

86-120437/19 E17 H04 J04 SHEL 02.11.84
SHELL INT RES MIJ BV *EP -180-269-A

02.11.84-NL-003335 (07.05.86) B01j-23/74 B01j-37/02
Preparing Fischer-Tropsch catalyst comprising cobalt on carrier -
contg. silica, with pretreatment of carrier by defined silicon cpd.,
giving catalysts of increased activity
C86-051245 E(BE FR GB IT NL)

Prepn. of catalysts comprising Co on a SiO₂-contg. carrier
includes:

(a) treating the carrier with a Si cpd. of formula



X = halogen, alkoxy and/or acyloxy.

Y = H and/or hydrocarbyl.

Z = halogen or a N-contg. or O-contg. gp..

n = 0-3.

(n+m) = 3;

(b) further treating the carrier with a Co cpd. in
presence of an organic liq.;

(c) removing the organic liq.; and

(d) calcining and activating the compsn. obtd.

USE/ADVANTAGE

The catalysts are useful for prodn. of hydrocarbons from

E(10-J2D) H(4-B3, 4-E5, 4-F2B, 4-F2E) J(4-E4) N(2-B, 2-E, 3-B,
3-D)

H₂-CO mixts.: esp. followed by hydrocracking, in a 2-step
process for middle distillate prodn. Step (a) increases the
final catalyst activity, since the Co when added does not form
inactive hydroxysilicate e.g. the (H₂+CO) conversion was
increased from 55 to 81 %.

CATALYST PREPARATION

The carrier is pref. SiO₂. Pref. Si cpds (I) include those
in which X = Cl, MeO, EtO or CH₃COO; Y = Me or Et; and
Z = OSiY₃ or -NHSiY₃. Cpd. (I) may be e.g. Si(OEt)₃H;
SiMe₃Cl or SiCl₄. Step (a) is pref. effected in a solvent
without OH gps. e.g. octane, benzene or acetonitrile,
pref. for 1-24 (esp. 4-20) hr. at 40-200 (esp. 80-150)°C e.g.
in the soln. boiling unde reflux. Step (b) can be effected
with a Co cpd. in MeOH, EtOH or glycol. To obtain catalysts
of improved activity owing to inhomogeneous Co distribution
the treated carrier may be submersed one or more times in
the Co-contg. soln under conditions such that

$$10,000 (\log v)/(t \times T) = \text{at least } 1,$$

where v = viscosity (cS at 60°C), T = temp (K) and
t = submersion time (sec.)

The catalysts are activated at 200-350°C with H_2 or a H_2 -contg. gas.

PREFERRED CATALYST

The catalyst pref. comprises (pts.wt.): 100 carrier, 5-50 Co and 0.1-5 of a promoter, pref. Ti, Cr, Ru or esp. Zr. The promoter is pref. deposited on the Co-loaded catalyst after calcination.

EXAMPLE

Catalysts comprising (pts.wt) 100 SiO_2 and 25 Co were prepd by impregnation of SiO_2 with $Co(NO_3)_2$ in EtOH and calcination at 500°C the SiO_2 for catalyst A being a calcined globular SiO_2 and that for catalyst B being the same SiO_2 after refluxing for 12 hr. with a soln. of triethoxysilane in toluene. With an H_2/CO (2:1 molar) mixt. at 20 bar, 220°C and GHSV 600 $Nl/l \times h$, fixed beds of the catalysts activated by H_2 at 250°C gave conversion (% vol) of (A) 55, and (B) 81. (12pp1492RKMHDwgNo0/0).
(E) ISR: No Search Report.