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Rhodium-BiPhePhos catalyzed hydroformylation studied by operando FTIR spectroscopy: Catalyst activation and rate determining step

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Abstract

The homogeneously rhodium catalyzed hydroformylation of 1-decene was studied using operando FTIR spectroscopy. The bulky chelating diphosphite ligand BiPhePhos was used for catalyst modification. Special emphasis was given to the transformation of the Rh-precursor $Rh(acac)(CO)_2$ to the activated $HRh(BiPhePhos)(CO)_2$ catalyst. Under hydroformylation conditions, this complex was found to be the most abundant catalyst species over a wide range of olefin conversion. Other inactive or non-selective rhodium species were not detectable. Analysis of the turnover frequency revealed a first order dependence of the hydroformylation rate with respect to the concentration of 1-decene. These findings indicate that the coordination of the olefin to the Rh-BiPhePhos catalyst is determining the hydroformylation rate of 1-decene.

Keywords: BiPhePhos, 1-decene, hydroformylation, rhodium

1. Introduction

The reaction of olefins with synthesis gas (CO, H_2) in presence of a transition metal complex as catalyst has been known for decades as hydroformylation. It is one of the most important industrial applications of homogeneous catalysis [1]. The Rh-complex catalyzed hydroformylation of long-chain olefins using the bulky chelating diphosphite ligand BiPhePhos [2] was investigated intensively in the literature [3–6]. Usage of this catalyst enables the double bond isomerization of straight-chain olefins [7, 8] which can be exploited in tandem isomerization-hydroformylation reactions to produce linear aldehydes from mixtures of internal olefins [9–11] or renewable feedstocks [12, 13]. However, desired mechanistic kinetic models of these reactions for efficient reactor design and operation are not available in the literature.

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