89-172713/23 E17 H06 J04 DOWC 30.07.84
DOW CHEMICAL CO *US 4831-060-A
06.06.88-US-202754 (+US-636000) (16.05.89) C07I-27/06

Selective production of mixed alcohol(s) from syn gas - by contacting mixt. of hydrogen and carbon mon oxide over co-catalyst of molybdenum, tungsten or rhenium and cobalt, nickel or iron

C89-076483

Div. ex. 4752623

Other Priorities 25.09.85-US-779906 17.12.86-US-942933

A process for selectively producing mixed alcohols from synthesis gas comprises contacting a mixt. of hydrogen and carbon monoxide with a catalyst contg. components of:
(1) A catalytically active metal of molybdenum, in free or combined form;
(2) A co-catalytic metal of iron, in free or combined form; and
(3) a Fischer-Tropsch promoter of an alkali or alkaline earth series metal, in free or combined form.

The components are combined by dry mixing, mixing as a wet paste or wet impregnation and then sulphided. The catalyst excludes rhodium, ruthenium and copper. The reaction is conducted at a pressure of at least 500 psig and under conditions sufficient to form the mixed alcohols in at least 50% CO_2 free C selectivity. The mixed alcohols contain a 1C to 2-5C alcohol wt. ratio of less than 1:1.

E(10-E4E) H(6-B, 6-D) J(4-E1) N(1-A, 1-B, 2-A1, 3-D)

USE/ADVANTAGE

The mixed alcohols are useful as motor fuel or motor fuel additive, combustive fuels, solvents etc.

The process affords high production rates at high selectivities of the mixed alcohols without the use of rhodium, copper, ruthenium or zinc. The case of catalyst preparation, simplicity and efficiency of the catalyst mix are unique.

PREFERRED PROCESS

The co-catalyst metal used is not susceptible to oxidation at ambient air at NTP or other normal conditions.
The Fischer-Tropsch promoter is potassium in free or combined form and is present in an amt. of 0.05-20 wt.% calculated as free element in the finished catalyst.
The mixed alcohols are produced in about 75% or greater CO_2 carbon selectivity

EXAMPLE

A soln. contg. K_2CO_3 (1 part by wt.), $(NH_4)_6Mo_7O_{24}.4H_2O$ (5 parts), aq. 22% $(NH_4)_2S$ (30 parts), heated to 50-

60°C was used in each of four impregnations of pelleted 4-6 mesh MBV activated carbon. The hot soln. was added dropwise to C until it was satd. Following each impregnation, the wet compsn. was air dried at room temp. until the C was dry. The compsn. was heated at a temp. increasing by 2°C/min., until 300°C was reached. This temp. was held for 1 hr.

A hot soln. contg. $Co(O_2CCH_3)_24H_2O$ (1.3g) dissolved in deionised water (5 ml) was added dropwise over 5.2g of a -20 + 20 mesh sample of the supported molybdenium sulphide catalyst. After air drying at room temp. for few hrs. the impregnated compsn. was heated in flowing N_2 at temp. rising by 2°C/min. until 300°C and held at this temp. for 1 hr.

The N_2 treated impregnated compsn. was treated in flowing H_2 + 3% H_2S for 2 hr. at 380°C prior to exposure to syngas feed. After 382 hr. onstream, the catalyst was treated in flowing H_2 at 500°C for 2 hr. and flowing H_2 + 3% H_2S at 400°C for 2 hrs.

After 428 hr. onstream at 318°C and a pressure of 1472 psig, H_2/CO mol. ratio of 1.11, GHSV (1455 hr.), a CO conversion of 27.3% was obtained.

The liquid phase contained MeOH (13.1), EtOH (24.7), Propanols (14.2), butanols (5.8), pentanols (1.2), wt.% to give a 1C/2C+ alcohol wt. ratio of 0.42.(11pp1917RBHDwgNo 0/0).

US4831060-A

88-190348/27 E17 J04 DOWC 30.07.84
DOW CHEMICAL CO *US 4752-623-A
25.09.85-US-779905 (+US-636000) (21.06.88) C07c-27

Prodn. of higher alcohol(s) from syngas with catalyst - contg. molybdenum or tungsten with cobalt or nickel and Fischer-Tropsch promoter, intimacy of contact governing prod. compsn.

C88-085077

Process for selective prodn. of mixed alcohols from syngas comprises contacting H_2 and CO with a catalyst contg.

(a) as catalytic metal, free or combined Mo or W,

(b) as cocatalytic metal, free or combined Co or Ni, and

(c) as Fischer-Tropsch promoter, a free or combined alkali(ne earth) metal and not contg. Rh, Ru or Cu. The components are combined by dry mixing, mixing as a wet paste or wet impregnation, and then sulphiding.

The syngas is contacted with the catalyst at at least 500 psig and under conditions to form the mixed alcohols, contg. a 1C/2-5C alcohol wt. ratio of less than about 1:1, in at least 20 % CO_2-free C selectivity.

WIDER DISCLOSURE

Component (a) may also be Re, and component (b) may also be Fe, both Re and Fe being free or combined. The catalyst may also contain a support.

E(10-E4E) J(4-E1) N(1-A, 1-B, 2-A1, 2-B1, 2-C1, 3-C, 3-D, 3-E)

USE/ADVANTAGE

The mixed alcohols are useful as motor fuel, motor fuel additive, other fuel and solvents. Control of the product mixt. is uniquely simple and efficient. The compsn. of the mixed alcohols fraction can be selected by selecting the intimacy of contact of (a) and (b). Up to about 1.4 g 1-5C alcohol/g catalyst x hr may be obtd.

The alcohol prod. may have low acidity and high octane blending value, and so may be lendable into hydrocarbon fuels without elaborate processing. The catalyst may be stable and active for 6000 hr or more.

CONTACTING IN CATALYST

Low intimacy of contact is provided by components (a) and (b) being of a size of about 35 mesh or smaller. High intimacy of contact is provided by mixing as a wet paste or preparing by impregnation. Combination by dry mixing is pref. With increasing intimacy of contact, the wt. ratio of higher alcohols to MeOH usually increases; the selectivity to mixed alcohols at high conversion increases; and the process becomes less sensitive to feed gas S level.

PREFERRED CATALYSTS

Component (a) is pref. Mo; component (b) is pref. Co. present in at least about 30 wt. % of the Mo; and component (c) is pref. an alkali metal, esp. Cs or K. More specifically, the catalyst contains $Co(OAc)_2.4H_2O$ and MoS_2.

SELECTIVITY

The CO_2-free C selectivity of prodn. of mixed alcohols is pref. at least 50 %, esp. at least 75 % with K as component (c). The 1C/2-5C alcohol wt. ratio is pref. less than about 0.8:1. (11pp1492RBHDwgNo0/0).

US4752623-A

86-056735/09 E17 H06 DOWC 30.07.84
DOW CHEMICAL CO *EP -172-431-A
30.07.84-US-636000 (26.02.86) C07c-29/15 C07c-31/04

Converting synthesis gas to alcohol mixt. for blending in motor fuels - with high selectivity and output rate using 3 component catalyst, pref. co-pptd. molybdenum and cobalt sulphide with activator

C86-023996 E(BE DE FR GB IT NL)

E(10-E4E) H(6-B1) N(2, 3-C, 3-D)

Process for making alcohols boiling in the motor gasoline range in at least 20% selectivity, neglecting CO_2, comprises reacting H_2 and CO with a catalyst comprising: (a) Mo or W; (b) alkali (ne earth) metal, as promoter; and (c) one or more of Fe, Co or Ni; all elements named being free or combined.

USE/ADVANTAGE

The prod. is useful for blending into motor fuels, and can have high octane value. High prodn. rate and high 1-5C alcohol selectivity can be combined: up to 1.4 g 1-5C alcohol/g catalyst x hr. can be made. The ratio 1C:(2-5C) alcohols in the prod. is reduced (pref. to less than 1:1 by wt.) by catalyst component (c) and does not rise at higher temps. The mixed alcohol has low S level and low acid content and it may be possible to blend it into the fuel without complex purification.

PREFERRED CATALYST

The catalyst pref. also contains a support, e.g. as pellets granules, beads or extrudates.

Component (c) may be Fe; or component (a) may be Mo and component (c) Co. Components (a) and (c) are pref. present as co-pptd. sulphides. The atomic ratio of (a) : (c) is pref. 1:4 to 4:1.

Component (b) may be e.g. K_2CO_3. Most pref. the catalyst comprises agglomerated Co/Mo copptd. sulphides.

PROCESS

The molar ratio H_2/CO is pref. less than 2:1. The more pref. reaction conditions are about 310°C, 1500 psig, GHSV 3800, and H_2/CO ratio of about 1:1, with a 2Mo/Co catalyst. At least 0.3 g alcohol/g catalyst x hr. is then obtd.

EXAMPLE

A catalyst was made by (i) reacting an aq. soln. contg. 0.142 mole $(NH_4)_2MOS_4$ (made from ammonium molybdate) and 0.071 mole Fe $(OCC.CH_3)_2$ with acetic acid at 60°C; (ii) filtering and washing the copptd. sulphides; (iii) calcining at 500° C under N_2; and (iv) blending to give a mixt. of 66% Mo/Fe

sulphide, 20% bentonite clay, 10% K_2CO_3 and 4% Sterotex (RTM) The catalyst was combined with an equal vol. of tabular Si_2O_3 before use.(31pp1492RKMHDwgNo0/0).
(E) ISR:- No Search Report.