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(54) Process for Production of Hydrocarbons

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Abstract:

Process for production of hydrocarbons

Disclosed is a process for producing hydrocarbons by bringing synthetic gas into contact with a catalyst bed comprising a crystalline aluminosilicate and an active metal or metal compound, which comprises using a slurry bed comprising a liquid for slurry formation added therein as said catalyst bed.

Process for production of hydrocarbons

BACKGROUND OF THE INVENTION

This invention relates to a process for production of hydrocarbons from synthetic gas, more particularly to a process for production of hydrocarbons in which a slurry bed is used as the catalyst bed and the reaction can be carried out continuously.

A process for producing a mixture of various hydrocarbons by bringing synthetic gas of carbon monooxide and hydrogen into contact with a catalyst has been known in the art. For example, Japanese Patent Publication No. 39131/1983 discloses a process for producing selectively gasoline fraction directly from synthetic gas by use of a catalyst comprising a crystalline aluminosilicate and an active metal or a metal compound capable of reducing carbon monooxide such as thorium or zinc. The reaction system in this case is a system in which a fixed-bed of a catalyst is formed and synthetic gas is passed therethrough.

However, in the case of the fixed-bed system, pressure loss through the fixed-bed will be increased within a short period of time due to precipitation of free carbon

in the fixed-bed as the hydrocarbons are produced, and regeneration of the fixed-bed is required in a cycle of about 20 days. Thus, a trouble is brought about in industrial practice.

On the other hand, it is also known in the art to produce hydrocarbons by forming a slurry of fine powdery catalyst suspended in an appropriated medium oil and blowing synthetic gas into the slurry bed. This is the so called slurry system Fischer-Tropsch synthesis (F-T synthesis). As the medium oil in this case, heavy hydrocarbons formed during the reaction are generally utilized by permitting them to reside as such within the system without removing them out of the system.

In such a slurry bed, when the catalyst consists of, for example, a crystalline aluminosilicate and an active metal or metal compound as mentioned above, of the hydrocarbons formed, those having 10 or more carbon atoms will be decomposed by the crystalline aluminosilicate. Accordingly, it has been impossible to maintain the slurry bed continuously.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a process for producing hydrocarbons continuously from synthetic gas in a slurry bed by use of a catalyst comprising a crystalline aluminosilicate and an active metal or metal compound.

The present inventors have found that, as different from formation of the slurry bed in F-T synthesis of the prior art, when a slurry bed is formed by addition of a liquid for formation of slurry as described hereinafter from outside of the system, the problem as described above can

be inhibited to a great extent, whereby continuous reaction is rendered possible, to develop the process of the present invention. More specifically, the process for producing hydrocarbons of the present invention is a process for producing hydrocarbons by bringing synthetic gas into contact with a catalyst bed comprising a crystalline aluminosilicate and an active metal or metal compound, which comprises using a slurry bed comprising a liquid for slurry formation added therein as said catalyst bed.

BRIEF DESCRIPTION OF THE DRAWING

The accompanying Figure 1 is a flow sheet showing an example of the reaction apparatus to be used in practicing the process of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

First, the catalyst to be used in the process of the present invention is a mixture of a crystalline aluminosilicate and an active metal or metal compound. As the crystallin aluminosilicate, either natural product or an artificial product referred to as Zeolite may be available. For example, the ZSM-5 type zeolite having intermediate pores with pore sizes of 5 to 9 Å may preferably be employed. Its particle size should preferably be 1 to 500 μm in view of the relationship with formation of the slurry bed.

As the active metal or metal compound, there may be employed any of those capable of reducing carbon monooxide at low temperature region of 280 to 350 ^{o}C, as exemplified by Fe, Cu, Ni, Co or Fe_2O_3-K_2O-Al_2O_3 which is a catalyst for ammonia synthesis. These catalysts should preferably have particle sizes of 1 to 100 μm, more preferably of 10 to 100 μm.

The catalyst to be used in the present invention may be prepared by mixing the respective powders of the crystalline aluminosilicate and the active metal or metal compound at a weight ratio of 95 : 5 to 10 : 90, preferably of 75 : 25 to 25 : 75.

The slurry bed of the present invention is constructed by adding a liquid for slurry formation as described below to the above catalyst.

The liquid for slurry formation according to the present invention may be any compound, provided that it is a liquid compound of a macromolecular structure having heat resistance to the temperature in the reaction system, and is not decomposed by the above catalyst system. For example, an aromatic hydrocarbon, a heavy petroleum hydrocarbon and various kinds of silicone oils may preferably be used. Of the aromatic hydrocarbon, heavy petroleium hydrocarbon and various kinds of silicone oils, the aromatic hydrocarbon is most preferred.

Among aromatic hydrocarbons, naphthalene, anthracene, phenanthrene, etc. which are aromatics of poly-fused rings and substituted derivatives thereof, of which hydrogen atoms are substituted with a plurality of alkyl groups having 1 to 4 carbon atoms are preferred. These compounds may be used either singly or suitably in a combination of two or more compounds. Further, the lubricant fraction of vacuum middle distillate having a boiling point of 300 to 550°C obtained in the course of petroleum refining may also effectively be used.

The mixing ratio of the catalyst to the liquid for slurry formation may be 5 : 95 to 40 : 60 in terms of weight ratio, preferably 10 : 90 to 20 : 80. This weight ratio may be selected suitably in view of the relationship with

the reaction conditions such as the pressure in the slurry bed, the reaction rate regulated by the catalyst amount, etc.

The reaction apparatus may be any one which can be used for the slurry bed, for example, a bubble tower.

The reaction may be carried out under the conditions of a temperature of 280 to 350 °C, preferably 300 to 340 °C and a pressure of 1 to 60 Kg/cm^2, preferably 10 to 20 Kg/cm^2, and a H_2/CO molar ratio in synthetic gas of 0.1 to 5, preferably 0.5 to 2.0.

Example

First, a zeolite converted to H-form by ion-exchange (HZSM-5) was prepared as follows.

A solution comprising 7.52 g of aluminum sulfate (18 hydrate), 17.6 g of sulfuric acid (97 %), 26.3 g of tetrapropylammonium bromide and 100 ml of water is called Solution A, a solution comprising 211 g of water glass (29.0 wt. % of SiO_2, 9.4 wt. % of Na_2O, 61.6 wt. % of water) and 250 ml of water called Solution B and a solution comprising 79 g of sodium chloride and 1250 ml of water Solution C. Into Solution C were added dropwise gradually simultaneously Solution A and Solution B to be mixed therein, followed by adjustment of pH to 9.5 by addition of 6.0 g of a 50 % sulfuric acid. The mixture was then charged into a one-liter autoclave and the reaction was carried out with stirring under the self-pressure at 170 °C for 20 hours.

After the reaction mixture was cooled, the product was washed 5 times with 1.5 liter of water. Subsequently, the solid obtained by filtration was dried at 120 °C for

6 hours to obtain a crystalline silicate of 55.0 g. The product was calcined in the air at 550 °C for 6 hours to give a composition (molar ratio) of 0.8 $Na_2O \cdot Al_2O_3 \cdot 65.1\ SiO_2$.

As the next step, ion-exchange was carried out overnight at room temperature by use of 5 ml of 1 N aqueous ammonium nitrate solution per 1 g of the silicate. Then, the product was washed with pure water, dried at 120 °C for 6 hours and calcined at 550 °C for 6 hours, followed further by the same treatments to make the zeolite H-form. Further, alumina sol corresponding to 35 wt. % of alumina was added as the binder to this zeolite, and the mixture was extrusion molded and calcined in the air at 550 °C for 6 hours. Particle sizes: 1 - 10 μm.

The zeolite HZSM-5 (14.6 g) and 10.4 g of a catalyst for ammonia synthesis (Fe_2O_3-K_2O-Al_2O_3) were suspended in (A): 117.2 ml (103.8 g) of straight-run heavy light oil, (B): 117.2 ml (119 g) of dimethylnaphthalene and (C): 117.2 ml (105.4 g) of lubricant oil fraction of vacuum middle distillate, respectively, to form three kinds of slurries.

Each of these slurries was charged into the reaction apparatus as shown in the Figure 1 to carry out the reaction. In the Figurel, 1 shows a hydrogen flow-meter, 2 a carbon monooxide flow-meter and 3 a reactor, which is embedded in a sand bath 4, and the above slurry 5 is housed therein. Into the slurry 5 is blown a synthetic gas at a predetermined molar ratio through a conduit 6a. The hydrocarbons formed reach the trap 7 through a conduit 6b, wherein a part is captured, while the other being blown again into the reaction system through a conduit 6c at a predetermined recycle ratio. 8 is an off-gas flow-meter.

The reaction conditions were a temperature of 300 °C or 320oC, a pressure of 20 Kg/cm^2 or 60 Kg/cm^2, a H_2/CO molar ratio of 0.7, GHSV (Gas Hourly Space Velocity; relative to the catalyst for ammonia synthesis) of 2000, 2700 or 3000 hr^{-1}, a recycle ratio of 6, etc. as shown in Table 1.

The reaction results obtained are also listed in the Table 1.

Table 1

	Liquid for slurry formation							
	Straight-run heavy light	Dimethyl-naphthalene	Lubricant oil* fraction of vacuum middle distillate					
Reaction time (hr)	0	9.0	7.5	54	57	75	123	235
Reaction pressure (Kg/cm^2)	20	60	20	20	20	20	20	20
Reaction temperature (^oC)	300	300	300	320	300	300	300	300
H_2/CO ratio	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
GHSV (Relative to the catalyst for ammonia synthesis)	2700	2700	2700	2000	3000	2000	2000	2700
CO conversion rate (%):	The liquid decomposed during temp. elevation to give no slurry bed	78	60	60.0	56.0	55.8	59.5	80
Hydrocarbons of C_5 or higher(wt.%)		51	64	57.6	80.8	73.2	70.5	63
Aromatics/Hydrocarbons of C_5 or higher(%)		25	15	28.9	13.0	13.7	12.6	14
Distribution of hydrocarbons of C_5 or higher								
C_5		56.6	20.5	20.2	13.9	17.4	17.6	17.3
C_6		6.5	9.3	7.4	17.6	11.8	11.7	11.9
C_7		9.2	13.7	12.5	19.3	16.4	17.4	17.1
C_8		6.5	25.3	25.7	23.8	26.7	26.4	26.3
C_9		8.7	17.6	19.5	13.8	15.3	15.1	15.1
C_{10}		9.7	9.7	10.7	8.9	9.8	9.5	9.9
C_{11}^+		2.8	3.9	4.0	2.7	2.6	2.5	2.4
Composition of hydrocarbons of C_5 or higher(**)								
Paraffins					8.6			
iso-Parrafins					17.5			
Olefins					25.7			
Naphthenes					0.9			
Aromatics					13.0			
(unknown)					(34.3)			

(*): Naphthenic lubricant oil fraction, b.p. 337-544 ^oC; Viscosity (100 ^oC) 9.18 cST; Composition (ring analysis): $\%C_A$ 4.9, $\%C_N$ 40.4, $\%C_P$ 54.7, no wax.

(**): By gas chromatograph analysis

As apparently seen from the above description, according to the process of the present invention, the slurry bed can be maintained over a long term, whereby the reaction for producing hydrocarbons from synthetic gas can be carried out continuously. Accordingly, it can be applied in the field of petroleum industries attempting to procure gasoline fraction as well as various chemical industries, and its commercial value is great.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for producing hydrocarbons by bringing synthetic gas into contact with a catalyst bed comprising a crystalline aluminosilicate selected from a natural crystalline aluminosilicate and a zeolite and an active metal or metal compound capable of reducing carbon monooxide at low temperature region of 280 to 350°C, which comprises using a slurry bed comprising a liquid for slurry formation added therein as said catalyst bed.

2. The process according to claim 1, wherein said luqid for slurry formation is an armoatic hydrocarbon, a heavy petroleum hydrocarbon or a silicone oil.

3. The process for proudcing hydrocarobns according to claim 1, wherein the crystalline aluminosilicate is an intermediate pore zeolite.

4. A process according to claim 3, in which the zeolite is a ZSM-5 type zeolite having intermediate pores with pore sizes of 5 to 9 Å.

5. A process according to claim 4, in which the particle size of the zeolite is from 1 to 500 μm.

6. The process according to claim 3, wherein thea ctive metal or metal compound is Fe, Cu, Ni, Co or Fe_2O_3–K_2O–Al_2O_3 which is a catalyst for ammonia synthesis.

7. The process according to claim 6, wherein the catalyst for ammonia synthesis have particle sizes of 1 to 100 μm.

8. The process according to claim 7, wherein the catalyst for ammonia synthesis have particles sizes of 10 to 100 μm.

9. The process according ot claim 3, wherein the catalyst is prepared by mixing the respective powders of the crystalline aluminosilicate and the active metal or metal compound at a weight ratio of 95:5 to 10:90.

10. The process according to claim 9, wherein the catalyst is prepared by mixing the respective powders of the crystalline aluminosilicate and the active metal or metal compound at a weight ratio of 75:25 to 25:75.

11. The process according to claim 2, wherein said liquid for slurry formation is petroleum hydrocarbons or lubricating oil fraction.

12. The process according to claim 11, wherein said aromatic hydrocarbon is naphthalene, anthracene or phenanthrene which is aromatic of poly-fused rings and substituted derivative thereof, of which hydrogen atoms are substituted with a plurality of alkyl groups having 1 to 4 carbon atoms.

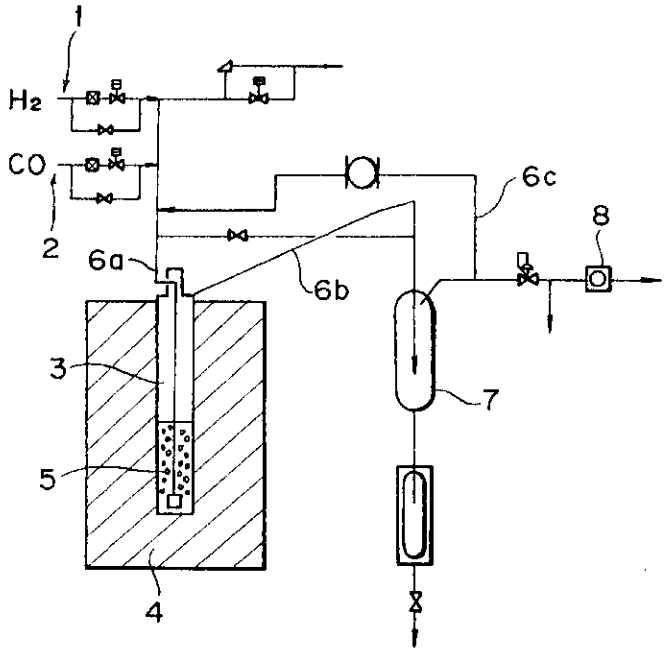
13. The process accordign to claim 3, wherein the mixing ratio of the catalyst to the liquid slurry formation is 5:95 to 40:60 in terms of weight ratio.

14. The process according to claim 13, wherein the mixing ratio of the catlayst to the liquid slurry formation is 10:90 to 20:80 in terms of weight ratio.

15. The process according to claim 3, wherein the reaciton is carried out under the conditions of a temperature of 280 to 350°C, a pressure of 1 to 60 Kg/cm^2 and a H_2/CO molar ratio in synthetic gas of 0.1 to 5.

16. The process according to claim 15, wherein the reaction is carreid out under the conditions of a temperature of 300 to 340°C, a pressure of 10 to 20 Kg/cm^2 and a H_2/CO molar ratio in synthetic gas of 0.5 to 2.0.

FIG. 1



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