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BRITISH PETROLEUM PLC (BALL/) *WO 8600-545-A
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Prepn. of catalyst precursor for use in prodn. of methanol - by precipitating thermally decomposable copper thorium cpds.

C86-017882 N(AU DK JP NO SU US)

Full Patentees: British Petroleum Co. PLC; W.J.Ball (US only).

Additional Priority: 26.1.85-GB-001981.

Prodn. of a catalyst precursor of formula (I), for use (after reductive activation) in the conversion of synthesis gas to MeOH is as follows;
(a) copper and thorium are pptd. at below 50°C in a thermally decomposable form (II) by addn. of M_2CO_3 or $MHCO_3$ (M = alkali metal and/or NH_4) to final pH 5-7;
(b) pptd. (II) is recovered; and
(c) (II) is thermally decomposed at 300-600°C to give (I).

$$Cu_aThA_bO_x \qquad (I)$$

A = alkali metal;
a = 0.1-4 (pref. 0.5-3);

E(10-E4E1, 35-A) N(2-D, 3-A)

b = 0-0.5 (pref. 0);
x = no. to satisfy valencies.

Also claimed is a catalyst compsn. comprising elemental copper and an oxide of thorium in the atomic ratio Cu_aThO_x, in which at least 30% of the Cu particles have size ≤ 20Å.

ADVANTAGE

The prepd. catalyst is resistant to decay, is very reproducible, and is an excellent MeOH prodn. catalyst giving very high MeOH space time yields and MeOH selectivities as high as 99%.

CATALYST PREPARATION

Pptn. is pref. at < 30(esp. 0-25)°C under CO_2, with final pH 5.5-65. Cu and Th are pref. in aq. soln. as the nitrate salts. Pref. Cu is added and pptd. after Th has been pptd. (opt. sepd., washed, and re-dispersed). The prefd. precipitants are $(NH_4)_2CO_3$ or NH_4HCO_3.

Pptd. (II) is pref. washed and dried at < 150°C.

Thermal decompsn. is pref. at 400-500 (esp. 440-460)°C in N_2 or air.

CATALYST ACTIVATION

Prepd. (I; b=0) is reductively activated by contact with synthesis gas as e.g. 80-300 (pref. 150-250)°C and 0-100 bar under MeOH prodn. conditions.

Prepd. (I; b is not 0) is pref. reductively at least initially with reducing gases in the absense of CO as a discrete step prior to MeOH prodn.

EXAMPLE

K_2CO_3 (207.3g) in H_2O (1.5 l) was added dropwise to $Cu(NO_3)_2.3H_2O$ (120g) and $Th(NO_3)_4.H_2O$ (180g) in H_2O (3 l) at room temp. (final pH 6, using 1.15 l of K_2CO_3) soln). Sepd. solid was washed, dried at 120°C, and calcined in air at 450°C for 6 hr. to give a catalyst precursor contg. 19% Cu and 44% Th.(39pp478DAHDwgNo0/5)

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