83-724818/31 A60 E17 TEXC 13.01.82
TEXACO DEV CORP *GB 2113-206-A
01.02.82-US-344431 (+ US-339233) (03.08.83) C07c-67/36

Lower alkyl carboxylate prodn. from corresp. acid - and synthesis gas, using catalyst contg. ruthenium and cobalt cpds.

A(8-P4, 8-S2) E(10-G2E) N(2-B, 2-E, 5)

C83-072424

Prodn. of lower alkyl carboxylate (I) comprises reacting, at elevated temp. and pressure, the appropriate carboxylic acid with carbon monoxide and hydrogen in presence of a catalyst consisting of (1) a ruthenium cpd., (2) a cobalt cpd. and (3) a quat. onium salt or base. Pref. the reaction mixt. also contains methanol and an inert solvent (esp. 1,3- or 1,4-dioxano, dipropyl or dibutyl ethers or diethylene glycol dimethyl ether) can be present.

Pref. Ru cpds. are the (hydrated) dioxide, tetraoxide, acetate, propionate, or acetylacetonate, or $(Ru)_3(CO)_{12}$. Co cpds. are esp. carbonyls, halides or the perchlorate and (3) is pref. a quat. phosphonium or ammonium salt.

USE/ADVANTAGES

The method is esp. used to make ethyl and propyl esters which are useful in prodn. of e.g. anhydrides, propylene or ethylene and as solvents, diluents, plasticisers and softeners for resins. This catalyst provides improved yields (49-63% in presence of methanol) and selectivity.

DETAILS

Most pref. the mole ratio of components (1) : (2) : (3) is 1-4: 0.25 - 1 : 10-50, and pref. reactants are 1-12 C mono- or di- carboxylic aliphatic acids and H_2 : Co mixts. of mole ratio 1 : 5 - 5 : 1. Reaction is at 150-350 (180)250°C and 1000-7500 psi.

EXAMPLE

A reactor was charged with 0.19g hydrated Ru oxide; 4.25g n-heptyltriphenylphosphonium bromide; 0.085g $(Co)_2(CO)_8$ and 10 g propionic acid. It was brought to 200 psi with 1:1 synthesis gas, heated to 220°C and held at 6280 psi for 18 hr. The reactor was cooled, vented and the liq. prod. (16.9g) analysed: 30.3% ethyl propionate (Ia); 15.6% n-propyl propionate (Ib); 2.4% methyl propionate; 1.9% n-butyl propionate and 41.4% unreacted acid. Selectivities were 56% for (Ia) and 25% for (Ib) and corresp. yields 27% and 12%. In presence of 5.2g methanol, yield of (Ia) was 45% and of (Ib) 7%.(10pp1251DwgNo0/0)

GB2113206