Paramagnetic Ionic Liquids as “Liquid Fixed-Bed” Catalysts in Flow Applications

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Introduction

The main drawback of homogeneous catalysis is the separation of products from the catalyst. Therefore two or multi-phase systems are used to keep the catalyst in and the reactants and/or products in separate phases. The reaction takes place at the phase boundary of the two immiscible liquids. Usually between an aqueous- and an organic liquid. Since a couple of years transition metal based ionic liquids are under investigation[1]. The chemical and thermal stability as well as the magnetic properties of e.g. [BMIM][FeCl4] are remarkable [2,3]. Imidazolium-based ferrocirhates are of interest due to their low-cost preparation procedure and high Lewis-acidity. Absorption spectroscopy (VIS) indicate that the reason for the magnetic properties of this compound is provided by high-spin FeCl4− anions. The magnetic susceptibility of 40.6 x 10−6 emu g−1 was determined by SQUID measurement[4]. Due to the preparation conditions an equilibrium of different liquid ferrocirhates appears, mostly [BMIM][FeCl4] and [BMIM][FeCl3], determined by Mössbauer spectroscopy [5]. Magnetic forced manipulation of such molecules is strongly restricted by the magnetic susceptibility of both, the magnetic fluid and the magnet, and also a function of their proximity respectively. It is obvious, that the twofold properties of [BMIM][FeCl4], hard Lewis acidity and paramagnetic behavior, combined with flow chemistry in confined space, i.e. within micro- or mesosstructured reactors opens up numerous unusual applications. A promising application reported here is the combination of the magnetic fixation of a magnetic ionic liquid catalyst (MILC) in a micro/meso-sized channel to form a liquid fixed-bed (LFB) and a reactant mixture flow through, an analogue to common heterogeneous catalysis.

Reference Reaction

\[
\text{C} + \text{H}_2 \rightarrow \text{CH}_3\text{OH} \\
\text{FeCl}_3 + \text{H}_2 \rightarrow \text{HCl} + \text{FeCl}_2
\]

Paramagnetic Liquid

- The permanent magnetic moment of the molecule arises from unpaired electrons
- Every angular momentum of an electron is connected with a magnetic moment
- \[ \mu = \frac{e}{2m} \] magnetic moment e = en, s = orbital angular momentum
- Paramagnetic liquids are functional ionic liquids composed of magento active metal complex anions
- The magento active centers in the liquid are isolated from each other and the ionic liquid behaves simply paramagnetic
- Response of [BMIM][FeCl4] to a strong external magnetic field
- Temperature dependence of the susceptibility can be described with the Curie-Law

Results

- Every droplet has a diameter of about 500 μm and therefore can be considered solid-wall-free micro reactor
- Due to the magnetically fixed symmetric LFB the droplets do not touch the glass walls of the reactor
- The reaction chamber is not in the scale of a micrometer
- The reaction mixture and catalyst are immiscible so the reaction kinetics is strongly connected to the interfacial area and diffusion inside the droplet
- Regular droplet flow offers a specific phase boundary of nearly 10000m^3

Summary

- The esterification reaction described here is known as a batch reaction [6]
- A two-phase system of pure [BMIM][FeCl4] and a reactant solution was used
- The catalyst is a paramagnetic ionic liquid
- The reaction mixture was delivered as micro droplets to a magnetically fixed catalyst bed
- The concentration of [BMIM][FeCl4] can be assumed as infinite.
- A yield of 78.5% was achieved within 1.3 seconds
- The next step will be the shift from single droplet formation to a multi-stream, at least to generate dispersions within a fixed bed of a liquid catalyst.

References