

## Catalyst Recycling by a Crystallisation of the Ethylene Carbonate-based Catalyst Phase in the Hydroformylation of 1-Octene

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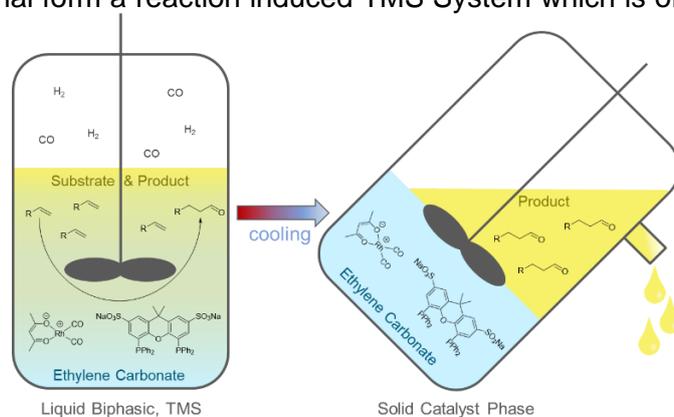
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### Abstract

The hydroformylation reaction is one of the most important and most used homogeneously catalysed processes.<sup>[1]</sup> Olefins react to aldehydes using transition metal complexes such as rhodium carbonyls modified with phosphine ligands. The recycling of such catalysts and their removal from the product are a focus in research and industry.<sup>[2]</sup> A method to achieve this is through multiphase catalysis. A well-known system for the hydroformylation of short chain olefins such as ethylene and propylene is the Rhône Poulenc/Ruhrchemie process using water soluble ligands, resulting in the separation of a pure product phase from the catalyst phase.<sup>[3]</sup> However, this method is not suitable for long chain olefins.<sup>[3]</sup> Less polar solvents need to be applied for the catalyst phase such as glycols and carbonates.<sup>[4]</sup> Using two solvents with a smaller polarity gap a thermomorphic multicomponent systems (TMS) may form. In these systems, the solvents are miscible at increased temperatures and turn biphasic again after the reaction at low temperatures.<sup>[5]</sup>

Herein, we present the development of an ethylene carbonate-based catalyst recycling system using Rh/sulfoXantphos as a water-soluble catalyst in the highly selective hydroformylation of 1-octene. The catalyst was recycled by a crystallisation of the entire catalyst phase. Ethylene carbonate and the reaction product nonanal form a reaction induced TMS System which is of disadvantage in the reaction as it causes a precipitation of the catalyst with increasing yield. Modifications have been investigated in order to increase the phase change temperature to remain in the biphasic regime. The addition of less polar solvents to the catalyst phase such as *n*-decane or the addition of water to the catalyst phase result in a slower but improved reaction system with an increased yield which is well recyclable.



### References

[1] P. W. N. M. van Leeuwen, C. Claver, *Rhodium Catalyzed Hydroformylation*, Kluwer Academic Publishers, New York, Boston, Dordrecht, London, Moscow, **2002**.

[2] B. Cornils, W. A. Herrmann, I. T. Horváth, W. Leitner, S. Mecking, H. Olivier-Bourbigou, D. Vogt, *Multiphase Homogeneous Catalysis, Vol. 1*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, **2005**.

[3] C. W. Kohlpaintner, R. W. Fischer, B. Cornils, *Appl. Catal. A: Gen.* **2001**, 221, 219.

[4] M. Strohmam, J. T. Vossen, A. J. Vorholt, W. Leitner, *Green Chem.* **2020**, 22, 8444.

[5] J. Bianga, K. U. Künnemann, T. Gaide, A. J. Vorholt, T. Seidensticker, J. M. Dreimann, D. Vogt, *Chem. Eur. J.* **2019**, 25, 11586.