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

Conversion of MeOH to hydrocarbons is effected at 150-350 °C. and a MeOH partial pressure of 100-1000 psia, with a MeOH : H_2 ratio above 4 : 1 and a LHSV of 0.1-10, using a catalyst comprising Co and a promoter (M) on TiO_2 or a TiO_2-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 C_{2+} hydrocarbon prodn., and also reduces loss of activity after regeneration by burning off coke and contacting with a reducing gas.

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 synthes s gas to hydrocarbons.

PREFERRED CATALYSTS

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

EXAMPLE

A feed comprising MeOH, H_2 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 TiO_2. The MeOH conversion was 49%, with 74 wt.% selectivity for C_{2+} hydrocarbons. The corresp. values for a catalyst comprising 5% Co on TiO_2 were 31% and 68 wt.% respectively (10pp367CGDwgNo0/2).

US4762959-A

88-205044/29 E17 H04 J04 ESSO 27.12.85
EXXON RES & ENG CO *US 4755-536-A
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 that 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 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. (5pp1492(DwgNo0/2).

E(10-J2D) H(4-E5, 4-F2E, 4-J4E1, 4-E4, 4-E5) N(2-B, 3-A, 3-B)

87-143206/20 E17 H04 ESSO 27.12.85
EXXON RES & ENG CO *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 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.

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

86-055230/08 E17 H06 J04 ESSO 29.06.84
EXXON RES & ENG CO *US 4568-663-A
29.06.84-US-626022 (04.02.86) B01j-21/06 B01j-23/12

Catalyst for converting methanol or synthesis gas to hydrocarbons - comprises cobalt, rhenium and opt. thoria composited with an inorganic oxide support

C86-023468

A catalyst useful for the conversion of methanol or synthesis gas to hydrocarbons comprises Co and thoria in catalytically active amts. and Re, composited with an inorganic oxide support in wt. ratio of Re:Co of 0.025:1 to 0.10:1.

The catalyst may contain 2-25% Co and 0.1-10% thoria based on the total wt. of catalyst, with the Co:thoria ratio being 20:1 to 1:1.

When the support is titania or titania-contg., no thoria need be present and the catalyst pref. contains 2-25% Co. The The rutile: anatase ratio of the titania may be at least 2:3.

USE/ADVANTAGE

Using the catalysts, methanol and synthesis gas are converted at high conversion levels and at high yields to premium grade transportation fuels, esp. 10+C distillate fuels, partic. without the prodn. of excessive amts. of CO_2. The catalyst are highly active and exhibit high stability.

E(10-J2D3) H(4-E5, 4-F2E, 6-B) J(4-E4) N(2-B1, 3-A, 3-E, 6-E)

PREFERRED CATALYSTS

5-15% Co and 0.5-5% thoria are present. The rutile:anatase content of the titania is 3:2 to 100:1 or higher. The wt. ratio of Co:thoria is 15:1 to 2:1.

EXAMPLE

TiO_2 was impregnated with cobaltous nitrate and perrhenic acid from acetone soln., dried at 15=°C and calcined for 3 hrs. The catalyst contained 12 wt.% Co and 3 wt.% Re on 16-20 Mesh TiO_2 (56% rutile) having a rutile:anatase ratio of 1.3:1. It was calcined in air at 500°C for 3 hr.

The catalyst was charged to a reactor, reduced in H_2 at 450°C for 1 hr and then reacted with syn.gas at 200°C, 280 psig, GHSV=1000 and H_2:CO=2.15 for at least 16 hrs. The performance of the catalyst was monitored by GC analysis. CO conversion was 81%.

When a similar catalyst but contg. no Re was used, CO conversion was 54%. The Re has adequate to stabilize the Co metal against agglomeration or loss of Co dispersion. (12pp1685 RBHDwgNo0/5)