

87-101186/14 E17 H04 J04 AIRP 03.07.85
 AIR PRODUCTS & CHEM INC US 4652-587-A
 18.06.86-US-675803 (+US-752203) (24.03.87) C07c-01/04
 Fischer-Tropsch catalyst for hydrocarbon prodn. - comprises porous particles of mixed zirconium and titanium di:oxide(s) with, on particle surface or inter-dispersed, iron or iron di:oxide
 C87-042101

Div. ex. 4624942(86-331807/50)

(A) Process for selective hydrogenation of CO to 9-25C hydrocarbons in a Fischer-Tropsch reaction, comprising reacting CO and H₂ at high temp. and pressure in presence of a previously-activated Fischer-Tropsch catalyst, is improved by use of a catalyst comprising porous solid particles, contg. (a) a mixt. of ZrO₂ and TiO₂, (b) at least on the particles' surface, Fe or iron oxide, and (c) up to 10 wt.% of an alkali metal cpd.
 (B) The same process is claimed, except that in the catalyst the Fe or iron oxide is interdispersed.

USE

The process is useful e.g. for making diesel-range hydrocarbons from synthesis gas, which can be made by coal gasification.

E(10-J2D3) H(4-E5, 4-F2E) J(4-E1) N(1-A1, 2-A1, 3-B, 5-B)

PREFERRED CATALYST

The pref. catalyst contains 5-15 wt.% Fe, and has an atomic ratio Zr:Ti of the order 1:1. Its surface area is at least 100 m²/g.

CATALYST PREPARATION

The iron component may be introduced by impregnating the ZrO₂/TiO₂ support, by dry-blending the support with an Fe cpd., or by coprecipitating a mixt. of Fe, Zr and Ti oxides.

EXAMPLE

An impregnated catalyst was prepd. by: (i) adding a mixt. of isopropanol (50%) and water to an equimolar soln. of Zr(OC₃H₇)₄ and Ti(OC₃H₇)₄ in isopropanol to ppte. a mixt. of Zr and Ti hydroxides; (ii) washing and drying the ppte. and calcining in air at 550°C; (iii) impregnating 25.5 g of the oxide support thus prepd. with a soln. of 32.54 g Fe(NO₃)₃.9H₂O in 30 ml water, to which NH₄OH was added; and (iv) drying the prod. and calcining at 510°C in air. After activation with H₂/CO (1:1 molar) at up to 275°C, this catalyst was used at 275°C and 300 psi to convert the same

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CG/H₂ mixt. at GHSV = 1000. There was 31.8% conversion, and the prod. contained 33.6 wt.% diesel-range hydrocarbons. (5pp1492RKMHDwgNo.0/0).

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03.07.85-US-752203 (25.11.86) B01j-21/06 B01j-23/74

Compsn. contg. iron and mixed zirconia and titania - of use as Fischer-Tropsch catalyst for synthesis of liquid hydrocarbon(s)

C86-143914

Compsn. (I) comprises porous solid particles contg.

- (a) a mixture of zirconium and titanium dioxides,
 (b) at least on the surface of, or interdispersed with (a), iron or iron oxide, and
 (c) up to 10 wt. % of an alkali metal cpd. (II).

A catalytically active material (Ia) is prepd. by

- (a) coprecipitating zirconium dioxide and titanium dioxide precursors (III) and (IV),
 (b) drying and calcining the coprecipitate in an oxygen-contg. atmosphere to form porous solid particles comprising a mixture of zirconium and titanium dioxides,
 (c) combining with the coprecipitate an iron precursor (V), and
 (d) drying and calcining in an oxygen-contg. atmosphere to convert the precursor to iron oxide.

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L(00-02, 00-01, 00-02, 00-03) P(4-E5, 4-F2E) J(4-E4) N(1-A1, 2-A1)

USE

(I) and (Ia) are Fischer-Tropsch catalysts of use for hydrogenation of carbon monoxide, esp. in CO-rich synthesis gas, to produce liquid hydrocarbons, esp. those in the diesel fuel range.

PREFERRED COMPOSITION

(I) contains 5-15 wt. % Fe; Zr:Ti ratio is 2:1 to 1:2; surface area is at least 100 m²/g. (II) is potassium bicarbonate to carbonate.

PREFERRED METHOD

(III) and (IV) are coprecipitating by hydrolysing a solution of zirconium and titanium (1-5C) alkoxides in an anhydrous non-reactive solvent. (V) is iron oxide, hydrated iron oxide, iron hydroxide, acetate, benzoate, maleate, nitrate, gluconate, citrate, lactate or sulphate; it may be coprecipitated with (III) and (IV). (II) is added by impregnation or deposition on the particulate material.

ACTIVATION

Before use as catalyst, the iron oxide is converted to iron by exposure to a reducing atmosphere, e.g. hydrogen.

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EXAMPLE

50g $Ti(OC_3H_7)_4$ and 57.5g $Zr(OC_3H_7)_4$ (equimolar mixture) was dissolved in 200ml dry 1-propanol, and 200ml 50% aq. isopropanol added thereto to precipitate the hydroxides. The precipitate was washed, dried and calcined for 2 hr. in air at 550°C. Surface area of product was 200m²/g.

25.5g product was impregnated with 32.54g $Fe(NO_3)_3 \cdot 9H_2O$ in 30ml water, and ammonium hydroxide added to precipitate iron nitrate. The product was dried and calcined in air for 2 hr. at 510°C to convert the nitrate to Fe_2O_3 .

After activation the product was contacted with 1:1 CO/H₂ at 275°C, 300 psi. CO conversion was 31.8%; product contained 33.6% hydrocarbons in the 9-25C range. (6pp1644RKMHDwgNo0/0).

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