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**Prepn. of hydrocarbon mixt. from synthesis gas - in stage catalytic process, increasing yield of higher hydrocarbon(s)**

E(10-E4E, 10-H1, 10-J20) H(4-E5) J(4-E1) N(1, 2, 3)

001

In the prepn. of a hydrocarbon mixt., (1) a mixt. of CO and $H_2$, with a molar ratio of $H_2$:CO of 1-2, is contacted with a bi- or tri- functional catalyst contg. (I) at least 1 metal component which catalyses the conversion of $H_2$ + CO mixt. to acylic hydrocarbons and/or oxygenated acyclic hydrocarbons and (II) a crystalline silicate which, after calcination for 1 hour in air at 500 ° C, is stable at up to above 600 °C, has an X-ray diffraction pattern with four specified sdrong lines, and contains oxides of H, an alkali(ne earth) metal, Si and a trivalent metal A, which is Al, Fe, Ga, Rh, Cr or Sc, with a ratio (m) of $A_2O_3$:$SiO_2$ of less than 0,1, and (III) if the ratio of $H_2$:CO is less than 1.5, at least 1 metal component which catalyses the conversion of a water/CO mixt. to a $H_2/CO_2$ mixt., and (2) at least the not more than 2C fraction from stage (1) is contacted with (IV) a catalyst contg. Co, Ni or Ru as component which catalyses the conversion of a $H_2$/CO mixt. to acyclic hydrocarbons, and (V) if the ratio of $H_2$:CO in the feed to the second stage is less than 1.5 at least 1 metal component which catalyses the conversion of a water/CO mixt. to a $H_2/CO_2$ mixt.; if catalyst component V is used, water is added to the feed to stage (2).

ADVANTAGES

Acceptable feed space velocities can be used. Mixts. contg. more than 12C hydrocarbons are obtd.

PROCESS

(1) The $H_2$/CO mixt. is pref. obtd. by steam-gassing a carbonaceous material at 900-1500 °C and 10-100 bars. Pref. the ratio of $H_2$:CO is above 0.25. Reaction is at 200-500 (250-450) °C, 1-150 (5-100) bars and space velocity 50-5000 (300-3000) vol./vol./hour. (I) Fischer-Tropsch catalysts are used, esp. contg. Fe + Mg on alumina, or Fe + Cr on silica, or Co + Zr, Ti or Cr on silica. (II) Pref., only 1 trivalent metal, esp. Al, Fe or Ga, is present; m is esp. 0.002-0-05. In partic., an Al silicate, with m greater than 0.005, and contg. 0.1-10 wt. % of Mn, Ca, Mg or Ti, is used. The alkali metal content is partic. less than 0.1 wt. %. (III) If catalyst I also catalyses the conversion of a water/CO mixt. to a $H_2/CO_2$ mixt., catalyst III can be omitted. Catalyst I esp. converts a $H_2$/CO mixt. to methanol

and/or dimethyl ether, and partic. consists of $ZnO/Cr_2O_3$. If a Co/Zr, Ti or Cr catalyst is used as I, catalyst III must be included. (2) The feed may be the not more than 2C fraction, the not more than 4C fraction, or the whole prod. from stage (1). The $H_2$:CO ratio is pref. not less than 1.5 (1.75-2.25); this is esp. obtd. by addn. of water in stage (1) and by use of the trifunctional catalyst. Reaction is at 125-350 (175-275) °C and 1-150 (5-100) bars. (IV) a Co catalyst prepd. by impregnation is pref. partic. of type III. (V) The usual CO-shift catalysts are used.

EXAMPLE

In two-stage runs, a catalyst contg. 2 pts. vol. of a $ZnO-Cr_2O_3$ catalyst and 1 pt. vol. of an Al silicate with 3% Mn was used in the first stage, and a $Co/Zr/SiO_2$ (25:1.8:100) catalyst in the second stage. The ratio of $H_2$:CO in the first stage was (A) 0.8 (for comparison), or (B) 1.3, and in the second stage was (A) 1.7, or (B) 2.0. The conversions were: A 95%, B 97%. The compsn. of the prod. was: not more than 4C, A 45%, B 18%, 5-12C, A 38%, B 43%; 13-19C A 7%, B 16%; and not less than 20C, A 10%, B 23%.(28pp510)