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Influence of hydroperoxides on the Rh/diphosphite-catalyzed hydroformylation

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Highlights

- Systematic investigation of long-chain olefin feeds in hydroformylation kinetics.
- Characterization and quantification of feed intrinsic hydroperoxides as critical impurities.
- Significant loss of chemo- and regioselectivity for increasing hydroperoxide concentrations.
- Restoring catalyst performance by different compensation strategies.

1. Introduction

Identification of reaction mechanisms and quantification of kinetics in homogeneous catalysis are typically performed under ideal conditions excluding impurities that eventually affect results. The resulting kinetic models are then often applicable in a broad range of operation conditions in the laboratory. In industry, the exclusion of impurities is often not feasible and a loss of catalytic performance has to be accepted which is not reflected by the derived kinetic models. In particular, for the Rh/diphosphite hydroformylation process of long-chain olefins (Figure 1) an understanding of hydroperoxides as critical impurities and their impact on the catalytic performance is still missing.

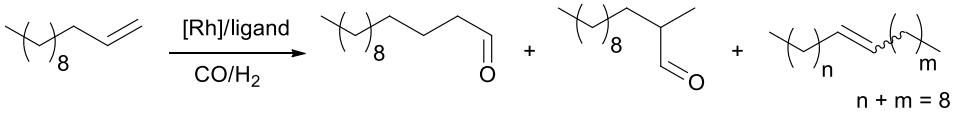

Figure 1. Rh-catalyzed hydroformylation of 1-dodecene producing the desired n-aldehyde and the side products iso-aldehyde and dodecene isomers.

2. Methods

Impurities in commercially supplied olefin (1-dodecene) samples were purified by vacuum distillation and analyzed using ^{1}H and ^{13}C NMR as well as UV/vis spectroscopy.
Kinetic hydroformylation experiments using four olefin feed samples differing in their impurity composition were carried out in a high-pressure reactor system equipped with temperature and pressure controllers. The reactions were performed in a thermomorphic solvent system that consisted of 1-dodecene, decane and *N*,*N*-dimethylformamide (DMF) (13/38/49/ mol%). $Rh(acac)(CO)_2$ (0.01 mol%) and BiPhePhos were used as catalyst precursor together with diphosphite ligand (Rh/ligand = 1:3), respectively. The reactions were carried out at constant pressure of 30 bar CO/H_2 (1:1) and constant temperature of 105 °C for 90 min. Samples were taken in discrete time steps and analyzed using gas chromatography [1].

3. Results and discussion

In the four different industrial 1-dodecene feed samples hydroperoxides could be identified as main impurities. The structures of three different unsaturated hydroperoxides (Figure 2a) were validated using NMR correlation spectra. UV/vis quantification of hydroperoxides in the feeds indicated concentrations varying from 0.01 to 0.26 mol%. This corresponded to hydroperoxide/ligand ratio of up to 7.9.
In the kinetic experiments significant effects of hydroperoxides on the catalytic performance were observed (Figure 2b). The final chemoselectivity to the desired n-aldehyde strongly decreased from 81 to 50 % for hydroperoxide concentrations from 0.01 to 0.26 mol%, respectively. In parallel, a significant loss of regioselectivity in terms of the n- to iso-aldehyde (n/iso) ratio from 98/2 to 93/7 was observed. Connected to

the change in catalytic performance the complete degradation of the diphosphite ligand was verified by ^{31}P NMR spectroscopy. To compensate for this loss of ligand, the hydroperoxide/ligand ratio was decreased purifying the olefin feed by distillation or feeding additional ligand. Both compensation strategies restored the catalytic performance leading to a n-aldehyde selectivity of more than 85 % and a n/iso ratio of more than 98/2 [2]. In addition, increasing the content of the solvent DMF by completely substituting decane a similar positive effect on catalytic performance was observed. A participation of the amide DMF in the hydroperoxide induced hydrogen atom transfer can be assumed, thus protecting the diphosphite ligand BiPhePhos [3].

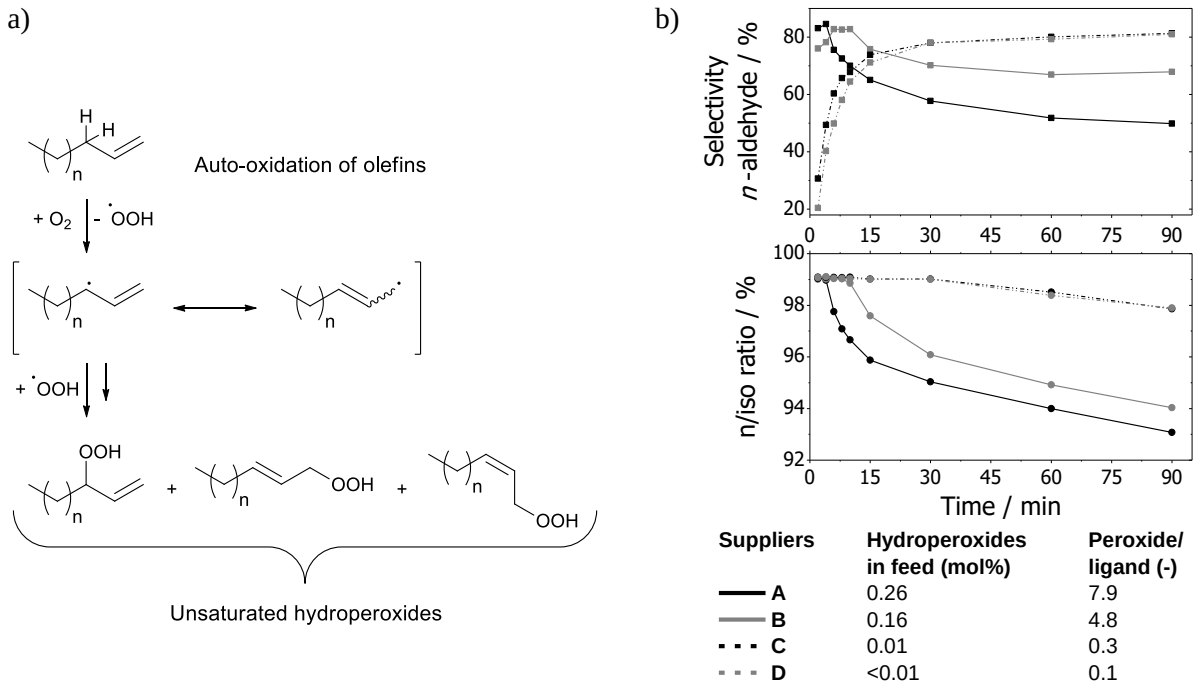

Figure 2. a) Auto-oxidation of long-chain olefins leading to unsaturated hydroperoxides, b) Hydroperoxide dependent chemo- and regioselectivities of n-selective hydroformylation of 1-dodecene using a Rh/BiPhePhos catalyst (c_{Rh} = 0.01 mol%, Rh/ligand = 1/3, T = 105 °C, $p_{CO/H2}$ = 30 bar, results partly published in [2]).

4. Conclusions

In commercially available olefin feed samples, significant amounts of hydroperoxides are present as critical impurities. These can be characterized and quantified using NMR and UV/vis spectroscopy. Four different feed samples were systematically investigated in the Rh/BiPhePhos-catalyzed hydroformylation. Kinetic experiments revealed a time dependent loss of chemo- and regioselectivity to the desired n-aldehyde for high hydroperoxide concentrations in the feed. Restoring the catalytic performance was possible by a) decreasing the hydroperoxide/ligand ratio through preliminary purification of the olefin feed or feeding of additional ligand and b) by increasing the amount of the solvent DMF in the thermomorphic solvent system.
This contribution emphasizes the importance of considering catalyst deactivation by hydroperoxides in homogeneous Rh/diphosphite hydroformylation.

References

[1] G. Kiedorf, D.M. Hoang, A. Müller, A. Jörke, J. Markert, H. Arellano-Garcia, A. Seidel-Morgenstern, C. Hamel, Chem. Eng. Sci. 115 (2014) 31-48.
[2] M. Gerlach, D. Abdul Wajid, L. Hilfert, F.T. Edelmann, A. Seidel-Morgenstern, C. Hamel, Catal. Sci. Technol. 7 (2017) 1465-1469.
[3] M. Salamone, M. Milan, G.A. DiLabio, M. Bietti, J. Org. Chem. 78 (2013) 5909-5917.

Keywords
Hydroformylation; deactivation; diphosphites; hydroperoxides