

Multiphase Hydroformylations of long chain alkenes and the liquid-liquid interface

K. E. Naße,¹ M. Schrimpf,¹ F. S. Heinen,¹ N. Pawlowsky,¹ Andreas J. Vorholt,¹ W. Leitner^{1,2}

¹Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany

²Institute of Technical and Macromolecular Chemistry, RWTH Aachen University, Aachen, Germany

Abstract

Multiphase catalysis in hydroformylation are well known by the Ruhrchemie/Rhône-Poulenc process. In here the water-soluble catalyst is dissolved in the polar aqueous phase. The product forms a second organic, non-polar phase, which allows an easy separation of both phases. Nevertheless, the substrate in the Ruhrchemie/Rhône-Poulenc process is quite water soluble. In contrast, for long chain alkenes this easy separation technique is accompanied with transport limitations during the reaction and still the exact steps for the reaction are discussed.

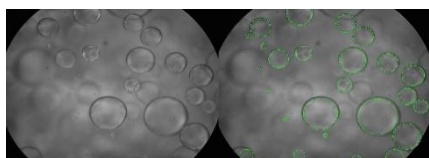


Figure 1: Emulsion of the biphasic reaction mixture recorded and analysed by the SOPAT borescopy technique

With borescope measurements we investigated the steps for multiphase hydroformylation of long chain substrates. This technique allows us to investigate interfaces during the reaction in situ, even with enhanced pressures. It takes pictures of the reaction solution under reaction conditions. Afterwards, an algorithm evaluates these pictures for calculating the liquid-liquid interface size or the Sauter diameter and is able to distinguish between liquid droplets and gaseous bubbles.

We investigated the liquid-liquid interface of the hydroformylation of 1-octene with the water soluble Rh/TPPTS. In artificial samples TPPTS concentration from 0 mol m_{aq}⁻³ to 100 mol m_{aq}⁻³ in the aqueous phase lead to an increase of the liquid-liquid interface of 48%. An addition of 40 mol% nonanal into the organic phase resulted in an increase of the interfacial area of 322%. Of more significance is the relationship between catalytic activity and the interfacial area during the reaction. Opposing the assumption that the catalyst accumulates in the liquid-liquid interface, our results show that this is unlikely. A non-linear relationship between the interface and the catalytic activity was observed. On basis of these results, the effective available interface for the catalyst seems to be reduced by the amphiphilic nonanal.

In actually research projects we investigate the liquid-liquid interfaces by assisted hydroformylation with cyclodextrins and the interfacial area in multiphase enzymatic systems.

References:

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[2] M. Schrimpf, P. A. Graefe, A. Holl, A. J. Vorholt, W. Leitner, *ACS Catal.* 2022, 12, 7850–7861.

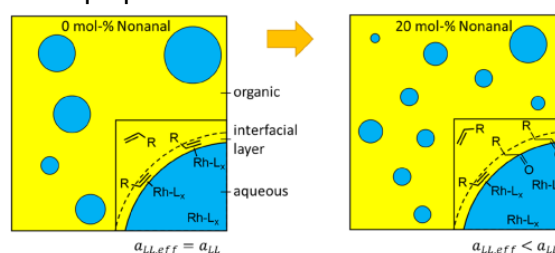


Figure 2: Proposed effect of the accumulation of nonanal with the reduction of the available interfacial area for the catalyst.