Acetaldehyde

Industrial Chemistry

Synthesis of acetaldehyde

Acetaldehyde is an important precursor for major organic chemicals such as:

- Acetic acid, anhydride

- Ketene,

- Ethyl acetate

- 1-butanol

- 2-ethylhexanol

Its importance is declining in the chemical industries due to the discovery of more efficient routes (Carbonylation of methanol for acetic acid, and hydroformylation for 1-butanol and 2-ethylhexanol). It is still highly relevant and has unique uses: it is produced mainly in the US and Japan for the manufacture of paracetic acid and for the oxidation of p-xylene to terephthalic acid.

Synthesis of acetaldehyde

- Oxidation of ethylene (Wacker process)

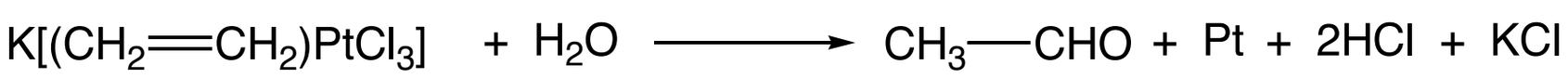
- Ethanol dehydrogenation

- C3/C4 alkane oxidation (not discussed here)

Wacker process - Chemistry

Preliminary Observations

F. C. Phillips, Am. Chem. J. 1894, 16, 255.



J. S. Anderson, J. Chem. Soc. 1934, 971.

Pd and Pt can oxidize ethylene to acetaldehyde stoichiometrically

How can it be done catalytically?

Kinetic-driven multistep redox

Ethene is converted to acetaldehyde in the presence of tetrachloropalladate(2–) and water.

$$CH_2{=}CH_2 + [PdCl_4]^{2-} + H_2O \rightarrow CH_3CHO + 2\ H^+ + 4\ Cl^- + Pd(0)$$

Ethene is oxidized, palladium(II) is reduced to palladium(0). Therefore, palladium can be used as catalyst in the presence of an oxidant whose E^0_{red} is more positive than E_0(Pd(II)/ Pd(0)). Such an oxidant will reoxidize Pd(0) to Pd(II)

$$Pd(0) + 2\ Cu^{2+} + 8\ Cl^- \rightarrow [PdCl_4]^{2-} + 2\ [CuCl_2]^-$$

An appropriate oxidant for the oxidation of Cu(I) is O_2:

$$2\ [CuCl_2]^- + \frac{1}{2}\ O_2 + 2\ H^+ \rightarrow 2\ Cu^{2+} + 4\ Cl^- + H_2O$$

The sum is:

$$CH_2{=}CH_2 + \frac{1}{2}\ O_2 \xrightarrow[H_2O]{[PdCl_4]^{2-}\ /\ Cu^{2+}} CH_3CHO$$

Water is essential as the formation of acetaldehyde occurs via nucleophilic attach of an OH- to the coordinated alkene in the palladium complex (see step 1)

Process operation

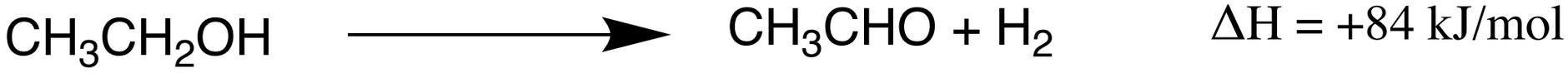
Two versions are possible:

1) Single step: Reaction and regeneration with O_2 are carried out in the same reactor. Pure O_2 must be used as oxidant to avoid alkene loss. 3 bar pressure of ethylene and O_2 at 120-130 °C. 35-45% conversion. The reaction is exothermic and the heat is used to distill offf acetaldehyde and water.

2) Two-step process: One step for the reaction and one for the regeneration, which now can use air as oxidant. After reaction, acetaldehyde is distilled off and the catalyst is regenerated at 100 °C ad 10 bar of air. Advantage: Total ethylene conversion, Disadvantage: Double reactor.

Acetaldehyde from ethanol

Reaction:



Two modifications:

1) Endothermic dehydrogenation with Ag or Cu catalysts activated with Zn, Co, or Cr. Conversion limited to 30-50 % at 270-300 °C. Selectivity 90-95%. The hydrogen produced can be used for hydrogenation in separate processes.

2) Oxidative dehydrogenation with air or oxygen. The heat of the oxidation of H_2 to H_2O will compensate for the endothermic dehydrogenation. Ideally the reaction should be operated at thermoneutral conditions. Oxygen amount regulates the temperature. Vapor phase reaction at 3 bar and 450-550 °C with a solid phase catalyst. The aim is to get a thermoneutral reaction. 30-50% ethanol conversion with 85-95% selectivity.

Acetaldehyde is then separated by distillation and ethanol recycled to the reaction.