

89-137922/18

E17 H04 J04

ESSO 02.07.86

*US 4822-824-A

EXXON RES & ENG CO

07.12.87-US-129747 (+US-881347) (18.04.89) C07c-01/04

Prod'n. of hydrocarbon(s) from synthesis gas - using a pretreated catalyst comprising cobalt and ruthenium supported on titania

C89-061035

E(10-J2D3) H(4-E5, 4-F2E) J(4-E1, 4-E5) N(2-B1, 2-E, 3-B)

Div. ex.: 4738948 (88-126192/18)

In a hydrocarbon synthesis process, hydrogen and carbon monoxide are reacted in the presence of a catalyst (A) comprising cobalt and ruthenium on titania, under reaction conditions suitable for the formation of higher hydrocarbons; (A) is prepd. by impregnating titania with solns. of cobalt and ruthenium salts, drying, reducing the cobalt and ruthenium, treating the reduced metals with an oxygen-contg. stream to form oxides of cobalt and ruthenium, and reducing the oxides.

ADVANTAGE

Catalyst (A) gives lower methane and higher C₅⁺ yields than conventional Co or Co/Ru catalysts, and greater conversion in unit time per gram atom Co. It has the ability to be regenerated in situ under low temp. flowing hydrogen;

high temp. carbon burning operations which generally necessitate removal of the catalyst from the reactor are not here required.

REACTION CONDITIONS

Conventional synthesis conditions are used, e.g. H₂/CO ratio 1.0 to 2.5, GHSV 300-1500, temp. 100-260°C, pressure 140-400°C; prods. are largely paraffins, e.g. in the 5-40C range.

CATALYST

(A) contains pref. 10-15 wt. % Co and 0.1-0.2 wt. % Ru; Co:Ru atomic ratio is 100-200:1. The titania is of high rutile:anatase ratio, e.g. 4:1 to 100:1, esp. 100% rutile; surface area is less than 50 m²/g (BET).

The metal salts may be introduced in the same solution or separately. Hydrogen is used for the first reduction, and air or 20% oxygen in helium may be used for the oxidation at 250-300°C. Final reduction takes place with hydrogen e.g. at 400°C.

In preps. described (Method 2), the titania is first impregnated with cobalt solution, dried, reduced with

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hydrogen, impregnated with ruthenium solution, dried and again reduced with hydrogen; the specified oxidation and final reduction then follow.

CATALYST REGENERATION

This takes place at a temp. at or slightly above synthesis temp., e.g. at 190-260°C for 10 hr. or more; catalyst activity is thereby largely or completely recovered; C5+ yield may be greater than that initially obtained.

EXAMPLE

A catalyst prep'd. by method 2 contained 11.6 wt.% Co and 0.14% Ru. Synthesis results (initial/after 10-30 days use but before regeneration/after hydrogen regeneration) were: Co time yield (hr^{-1}) 4.5/3.9/4.8; CH_4 wt.% 5.5/6.4/4.9; C5+ wt.% 91.0/88.8/91.5. (10pp1644CGDwgNo0/4).

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H(4-E4, 4-E5, 4-F2, 4-F2E) J(4-E4, 4-E5) N(2-B1, 2-E, 3-B, 6-E)

02.07.86-US-881347 (19.04.88) B01j-23/89
Catalyst for hydrocarbon synthesis - prep'd. by impregnating titania support with cobalt and ruthenium, redn., oxidn. and re-redn.
C88-056545

ated in situ under low temp. flowing H_2 , instead of requiring C oxidn. at e.g. 400°C.

PREFERRED CATALYST COMPOSITION

The catalyst contains 5-25wt.% Co. The atomic ratio Co-Ru is 10:1 to 400:1. In the TiO_2 support, the ratio of rutile to anatase is at least about 2:3. The support has BET surface area below $50m^2/g$.

Hydrocarbon synthesis catalyst is prep'd. by:

- (i) impregnating a refractory support comprising TiO_2 with solns. of catalytically active amts. of Co and Ru salts;
- (ii) drying the impregnated support;
- (iii) reducing the Co and Ru;
- (iv) treating the reduced metals with an O_2 -contg. stream at conditions sufficient to form Co oxides and Ru oxides; and
- (v) reducing the Co and Ru oxides.

CATALYST PREPARATION

The Co and Ru impregnations may be simultaneous. Or Co may be impregnated first, reduced to metal, and followed by Ru impregnation and Ru redn. The Co and Ru salts used are pref. aq.. The reduced metals may be treated with an O_2 -gas stream at 250°C for a sufficient time to form Co and Ru oxides or a bimetallic Co-Ru oxide. The Co and Ru oxides can then be reduced by H_2 at about 200-500°C.

USE/ADVANTAGE

The catalyst is useful for synthesis of hydrocarbons (chiefly 5-40C or higher paraffins) from syngas. The CH_4 yields are lower and the $5C+$ yields are higher than from a Co or Co-Ru catalyst that has not been oxidised and re-reduced. The conversion of CO and H_2 per g atom of Co per unit of time is increased. The catalyst can be regener-

EXAMPLE

H_2 and CO (2:1) were reacted at 200°C and 2930 kPa over catalysts contg. Co (11.6%) and Ru (0.14%), which had been (A) simply reduced in H_2 and passivated, or (B) (according to the invention) reduced in H_2 , oxidised, re-

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reduced and passivated.

The GHSV was (A) 800 and (B) 1200. The CO conversion (%) was (A) 50.7, (B) 61.0. The CH₄ selectivity (wt. %) was (A) 7.5, (B) 5.0. The 5C+ selectivity (wt. %) was (A) 86.1, (B) 91.4. (10pp1492CGDwgNo0/4)

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