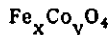


87-170338/25 E17 H04 J04 ESSO 30.09.85
 EXXON RES & ENG CO *AU 8548-135-A
 30.09.85-AU-048135 (02.04.87) C07c-01/04 C07c-11/02
 Fischer-Tropsch hydrocarbon synthesis - using iron-cobalt spinel
 catalyst
 C87-071008

Prod'n. of hydrocarbon mixts. contg. 2-20C olefins is effected
 by contacting a mixt. of CO and H₂ with a carbided and
 reduced, unsupported Fe/Co single-phase spinel catalyst.
 The spinel has the initial empirical formula:



x and y are nonzero nos. such that $x+y = 3$ and $x/y = 7$ or
 more.

It exhibits a single-phase X-ray diffraction pattern
 isostructural with that of Fe₃O₄ and has a BET surface area
 of at least 0.1 m²/g.

ADVANTAGE

The catalysts have high activity and high selectivity
 for 2-6C olefins, e.g. giving hydrocarbon prods. contg.
 25-80 wt. % of 2-6C olefins.

E(10-J2C3) H(4-E5, 4-F2E) J(4-E1) N(2-A1, 2-B1)

PREFERRED CATALYSTS

The spinel has x/y values of 2.85/0.15, 2.625/0.375,
 2.97/0.03 or 2.25/0.75. The catalyst also contains 0.1-10
 atom% of an alkali(ne earth) metal cpd. as promoter, esp.
 K₂CO₃. The catalyst may be mixed with a solid diluent.

PREFERRED CONDITIONS

The reaction is effected in a slurry-phase or fixed-bed
 reactor at 200-300 deg. C and 50-1000 psig with an H₂:CO
 molar ratio of 0.1-10:1 and a GHSV of 200-4000.

EXAMPLE

An Fe_{2.85}Co_{0.15}O₄ catalyst contg. 1% K was reduced
 with H₂ at 500 deg. C for 5-7 hr and contacted in a fixed bed
 with a 1:1 H₂/CO mixt. (570 GHSV) at 270 deg. C and 300
 psig. The CO conversion was 98%, with 56% selectivity for
 hydrocarbons, which included 9.8 wt. % C₂H₄, 20.3% C₃H₆,
 9.3% C₄H₈ and 45.2% C₅₊ hydrocarbons. (66pp367RKMHDwgNo
 0/0).

AU8548135-A

85-262892/42 A41 E17 H04 J04 ESSO 14.12.83
 EXXON RES & ENG CO *US 4544-674-A
 14 12 83-US-561193 (01.10.85) C07c-01/04
 Fischer-Tropsch synthesis of olefin(s) - using as fixed bed catalyst iron-cobalt spinel

A(1-D13) E(10-J2C3) H(4-E5, 4-F2E) J(4-E1) N(1-A, 1-B, 2-A1, 2-B1)

845

C85-113932

A hydrocarbon mixt. contg. 2-6C olefins is synthesised by contacting carbon monoxide and hydrogen with a fixed bed of catalyst comprising an unsupported iron-cobalt spinel promoted with a Gp. Ia or IIa metal salt; the spinel exhibits a single phase isostructural with Fe_3O_4 by X-ray diffraction, has BET surface area up to $5m^2/g$ and Fe:Co ratio 7 : 1 or above.

ADVANTAGE

The catalyst is stable and highly active, giving a high level of 2-4C olefins and little methane.

CATALYST PREPARATION

Stoichiometric mixtures of the oxides or metals are sintered at 600-1100°C in an inert or vacuum atmosphere, and the spinel obtd. is treated with the promoter salt.

WIDER DISCLOSURES

The specified catalyst, and the reduced and carbided form in which it is catalytically active, are new catalyst compositions.

PREFERRED FEATURES

The spinel is of formula $Fe_xCo_yO_4$, where x:y is 7:1 to 35:1; it is e.g. :



The promoter is a bicarbonate, carbonate, acid salt, nitrate, sulphate, halide or hydroxide, esp. potassium carbonate; it is added at 0.1-10g. atom % Gp. Ia or IIa metal/total metal. A solid diluent may be present to assist heat removal.

Reaction takes place at 200-350°C, 50-1000 psig, space velocity 200-4000 v/v/hr, H_2CO ratio (0.5-2.5):1.

EXAMPLE

A spinel of formula $Fe_{2.85}Co_{0.15}O_4$ was made by sintering at 800-1000°C under vacuo a mixture of Fe_2O_3 , Fe metal and Co_3O_4 ; it was then impregnated with aq. potassium carbonate to give a catalyst contg. 1g atom %

US4544674-A*

K on total metals; the product had surface area 0.29.
8.8g catalyst, 20-80 mesh, in a tube was pretreated with H_2/N_2 at $500^\circ C$, and H_2/CO (1:1) then passed at 570 v/v/hr, 300 psig, $270^\circ C$. CO conversion was 98% (79), conversion to hydrocarbons 56% (43); of the latter, methane was 9.1 wt.% (8.5) and 2-4C olefins 39.4 wt. % (26.6). Figures in brackets are for a comparison expt. using as catalyst $Fe_3O_4/1\% K$. (8pp1644RKMHDwgNo0/0).