

87-220977/31 E17 H04 J04 AIRP 05.06.85
 AIR PRODUCTS & CHEM INC *US 4681-867-A
 13.05.86-US-862844 (+US-741403) (21.07.87) B01j-21/06 B01j-
 23/46

Prepn. of Fischer-Tropsch catalyst - by impregnation of a silica support with non-aq. solns. of a GP/IVB metal and a Fischer-Tropsch catalyst metal

C87-092975

C.i.p. 4619910 (86-318126/48)

A catalyst (I) is made by:

- (a) treating a silica base material with a non-aq. soln. of a decomposable salt or organic cpd. (II) of a Gp. IVB metal, and removing remaining solvent;
- (b) impregnating the prod. with a non-aq. soln. of a decomposable salt or organic cpd. (III) of a Fischer-Tropsch metal catalyst, consisting of cobalt, iron or ruthenium, and removing remaining solvent; and
- (c) exposing the prod. to a reducing atmos.

Materials and prods. are maintained under conditions to avoid hydrolysis, oxidn. or calcination.

USE/ADVANTAGE

(I) is a Fischer-Tropsch catalyst, of use in converting

E(5-L1, 5-M, 5-N, 10-J2D, 35-V) H(4-E5, 4-F2E) J(4-E4) N(5-A, 5-B)

synthesis gas to a hydrocarbon prod. of relatively narrow carbon number range. It is used, pref. in slurry phase, under mild conditions.

PREFERRED MATERIALS

(II) is Zr, Ti or Hf alkoxide. (III) is a carbonyl of Co, Fe or Ru. A suitable solvent is cyclohexane.

WIDER DISCLOSURE

Other materials may be used as support, e.g. a metal oxide, esp. alumina, or a clay, kieselguhr or zeolite.

EXAMPLE

87.2 g silica was treated with 300 cc of a solution of 50.8 g zirconium propoxide in hexane, and the solvent evaporated off under vacuum. 200 cc of a solution of 17.5 g cobalt carbonyl in 60/40 toluene/hexane was then added, and the solvent removed under vacuo to obtain 132 g catalyst containing 3.5 wt. % Co and 6.6 wt. % Zr.

The catalyst, after activation in hydrogen at 300° C, was used slurried in paraffin oil to convert CO/H₂ to hydrocarbons at 240° C, 300 psig, 1000 GHSV, conversion of CO 33%, selectivity C5-25 72%. (8pp1644RKMHDwgNo0/0)

87-170181/24 E17 H04 AIRP 05.06.85
 AIR PRODUCTS & CHEM INC *US 4670-472-A

13.05.86-US-862744 (+US-741403) (02.06.87) C07c-01/04

Converting syn:gas pref. to 5-25C hydrocarbon(s) using catalyst -
 prepd. by reacting alumina or silica with zirconium, titanium or
 hafnium alkoxide, then impregnating with iron or ruthenium
 carbonyl

C87-070919

Cip 4619910

Process for converting syngas preferentially to 5-25C hydro-
 carbons at CO:H₂ mole ratio 1:1 to 3:1, GHSV 200-1000,
 200-350°C and 200-1000 psig is improved by using a catalyst
 prepd. by: (a) treating an inert, Al₂O₃ catalyst base with
 a non-aq. soln. of a Zr, Ti or Hf alkoxide, and removing
 the non-aq. soln.; (b) impregnating the prod. of step (a)
 with a non-aq. soln. of Fe or Ru carbonyl, and removing
 the non-aq. soln.; and (c) exposing the prod. of step (b)
 to a reducing atmos.; all while maintaining the Al₂O₃ and
 prods. under conditions avoiding their hydrolysis, oxidn.
 and calcination.

A process as above, except that Al₂O₃ is replaced by
 SiO₂, is also claimed.

E(10-J2D3) H(4-E5, 4-F2E) N(1-C2, 1-D, 2-A, 2-E, 3-B, 6-E)

USE/ADVANTAGE

E.g. a Ru/Zr/Al₂O₃ catalyst showed a selectivity to
 produce high yields of 5-11C gasoline-range hydrocarbons,
 with a sharp cutoff at 28-30C, preventing the formation of
 heavy waxes and so minimising the need for withdrawal of
 catalyst and slurry from a reactor. A Fe/Zr/Al₂O₃ catalyst
 showed a hydrocarbon selectivity centred in the 4-5C range.
 The selectivity of these catalysts is maintained as a function
 of time, and the deactivation rate is low. CO-rich syngas,
 as produced by advanced generation coal gasifiers, can be
 accepted directly.

EXAMPLE

Zr(OC₃H₇)₄ was reacted by mixt. with Al₂O₃ in cyclo-
 hexane in an inert atmos. until 1 mol. Zr cpd. had deposited
 by reaction and loss of C₃H₇OH, per Al-OH gp., and the
 support was then dried in vacuo. The support was then
 impregnated in several stages by the incipient wetness
 technique with Ru₃(CO)₁₂ in soln. in hexane, with O₂ and
 H₂O absent, removing unreacted carbonyl and solvent in
 vacuo after each stage. When the catalyst after redn. was
 used as a 12wt.% slurry in oil to convert CO + H₂ (1:1) at

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280°C and 300 psig, there was 22.6% conversion of CO, and the prods. included (wt.%) 35.65 5-11C, 27.0 IC, 22.9 2-4C and 4.5 18C+. (8pp1492RKMHDwgNo0/0)

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 AIR PRODUCTS & CHEM INC *US 4619-910-A
 05.06.85-US-741403 (28.10.86) B01j-21/04 B01j-23/46
 Prepn. of fischer-tropsch catalyst - of use for converting synthesis gas
 to higher hydrocarbon(s) of narrow carbon number range
 C86-137824

H(4-E5, 4-F2E) J(4-E4) N(2, 3-B)

fiers) to a hydrocarbon product of relatively narrow carbon number range. A higher proportion of n-alkanes in the diesel fuel range may be obtained than by prior processes.

PREFERRED MATERIALS

(II) is e.g. silica, magnesia, clay or esp. alumina, (III) is Ti, Hf or esp. Zr alkoxide, esp. propoxide; the metal forms 1-20 wt. % of (II). (IV) is Co, Fe or Ru carbonyl, or an organic complex; the metal forms 0.1-10 wt. % of (I). Solvent is cyclohexane.

UTILISATION

Syngas, CO:H₂ ratio 1.4:1 to 2:1, is contacted with the catalyst at space velocity 300-600 hr⁻¹, 230-275°C, 250-450psig. Hydrocarbon products range from C1 to C18+.

EXAMPLE

Zr(OC₃H₇)₄ was mixed with alumina in cyclohexane in an inert atmosphere; sufficient Zr was used to combine with all the Al-OH groups of the alumina. The product was dried, and Co₂(CO)₈ dissolved in 1/1 hexane/toluene was added in several steps in the absence of oxygen and water. Residual solvent was removed under vacuo. The catalyst so prep'd. was

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Making a catalyst (I) comprises the steps

(a) treating an inert inorganic metal oxide catalyst base material (II) with a non-aq. soln. of a decomposable salt or organic cpd. of a Gp. IVB metal (III), and removing remaining soln;

(b) impregnating the product with a non-aq. soln. of a decomposable salt or organic cpd. of a Fischer-Tropsch metal catalyst comprising cobalt, iron or ruthenium (IV) and removing remaining soln.; and

(c) exposing the product to a reducing atmos.

All steps are carried out under conditions to avoid hydrolysis, oxidn. or calcination of the materials and products.

USE

Catalyst is of use in a conventional slurry phase reactor for converting synthesis gas, esp. CO-rich synthesis gas, e.g. of CO:H₂ mole ratio 1:1 to 3:1 (as produced in some coal gasi-

activated with CO/H₂, and used as a slurry in paraffin oil.
(8pp1644RKMHDwgNo0/0)

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