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 BRITISH PETROLEUM PLC (BUTL/) \*WO 8704-085-A  
 09.01.86-GB-000445 (16.07.87) B01j-23/58 C07c-01/04  
 Compsn. contg. ruthenium-cerium mixed oxide and opt. alkali metal  
 - for reductive activation and use as catalyst in conversion of  
 synthesis gas to hydrocarbon(s)  
 C87-086348 N(AU JP NO US)

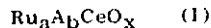
Full Patentees: British Petroleum Co. plc;  
 Butler G (for U.S. only).

A compsn. (I) for use, after reductive activation, as a catalyst in conversion of synthesis gas to more than 1C hydrocarbons, is prepd. by:

(A) adding a soln. of cpds. of Ru and Ce, and opt. an alkali metal cpd., to a soln. of a precipitant which is a (bi)-carbonate and/or hydroxide of an alkali metal or  $\text{NH}_4$ , to form a ppte. comprising Ru and Ce, and opt. an alkali metal, as cpds. thermally decomposable to the metals and/or oxides, and

(B) recovering the ppte.

(I) is of formula



E(10-J2D) H(4-E5, 4-F2E) J(4-E4) N(1-A, 2-E, 3-A, 6-E)

A = alkali metal;

x = number such that the valency requirements of the other elements for O is satisfied;

a = 0-5 wt.%, w.r.t. total wt. of the compsn.;

b = 0-10 wt.%, w.r.t. total wt. of the compsn.;

#### USE

Prodn. of more than 1C hydrocarbons by contacting synthesis gas with the reductively activated catalyst at 190-400°C and 1-100 bars, opt. with periodic treatment of the catalyst with  $\text{H}_2$ , is claimed. The hydrocarbons are esp. aliphatic hydrocarbons in the gasoline boiling range.

#### ADVANTAGE

The catalysts have high activity, long life, and low selectivity to  $\text{CH}_4$  and  $\text{CO}_2$ .

#### PREFERRED CATALYST

a = less than 2 wt.%

#### PREFERRED PROCESS

Step (A) is carried out continuously by simultaneous feeding and mixing, in a pptn. zone, or a soln. of cpds. of

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Ru and Ce and opt. an alkali metal, and a soln. of the precipitant, at pH 6-10 which is pref. constant during the pptn., and at below 30°C.

(C) The recovered ppte. is thermally decomposed in a separate step.

#### EXAMPLE

(I) A soln. of 0.3974 g of  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  in 100 cc water was added dropwise to a stirred soln. of 75.4 g of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  made up to 750 cc with water, followed by dropwise addn. of a soln. of 1.1421 g of  $\text{KNO}_3$  in 50 cc of water. During 1 h, this mixed soln. was added to a soln. of 299.7 g of  $\text{NH}_4\text{HCO}_3$  made up to 2500 cc with water; the pH of the alkali was a constant 8.7-8.8 during the pptn.

After stirring for a further 0.25 h, the mixt. was vacuum filtered. The sludge was stirred 4x with 3000 cc of water for 0.25 h, and filtered, and finally dried at 116°C and 17 mm Hg for 24 h. The dried solid, 25 g, was ground, pressed, crushed and sieved.

(II) A mixt. of 4 cc of the catalyst and 6 cc of crushed ceramic beads was reduced, in a fixed bed reactor, for 16 h at 225 cc  $\text{H}_2$ /min. at atmos. pressure, and then pressurised under syngas (2:1  $\text{H}_2$ :CO) to 30 bar and heated to varying bed temps. during 2 h. The CO flow was stopped for 2 h, and then re-admitted, with redn. in bed temp.

Results were: bed temp. 300°C, CO conversion 37.1%, molar selectivity to 1C 8.3%, 2C 3.2%, 3C 11.2%, 4C 12.5%, 5+C 62.2%,  $\text{CO}_2$  2.3%, oxygenates 0.3%; productivity, g/l/h. 2+C 166, 5+C 120; bed temp. 314°C, CO conversion 88%, molar selectivity, 1C 17%, 2C 2.8%, 3C 11.9%, 4C 11.7%, 5+C 53.8%,  $\text{CO}_2$  2.4%, oxygenates 0.4%; productivity g/l/h. 2+C 373, 5+C 259. (28pp510RBHDwgNo0/0).  
(E)ISR: EP-169743 WO8600885 US4001143 US4060500 US2358050.

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