

87-051732/08 E17 H04 (H06) BRPE 31.07.85  
 BRITISH PETROLEUM PLC \*EP -211-577-A  
 31.07.85-GB-019321 (25.02.87) B01j-23/58 C07c-01/04  
 Fischer-Tropsch catalyst with reduced selectively to methane - prepd.  
 via pptn. by hydroxide or carbonate of ruthenium cpd. soln. mixed  
 with rare earth metal oxide  
 C87-021545 E(BE DE FR GB IT NL)

E(35-X) H(4-E5, 4-F2E) N(2-E)

(C) thermally decomposing the decomposable cpds. in the mixt. from step (B). The reductively activated catalyst can be combined with a zeolite, pref. ZSM-5.

#### ADVANTAGE

The disadvantages of high  $\text{CH}_4$  yield and low selectivity to olefins of prior art Ru-impregnated catalysts are largely overcome. E.g. molar selectivities (%) at 36% conversion were 2.2  $\text{CO}_2$ , 13.5  $\text{CH}_4$ , and 46.6  $\text{C}_5+$  hydrocarbons.

#### PREFERRED CATALYST

Pref. A = Na or K, X = Ce, and b and a = less than 1 wt. %.

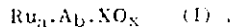
#### CATALYST PREPARATION

Step (A) is pref. effected at below  $30^\circ\text{C}$ ; and step (C) in a non-reducing atmos. at  $250-600^\circ\text{C}$ . Subsequent reductive activation may comprise contacting with a reducing gas at  $150-300^\circ\text{C}$  and 1-100 bar.

#### PROCESS

For hydrocarbon synthesis, synthesis gas is pref. contacted with the reductively activated catalyst in the slurry

Prodn. of compsn. of formula



A = alkali metal.

X = rare earth (RE) metal,

a = above 0 and up to 5 wt. %.

b = 0-5 wt. %.

x satisfies the valency requirements,

for use after activation as catalyst for converting synthesis gas to hydrocarbons higher than  $\text{C}_2\text{H}_4$ , comprises:

(A) contacting below  $50^\circ\text{C}$  an RE oxide, a soln. of a Ru salt and as precipitant a carbonate and/or bicarbonate and/or hydroxide of an alkali metal or ammonium, so precipitating Ru as a heat-decomposable cpd.;

(B) recovering the mixt. of RE oxide and pptd. Ru cpd. from step (A); and

EP-211577-A\*

phase at 190-400 (esp. 250-350)°C and 0-100 (esp. 10-50) bar.

#### EXAMPLE

A catalyst comprising 0.5 wt. % Ru on CeO<sub>2</sub> was made by: (i) slow addn. of aq. ammonium carbonate soln. at about 20°C to a mixt. of CeO<sub>2</sub> and an aq. RuCl<sub>3</sub> soln.; (ii) boiling to complete RuCl<sub>3</sub> hydrolysis; (iii) cooling, filtering and washing; (iv) drying at 125°C for 16 hrs.; and (v) activating with H<sub>2</sub>. When used with a mixt. of CO and H<sub>2</sub> (1:2 molar) in a slurry phase reactor at 20 bars, 290°C and GHSV 268 (based on wax), the catalyst gave the above results (ADVANTAGE). (14pp1492RKMHDwgNo0/0).  
(E) ISR: EP-169743, FR2194482, GB2119277.

EP-211577-A