

Hydroformylation of olefins with cobalt/phosphonate- and cobalt/sulfonate-phosphines

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[#] A member of the EU-funded Coordination Action of Nanostructured Catalytic Oxide Research and Development in Europe (CONCORDE)

Water-soluble cobalt/phosphonate-phosphine catalysts were prepared and used in the two-phase hydroformylation of a mixture of internal C₁₀-olefins. The preparation of the cobalt complexes was carried out in the two-phase system hexane/water. Phosphonate-phosphines and sulfonate-phosphines were employed as complex ligands using the following structures: Ph₂P-(CH₂)₂-PO₃Na₂, Ph₂P-(CH₂)₃-PO₃Na₂, Ph₂P-(CH₂)₁₀-PO₃Na₂, PhP(-(CH₂)₁₀-PO₃Na₂)₂, PhP(-C₆H₄-PO₃Na₂)₂, Ph₂P-(CH₂)₃-SO₃Li, Ph₂P-C₆H₄-SO₃Li and Ph₃P-(SO₃Na)₃ (TPPTS). The investigations on the hydroformylation were carried out at temperatures between 150 and 190 °C, syngas (CO/H₂ = 1) pressures from 60 to 200 bar (at room temperature) and reaction times between 12 and 46,5 h. 25 and 100 ml stainless-steel autoclaves (Parr) were used for the investigations. The aqueous catalyst solution (20 or 30 ml) contains 0.25 % of cobalt with a ligand/Co-ratio between 2 and 10. 10 or 15 ml of an industrial decene mixture containing terminal and internal olefins were loaded depending on the volumes of the used autoclaves. Product analyses were carried out mainly using GC (FID)

Highest aldehyde yields of ca. 60-65 mol% beside 12-13 mol% decane, 1-5 mol% decenes and 2-5 mol% of other oxo-products were formed at a reaction temperature of 170 °C, a syngas-pressure of 160-200 bar and a reaction time of 12-16 h. The remainder is a fraction of non-GC-detectable heavy oligomers (15-20 %). Best olefin conversion was reached with Ph₂P-C₆H₄-SO₃Li and TPPTS as ligands, best stability of biphasic system with TPPTS and Ph₂P-(CH₂)₃-SO₃Li. The activity of the catalysts rises with increasing reaction pressure and temperature whereas the differences between 160 and 200 bar starting pressure were only small. At these higher pressures the selectivity is not significantly affected by the structure of the ligand with regard to the terminal aldehyde. The terminal aldehyde selectivity amounted to 36-42 mol% of the aldehyde pool. Cobalt/phosphonate-phosphine catalysts are not suitable at pressures higher than 100 bar due to their instability.