**Kinetic modeling of catalyst deactivation in the rhodium diphosphite catalyzed hydroformylation of long chain olefins**

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**Highlights**

* Kinetic study of industrially relevant impurities
* Detailed experimental investigation of deactivation kinetics
* Operando FTIR spectroscopic validation of catalyst deactivation
* Extension of mechanistic kinetic models by deactivation model

**1. Introduction**

In the Collaborative Research Center Transregio 63 of the German Research Foundation the concept of thermomorphic multi component solvent systems (TMS systems) is investigated for the Rh/BIPHEPHOS-catalyzed hydroformylation of long chain olefins and esters. For a TMS system consisting of *N,N*-dimethylformamide (DMF), decane and 1-dodecene reaction kinetics and solvent effects on the chemical equilibrium were investigated in detail [1,2,3]. Previous studies on feed impurities revealed a significant kinetic influence of hydroperoxides on the isomerizing hydroformylation network of long chain olefins [4]. In particular, a loss of active ligand specific n- to iso-aldehyde production could be correlated to the decomposition of the diphosphite ligand which was observed by 31P NMR [4]. In parallel, industry is facing reduced aldehyde space-time yield and selectivity by decomposition of catalyst due to unavoidable traces of peroxides in the olefin feed [5]. This work aims to contribute to a better understanding of the deactivation kinetics which is necessary to be optimized in the rhodium catalyzed hydroformylation process using highly active diphosphite ligands.

**2. Methods**

Hydroformylation experiments were carried out in a high pressure reactor system equipped with temperature and pressure controllers. The TMS system consisted of 1-dodecene (*c0substrate* = 0.9 mol L- 1), decane and DMF. Rh(acac)(CO)2 and BIPHEPHOS were used as catalyst precursor and ligand (Rh/ligand = 1:3, *ccat* = 13 ppm), respectively. Two hydroperoxide species, *tert*-butyl hydroperoxide and a mixture of unsaturated hydroperoxides, generated by autoxidation of 1-dodecene, were used as model and substrate derivative hydroperoxides, respectively. These hydroperoxides were separately spiked to 1-dodecene according to different peroxide/ligand ratios. The hydroformylation was performed at temperatures ranging from 95 °C to 115 °C at a constant CO/H2 (1:1) pressure of 30 bar. In addition, operando FTIR hydroformylation experiments were conducted at 60 °C and 10 bar CO/H2 (1:1) in toluene using an increased catalyst concentration of *ccat* = 500 ppm.

**3. Results and discussion**

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| a) | b) |
| **Figure 1.** Results of the kinetic deactivation study for the Rh/BIPHEPHOS-catalyzed hydroformylation of 1-dodecene at 105 °C and 30 bar CO/H2 (1:1) for different peroxide/ligand ratios: a) n/iso Aldehyde regioselectivity, b) Simulation of ligand decomposition | |

The kinetic influences of hydroperoxides on the hydroformylation of terminal olefins were investigated at different temperatures and different hydroperoxide to ligand ratios (Fig. 1a). Both hydroperoxide species revealed different activity in the hydroformylation experiments.

The decomposition of the ligand BIPHEPHOS by hydroperoxides was assumed to proceed as a second order irreversible reaction. Thus, a kinetic model for the decomposition could be derived and parameterized. The resulting simulation of ligand/Rh ratio shows a good correlation to the experimental findings (Fig. 1b) whereas a decline of the ligand/Rh ratio below 1 is supposed to significantly change the regio- and chemoselectivity of the catalysis. In addition, a change of the catalytic species could be observed during the decomposition using FTIR spectroscopy.

**4. Conclusions**

The kinetic influence of industrially relevant hydroperoxides was studied in detailed kinetic experiments. The kinetic data was used to derive and parameterize a kinetic model for a mathematical description of decomposition of the ligand as well as the corresponding deactivation of the catalyst. Thus, already existing mechanistic kinetic models for Rh/BIPHEPHOS-catalyzed hydroformylation could be extended to an improved prediction of the reaction kinetics allowing a description, simulation and optimization of the reactor behaviour using real feedstocks in industry.

**References**

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