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PROCESS FOR THE HYDROGENOLYSIS OF LIGHT HYDROCARBONS

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This invention relates to hydrogenolysis of light hydrocarbons and more particularly to a process for the hydrogenolysis of non-cyclic aliphatic light hydrocarbons to produce gaseous reaction products comprising methane.

Use of base metals as catalysts for the hydrogenolysis of ethane under static conditions has been reported in the prior art. Cracking catalysts, which occasionally may contain platinum, are known for use in cracking heavy hydrocarbons such as gas oils boiling at 450° F. and higher. However, little is known in the prior art concerning the use of precious metal catalysts for the hydrogenolysis of light hydrocarbons.

In accordance with the present invention, a novel and meritorious process is provided for the hydrogenolysis of non-cyclic, aliphatic light saturated and/or unsaturated hydrocarbons characterized by having 2–7 carbon atoms per molecule, to produce methane. In its broader aspects, the process involves passing an admixture of hydrogen and the light hydrocarbon into contact with a platinum group metal catalyst, preferably a supported catalyst, at an elevated temperature, preferably from about 80° C.–600° C. By reason of such catalytic contacting at a temperature within the range specified, hydrogenolysis of the light hydrocarbon molecules is effected and the methane is produced. The process is of merit because achieving the following advantages: (1) effects hydrogenolysis of the light hydrocarbons efficiently and with relative ease, cracking of light hydrocarbons heretofore being attended with relative difficulty; and (2) produces a methane-containing product gas which is a good fuel gas and interchangeable with natural gas and other fuel gas.

Natural gas, which consists mainly of CH_4, is frequently used as a fuel for reasons of economy and convenience, and fuel burners using natural gas are adjusted for the proper intake of fuel and air. It has been one of the major problems of the utility gas industry to develop processes for peak-load substitutes for natural gas. Where a low molecular weight feed is available, this invention is eminently adapted for the production of CH_4.

It is also noteworthy that one of the major problems in developing a substitute for natural gas is the reduction of unsaturated hydrocarbons, since combustion of unsaturated hydrocarbons results in yellow-tipping and soot deposition. It has been difficult to reduce the unsaturated hydrocarbons to CH_4, i.e. it could be accomplished only at high temperatures with resultant high rates of carbon formation. According to this invention the unsaturated hydrocarbons react with H_2 to form CH_4 at relatively low temperatures.

The attainment of hydrogenolysis of the light hydrocarbons of this invention with relative ease was unexpected and surprising, inasmuch as heretofore cracking of such light hydrocarbons was difficult as compared with cracking of higher molecular weight hydrocarbons containing more than 7 carbons per molecule. The hydrogenolysis of hydrocarbons having from 2–4 carbon atoms

per molecule with ease in accordance with this invention was deemed to be especially an achievement.

The platinum group metals which are employed as catalysts in the present invention are preferably carried on a suitable support, for instance activated alumina, carbon, silica gel and diatomaceous earth, and any combination thereof. The platinum group metal is preferably rhodium, ruthenium, palladium, platinum and combinations of such metals, for instance ruthenium and platinum, ruthenium and palladium, and rhodium and platinum. The catalyst metal is preferably present in amount of about 0.1–5 weight percent, more preferably about 0.3–2 weight percent of the catalyst metal and support. The extent of the cracking varies with the particular catalyst used, the support, and the concentration of catalyst.

Temperatures of from about 80° C–600° C. are preferred in the present invention inasmuch as temperatures much above 600° C. tend to result in greater coke formation. Temperatures much below 80° C. should be avoided, as the hydrogenolysis will not be affected to any appreciable extent at such temperatures. The optimum temperature employed depends upon the nature and concentration of the catalyst as well as the nature and concentration of the reactants. More preferably, for the hydrogenolysis of ethane-containing gas, temperatures between 200° C. and 300° C. are employed when utilizing a rhodium catalyst, between 125° C. and 400° C. when using a ruthenium catalyst, between 300° C. and 400° C. when employing a palladium catalyst, between 210° C. and 300° C. when employing a ruthenium-platinum catalyst, and between 220° C. and 450° C. when utilizing a ruthenium-palladium catalyst.

Hydrocarbons which are subjected to the hydrogenolysis of the present invention are non-cyclic aliphatic light hydrocarbons which may be saturated and/or unsaturated, and substituted and/or unsubstituted. The number of carbon atoms per molecule of the hydrocarbon can range from 2–7. Examples of such hydrocarbons include ethane, ethylene, propane, propylene, butane, 1-butene, hexane, n-hexylene, pentane, 1-pentene, heptane, heptylene, and 2,2-dimethyl butane.

The proportion of hydrogen in the input mixture can be varied and the extent of the hydrogenolysis depends on the ratio of hydrocarbon to hydrogen in the input mixture. For greatest percentage yield of methane a quantity of hydrogen is utilized which is that stoichiometrically required for reaction with all the hydrocarbon to produce methane. Exemplary hydrogenolysis reactions of this invention utilizing ethane as hydrocarbon in reaction (1) and pentane as hydrocarbon in reaction (2) are set forth below:

$$C_2H_6+H_2\rightarrow 2CH_4 \quad (1)$$

$$C_5H_{12}+4H_2\rightarrow 5CH_4 \quad (2)$$

It is desirable when possible to use relatively pure gas streams of reactants as this normally will increase the useful life of the catalyst. In the case of fouling of the catalyst surface by coke deposition or sulfur compound adsorption, it is frequently possible to regenerate the catalyst by burning off the coke and/or sulfur by treatment with oxygen-containing gas.

Space velocities employed can range up to 20,000 standard volumes of gas per volume of catalyst per hour, preferably from about 1000 to 10,000 standard volumes gas per volume of catalyst per hour. The reaction will proceed at pressures ranging from about 0–1000 p.s.i.g.

The invention will be further illustrated by reference to the following examples.

EXAMPLE I

A mixture of 55 mol percent ethane and 45 mol percent hydrogen was metered through a rotameter into a reactor of 1" diameter containing 20 ml. of 0.5 percent Ru on 1/8" activated Al_2O_3 pellets at a temperature of about 220° C. The resultant gaseous products were analyzed by an infrared spectrophotometer and 85 mol percent methane was noted.

Other mixtures of hydrocarbon and hydrogen gases set forth in Table I, were similarly tested for hydrogenolysis with the ruthenium catalyst.

Results of these experiments are listed in Table I.

The data in Table I show that a ruthenium catalyst in the presence of hydrogen promoted the cracking of light, aliphatic, saturated hydrocarbons to form methane.

In tabulating the data in Table I, minor ingredients in inlet and outlet gases are omitted to simplify interpretation of the data. Apparent discrepancies in the determination of yields and in the analysis of total product gases present are within the limits of experimental and analytical error with the methods used.

EXAMPLE II

Using the procedure described in Example I, gas mixtures ranging from 5 mol percent ethane and 95 mol percent hydrogen to 99 mol percent ethane, 0.15 mol percent methane, 0.85 mol percent ethylene and no hydrogen were employed to determine the yield of methane at various temperatures.

Table I

CATALYTIC HYDROGENOLYSIS OF HYDROCARBONS

Catalyst: 20 ml. of 0.5% Ru on 1/8" activated Al_2O_3 pellets
Pressure: 0 p.s.i.g.
Space velocity: 2000-3000 s.c.f.h./c.f.

Hydrocarbon	Temp., ° C. Bed	Inlet, mol percent			Outlet, mol percent		
		H_2	Hydrocarbon [1]	CH_4	H_2	Hydrocarbon [1]	CH_4
Ethane	147	95	5.0	<0.02	95	4.6	0.2
	249	95	5.0	<0.02	93	2.1	4.3
	297	95	5.0	<0.02	90	0.6	11
Propane	159	97	3.5	<0.02	90	some	3.5
	246	97	3.5	<0.02	84	(2)	16

[1] As indicated in first column.
[2] Not analysed.

Table II

EFFECT OF CATALYST ON ETHANE-HYDROGEN MIXTURES

Catalyst: 0.5% Ru on 1/8" activated Al^2O^3 pellets
Conditions:
Pressure—0 p.s.i.g.
Space velocity—2000-3000 s.c.f.h./c.f.

Temp., ° C. bed	Inlet, mol percent [1]			Outlet, mol percent			Calc. temp. for 100% yield of CH_4, ° C.
	H_2	C_2H_6	CH_4	H_2	C_2H_6	CH_4	
147	95	5.0	<0.02	95	4.6	0.2	330
202	95	5.0	<0.02	94	4.6	1.5	
249	95	5.0	<0.02	93	2.1	4.3	
297	95	5.0	<0.02	90	0.6	11	
329	95	5.0	<0.02	90	<.02	12	
150	86	14	<0.02	85	14	0.09	250
202	86	14	<0.02	85	6.0	13	
253	86	14	<0.02	74	<.002	28	
400	86	14	<0.02	72	<.002	28	
217	55	45	0.03	(2)	5.0	85	220
295	55	45	0.03	(2)	<0.02	86	
355	55	45	0.03	(10)	<0.02	88	
127	18	82	0.10	(2)	86	0.56	150
154	18	82	0.10	2.0	64	36	
194	18	82	0.10	<0.02	62	40	
326	18	82	0.10	<0.02	67	35	
246	0	99	0.15	(2)	(2)	0.14	----------
295	0	99	0.15	(2)	(2)	0.12	
383	0	99	0.15	(2)	96	[3] 0.30	

[1] Small amounts of C_2H_4 present as impurities.
[2] Not analyzed.
[3] Inlet mixture includes 0.9 mol percent C_2H_4, 0.72 mol percent CO_2; outlet mixture includes 0.46 mol percent C_2H_4, trace of CO_2 1.6 mol percent CO.

From the data in Table II it is evident that in the hydrogenolysis of ethane, where the catalyst and other conditions are constant, the extent of the hydrogenolysis varies with the temperature and the concentrations of ethane and hydrogen in the input mixture.

It is also evident from Table II that the Ru catalyst in the presence of H_2 promoted the cracking of ethane in a 82 mol percent ethane–18 mol percent hydrogen input mixture, approaching maximum yield at a temperature of approximately 150° C., while no appreciable cracking occurred in ethane (99 percent) through 383° C. in the absence of hydrogen.

EXAMPLE III

Using the procedure described in Example I, a mixture of 41 mol percent C_2H_6 and 49 mol percent hydrogen was metered into a reactor containing 10 ml. of 0.5 percent Ru on 1/8" activated Al_2O_3 pellets. Similarly, mixtures of approximately the same proportions of gases were metered into other reactors containing other catalysts as listed in Table III.

Table III

EFFECT OF CATALYSTS IN PROMOTING THE HYDROGENOLYSIS OF ETHANE

[Amount of catalyst—10 ml.; space velocity—4000 s.c.f.h./c.f.; pressure—0 p.s.i.g.]

Catalyst	Temp., ° C.	Inlet mol percent[1]					Outlet mol percent				
		CO	H_2	CH_4	C_2H_4	C_2H_6	CO	H_2	CH_4	C_2H_4	C_2H_6
0.5% Ru on 1/8" activated Al_2O_3 pellets	174 197 238	0.48 0.48 0.48	49 49 49	14 14 14	1.5 1.5 1.5	41 41 41	<.06 <.06 <.06	17 10 0	47 79 86	.03 <.02 <.02	27 5.0 <.002
0.5% Rh on 1/8" activated Al_2O_3 pellets	210	0.36	49	14	1.7	41	.0060	0.6	84	<.02	<.002
0.5% Pd on 1/8" activated Al_2O_3 pellets	360 400 420	0.36 0.36 0.36	49 49 49	14 14 14	1.6 1.6 1.6	41 41 41	<.0005 <.0005 <.0005	20 30 44	40 28 19	<.02 <.02 <.02	32 38 44
1% Pt on carbon	460	0.36	49	14	1.6	41	0.34	36	30	<.02	34
0.3% Pt+0.2% Ru on 5/32" activated Al_2O_3 pellets	210	0.36	49	14	1.7	41	<.0060	6.6	79	<.02	10
0.4% Pd+0.1% Ru on 5/32" activated Al_2O_3 pellets	240 490 370	0.40 0.40 0.40	49 49 49	14 14 14	1.6 1.6 1.6	41 41 41	<.0005 .50 (2)	6.0 48 8	75 15 75	<.02 0.69 0	11 45 4.5
5% Co on 1/8" Al_2O_3 spheres	280-350	0.36	49	14	1.6	41	0.26	45	14	.03	42
Hopcalite (Ag-Mn)	160 450	0.36 0.36	49 49	14 14	1.3 1.3	42 42	0.34 0.36	48 48	15 14	1.2 0.40	42 43
Finely divided copper	370 425	0.36 0.36	49 49	14 14	1.6 1.6	42 42	0.28 0.24	47 47	14 14	<.02 <.02	43 43

[1] Inlet mixture includes 0.07 mol percent O_2.
[2] Not analyzed.

The results tabulated in Table III indicate that the ease of hydrogenolysis of ethane varies with the catalyst. Furthermore, it is evident that ruthenium and rhodium are particularly effective in promoting this reaction at relatively low temperatures, and, ruthenium in combination with platinum, and ruthenium in combination with palladium are effective catalysts.

EXAMPLE IV

Using the procedure described in Example I, mixtures of ethane and hydrogen were passed over 10 ml. of Pd catalyst. As indicated in Table IV, the metal content of catalyst was varied.

Table IV

EFFECT OF VARIATION OF CATALYST METAL CONTENT ON HYDROGENOLYSIS OF ETHANE

Catalyst—10 ml.
Conditions:
Space velocity—4000 s.c.f.h./c.f.
Pressure—0 p.s.i.g.

Catalyst	Temp., ° C.	Inlet mol percent[1]					Outlet mol percent				
		CO	H_2	CH_4	C_2H_4	C_2H_6	CO	H_2	CH_4	C_2H_4	C_2H_6
0.5% Pd on 1/8" activated Al_2O_3 pellets	360 400 420	0.36 0.36 0.36	49 49 49	14 14 14	1.6 1.6 1.6	41 41 41	<.0005 <.0005 <.0005	20 30 44	40 28 19	<.02 <.02 <.02	32 38 44
2% Pd on 1/8" activated Al_2O_3 pellets	300-390 450	0.36 0.36	49 49	14 14	1.6 1.6	41 41	0.13 0.38	2.0 36	85 24	<.02 <.02	<.0020 43
0.4% Pd+0.1% Ru on 5/32" activated Al_2O_3 pellets.	240 490 370	0.40 0.40 0.40	49 49 49	14 14 14	1.6 1.6 1.6	41 41 41	<.0005 0.50 (2)	6.0 48 8	75 15 75	<.02 0.69 0	11 45 4.5

[1] Inlet mixture includes 0.07 mol percent O_2.
[2] Not analyzed

The data in Table IV indicate that the ease of hydrogenolysis increases with the metal content of catalyst used.

The general comments in Example I regarding reported data apply also to Tables II, III and IV.

EXAMPLE V

The following experiments are set forth to show the promotion of hydrogenolysis of an unsaturated and of a branched, aliphatic light hydrocarbon to form methane by a platinum group metal catalyst in the presence of hydrogen. The experiments were conducted at 0 p.s.i.g.

Using the procedure described in Example I, approximately 41 mol percent C_2H_6, 14 mol percent CH_4, 1.5 mol percent C_2H_4, 0.48 mol percent CO, 0.07 mol percent O_2 and the balance H_2 was metered through a rotameter into a reactor containing 10 ml. of 0.5 percent Ru on 1/8" activated Al_2O_3 pellets. The space velocity was 4000 s.c.f.h./c.f. The resultant gaseous products at various temperatures were analyzed by an infrared spectrophotometer. Analysis of the outlet mixtures showed 0.03 mol percent of unreacted ethylene at 174° C. and

<0.02 mol percent of unreacted ethylene at 197° C., and considerable quantities of CH_4 were formed.

In order to pass a mixture of neohexane (99 mol percent) and hydrogen over the catalyst, hydrogen was passed through a micro-bubbler filled with neohexane and over 20 ml. of Ru on ⅛″ activated Al_2O_3 pellets. The space velocity was 4750 s.c.f.h./c.f. The inlet mixture contained 45.5 mol percent neohexane and 54.5 mol percent H_2. A gas sampling bulb in series with a cold trap was used to collect the samples for analysis. Analysis of the effluent gases showed that 4.0 mol percent CH_4 was formed at 90° C. and considerable quantities of CH_4 were formed at higher temperatures. Infrared analysis of the outlet mixtures, with temperatures ranging to 432° C., did not show the formation of reaction products other than CH_4.

No attempt was made to determine exact quantities, but considerable quantities of CH_4 were formed at temperatures below 200° C.

It will be obvious to those skilled in the art that many modifications may be made within the scope of the present invention without departing from the spirit thereof, and this invention includes all such modifications.

What is claimed is:

1. A process for the hydrogenolysis of non-cyclic aliphatic light hydrocarbons which comprises passing a gaseous admixture of hydrogen and a gas containing primarily a hydrocarbon from the group consisting of non-cyclic saturated aliphatic light hydrocarbons having from 2–4 carbon atoms per molecule, ethylene, propylene, 1-butene, and mixtures of the saturated and olefin hydrocarbons aforesaid, into contact with a supported catalyst consisting essentially of a catalytic metal selected from the group consisting of ruthenium and a ruthenium-palladium combination, supported on activated alumina, at a temperature within the range of between 197° C. and 370° C. and a space velocity from about 1000 to 10,000 standard volumes of gas per volume of catalyst per hour, the catalytic metal being present in amount of about 0.1–5 weight percent based on catalytic metal plus support, whereby hydrogenolysis of the hydrocarbon occurs to produce gaseous reaction products comprising methane.

2. A process in accordance with claim 1 wherein the gas admixed with the hydrogen contains primarily ethane.

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