86-266516/41 E17 H04 J04 STAH 21.12.81
*EP -196-732-A
STANDARD OIL CO (OHIO)
00.00.86-EP-200700 (+US-332771) (08.10.86) B01j-23/89 B01j-27/24 C07c-01/04 C07c-29/15 C10g-69/02
E(10-E4E, 10-J2D, 35) H(4-E4, 4-F2E) J(4-E4) N(1-A, 2, 6-E)

Catalyst comprising mixed oxide of alkali metal - ruthenium, copper and noble metal, opt. nitrided, for upgrading synthesis gas

C86-115215 E(BE DE FR GB IT NL)

Priority: 21.12.81(2)-US-332771-2. Related to EP--82692 (83-701259/27).

A catalyst of compsn. $A_aRu_bCu_cM'_dN_zO_x$ is claimed.
A = alkali metal;
M' = Rh, Ir, Pd and/or Pt;
a = 0.02-0.5;
b,c = 0.5-3;
d = 0.05-0.5;
z = 0-1 wt.%
x = number of O needed to fulfill valency requirements of other elements.

USE

Synthesis gas is upgraded to obtain selectivity of alkanes and alcohols, by contacting CO and H_2 in the vapour phase, at at least 250 (275-375)°C and at least 35 (35-350)kg/cm², with the catalyst; the ratio of CO:H_2 is 10:1-1:10 (3:1-1:3).

The prods. of the upgrading step may be contacted with H_2, at increased temp. and pressure, in presence of a hydrogenation catalyst, esp. of formula $G_eRu_fD_gE_hO_x$.
G = Zn and/or Cd;
D = Co and/or Ni;
E = Fe, Cu, Rh, Pd, Os, Ir and/or Pt;
e,h = 0-1;
f, g = 0.01-3.

PREFERRED UPGRADING CATALYST

The catalyst is partially reduced, and is supported on an inert carrier, pref. Al_2O_3 and/or SiO_2, alundum, clay or SiC.
A = Na, K or Rb;
a = 0.02-0.4;
b, c = 1;
d = 0.1-0.5.

EXAMPLE

50% aq. NaOH was added dropwise to a soln. of Ru chloride and $CuCl_2$, to give 0.03 mols. of each metal, and the required amt. of promoter metal, in 250ml of water, until the pH remained at 8.3-8.5. The slurry was heated near boiling

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for 30 mins., and cooled, and the pH was brought to 7.5 if necessary. The mixt. was filtered and washed, and slurrying filtration and washing were repeated until the molar ratio of Na:Ru was 0.02-0.2:1. The solid mixed oxide was dried at 125°C for 6 h., calcined in air at 350°C for 3 h., and ground to pass 140 mesh. The catalyst was then coated onto Alundum, and the coated catalyst was dried at 125°C for 16 h. and calcined at 350°C for 3 h.

The catalyst was partially reduced in H_2, and nitrided in NH_3.

A catalyst of formula $Na_aRuCuRh_{0.5}N_ZO_X$/alundum (5:95) was used in upgrading synthesis gas. The prods. were mainly alkanes and alcohols.(19pp510RKMHDwgNo0/0)

(E)ISR: FR2231416 US4235798 GB1219281 US3901827 US4085157 US3953363 GB2074164

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84-282009/45 E17 H04 J04 STAH 21.12.81
STANDARD OIL CO (OHIO) *US 4478-955-A
16.11.83-US-552556 (+US-332772) (23.10.84) C07c-01/04 C07c-27/06

Upgrading synthesis gas - by reacting with ruthenium-copper complex catalyst, opt. followed by hydrogenation

C84-119791

CLAIMED HYDROCARBON SYNTHESIS PROCESSES

(A) Hydrocarbon synthesis with increased selectivity for olefins and carboxylic acids is effected by contacting synthesis gas ($CO + H_2$), in the vapour phase, at at least 250° C and at least 500 psi. with a catalyst (I) having the formula

$$M_aA_bRuCu_cN_zO_x$$

A = Na, Li, K, Rb, Cs and/or Mg;
M = Ce, Cr, Fe, Mn, Mo and/or Zn;
a = 0.05;
b = 0.002-2;
c = 0.5-3;
z = 0.1 wt.%; and
x is the no. of O determined by the valence requirements of the other elements.

E(10-C4E, 10-E4E, 10-G2E, 10-J2C3, 10-J2D) J(4-E1, 4-E4)
H(4-E5, 4-F2E) N(1, 2, 3)

(B) Prodn. of hydrocarbons, alcohols and esters for use in fuels is effected by hydrogenating the effluent of process (A) at at least 200° C and at 250-5000 psig(500-5000 psi if (I) includes M) in the presence of a catalyst (II) of the formula

$$G_eRu_fD_gE_hO_x$$

G = Zn and/or Cd;
D = Co and/or Ni;
E = Fe, Cu, Rh, Pd, Os, Ir and/or Pt;
e = 0.1;
f = 0.01-3;
g = 0-01-3;
u = 0-1; and
x is the no . of O determined by the valence requirements of the other elements.

PREFERRED EMBODIMENTS

(A) In the prefd. (I), a is 0.1-0.5, b is 0.02-1, and c is about 1. (I) is pref. supported on an inert carrier(alumina, silica, alumina-silica, alundum, clay or SiC) and is pref.

partially reduced. The reaction is pref. effected at 275-375° C, with a $CO:H_2$ ratio of 10:1 to 1:10 (esp. 3:1 to 1:3).

(B) The prefd. (II) is $RuCePdZn_{0.4}Ox$.

WIDER DISCLOSURES

(I) is disclosed as novel(9pp1639MHDwgNo0/0)

84-269514/43 E17 H04 STAH 21.12.81
STANDARD OIL CO (OHIO) *US 4476-247-A
12.01.83-US-457330 (+US-332771) (09.10.84) B01j-23/62 B01j-27/24

Catalysts for conversion of synthesis gas - to alkane(s) and alcohol(s), contains ruthenium, copper, alkali metal and platinum gp. metal

C84-114279 Div.ex. 4377643(83-34436K/14)

CLAIMED CATALYST

A catalyst has the formula

$$(A)a(Ru)b(Cu)c(M)d(N)z(O)x$$

A = alkali metal;
M = Rh, Ir, Pd, Pt or mixts. of these;
a = 0.02-0.5;
b = 0.5-3;
c = 0.5-3;
d = 0.05-0.5;
z = 0-1 wt.%; and
x = the number of oxygens needed to satisfy the valencies of the other elements.

MORE SPECIFICALLY

A = Na, K or Rb;

E(10-E4E, 35) H(4-E5, 4-F2E) N(1-A, 2)

a = 0.02-0.4;
b and c = ca. 1 and
d= 0.1-0.5.

ADVANTAGES

The catalyst gives high selectivity ot alkanes (e.g. 23-87 %) and to alcohols (e.g. 10-60%).

PREFERRED

The catalyst may be partially reduced, and supported on an inert carrier such as alumina, silica, alumina-silica, Alundum, clay or silicon carbide.

The parent specification relates to a process for conversion of synthesis gas to alkanes and alcohols using these catalysts at temps. of at least 250° C and 500 psi.(6pp513MH DwgNo0/0)

83-701259/27 A41 E19 H04 J04 STAH 21.12.81
STANDARD OIL CO (OHIO) *EP --82-692-A
21.12.81-US-332772 (+US-332771) (29.06.83) B01J-23/89 B01J-27/24 C07C-01/04 C07C-27/20 C07C-29/15 C07C-51/10

Copper based multielement oxide catalyst - for conversion of synthesis gas to fuel mixt.

C83-062388 D/S: BE DE FR GB IT LI

Processes and catalysts are claimed for (A) upgrading synthesis gas to hydrocarbons, alcohols and esters for fuels, and (B) upgrading synthesis gas with selectivity for alkanes and alcohols.

Process (A) comprises (a) converting synthesis gas with selectivity for olefins and carboxylic acids over a catalyst (I), and (b) contacting the hydrocarbon and oxygenate conversion products with a hydrogenation catalyst (III).

Process (B) comprises converting synthesis gas with selectivity for alkanes and alcohols over a catalyst (II), opt. followed by contacting the conversion product with a hydrogenation catalyst.

Catalysts (I) and (II) are claimed per se.

DETAILS

Catalyst (I) is of the formula $M_aA_bRuCu_cN_zO_x$ (where A is alkali(ne earth) metal; M is Ce, Cr, Fe, Mn, Mo, Th and/or Zn; a is 0-0.5, esp. 0.1-0.5, b is 0.002-2, esp. 0.02-1; c is 0.5-3, esp. 1; z is 0-1 wt. %; and x is the number of oxygens needed to fulfil the valency requirements of the other elements). The catalyst is pref. partially reduced and may be supported on an inert carrier, esp. Al_2O_3, SiO_2, Al_2O_3 -SiO_2, alundum, clay or SiC. Catalyst (II) is of the formula $A'_{a'}Ru_{b'}Cu_{c'}M'_dN_z O_x$ (where A' is alkali metal, esp. Na, K or Rb; M' is Rh, Ir, Pd and/or Pt; a' is 0.02-0.5, esp. 0.02-0.4; b' and c' are 0.5-3, esp. 1; d is 0.05-0.5, esp. 0.1-5; z' is 0-1 wt. %; and x is the number of oxygens needed to fulfil the requirements of the other elements). This catalyst is also pref. partially reduced and may be supported on an inert carrier (as with I).

Process conditions for step (a) of (A) and for (B) are ≥ 250 (pref. 275-375)°C and 500-5000 (pref. 500-1500) psi, a GHSV of 100-10000 (pref. 500-6000) and a $CO:H_2$ ratio of 10:1 to 1:10 (pref. 3:1 to 1:3). Reaction time is 10-200 (pref. 15-100) secs.

The hydrogenation step is pref. effected at 150-450°C and 250-5000 psig, using a catalyst (III) of the formula

A(1-D13) E(10-E4E, 10-G2H, 10-C4J, 10-C4K, 10-J2D, 33-A, 34, 35) H(4-E5, 4-F2E) J(4-E1, 4-E4) N(1-A, 1-B, 2,3)

$G_eRu_fD_gE_hO_x$ (where G is Zn and/or Cd; D is Co and/or Ni; E is Fe, Cu, Rh, Pd, Os, Ir and/or Pt; e is 0-1; f is 0.01-3; g is 0.01-3; h is 0-1; and x is the number of oxygens needed to fulfil the valancy requirements of the other elements). A prefd. catalyst (III) is $RuCoPdZn_{0.4}O_x$ (34pp920DwgNo0/0).
(E) No Search Report.

34436 K/14 E17 H04 (H06) STAH 21.12.81
STANDARD OIL CO (OHIO) *US 4377-643
21.12.81-US-332771 (22.03.83) C07c-01/04 C07c-27/06

Synthesis gas conversion to alkane(s) and alcohol(s) - using catalyst contg. ruthenium, copper, alkali metal and platinum-gp. metal

C83-033644 Conversion of synthesis gas to alkanes and alcohols is effected at ≥ 250°C and ≥ 500 psi and in the presence of a catalyst of formula:

$$(A)_a(Ru)_b(Cu)_c(M)_d(N)_z(O)_x$$

(where A is alkali metal; M is Rh, Ir, Pd and/or Pt; a = 0.02-0.5; b = 0.5-3; c = 0.5-3; d = 0.05-0.5; z corresponds to a N content of 0-1 wt. % ; and x is the no. of oxygens needed to satisfy the valences of the other elements).

ADVANTAGES

High selectivities for alkanes (e.g. 23-87%) and alcohols (e.g. 10-60%) can be achieved.

DETAILS

Prefd. catalysts are those where A is Na, K or Rb, a = 0.02-0.4, b = 1, c = 1 and d = 0.1-0.5. The catalyst may be partially reduced and/or supported on an inert carrier, e.g. Al_2O_3, SiO_2, SiO_2-Al_2O_3, alundum, clay or SiC.

The synthesis gas may have a CO:H_2 ratio of 10:1 to 1:10 (pref. 3:1 to 1:3). The reaction is pref. effected at 275-375°C and 500-5000 psi.

The prods. can be catalytically hydrogenated to remove by-products (alkenes, aldehydes, acids, etc.), thereby producing an alkane/alcohol mixt. suitable for use as a fuel. The hydrogenation catalyst is pref. of formula $(G)_e(Ru)_f(D)_g(E)_h(O)_x$ (where G is Zn and/or Cd; D is Co and/or Ni; E is Fe, Cu, Rh, Pd, Os, Ir and/or Pt; e = 0-1; f = 0.01-3; g = 0.01-3; h = 0-1).(6pp367).

E(10-E4E, 10-J2D) H(4-E5) N(1-A, 2)