

Effect of pH on rate and selectivity behavior in biphasic hydroformylation of 1-octene

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Abstract

The effect of pH on activity and selectivity of $(\text{RhCl}(\text{COD})_2)/\text{TPPTS}$ catalyzed hydroformylation of 1-octene in a biphasic medium has been studied. The pH of the aqueous catalyst phase shows a strong influence on the rate of reaction and *n/iso* ratio of the aldehyde products. The effect of P/Rh ratio, catalyst and 1-octene concentration, partial pressure of hydrogen and carbon monoxide was studied at 7 and 10 pH, which showed significantly different trends. The rates increased by two- to five fold when the pH was changed from 7 to 10. While the dependence of the rate was found to be linear on the olefin and hydrogen concentration at both 7 and 10 pH, the rate of hydroformylation was found to be inhibited with increase in catalyst concentration beyond $1 \times 10^{-3} \text{ kmol m}^{-3}$. The effect of partial pressure of carbon monoxide was linear at pH 7 whereas at pH 10 a substrate inhibited kinetics was observed. © 1997 Elsevier Science B.V.

1. Introduction

Hydroformylation of olefins to aldehydes using homogeneous catalysts is a well known industrial process [1,2] as a key step in the manufacture of oxo alcohols. Water soluble catalysts consisting of Rh complexes of sulphonated phosphine derivatives have gained considerable attention in recent years as these reactions can be carried out in a biphasic

medium, wherein the catalyst is soluble in the aqueous phase and the reactants and products are soluble in the organic phase [3,4]. This novel catalyst system with a possibility of simple catalyst and product separation is already commercialized by Ruhrchemie–Rhone Poulenc. A major drawback in two phase catalytic hydroformylation using water soluble catalysts, is that olefins, and in particular, higher olefins, have poor solubility in the aqueous phase, which results in lower reaction rates. To enhance the solubility of the olefins in the aqueous phase the use of co-solvents such as ethanol etc. has been proposed [5–7].

The reaction being in the aqueous medium, the pH of this solution has an important role to

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