

88-242564/34

E17 H04 J04 (H06)

ESSO 27.12.85

EXXON RES & ENG CO

*US 4762-959-A

04.06.87-US-057302 (+US-813918) (09.08.88) C07c-01

Conversion of methanol to hydrocarbon(s) - using catalyst comprising cobalt and promoter on titania

C88-108518

E(10-J2D) H(4-E5, 4-F2E) J(4-E1, 4-E4) N(2-B1)

WIDER DISCLOSURE

The catalysts may also be used to convert synthesis gas to hydrocarbons.

PREFERRED CATALYSTS

The catalyst contains 5-15 wt.% Co and has a M : Co wt. ratio of 0.04-0.25 : 1. M is esp. Ce and is added during impregnation of the support with Co.

EXAMPLE

A feed comprising MeOH, H₂ and Ar in 20 : 1 : 4 molar ratio was contacted at 230°C. and 400 psig (LHSV = 0.67) with a catalyst comprising 4.55% Co and 1% Ce on TiO₂. The MeOH conversion was 49%, with 74 wt.% selectivity for C₂₊ hydrocarbons. The corresp. values for a catalyst comprising 5% Co on TiO₂ were 31% and 68 wt.% respectively (10pp367CGDwgNo0/2).

Conversion of MeOH to hydrocarbons is effected at 150-350 °C. and a MeOH partial pressure of 100-1000 psia, with a MeOH : H₂ ratio above 4 : 1 and a LHSV of 0.1-10, using a catalyst comprising Co and a promoter (M) on TiO₂ or a TiO₂-contg. support.

The catalyst contains 2-25% Co. M is Zr, Hf, Ce or U. The M : Co wt. ratio is above 0.01 : 1.

ADVANTAGE

The promoter increases the activity of the catalysts and their selectivity for C₂₊ hydrocarbon prodn., and also reduces loss of activity after regeneration by burning off coke and contacting with a reducing gas.

US4762959-A

88-205044/29

E17 H04 J04

ESSO 27.12.8:

*US 4755-536-

EXXON RES & ENG CO

24.10.86-US-922885 (+US-813918) (05.07.89) C07c-01

Converting syngas to hydrocarbon(s) - with catalyst comprising cobalt and titania with zirconium, hafnium, cerium or uranium as promoter

C88-091563

Div. ex: 4663305 (87-143206/20)

Process for conversion of syngas feed to hydrocarbons comprises contacting the feed at reaction conditions with a catalyst contg. about 2-25 wt. % Co, which is composited with TiO_2 or a TiO_2 -contg. support, to which is added a Zr, Hf, Ce or U promoter in a wt. ratio of promoter metal to Co of more than about 0.010:1.

USE/ADVANTAGE

High-quality distillate fuels etc. can be produced, the catalysts being highly active and stable prior to regeneration. Unlike the unpromoted catalyst, the activity, selectivity and stability of the promoted catalyst after regeneration are essentially the same as that of a freshly prepd. unpromoted Co- TiO_2 catalyst which has never been regenerated by burning off the coke at high temp. in air under oxidising

E(10-J2D) H(4-E5, 4-F2E) J(4-E1, 4-E4, 4-E5) N(2-B, 3-A 3-B)

conditions.

PREFERRED CATALYST

The wt. ratio Zr, Hf, Ce or U to Co is 0.04:1 to 0.25:1. The Co constitutes 5-15 wt. % of the catalyst compsn. The rutile:anatase ratio of the TiO_2 is 3:2 to 100:1 and higher, esp. about 2:3 to 3:2.

PROCESS CONDITIONS

The syngas, of H_2 :CO ratio 0.5:1 to 4:1, is pref. converted at GHSV 100-5000, 160-290°C and total pressure about 80-600 psig. (Spp1492C (DwgNo0/2).

US 4755 6-A

87-143206/20 E17 H04
 EXXON RES & ENG CO

ESSO 27.12.85
 *US 4663-305-A

27.12.85-US-813918 (05.05.87) B01j-21/06 B01j-23/10

Catalyst for converting methanol or syn-gas to liq. hydrocarbon(s) - comprises cobalt on titania support, promoted by zirconium, hafnium, cerium or uranium to reduce activity loss on calcination
 C87-059718

Regeneration-stable catalyst for converting MeOH or synthetic gas to liq. hydrocarbons consists of 2-25 wt. % Co composited with TiO_2 or a TiO_2 -contg. support with sufficient of a Zr, Hf, Ce or U promoter to provide a wt. ratio of the Zr, Hf, Ce or U metal to Co of greater than 0.101:1. (sic).

ADVANTAGE

The promoters reduce the loss of activity, esp. for MeOH prodn., of the Co- TiO_2 catalysts during regeneration by calcination in air. E.g. loss of activity (CO conversion) on regeneration at 500°C. is reduced from about 30% to a small value.

PROCESS

Process comprises contacting MeOH or CO/ H_2 or a precursor of CO/ H_2 with a bed of the catalyst to produce a middle distillate fuel prod., consisting chiefly of linear, esp. 10C+, paraffins and olefins. MeOH (1 mole) is pref. mixed

E(10-J2C3, 10-J2D3, 34-E, 35, 35-K4) H(4-E5, 4-F2E) N(2-B1, 3, 6-E)

with H_2 (0.125 mole or less), with MeOH partial pressures of 200-700 psia and reacted at 180-250°C. and LHSV 0.2-2. H_2 and CO (pref. 0.5-4 by vol.) are pref. reacted at 140-400 psig, 190-260°C. and GHSV 300-1500.

PREFERRED COMPOSITION

In the TiO_2 , the rutile:anatase ratio is at least 2:3, or at least 3:2, or at least about 100:1 or higher. The wt. ratio of Zr, Hf, Ce or U metal to Co is pref. 0.04:1 to 0.25:1. The catalyst compsn. pref. contains about 5-15 wt. % Co.

PREPARATION

The catalyst can be prepd. e.g. from spherical TiO_2 beads by impregnation with an aq. soln. contg. $Co(NO_3)_2$ and a salt of Zr, Hf, Ce or U (e.g. $ZrO(O_2CMe)_2$), drying, calcining in air to 500°C. and reducing in H_2 at 450°C..

EXAMPLE

Catalysts prepd. as above contained TiO_2 and (wt. %): (A) 5.00 Co; (B) (according to the invention 4.34 Co + 1 Zr. A mixt. of (moles) 20 MeOH:1 H_2 :4 Ar was passed over the catalysts at MeOH LHSV = 0.67, 230°C. and 400 psig.