85-276096/44 H04 J04 BRPE 05.04.84
BRITISH PETROLEUM PLC (ATKI/) *WO 8504-598-A
19.09.84-GB-023742 (+GB-008803) (24.10.85) B01J-23/89
B01J-27 B01J-32 C07c-1/4

Fischer-tropsch catalyst contg. active metals uniformly distributed - through amorphous matrix, pref. contg. silicon and aluminium, and prepd. by hydrolysing precursor mixt., is more active and selective

C86-056430 E(AU JP NO US)

Reissued in Week 8621; abstract is additionally classified in Section H.

Full Patentees; B.P. Co. plc; Atkins M (for US only).

Compsn. useful after activation as catalyst or catalyst support in converting synthesis gas to hydrocarbons comprises:
(a) a porous amorphous framework matrix contg. at least one element (A) present as a hydrolysis prod. and
(b) element(s) from Gps. VIa and VIII, uniformly distributed through (a).

Prodn. of the compsn. via hydrolysis of a mixt. of components is also claimed.

ADVANTAGE

Compared with catalysts of similar compsn., but having the active components impregnated onto the support, the catalyst shows:
(i) lower selectivity to CO_2 (e.g. 5.0 instead of 27.6 mole %);
(ii) greater selectivity to liq. aliphatic hydrocarbons (e.g. 36.0 mole % instead of trace);
(iii) greater selectivity to oxygenates (e.g. 4.2 instead of 0.3 mole %); and
(iv) lower reaction temps. (e.g. 294 instead of 395°C).

PREFERRED COMPOSITION

The element (A) is Ga, Mg, Ca, P, Ti, Be, V, La or Ce, or esp. Si and/or Al. Element (b) is Fe, Co, Ni or Ru. The compsn. may also contain alkali(ne earth) or rare earth metal(s) and a halide.

Esp. pref. is a compsn. with framework contg. Si and/or Al, either or both being present as a hydrolysed prod. and Ru, Fe and K distributed uniformly through it. Pref. concns. (wt.%) are: 0.5-15 Ru and Fe, 0.1-5 K and 0.1-2.5 halide, the Si/Al ratio exceeding 1.

PREPARATION

Pref. a homogeneous mixt. of water, a hydrolysable Si

cpd. (e.g. $Si(OEt)_4$)$_4$, a water-sol. Al cpd. (e.g. $Al(NO_3)_3$) and sources of Cl, Ru, K and e.g. Fe, is hydrolysed, and the water and the by-prod. of hydrolysis are removed. Then compsn. is then heated, pref. under reducing consitions at 200-600°C.

PROCESS

Pref. the synthesis gas (CO/H_2 = 5-0.2 molar) is contacted with the catalyst at 225-375°C. and pressures from atmospheric to 100 bars, with contact time in a continuous process of 1-30 sec.

EXAMPLE

To 52.1g, $Si(OEt)_4$ were added with rapid stirring 1.68g $RuCl_3$, 6.51g. $Fe(NO_3)_3$, and 1.08g, KOH, followed by 20.1g $Al(NO_3)_3$ in 146 ml. deionised water. The suspension was heated to 70°C and stirred until hydrolysis of the $Si(OEt)_4$ was complete.

The prod. was then heated at 80-100°C for 12 hr. to give a catalyst as a brown glassy solid, contg. 1.6 wt.% Ru, 2.2 wt.% Fe and with a Si/Al ratio of 5:1.(21pp1491RBHDwgNo0/0)

(E) ISR: US3243368 FR1553174 FR2334415 NL7708307 EP--71770.

AU-A-42133/85