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[54] **AROMATICS FROM SYNTHESIS GAS**

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[63] Continuation-in-part of Ser. No. 722,292, Sep. 10, 1976, abandoned.

[51] **Int. Cl.**[2] **C07C 1/04**
[52] **U.S. Cl.** .... **260/449.6 R**
[58] **Field of Search** .... 260/449.6 R, 449 R

[56] **References Cited**

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[57] **ABSTRACT**

Aromatic hydrocarbons useful as fuels are formed by passing a mixture of CO and hydrogen (synthesis gas) over a mixture of a copper-chromium promoted iron catalyst and a type Y mole sieve at elevated temperatures and pressures.

4 Claims, No Drawings

AROMATICS FROM SYNTHESIS GAS

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of Ser. No. 722,292, filed Sept. 10, 1976 now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to a process for the conversion of CO and hydrogen to aromatic hydrocarbon mixtures which are useful as fuels in automobile engines and the like. More particularly, this invention relates to a one-step conversion of CO and hydrogen to said aromatics in the presence of a novel catalyst composition comprising a mixture of a promoted iron catalyst defined hereinbelow and a mole sieve also defined below.

Belgian Pat. No. 828,228 (together with corresponding British Pat. No. 1,495,794 and French Pat. No. 2,268,771) describes a process for the conversion of synthesis gas to a liquid product containing a high proportion of C_5^+ olefins, isoparaffins and/or aromatics, using a CO-reduction catalyst in combination with a crystalline aluminosilicate (zeolite). This patent, however, requires that said zeolite have (1) an SiO_2/Al_2O_3 ratio of greater than 12; and, as defined by said patent, (2) a "constraint index" of 1 to 12; and (3) a "crystal framework density" of not less than 1.6 grams/cc.

By contrast, the present invention employs as the zeolite component a Y zeolite having an SiO_2/Al_2O_3 ratio of no greater than 6. Moreover, as the Belgian patent itself teaches, Y zeolites do not fall within its defined ranges of the constraint index and crustal framework density.

U.S. Pat. No. 3,972,958 and Storch et al, Fischer-Tropsch and Related Synthesis, John Wiley, New York, 1951, pp. 428–434 also bear on the subject of this invention.

SUMMARY OF THE INVENTION

In accordance with the present invention, it has now been found that synthetic fuels having a high aromatic content may be prepared in one step from synthesis gas, i.e., a mixture of CO and H_2, by contacting said gas with a novel catalyst composition comprising a mixture of a copper-chromium promoted iron catalyst and an aluminosilicate, both of which components are defined hereinbelow.

DESCRIPTION OF THE INVENTION

The process of this invention may readily be carried out by simply passing the synthesis gas over the catalyst mixture, preferably in pelleted form, in a conventional manner, e.g., in a fixed bed reactor. The synthesis gas should comprise an essentially pure mixture of CO and H_2, and especially should be free of H_2S, which would poison the catalysts of this invention.

The CO—H_2 mixture used herein is a well-known mixture of gases obtainable by conventional methods from methane, methanol, coal, or the like. The mole ratio of CO to H_2 should desirably be in the range of from about 1.5:1 to 1:1.5, and preferably should be about 1:1.

The rate at which the gas is passed over the catalyst, i.e., the gas hourly space velocity, is in the range of 1000 to 10,000, and preferably is 2000 to 4000. The temperature should be in the range of 300° to 350° C., preferably about 325° C., while the pressure is desirably 100–1500 psig, preferably about 500–750 psig.

The catalyst, as described above, comprises a physical mixture of a copper-chromium promoted iron catalyst and an aluminosilicate, i.e., a type Y mole sieve, both of which components are commercially available materials. This mixture desirably contains the two components in ratios of 0.1 to 10.0 by volume of the promoted iron catalyst to mole sieve, preferably about 1.0. The mixture is desirably used in pelleted form, as, for example, by using 20% by weight of an acid-washed inorganic oxide binder such as alumina.

The copper-chromium promoted iron catalyst component should desirably comprise about 1 to 20 wt.% copper; 1 to 20 wt.% chromium, and the remainder iron, i.e., from 60 to 98 wt.% iron. One example of this type of catalyst is a commercial preparation known as Girdler "G-8" (Girdler Catalysts, Louisville, Ky., a division of Chemtron Corporation), which contains 90 wt.% iron, 7 wt.% copper (as the oxide) and 3 wt.% chromium (as the oxide).

Alternatively, a like promoted iron catalyst component may be routinely prepared using a simple mixture of copper chromite and iron, preferably but not essentially in a 1:1 to 1:2 volume mixture.

In some cases it is desirable, but not essential, to promote the iron further with less than about 2% alkali or alkaline earth oxides in order to maximize the yield of liquids as opposed to gaseous products.

The aluminosilicate is a commercially available material, i.e., an HY mole sieve (conventionally obtained by heating an ammonium-exchanged Y mole sieve, e.g., at 450°-500° C., to drive off water and ammonia) which contains less than 0.2 wt.%, of sodium cations, generally about 0.12%, an NH_4O content of less than 4 wt.%, generally about 3.9%, (Linde Catalyst Base 33-200; Union Carbide Corp.), and has an SiO_2/Al_2O_3 ratio of less than about 6, preferably about 5.9. After pelletizing with an alumina binder, the SiO_2/Al_2O_3 ratio may decrease, for example, to about 3.3.

The product of this novel process is a liquid mixture having a boiling range of about 38° to 350° C., and typically contains about 25–50% by weight aromatics and a low concentration of carbonyl compounds, generally not more than about 10%, which mixture is useful as an automotive fuel.

EXAMPLE 1

The invention will now be illustrated by the following examples in which a series of cuts of synthesis gas was contacted with the iron-mole sieve catalyst of the invention at varying GHSV's, temperatures, pressures, and the like.

The various parameters and results are shown in Table I below. It should be noted that in a similar run using the iron catalyst alone without the mole sieve produced a mixture showing high carbonyl and low aromatic content, while a run using the mole sieve alone under the given conditions gave no product at all.

In the following runs a pelleted mixture of 14–20 mesh catalyst comprising 5 cc Girdler "G-8" copper-chromium promoted iron catalyst and 5 cc Linde "33-411" (i.e., 33-200 base catalyst plus binder) ultrastable hydrogen Y catalyst was charged into a fixed-bed reactor. A mixture of CO-H_2 was fed down over the catalyst at 75 psig. The product was condensed in an ice water condenser and the gases passed through a dry ice trap and wet test meter. The conditions and results are set forth in Table I.

TABLE I

LIQUID PRODUCTS FROM CO/H_2

Hourly Cut	Catalyst	T° C	GHSV	H_2/CO	Wt. % Yield	% By FIA* Ar.	Olef.	Sat.	BOILING RANGE ° F 5%	50%	95%
1	G-8 + HY	300	1100	1.3	5.7	40			150	275	371
2		300	1100	1.3	8.6	33			137	265	443
3		300	1100	1.1	12.4	33.0	32.6	34.4	108	283	572
4		300	2200	1.1	8.9	40.7	39.0	20.3	109	259	510
5		300	2200	1.1	7.1	25			155	236	576
6		325	2200	1.1	5.3	47.2	27.9	22.9	196	366	615
7	325	2200	1.1	7.1	24			114	258	525	
8		325	3300	1.1	2.4	50			146	302	582
9	G-8	300	1100	1.1	10.3	17.4	19.6	63.0	167	308	560
10		325	1100	1.1	8.3				157	298	544
11		300	2200	1.1	18.6	15.7	62.8	21.5	108	283	572
12		300	2200	1.1	8.6	14.6	72.6	12.8	197	321	544
13	HY	325	200	1.3	0						

*Fluorescent Indicator Analysis

EXAMPLE 2

Iron (ferric) and copper (cupric) in the ratio of 100:10 as nitrates were dissolved in water and a 5% excess of sodium carbonate was added to precipitate out the metal hydroxides. This solid was washed fairly well with water (but not until nitrate free) and 0.5 part K_2CO_3 added with enough water to make a paste. Following this the precipitate was dried in the oven, charged to the reactor and reduced in hydrogen at 450°–475° C. to yield a Fisher-Tropsch catalyst comprising 100 Fe:10 Cu:.5K_2CO_3.

This material was then mixed in a 1:1 ratio by volume with a HY mole sieve containing about 0.12 wt.% of sodium cations, an NH_4O content of about 3.9 wt.%, (Linde Catalyst Base 33-200; Union Carbide Corp.), and having an SiO_2/Al_2O_3 ratio of about 5.9, as defined above.

A similar catalyst was prepared by adding 100 parts of a copper-and-chromium promoted iron catalyst (Girdler "G-8"-Girdler Catalysts), as defined above, to 2 parts of K_2CO_3 in water to make a paste and heating the same until dry to yield a catalyst comprising 100G-8:2K_2CO_3. This material was then mixed with the HY mole sieve in a 1:1 ratio by volume.

The CO and H_2 were then passed over the resulting catalysts under the conditions set forth below in Table II, and the liquid products analyzed with the following results:

TABLE II

LIQUID PRODUCTS FROM CO/H_2

RUN	CATALYST	Press. (psig)	T° C	GHSV	H_2/CO	Yield, % C	Boiling Range ° F 5%	50%	95%	I.R. Absorbance C = O	C = C AR	Olefin Trans	Vinylidene
A	[G-8 + 2% K_2CO_3] + HY	750	325	1100	1.1	15.4	92	301	554	None	.242	Low	Low
B		750	300	2200	1.1	21.5	92	226	419	Low	.123	High	.423
1	100FE:10 Cu: 0.5 K_2CO_3 + HY	500	300	1100	1.1	24.3	135	338	633	N.A.	N.A.	N.A.	N.A.
2		350	300	1100	1.1	10.2	196	430	809	Very High	Low	High	High
3		500	300	1100	1.1	16.6	171	558	811	"	"	"	"
4		500	325	1100	1.1	27.2	116	348	771	"	"	"	"
5		500	325	2200	1.1	25.4	146	363	766	"	"	"	"

N.A. + No Aromatics

Based on the above results, in Runs 1 to 5, it will be seen that the combination of a Fisher-Tropsch catalyst, as taught by Storch, when mixed with an HY zeolite, and contracted with CO and H_2 yields, at most, insignificant traces of aromatic products as compared with the yields provided by the novel catalyst claimed herein, and as compared with a like copper-chromium-containing catalyst shown in Runs A and B above.

EXAMPLE 3

A series of seven runs, similar to those of Example 1, was carried out using varying combinations of catalyst components. As will be seen below in Table III, Run A employed no chromium, Runs B and C employed no copper, while Run D employed neither copper nor chromium. From these four runs the high carbonyl content of the resulting product confirm that both copper and chromium are needed for aromatization. That is to say, it has been found from studies made in the course of the invention that aromatization is always accompanied by low carbonyl content so that the key analysis of the liquid products is the infra red analysis for carbonyls.

The findings that both copper and chromium are needed for aromatization is confirmed in Run E, where the presence of both of these components with the zeolite-iron mixture yields aromatics.

In Run F, containing 50—50 volume ratio of iron and copper chromite, the carbonyl content of the product was relatively low, even without the zeolite. This product was analyzed further, as was the liquid from Run G which was made with all four components, i.e., copper, chromium, iron and zeolite.

In Table IV the products from Runs F and G were analyzed by fluorescent indicator analysis to give an "aromatics" fraction. Since carbonyls would also come out in this fraction, it was further analyzed by mass spectrometry to find the true aromatic content. This turned out to be 3% when no zeolite was used, compared with 19% in the four component system.

TABLE III

Dependence of Aromatization on Catalyst Composition

Catalysts reduced at 450° C for 1 hour at 1 atmos. H_2, then ½ hour at 475° C and 68 atmos H_2. Charge 1:1 H_2:CO at 50 atmos.

Run	Catalyst (Volume Ratio)*	GHSV	° C	CO Conversion	% Liquid Yield	Carbonyls (by I.R.)
A	Iron (40), YZ (40), Copper (20)	1200	300	60	27	High
B	Iron + 5% Cr_2O_3(50), YZ (50)	1200	290	81	56	High
C	Iron (40), YZ (40), Chromia (20)	1200	290	83	57	High
D	Iron (50), YZ (50)	1200	290	74	47	High
E	Iron (40), YZ (40), CuCr (20)	1800	296	95	67	Low
F	Iron (50), CuCr (50)	1200	300–325	80	40	Low
G	Iron (40), YZ (40), CuCr (20)	1200	300–325	84	31	None

*Iron = ICI 35-4, (Imperial Chemical Industries) iron catalyst; YZ = 33-411, Linde Y zeolite; Copper = T-317, Girdler copper catalyst; Chromia = CrO 101, Harshaw chromia-alumina; CuCr = G-13, Girdler copper chromite.

TABLE IV

ANALYSES OF LIQUID PRODUCTS

	Fluorescent Indicator Analysis			M.S.*.% Aromatics	
Run	% "Aromatics"	% Olefin	% Saturates	in FIA "Aromatics"	Actual % Aromatics
F	23	20	57	13	3
G	33	49	18	56	19

*M.S. = mass spectrometer

The invention claimed is:

1. The process for the preparation of a liquid aromatic fuel mixture suitable for use in automobile engines which comprises passing at an hourly space velocity of from about 1,000 to 10,000, a mixture of substantially pure CO and hydrogen at temperatures of from about 300° to 350° C., and pressures of from about 100 to 1500 psig over a catalyst comprising a physical mixture of a copper-chromium promoted iron and a type Y molecular sieve having a sodium cation content of less than about 0.2 wt.%, an SiO_2/Al_2O_3 weight ratio of less than about 6.0, and an NH_4O content of less than about 4 wt.%, wherein the mole ratio of CO to H_2 is in the range of about 1.5:1 to 1:1.5, and the ratio of iron catalyst to molecular sieve is about 0.1 to 10.0 by volume, and recovering said liquid aromatic mixture.

2. The process according to claim 1 wherein the product comprises about 25 to 50% by weight of aromatics, and has a boiling range of from about 38° to 350° C.

3. The process according to claim 1 wherein the promoted iron catalyst component comprises 1 to 20 wt.% copper, 1 to 20 wt.% chromium, and 2 to 98 wt.% iron.

4. The process according to claim 1 wherein the promoted iron catalyst component is a 1:1 to 1:2 volume ratio mixture of copper chromite and iron.

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