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 EXXON RES & ENG CO *US 4977-126-A

14.11.88-US-270596 (+US-046649) (11.12.90) B01j-21/06
 B01j-23/74 C07c-27/06

Fischer-Tropsch cobalt catalyst prodn. - by spraying liq. cobalt cpd. onto fluidised bed of porous oxide support particles, dispersing cobalt on surface of particles

C91-046923

In prodn. of catalysts in which Co is impregnated and dispersed on the outer surface of particles of a porous inorganic oxide support:

(a) a bed of the particles is fluidised at 50 - 100°C by contact with a gas at 50 - 100°C; and

(b) the bed is sprayed with a liq. in which a Co cpd. is dispersed, at a flow rate to give a ratio between the flow rate of the liq. : flow rate of the fluidising gas below 0.6 g of liq./ft³ of fluidising gas, to form a surface layer, 20 - 150 μ thick, of Co cpd. on the particles; the loading of Co cpd. is 0.01 - 0.15 g/cc, calculated as metallic Co, w.r.t. packed bulk vol. of catalyst.

USE

The catalyst is a Fischer-Tropsch catalyst for conversion of synthesis gas to hydrocarbons.

E(10-J2D, 35-V) H(4-E5, 4-F2E) J(4-E4) N(2-B, 6-E)

PREFERRED

The support is Al₂O₃, SiO₂, SiO₂-Al₂O₃, TiO₂, or a mixt. of Al₂O₃, SiO₂ or TiO₂, pref. TiO₂ with ratio by wt. of rutile : anatase of at least 3 : 2 (3 : 2 - 100 : 1 and higher).

The Co cpd. is dispersed in water, and the fluidising gas is air at 70 - 90°C. The ratio of the flow rate of liq. : flow rate of gas is 0.3 - 0.5 g/ft³. The thickness of the catalytically active surface layer is 40 - 150 μ, with Co loading of 0.03 - 0.09 g/cc.

The Co cpd. is converted to CoO at below 500°C. The spray liq. may contain a decomposable cpd. of Re, Hf, Zr, Ce, Th and/or U as promoter, in ratio by wt. of Co : promoter of 30 - 2 : 1.

EXAMPLE

The support was 1 kg of 96.5% TiO₂ + 3.5% Al₂O₃, as 0.8 mm extrudates. An aq. soln. contg. 11 - 13%wt. Co as Co(NO₃)₂ and 1 - 1.3% of Re as perrhenic acid was sprayed at 21 g/min. onto a bed of the support at (a) 95°C or (b) 73°C, fluidised with air at (a) 56 or (b)

76 cubic feet/min., followed by calcination at 300°C in the tube unit.

The catalyst contained (a) 4.5 or (b) 4.6 wt. % of Co, and the thickness of the Co/Re layer on the surface of the particles was (a) 123 μ or (b) 203 μ . (6pp510SLDwgNo0/0).

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*US 4962-078-A

03.10.88-US-252215 (+US-046649) (09.10.90) B01j-21/06

B01j-23/84 C07c-01/04

Catalyst for prepn. of hydrocarbon(s) - esp. distillate fuels from synthesis gas, comprises titania support with surface layer contain cobalt

C90-142136

A novel catalyst compsn. (I) useful for conversion of synthesis gas to liq. hydrocarbons comprises cobalt dispersed and impregnated as a catalytically active layer on a support. The layer is of thickness 0.02-0.20 mm., and cobalt loading is 0.04-0.15 g./cc., calculated as metallic cobalt per packed bulk volume of (I). The support is at least 80 wt. % titania.

Productivity of (I) (vol. CO converted/vol. catalyst/hr.) is at least 150-200°C. and selectivity to methane not more than 10 mole %.

USE/ADVANTAGE

Synthesis gas is converted to C10+ distillate fuels and other valuable products with high productivity, with low selectivity to methane. (I) may match the performance of a powder catalyst, but be of a size suitable for commercial use.

E(10-J2D3, 35-V) H(4-E5, 4-F2E) N(2-B)

PREFERRED COMPOSITION

Cobalt loading is 0.05-0.09 g./cc.. The titania support has a rutile/anatase ratio at least 3:2, esp. 4:1 to 100:1 or more.

(I) may additionally contain hafnium or esp. rhenium as promoter, in wt. ratio Co:(Hf or Re) 30:1 to 2:1.

CLAIMED PREPARATION

The support is heated to more than 140°C., and repeatedly contacted with a spray of a solution containing 0.05-0.25 g./ml. (calculated as metallic Co) of a cobalt compd., e.g. cobalt nitrate, with drying and calcining between each contact.

(10pp1644SLDwgNo0/1).

EXAMPLES

Catalyst were prepd. using as support TiO₂ spheres (14-20 Tyler mesh, 86-95% rutile, 14-17 m²/g BET surface area, 0.11-0.16 pore column (Hg)). The support was impregnated with a cobalt nitrate/perrhenic acid solution by a variety of techniques.

Surface impregnated catalysts had in general higher productivity and lower selectivity to methane than did uniformly impregnated catalyst.

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