 50% by weight of the H-type high silica zeolite and 50% by weight of iron oxide, prepared in an analogous manner to Example 1 but containing not ruthenium, and Examples 9 and 10 use catalysts consisting of ruthenium supported on the same H-type high silica zeolite, prepared by impregnating in known manner with a solution of ruthenium trichloride in the former case and by ion exchange of ruthenium in known manner using a solution of hexammine ruthenium trichloride in the latter case.

When using the ruthenium-free catalyst of Example 8, the CO conversion was lowered and the yield of hydrocarbons was largely lowered with an increased quantity of $CO_2$. The resultant hydrocarbons contained mainly $C_4$ or lower paraffins, in particular, methane.

On the other hand, when using the iron component-free ruthenium-supported catalyst, there was found no CO conversion activity irrespective of whether calcination of the catalyst was carried out or not in Example 9, while in Example 10, there was found no CO conversion activity in the case of calcining the catalyst at 500°C for 3 hours, but the non-calcined catalyst gave a higher CO conversion, i.e. 95.2%. However, the resulting hydrocarbons contained 94.5% of methane and $C_{5+}$ gasoline fraction was scarcely recovered.

EXAMPLES 11 to 17

Using catalysts prepared in an analogous manner to Example 1 except supporting rhodium, platinum, palladium, iridium, cobalt and molybdenum instead of the ruthenium, the conversion reactions of the synthesis gas were carried out to obtain results as shown in Table 3 and 4.

*In Example 11,* the catalyst containing 1.0% by weight of rhodium supported using rhodium trichloride gave 85.9% by weight of a $C_{5+}$ gasoline fraction having a high octane number, i.e. 89 with a high CO conversion as well as a high selectivity to hydrocarbons.

*In Example 12,* the catalyst containing 1.0% by weight of ruthenium and 1.0% by weight of rhodium supported using ruthenium trichloride and rhodium trichloride gave a higher selectivity to hydrocarbons and much more improved yield of $C_{5+}$ gasoline fraction than the catalyst free from these metals.

*Example 13:* Catalyst containing 0.6% by weight of platinum supported using chloroplatinic acid.

*Example 14:* Catalyst containing 1.0% by weight of palladium supported using palladium chloride.

*Example 15:* Catalyst containing 0.6% by weight of iridium supported using ammonium hexachloroiridate.

In the conversion reaction of the synthesis gas with an $H_2$/CO mole ratio of 2, any of these catalysts gave a high CO conversion, i.e. at least 80% as well as a high selectivity to hydrocarbons, i.e. at least 77%, the hydrocarbons containing a large proportion of $C_{5+}$ gasoline fraction with a decreased quantity, i.e. about 22% of methane formed and having an octane number of 85 to 89.

It will be understood from these results that supporting of the noble metals on an iron component can give a markedly improved effect in the production of hydrocarbons from the synthesis gas.

*In Examples 16 and 17,* a catalyst containing 5.0% by weight of cobalt supported using cobalt nitrate and a catalyst containing 5.0% by weight of molybdenum supported using ammonium molybdate were respectively used and gasoline with high octane number was obtained in any case.

TABLE 2

| | Example 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|
| Catalyst Component (wt %) | | | | | |
| Zeolite | 50 | 50 | 50 | 100 | 100 |
| Iron as $Fe_2O_3$ | 50 | 50 | 50 | 0 | 0 |
| Ru | 1.0 | 1.0 | 0 | 1.0 | 1.0 |
| Reaction Condition | | | | | |
| Temp. (°C) | 320 | 320 | 320 | 320 | 320 |
| Press. (Kg/cm$^2$g) | 20 | 20 | 20 | 20 | 20 |
| GHSV (h$^{-1}$) | 1,000 | 1,000 | 1,000 | 1,000 | 1,000 |
| CO Conversion (%) | 90.9 | 86.7 | 75.8 | 0 | 95.2 |
| Selectivity (%) | | | | | |
| to $CO_2$ | 26.7 | 21.6 | 41.8 | — | 25.0 |
| to Hydrocarbons | 73.3 | 78.4 | 58.2 | — | 75.0 |
| Components of Hydrocarbons (wt %) | | | | | |
| $C_1$ | 31.2 | 23.6 | 42.6 | — | 94.5 |
| $C_2$ | 7.4 | 5.0 | 7.6 | — | 0.7 |
| $C_3$ | 5.0 | 5.6 | 15.6 | — | 1.0 |
| $C_3^=$ | 0.4 | 0.5 | 0.0 | — | 0.0 |
| $C_4$ | 10.7 | 14.0 | 20.9 | — | 1.1 |
| $C_4^=$ | 0.8 | 1.1 | 0.0 | — | 0.0 |
| $C_{5+}$ Gasoline | 44.5 | 50.2 | 13.3 | — | 2.7 |

TABLE 3

| | Example 11 | 12 | 13 | 14 | 15 |
|---|---|---|---|---|---|
| Catalyst Component (wt %) | | | | | |
| Zeolite | 50 | 50 | 50 | 50 | 50 |
| Iron as $Fe_2O_3$ | 50 | 50 | 50 | 50 | 50 |
| Metal | 1.0 (Rh) | 1.0 (Rh)<br>1.0 (Ru) | 0.6 (Pt) | 1.0 (Pd) | 0.6 (Ir) |
| Reaction Condition | | | | | |
| Temp. (°C) | 350 | 320 | 320 | 320 | 320 |
| Press. ($Kg/cm^2G$) | 40 | 40 | 20 | 20 | 20 |
| GHSV ($h^{-1}$) | 1,000 | 1,000 | 1,000 | 1,000 | 1,000 |
| CO Conversion (%) | 94.0 | 62.4 | 81.1 | 82.4 | 83.9 |
| Selectivity (%) | | | | | |
| to $CO_2$ | 6.5 | 20.4 | 21.7 | 21.4 | 19.3 |
| to Hydrocarbons | 93.5 | 79.6 | 78.3 | 78.6 | 80.7 |
| Components of Hydrocarbons (wt %) | | | | | |
| $C_1$ | 7.1 | 37.3 | 19.6 | 23.9 | 20.6 |
| $C_2$ | 2.9 | 10.5 | 5.3 | 10.9 | 14.9 |
| $C_3$ | 2.5 | 9.1 | 5.0 | 5.3 | 9.3 |
| $C_3^=$ | 0.0 | 0.0 | 0.7 | 0.7 | 0.5 |
| $C_4$ | 1.6 | 7.0 | 13.2 | 10.0 | 10.8 |
| $C_4^=$ | 0.0 | 0.0 | 1.6 | 1.6 | 1.3 |
| $C_{5+}$ Gasoline | 85.9 | 36.1 | 54.6 | 47.6 | 42.6 |
| $C_{5+}$ ON F-1 Clear | 89 | 88 | 86 | 89 | 87 |

EXAMPLE 18

Using a catalyst prepared in an analogous manner to Example 1 except that the crystalline zeolite was an H-type synthesized erionite, the conversion reaction of the synthesis gas with an $H_2/CO$ mole ratio of 2 was carried out to obtain results as shown in Table 4. Under conditions of a temperature 350°C, pressure 20 $Kg/cm^2G$ and GHSV 1,000 $h^{-1}$, the CO conversion was 29.2% and the selectivity to hydrocarbons was 65.1%. The proportion of formed methane was less than in the case of using a ruthenium-free catalyst, but the proportion of $C_{5+}$ gasoline fraction was also small, i.e. 13.8% and there were formed large amounts of lower paraffins and olefins of up to $C_2$—$C_4$. This is possible due to that the pore size of the erionite used as one catalyst component is small, that is, about 5 Å and hydrocarbons having a molecular size capable of passing through the pores are selectively formed. Of course, the $C_3$ and $C_4$ fractions containing a large amount of olefins (56%) can readily be converted into gasoline, for example, by alkylation.

EXAMPLE 19

Using a catalyst prepared in an analogous manner to Example 1 except adding to the zeolite of

Example 1 alumina sol in a quantity sufficient to give $Al_2O_3$:$Fe_2O_3$:zeolite weight ratio of 30:40:30 before precipitating with aqueous ammonia, followed by coprecipitating with iron, the conversion reaction of the synthesis gas was carried out to obtain results as shown in Table 4.

It is evident from the results that the incorporation of alumina serves to improve the activity and selectivity without deteriorating the catalytic performance.

TABLE 4

| | Example 16 | 17 | 18 | 19 |
|---|---|---|---|---|
| Catalyst Component (wt %) | | | | |
| | | | | 30 ($Al_2O_3$) |
| Zeolite | 50 | 50 | 50 | 30 |
| Iron as $Fe_2O_3$ | 50 | 50 | 50 | 40 |
| Metal | 5.0 (Co) | 5.0 (Mo) | 1.0 (Ru) | 1.0 (Ru) |
| Reaction Condition | | | | |
| Temp. (°C) | 290 | 290 | 350 | 320 |
| Press. ($Kg/cm^2G$) | 40 | 20 | 40 | 20 |
| GHSV ($h^{-1}$) | 1,000 | 1,000 | 1,000 | 1,000 |
| CO Conversion (%) | 91.4 | 75.5 | 29.2 | 78.6 |
| Selectivity (%) | | | | |
| to $CO_2$ | 24.5 | 44.0 | 34.9 | 23.2 |
| to Hydrocarbons | 75.7 | 56.0 | 65.1 | 76.8 |
| Component of Hydrocarbons (wt %) | | | | |
| $C_1$ | 40.4 | 24.1 | 34.7 | 31.3 |
| $C_2$ | 14.0 | 9.0 | 17.4 | 9.6 |
| $C_3$ | 5.3 | 5.9 | 15.0 | 5.1 |
| $C_3^=$ | 0.3 | 0.1 | 4.1 | 1.2 |
| $C_4$ | 5.4 | 8.9 | 5.6 | 11.9 |
| $C_4^=$ | 1.1 | 0.2 | 9.4 | 3.7 |
| $C_{5+}$ Gasoline | 33.5 | 51.8 | 13.8 | 37.2 |
| $C_{5+}$ ON F-1 Clear | 94 | 91 | 82 | 91 |

CLAIMS

1. A catalyst for the production of hydrocarbons from synthesis gas, which comprises an iron-containing Fischer-Tropsch catalyst, a zeolite and at least one of ruthenium, rhodium, platinum, palladium, iridium, cobalt or molybdenum.

2. A catalyst as claimed in claim 1, wherein the zeolite is erionite, offretite or ferrierite.

3. A catalyst as claimed in claim 1, wherein the zeolite is X-zeolite, Y-zeolite or mordenite.

4. A catalyst as claimed in any one of the preceding claims wherein the zeolite has a pore size of from 5 to 9 Å and a silica to alumina mole ratio of at least 12.

5. A catalyst as claimed in any one of the preceding claims wherein a part or all of the aluminum in the zeolite is replaced by at least one trivalent metal selected from the group consisting of iron, chromium, vanadium, bismuth, lanthanum, cerium and titanium.

6. A catalyst as claimed in any one of the preceding claims wherein the Fischer-Tropsch catalyst is precipitated iron or fused iron.

7. A catalyst as claimed in claim 1 substantially as hereinbefore described in any one of Examples 1 to 7 or 11 to 19.

8. A process for the production of a catalyst, which comprises mixing intimately a high silica zeolite with a Fischer-Tropsch catalyst and then impregnating the mixture with a solution containing at least one metal salt of ruthenium, rhodium, platinum, palladium, iridium, cobalt or molybdenum.

9. A process as claimed in claim 8, wherein the mixing is carried out by a gel mixing process comprising mixing and kneading previously prepared iron oxide hydrated gel with a zeolite powder.

10. A process as claimed in claim 8, wherein the mixing is carried out by a gel mixing process comprising suspending a zeolite powder in a solution containing iron nitrate, chloride, sulfate, carbonate or oxalate, adding an alkali thereto to precipitate iron oxide and thus obtaining a mixture of iron and zeolite.

11. A process as claimed in claim 8, wherein the mixing is carried out by a dry mixing process comprising mixing and grinding iron oxide and zeolite powder and thus obtaining a mixture of iron and zeolite.

12. A process as claimed in any one of claims 8 to 11 wherein the impregnated mixture, after being dried, is further subjected to calcination at a temperature of 300 to 550°C.

13. A process as claimed in any one of claims 8 to 12 wherein the high silica zeolite has a silica to alumina mole ratio of at least 12.

14. A process as claimed in any one of claims 8 to 13 wherein at least one of alumina, silica, silica-alumina or hydrates thereof is further added.

15. A process as claimed in claim 10 wherein at least one of alumina, silica, silica-alumina or hydrates thereof is further added before the precipitation of iron oxide.

16. A process as claimed in any one of claims 8 to 15 wherein the zeolite and iron salt are mixed in an iron oxide ($Fe_2O_3$) to (iron oxide + Zeolite) ratio of from 5 to 80% by weight.

17. A process as claimed in any one of claims 8 to 16 wherein the metal salt is mixed with the zeolite and iron oxide in a metal to (iron oxide + Zeolite) ratio of from 0.3 to 5% by weight.

18. A process as claimed in claim 8 substantially as hereinbefore described in any one of Examples 1 to 7 or 11 to 19.

19. A process for the production of hydrocarbons from synthesis gas, which comprises subjecting the synthesis gas to conversion reaction in the presence of a catalyst as claimed in any one of claims 1 to 7.

20. A process as claimed in claim 19 wherein the synthesis gas has a hydrogen to carbon monoxide mole ratio of from 0.2 to 6.

21. A process as claimed in claim 19 or claim 20 wherein the conversion reaction is carried out at a temperature of from 200 to 500°C, a pressure of from 5 to 200 Kg/cm$^2$ and a GHSV of from 250 to 10,000 hr$^{-1}$.

22. A process as claimed in any one of claims 19 to 21 wherein the catalyst is in a fixed bed or in a fluidized bed.

23. A process as claimed in claim 19 substantially as hereinbefore described in any one of Examples 1 to 7 or 11 to 19.

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