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

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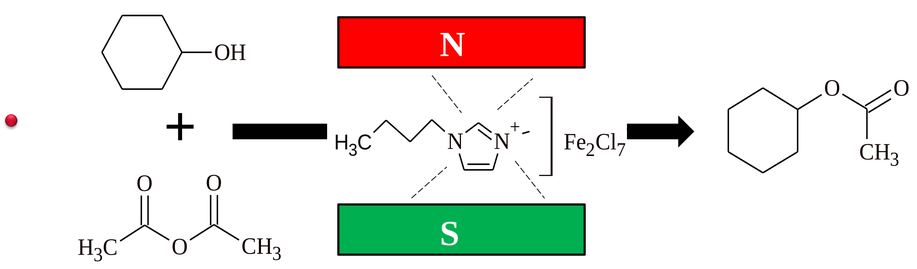
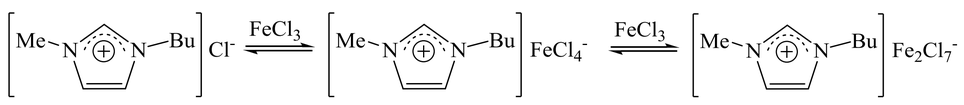
Introduction

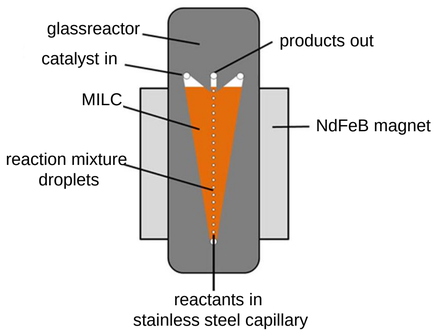
The main drawback of homogeneous catalysis is the separation of products from the catalyst. Therefore two or multi-phase systems are used to keep the catalyst in and the reactants and/or products in seperate phases. The reaction takes place at the phase boundary of the two immiscible liquids. Usually 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]$FeCl_4$ are remarkable [2,3]. Imidazolium-based ferrochlorates 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 $FeCl_4^-$ anions. The magnetic susceptibility of 40.6 x 10^{-6} emu g^{-1} was determined by SQUID measurements[4]. Due to the preparation conditions an equilibrium of different liquid ferrochlorates appears, mostly [BMIM]$FeCl_4$ and [BMIM]Fe_2Cl_7, determined by Moesbauer 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]Fe_2Cl_7, hard Lewis acidity and paramagnetic behavior, combined with flow chemistry in confined space, i.e. within micro- or mesostructured 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



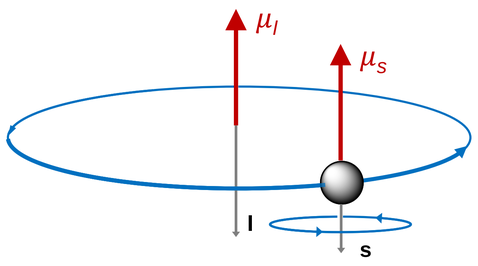


Solid wall free processing



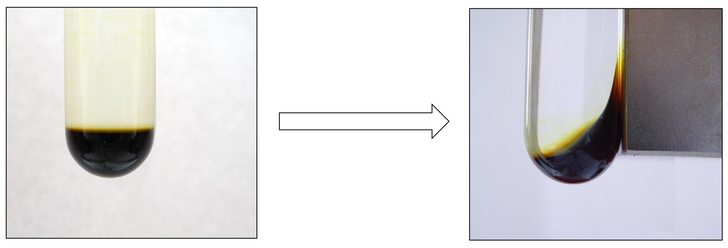
- Every droplet has a diameter of about 500 µm and therefore can be considered as **solid-wall-free micro reactor**
- Due to the magnetically fixed symmetric LFB the droplets do not touch the glass walls of the reactor
- The reaction chamber is not in the scale of a microreactor
- The reaction mixture and catalyst are immiscible so the reaction kinetics ist strongly connected to the interfacial area and diffusion inside the droplet
- Regular droplet flow offers a specific phase boundary of nearly 10000m^2m^{-3}

Paramagnetic Liquid

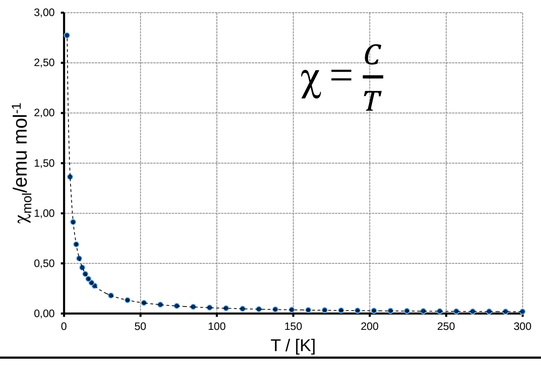


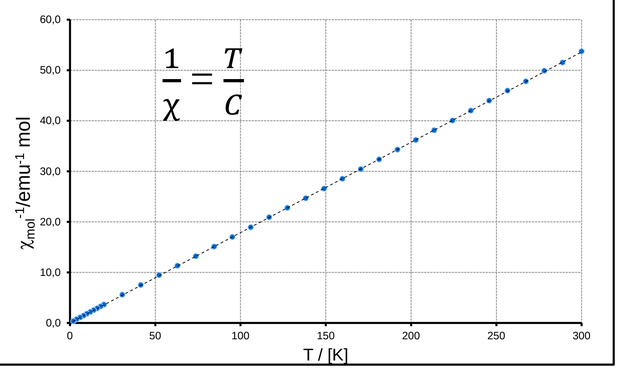
- The permanent magnetic moment of the molecule arises from unpaired electrons
- Every angular momentum of a electron is connected with a magnetic moment
- $\mu_s = -\frac{e}{m_e}\mathbf{s}$ $\quad\quad$ $\mu_l = -\frac{e}{2m_e}\mathbf{l}$

  μ: *magnetic moment*, **s**: spin, **l**: orbital angular momentum
  e : elementary charge, m_e: elektron mass
- Paramagnetic liquids are functional ionic liquids composed of magneto active metal complex anions
- The magneto active centers in the liquid are isolated from each other and the ionic liquid behaves simply paramagnetic

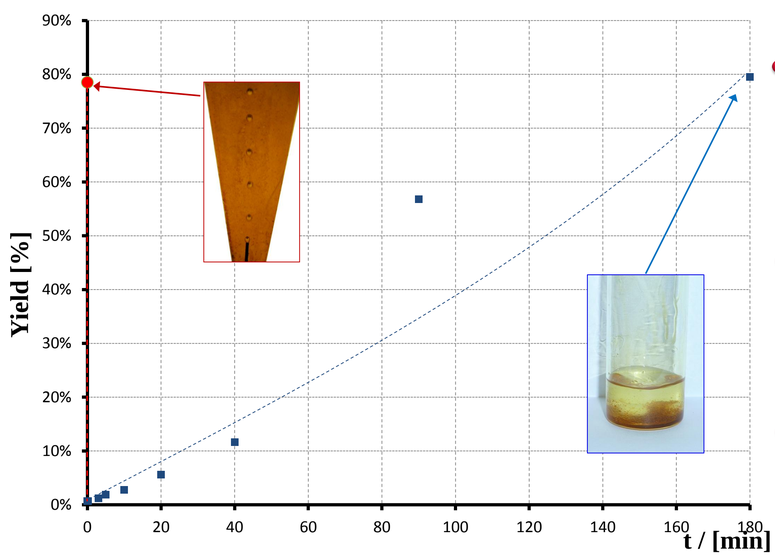


- Response of [BMIM]Fe_2Cl_7 to a strong external magnetic field
- Temperature dependence of the susceptibility can be described with the Curie-Law

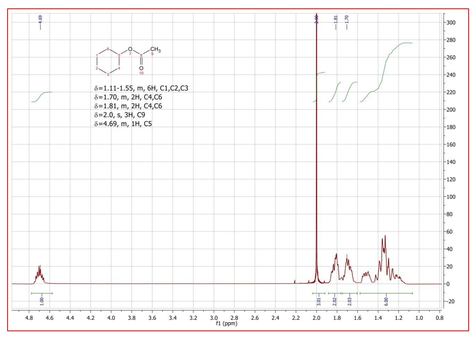


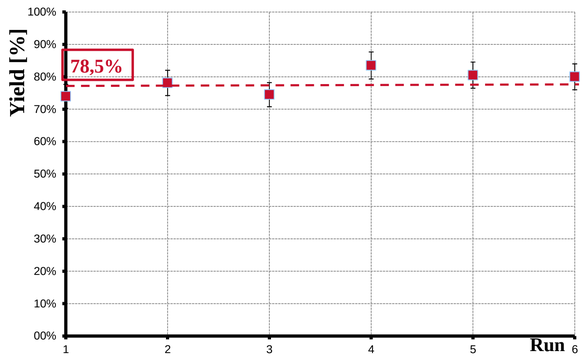


Results



- Pumping the reaction mixture through [BMIM]Fe_2Cl_7 – LFB gave a yield of about 78.5% of the desired ester in 1.3 seconds
- The same reaction as a stirred batch-process gave nearly the same yield after 3 hours
- The catalyst was reused for several cycles without loss of activity



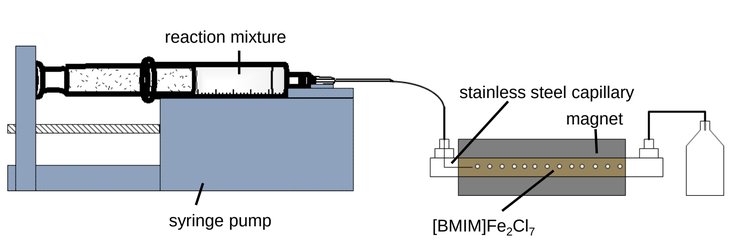


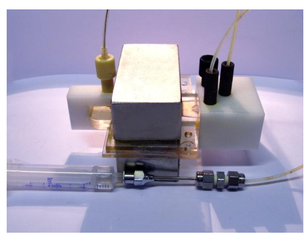
Summary

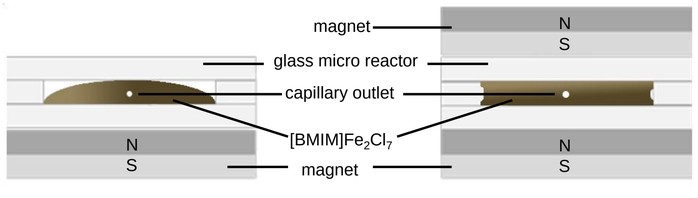
- The esterification reaction described here is known as a batch reaction [6]
- A two-phase system of pure [BMIM]Fe_2Cl_7 and a reactant solution was used
- The catalyst is a paramagnetic ionic liquid
- The reaction mixture was delivered as micro droplets into a magnetically fixed catalyst bed
- The concentration of [BMIM]Fe_2Cl_7 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.

Setup







- Observed shaping of the MILC inside the cavity under magnetic force. Single-sided mounted magnet gave a droplet-like shape with open spaces at the upper edges (left). A filled cavity appeared by applying two magnets on the opposite sides (right)

References

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