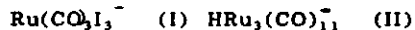


87-320678/45 E17 UNIC 11.11.79
 UNION CARBIDE CORP *US 4703-064-A
 28.11.83-US-555637 (+US-091242) (27.10.87) C07c-27/06 C07c-67
 Prodn. of ethylene glycol, methanol and ethanol from synthesis gas -
 using as catalyst a synergistic combination of ruthenium carbonyl
 complexes in soln.
 C87-136714

Other Priorities: 19.03.82-US-359778 30.06.81-US-279095

Methanol, ethylene glycol and ethanol are produced by reacting a mixt. of hydrogen and carbon monoxide in a solvent contg. liq. phase in the presence of a ruthenium carbonyl complex catalyst at 50-400°C, 500-15,000 psia. The catalyst is a synergistic combination of ruthenium complexes (I) and (II), characterised by three significant IR bands at 2100, 2015 and 1990 $\text{cm}^{-1} \pm 10 \text{ cm}.$



ADVANTAGE/USE

The process is stable, and significant loss of ruthenium from reaction or catalyst does not occur. The process can yield predominantly any one of the three specified prods.; it is esp. of use for the production of ethylene glycol at low cost.

E(10-E4B, 10-E4E1, 10-E4E2) N(5-B)

LIQUID PHASE

The solvent is polar or complexing; it may be water, a carboxylic acid (in which case carboxylates of the specified prods. are formed), a sulphone, lactam, ether (e.g. crown ether, alkylene glycol alkyl ether or polyalkylene glycol dialkyl ether) or lactone (e.g. butyrolactone).

A promoter is pref. present, esp. an iodide-contg. cpd., e.g. Li, Na, K or Cs iodide.

CATALYST

Ratio (I):(II) is 0.2:1 to 1:1; the average oxidation state of the ruthenium is between -0.2 and +0.25. The catalyst combination may be formed separately or in situ in the reaction solvent.

EXAMPLES

100 examples are given, with a range of conditions and results. In a typical example the reaction mixt. consisted of 3 mmole Ru (added as $\text{Ru}_3(\text{CO})_{12}$), 12 mmole KI and 75 ml 18-crown-6 ether as solvent; H_2/CO ratio was 1/1. In 0.83 hr at 230°C, 12,500 psig, 1.22g ethylene glycol, 6.73g methanol and 0.63g ethanol were obtained. (18pp1644LDDwgNo0/8).

US4703064-A

04956 K/03 E17 UNIC 30.06.81
 UNION CARBIDE CORP *EP--68-498
 30.06.81-US-279095 (05.01.83) C07c-29/15 C07c-31/04
 Prepn. of methanol, ethanol and ethylene glycol - from carbon monoxide and hydrogen in presence of ruthenium carbonyl complex catalyst

E(10-E4B, 10-E4E) N(5-B)

085

action of $\text{Ru}_3(\text{CO})_{12}$ with excess I^- .

Reaction is pref. at 100-350 (esp. 150-300) $^\circ\text{C}$ in a solvent (pref. polar of relatively high dielectric constant (i.e. above 2) and/or complexing solvent), e.g. a carboxylic acid (to give the prods. as carboxylates), a sulphone, lactam, ether (pref. crown ether), an alkyl ether of an alkylene glycol, a dialkyl ether of a polyalkylene glycol, tetraglyme or a lactone (pref. butyrolactone). Opt. the reaction is in the presence of an iodide promoter (pref. an alkali metal iodide, esp. NaI, LiI, KI or CsI; 0.1-10⁶ mol./g. atom of Ru). Mol. ratio CO : H₂ is 40-1 : 1-40 (esp. 10-1 : 1-10).

EXAMPLE

Mixt. of sulpholane (75 ml.), NaI (18 mmol), $\text{Ru}_3(\text{CO})_{12}$ (2 mmol) and 1 : 1 H₂/CO (12,500)psi) was heated at 230 $^\circ\text{C}$. to give ethylene glycol (0.38 mol/hr.) and MeOH (2.28 mol./hr.). (53pp478).

(E)ISR: EP--13008 US4301253 US4265828 GB2024811
 US4270015 US4233466 4.Jnl.Ref.

C83-004893 D/S: E(BE DE FR GE IT NL)

MeOH, ethylene glycol (I) and EtOH are prepd. directly by the liq. phase reaction of H₂ and CO at 50-400 $^\circ\text{C}$ and 500-15,000 (pref. 500-12,500) psia in the presence of a ruthenium carbonyl complex (II) catalyst. The IR spectrum of (II) has significant bands at 2100, 2015 and 1990 cm^{-1} (all $\pm 10 \text{ cm}^{-1}$).

ADVANTAGES

There is no significant loss of Ru from the reaction or catalyst.

DETAILS

(II) is a synergistic mixt. of the Ru carbonyl complexes (a) $\text{Ru}(\text{CO})_3\text{I}_3^-$ and (b) $\text{HRu}(\text{CO})_{11}^-$; has average oxidn. state -0.2 to +0.25, pref. 0 (i.e. mol. ratio (IIa) : (IIb) = 0.012-2, pref. 0.2-1). The catalyst system is prepd. by known methods (US 2535060 etc.), e.g. formed in situ by re-

EP--68498