

# DESIGN AND APPLICATION OF EFFICIENT AND RECYCLABLE GRAFTED ORGANOTIN CATALYSTS FOR TRANSESTERIFICATIONS

Proces monitoring by High-Resolution Magic Angle Spinning (HRMAS) NMR  
spectroscopy

Vanja PINOIE

The present Ph.D. thesis aims at contributing to the development and optimization of efficient solid-supported organotin catalysts and explores their application potential as sustainable, recyclable and environmentally benign transesterification catalysts. As such, the followed approach fits within the present “Zeitgeist” of pursuing “*green chemistry*”, addressing its specific goals by the design of novel catalytic systems for which the concomitant realization of economic advantages *and* the reduction of environmental and human health hazards serve as a strong incentive.

A novel straightforward synthesis procedure is presented toward a functionally pure monoalkyltin trichloride grafted onto *cross-linked polystyrene* through a C11-spacer. A parallel study focuses on enhancing the compatibility between the resin and polar solvents, targeting an improved swelling and site accessibility in the polar media typically involved in transesterification reactions. In this context, the suitability of a *HypoGel* support bearing oligomeric poly(ethylene glycol) chains to act as an insoluble carrier for organotin catalysts is investigated. In a subsequent part, in which the focus lies on the use of inorganic catalyst carriers, promising explorative results are presented on the immobilization of an organotin catalyst onto a *highly ordered mesoporous silica* support.

In order to evaluate the potential practical applicability of the developed organotin catalysts, the catalytic performance is assessed in the model transesterification reaction of ethyl acetate and *n*-octanol. A further extension of this study involves the use of secondary alcohols. Detailed investigations are conducted with regard to the chemical integrity, recycling ability, and leaching resistance of the various catalyst systems.

Finally, in terms of characterization of the grafted species, 1D and 2D  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{119}\text{Sn}$  high-resolution magic angle spinning HRMAS NMR spectroscopy evidence their full potential for monitoring solid-phase synthetic procedures and catalytic processes *in situ* at the solid-liquid interface. As such, the developed methodology offers wide applicability for the in-depth investigation of supported catalysts in general.