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TEXACO INC
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Prepn. of ethanol from carbon mon:oxide, hydrogen and methanol - using ruthenium-quat. ammonium or phosphonium cpd.-cobalt halide catalyst

D/S: E(AT BE DE FR GB IT NL SE)

Ethanol is prepd. by treatment of a mixt. of carbon monoxide, hydrogen and methanol with a catalyst at ⩾150 °C and ⩾ 35 bars. The catalyst system consists of (a) a ruthenium cpd. (I); (b) a quat. phosphonium or ammonium cpd. (II); and (c) cobalt(II) iodide, chloride or bromide.

ADVANTAGES

Use of the catalyst system gives high yields of EtOH, with high MeOH conversions. The catalyst is readily recovered and recycled.

DETAILS

(I) is pref. RuO_2 (and hydrate), RuO_4, $RuCl_3$, Ru acetate or propionate, Ru(III) acetylacetonate, or Ru_3CO_{12}. Pref. (II) are tetraalkyl (esp. tetrabutyl) or alkyltriaryl phosphonium salts or bases (pref. the bromide, chloride, iodide, acetate, chromate or hydroxide); esp. heptyl triphenylphosphonium chloride or bromide or methyltriphenylphosphonium bromide. Pref. mol. ratio (I) : (II) is 1:0.01-100, esp. 1:0.5-20. Pref. the reaction is at 150-350 (esp. 180-250) °C and 135-700 bars with mol. ratio $CO:H_2$ 20-1:1-20 (pref. 5-1:1-5); (II) concn. 1×10^{-5} - 5 wt.%; and Co concn. 1×10^{-5} - 5 wt.%.

The reaction is pref. in the presence of an oxygenated hydrocarbon solvent (pref. 3-12C and not more than 3 O's) esp. 1,3- or 1,4-dioxan, isopropyl propyl ethyl, dibutyl ether, ethyl butyl ether or ethylene glycol dibutyl ether.

EXAMPLE

A mixt. of hydrated RuO_2 (0.57 g), tetrabutylphosphonium bromide (10.2 g), CoI_2 (1.9 g), MeOH (30 ml), and p-dioxan (70 ml) was pressurised with CO/H_2 (1:2 mol. ratio) to 70 bars, then heated for 10 hr. at 200 °C and 235.5 bars. Analysis showed the prod. contained 74 mol.% EtOH (80 mol.% MeOH conversion).(25pp478).

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E(10-E4E) N(2-B, 2-E, 5-D, 5-E)

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