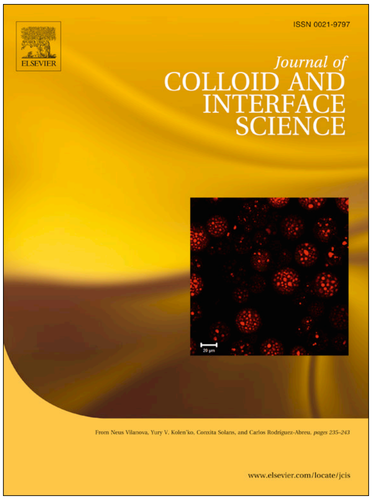

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Colloidal polymer particles as catalyst carriers and phase transfer agents in multiphasic hydroformylation reactions

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Hypothesis: Colloidal particles have been used to covalently bind ligands for the heterogenization of homogeneous catalysts. The replacement of the covalent bonds by electrostatic interactions between particles and the catalyst could preserve the selectivity of a truly homogeneous catalytic process.

Experiments: Functionalized polymer particles with trimethylammonium moieties, dispersed in water, with a hydrophobic core and a hydrophilic shell have been synthesized by emulsion polymerization and have been thoroughly characterized. The ability of the particles with different monomer compositions to act as catalyst carriers has been studied. Finally, the colloidal dispersions have been applied as phase transfer agents in the multiphasic rhodium-catalyzed hydroformylation of 1-octene.

Findings: The hydrodynamic radius of the particles has been shown to be around 100 nm, and a core-shell structure could be observed by atomic force microscopy. The polymer particles were proven to act as carriers for the water-soluble hydroformylation catalyst, due to electrostatic interaction between the functionalized particles bearing ammonium groups and the sulfonated ligands of the catalyst. The particles were stable under the hydroformylation conditions and the aqueous catalyst phase could be recycled three times.

Introduction

Biphasic catalysis is an elegant strategy to perform reactions with the characteristic high activity and selectivity of molecular catalysts. A further advantage is ease of separation of the reaction products, since the catalyst and the products are in different phases (Figure 1). Moreover, the possibility to dissolve the homogeneous catalyst in water can drive catalytic reactions towards cheaper and more environmentally friendly processes. The most prominent industrial application of this type of system is the hydroformylation of short chain alkenes in the Ruhrchemie/Rhône-Poulenc process.[1,2] Because of the low water-solubility of alkenes with chain lengths above C_4, these substrates are not suitable for this process. For longer chain alkenes cobalt catalysts are often used. However, harsh conditions are required[3] and the selectivity of the process is poor.

To make a water-organic biphasic system applicable for the hydroformylation of long chain alkenes, different approaches have been tested. A common way is to use phase transfer agents, for example cyclodextrins,[4–6] which can also be combined with poloxamines forming hydrogels.[7] Surfactants have been utilized as well[8,9] and have even been successfully applied in miniplants.[10,11] Another approach is to have a completely homogeneous reaction medium that can be switched into two phases for easy product separation after the reaction. This can be achieved by adding co-solvents[12,13] or additives with co-solvents[14] that can be switched in polarity by addition of CO_2.

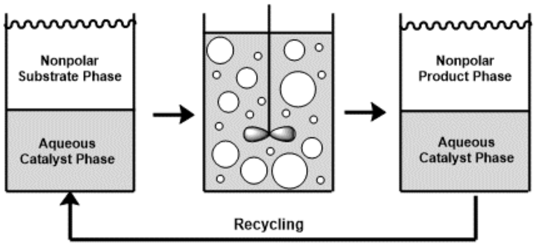

Figure 1. Biphasic catalytic batch process with a water-soluble homogeneous catalyst