

Synthesis of POSS Modified Xantphos Ligands for Their Application in a Continuous Flow Nanofiltration Loop-reactor

V. K. A. Söderholm, D. Vogt

Lehrstuhl für Technische Chemie, Fakultät Bio- und Chemieingenieurwesen, Technische Universität (TU) Dortmund, Germany

Abstract

Many transition metals (TM) that show good catalytic performance can be very expensive because of their scarcity. Also many ligands with interesting properties come at a considerable cost. There are therefore strong incentives to reuse and recycle these catalytic entities in industrial processes. But TM-complexes dissolved in a single liquid phase are intrinsically non trivial to separate from the reaction mixture. Nanofiltration membranes have previously been investigated as an energy efficient approach for mechanical differentiation of solutes based on their size. When catalyst retention is not sufficient, grafting a soluble support to the ligand, so-called Molecular Weight Enlargement (MWE), can significantly increase the catalyst/ligand rejection.^[1, 2] We have shown that MWE of ligands grafted with Polyhedral Oligomeric Silsesquioxane (POSS) units (figure 1) can lead to retention of ligand/catalyst as high as 99.99%. A POSS modified PPh_3 ligand was applied in continuous Rh-catalysed hydroformylation of 1-octene. After nearly 2 weeks of continuous operation an accumulated turnover number of $120\,000\text{ Rh}^{-1}$ with a steady l/b selectivity of ~ 2.5 was achieved.^[3]

The goal now is to extend this concept of MWE with POSS to other ligands, such as Xantphos. Herein we present the synthesis of two POSS modified Xantphos ligands (figure 2), with the POSS units attached either to the xanthene backbone or to the substituents on the phosphine moieties. With these ligands in hand, hydroformylation of 1-octene should be feasible with higher l/b selectivity while maintaining a high retention in the nanofiltration step.

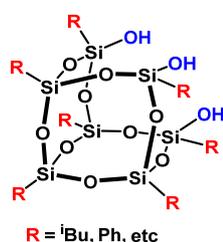


Figure 1

Polyhedral Oligomeric Silsesquioxane

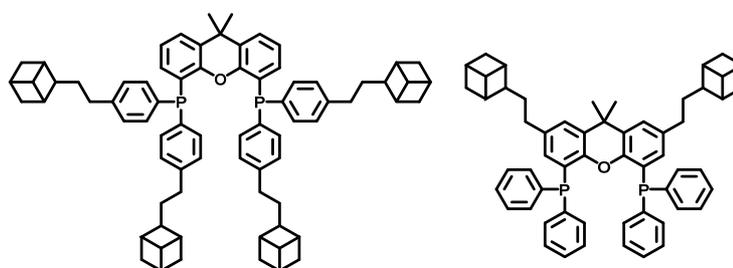


Figure 2

POSS-modified Xantphos ligands

[1] C. Müller, M.G. Nijkamp and D. Vogt, *Eur. J. Inorg. Chem.* **2005**, 4011-4021.

[2] M. Janssen, C. Müller and D. Vogt, *Dalton Trans.* **2010**, 36, 8403-8411.

[3] M. Janssen, J. Wilting, C. Müller, D. Vogt, *Angew. Chem., Int. Ed.*, **2010**, 49, 7738-7741.