

50158 E/24 E17
 TEXACO INC
 26.06.81-US-277527 (01.06.82) C07c-27/06
 Alkanol prodn. from synthesis gas - over mixed ruthenium and rhenium or manganese catalyst in molten quat. phosphonium cpd.

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 *US 4332-914

E(5-G3A, 5-L3A, 5-M, 5-N, 10-E4F, 35-S, 35-T, 35-X) N(2-E, 3-E, 5, 5)

0.00001-10 wt.% used with 0.00001-5 wt.% Re or Mn, and the atom ratio Ru:Mn or Re is 10:1-1:10. The synthesis gas used has CO:H₂ ratio 1:5-5:1 and can be diluted with N₂, argon, etc. Small amts. of formate and acetate esters, acetaldehyde, etc. are formed in the reaction.

EXAMPLE

2 mmoles RuO₂ hydrate and 8 mmoles Re₂CO₁₀ were dispersed in 10 g Bu₄NBr, charged to a reactor and brought to 2000 psig with 1:1 CO-H₂. The mixt. was heated at 220°C and 6350 psig for 6 hr., then cooled, and excess gas removed. The liq. prod. (23.9 g) comprised (wt.%) methanol 84.7 and ethanol 9.4. Liq. yield was 85 wt.% and turnover, of 1-2 C alkanols, was about 160 moles per g-atom Ru.(5pp1251).

Alkanol prodn. comprises reacting carbon monoxide and hydrogen at ≥ 500 (pref. 2000-9000) psig and ≥ 180 (pref. 180-250)°C over a catalyst system consisting of (1) a Ru cpd. (I); and (2) a halogen-free Re or Mn cpd. (II), dispersed in a low m.pt. quat. phosphonium base or salt (III), esp. a tetraalkyl- or mixed alkylaryl-phosphonium cpd.

Specified (III) are tetrabutylphosphonium bromide, chloride, iodide, acetate, chromate and hydroxide. (II) is esp. Re₂CO₁₀, MnCO₃ or Mn₂CO₁₀ and (I) is specifically RuO₂ or Ru₃CO₁₂.

ADVANTAGES

The catalyst system gives good yields (95% 1-2 C alkanols in the liq. prod.) with excellent selectivity for methanol (as high as 85%).

DETAILS

(III) has m.pt. < 180 (pref. < 150)°C and the mole ratio (I):(III) is 1:0.01-100 (esp. 1:0.5-20). Pref. the Ru concn. is