

86-266516/41 E17 H04 J04 STAII 21.12.81  
 STANDARD OIL CO (OHIO) \*EP -196-732-A  
 00.00.86-EP-200700 (+US-332771) (08.10.86) B01i-23/89 B01j-  
 27/24 C07c-01/04 C07c-29/15 C10g-69/02  
 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<sub>2</sub> in the vapour phase,  
 at at least 250 (275-375)°C and at least 35 (35-350)kg/cm<sup>2</sup>.

E(10-E4E, 10-J2D, 35) H(4-E4, 4-F2E) J(4-E4) N(1-A, 2, 6-E)

with the catalyst; the ratio of CO:H<sub>2</sub> is 10:1-1:10 (3:1-1:3).

The prods. of the upgrading step may be contacted with  
 H<sub>2</sub>, at increased temp. and pressure, in presence of a hydro-  
 genation 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<sub>2</sub>O<sub>3</sub> and/or SiO<sub>2</sub>, 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 chlor-  
 ide and CuCl<sub>2</sub>, 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  
 EP-196732-A+

for 30 mins., and cooled, and the pH was brought to 7.5 if necessary. The mixt. was filtered and washed, and slurry-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 nitrified in  $NH_3$ .

A catalyst of formula  $Na_aRuCuRh_{0.5}N_2O_x$ /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

EP-196732-A

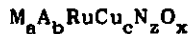
84-282009/45 E17 H04 J04 STA# 21.12.81  
 STANDARD OIL CO (OHIO) \*US 4478-955-A  
 16.11.83-US-552556 (+US-332772) (23.10.84) C07c-01/04 C07c-27/06

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 ( $\text{CO} + \text{H}_2$ ), in the vapour phase, at at least  $250^\circ \text{C}$  and at least 500 psi. with a catalyst (I) having the formula



A = Na, Li, K, Rb, Cs and/or Mg;

M = Ca, Cr, Fe, Mn, Mo and/or Zn;

a = 0.05;

b = 0.002-2;

c = 0.5-3;

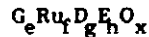
z = 0.1 wt. %; and

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)

409

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



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.

US4478955-A+

partially reduced. The reaction is pref. effected at 275-375°  
C, with a CO:H<sub>2</sub> ratio of 10:1 to 1:10 (esp. 3:1 to 1:3).

(B) The pref. (II) is RuCoPdZn<sub>0.4</sub>Ox.

WIDER DISCLOSURES

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

84-269514/43 E17 H04 STA# 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

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

462

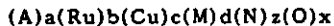
a = 0.02-0.4;  
 b and c = ca. 1 and  
 d = 0.1-0.5.

C84-114279

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

CLAIMED CATALYST

A catalyst has the formula



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;

ADVANTAGES

The catalyst gives high selectivity of 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 conver-  
 sion 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 STAII 21.12.81  
 STANDARD OIL CO (OHIO) \*EP --82-692-A  
 21.12.81-US-332772 (+US-332771) (29.06.83) B011-23/89 B011-  
 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 oxygen-  
 ate 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  $M_a A_b Ru C_u N_z O_x$  (where  
 A is alkali(ne earth) metal; M is Ce, Cr, Fe, Mn, Mo, Th

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)

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  $A'a'Ru^bCu^cM'dN_zO_x$  (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  $\geq$   
 250 (pref. 275-375) $^{\circ}C$  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 $^{\circ}C$  and  
 250-5000 psig, using a catalyst (III) of the formula

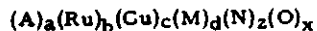
EP--82692+

$G_e R_u_f D_g E_h O_x$  (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 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) STA# 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  $\geq 250^\circ\text{C}$  and  $\geq 500$  psi and in the  
presence of a catalyst of formula:



(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

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

3 4 3

partially reduced and/or supported on an inert carrier,  
e.g.  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{SiO}_2\text{-Al}_2\text{O}_3$ , alundum, clay or SiC.

The synthesis gas may have a  $\text{CO}:\text{H}_2$  ratio of 10:1  
to 1:10 (pref. 3:1 to 1:3). The reaction is pref. effected at  
 $275\text{-}375^\circ\text{C}$  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).

US4377643