



Paramagnetic ionic liquids as “liquid fixed-bed” catalysts in flow application

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ABSTRACT

The structural diversity of Ionic Liquids is well-known and widely used to generate solvents designed for special applications. Magnetic as well as catalytic properties have been described previously. To our best knowledge we report the first time about the combination of both, the magnetic and catalytic behaviour of imidazole based magnetic ionic liquids was used to establish a so-called liquid fixed-bed (LFB) in a micro-/meso-structured reactor. As proof of principle the esterification of Ac_2O with cyclohexanol was investigated by bubbling generated regular microdroplets of the reaction mixture through the magnetically fixed ionic liquid catalyst. With residence times of approx. 1.4 s a yield of 78.5% of the target ester molecule was achieved.

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1. Introduction

In general, the main drawback of homogeneous catalysis is the separation of products from the catalyst. Therefore, two or multi-phase systems are commonly used to keep the catalyst in one and the reactants and/or products in the other phase. The chemical reaction takes place at the phase boundary of the two immiscible liquids, usually between an aqueous- and an organic liquid. Chaudhari et al. [1] showed that a catalytic reaction at the phase boundary of such an aqueous/organic solvent interface can be significantly enhanced with organic phase soluble carrier molecules containing so-called ‘promoter ligands’ which stabilize and promote the catalyst.

Tundo and Perosa discussing supported liquid phase catalysts (SLPC) in multi-phase systems [2]. Consequently, on silica supported ionic liquid phases (SILP) were investigated to perform numerous organic reactions [3]. To promote a Friedel-Crafts reaction the catalyst AlCl_3 is bonded to an ionic liquid [emim]Cl to form [emim] AlCl_4 . This results in a heterogeneous system where the homogeneous catalyst AlCl_3 is transferred via anion immobilization [4–6].

Since a couple of year’s transition metal based ionic liquids are under investigation [7]. Lanthanides containing ionic liquids provide a weak Lewis-acidity but comparably high paramagnetic response to an external magnetic field [8–10], while imidazolium-based ferrochlorates are of interest due to their low-cost preparation procedure and high Lewis-acidity and catalytic activity. The chemical and thermal stability as well as the mag-

netic properties of e.g. [bmim] FeCl_4 are also remarkable [11,12]. Absorption spectroscopy (VIS) indicate that the reason for the magnetic properties of this compound is provided by the possible local ordering and high-spin of the FeCl_4^- anions.

The magnetic susceptibility of $40.6 \times 10^{-6} \text{ emu g}^{-1}$ was determined by SQUID measurements [13]. Due to the preparation conditions of an equilibrium of different liquid ferrochlorates, [bmim] Fe_2Cl_7 , and [bmim] FeCl_4 , appear after removing the excess of solid FeCl_3 determined by Moesbauer spectroscopy [14].

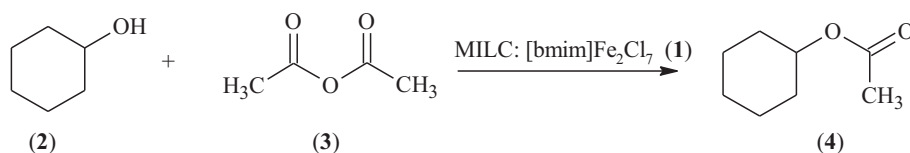
Unfortunately, magnetic forced manipulation of such molecules is strongly restricted by the magnetic susceptibility of both, the magnetic fluid and the magnet, and also a function of their proximity respectively. It is obvious, that the twofold properties of [bmim] Fe_2Cl_7 , hard Lewis-acidity and paramagnetic behaviour, combined with flow chemistry in confined space, i.e. within micro- or meso-structured reactors opens up numerous unusual applications [15–17], for example, shaking plugs of magnetic ionic liquids within a second phase at least intensively to form dispersions, magnetic enhanced phase separation, capture and release of magnetic fluid droplets [18], or transportation of magnetic droplets through borders of immiscible liquid phases.

A most 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.

For a proof of principle a comparably simple esterification of cyclohexanol (2) with acetic anhydride (3) to form acetic acid cyclohexylester (3) (see Scheme 1) was selected.

This reaction is described in literature as a batch reaction, where a mixture of 10 mmol (2), 15 mmol (3), and 20 mol% (1) as catalyst was stirred for 20 min. The homogeneous reaction mixture

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Scheme 1.

was extracted three-times with diethyl ether. The ether phase contained the organic substances was separated from the ionic liquid. A yield 90% (3) could be achieved and the catalyst was reused for several cycles without remarkable loss of activity [19].

2. Experimental

1-Chlorobutane (CAS 109-69-3; 99+%), FeCl_3 water free (CAS 7705-08-0; >97%), cyclohexanol (2) (CAS 108-93-0; 99%), acetic anhydride (3) (CAS 108-24-7; 98%), and diethyl ether (CAS 60-29-7; p.a.) was purchased from Sigma Aldrich. 1-Methylimidazole (CAS 616-47-7; 99%), from Carl Roth GmbH + Co. KG, Karlsruhe, Germany, and acetic acid cyclohexylester (4) (CAS 622-45-7; 99%) from ACROS ORGANICS, Geel, Belgium. All liquid substances were dried and freshly distilled before use.

For feeding the reactants solution a commercial available double-syringe pump, PHD 200 Infusion, Harvard Apparatus, USA, was used.

Necessary magnetic forces were applied by two NdFeB permanent magnets (N52 -1.4T, HKCM Engineering.K. Eckernförde, Germany; size: 60 mm × 30 mm × 20 mm).

GC-measurements were carried out at a Varian 3900 GC (column: 15 m (Factor Four VF-1, diameter 0.25 mm); detector: FID, temperature 280 °C; carrier gas flow: 1.5 ml min⁻¹; temperature ramp: 80–220 °C (20 °C min⁻¹).

Syntheses procedures of the MILC substance [bmim] Fe_2Cl_7 (1) are already published [20,21]. Crystalline [bmim]Cl, made from commercial available methylimidazole and butylbromide [17,22–25], was mixed with an excess of FeCl_3 powder. The solid/solid reaction turns immediately to a dark brown liquid by forming an equilibrium mixture of both substances, [bmim] Fe_2Cl_7 , and [bmim] FeCl_4 (1) [14,18]. After removing the excess of FeCl_3 the raw mixture MILC mixture was treated with dry diethyl ether to remove traces of moisture and organic waste.

To carry out the chemical reaction according to Scheme 1, a glass micro reactor, originally designed for in-flow phase separation experiments, provided by mikroglaschemtech GmbH, Mainz, Germany, was used. The reactor consists of two bonded glass layers with a one dimensional micro/meso structured cavity (2000 μm open space). The cavity has a triangular shape with one inlet at the bottom and three additional orifices on the top of the reactor (see Fig. 1).

The reactant mixture is feed in the inlet orifice through a stainless steel capillary (1.4301, outer diameter 400 μm , inner diameter 200 μm) which ensures a constant droplet flow through the micro cavity. Two of the three upper orifices are used: one to feed the catalyst into the cavity, and a withdrawal channel in the middle. The third orifice is not in use, except for maintaining the reactor by flushing, cleaning or drying. A low-pressure N_2/O_2 plasma was used for cleaning the inner surface subsequently followed by a plasma enhanced deposition of Si-organic compounds to achieve a long-term stable hydrophobic surface [26].

The necessary magnetic force is provided by a NdFeB permanent magnet mounted either as a single part on one or double-sided two parts with bucking polarity on the glass plate. In the case of a single sided magnet, a flat-shaped droplet appears independent of the amount of filled into the reactor cavity. It is obvious that due to the high viscosity of the magnetically captured MILC the fed reaction mixture does not flow regularly through the LFB, but rather along the MILC-free regions. To ensure a centered flow, the magnet must be mounted on both sides of the reactor (see Fig. 2). The stainless steel capillary delivers the feed stream of reactants and the magnetically fixed MILC ensures non-disturbed and centered droplet flow through the LFB (compare [12]).

The experimental set-up shown in Fig. 3 was used to perform the esterification reaction. Due to the small liquid volumes used, electronically controlled syringe pumps were used to feed the reactants into a triangular micro mixer with 150 μm internal structures (mikroglas chemtech GmbH, Mainz, Germany) and subsequently

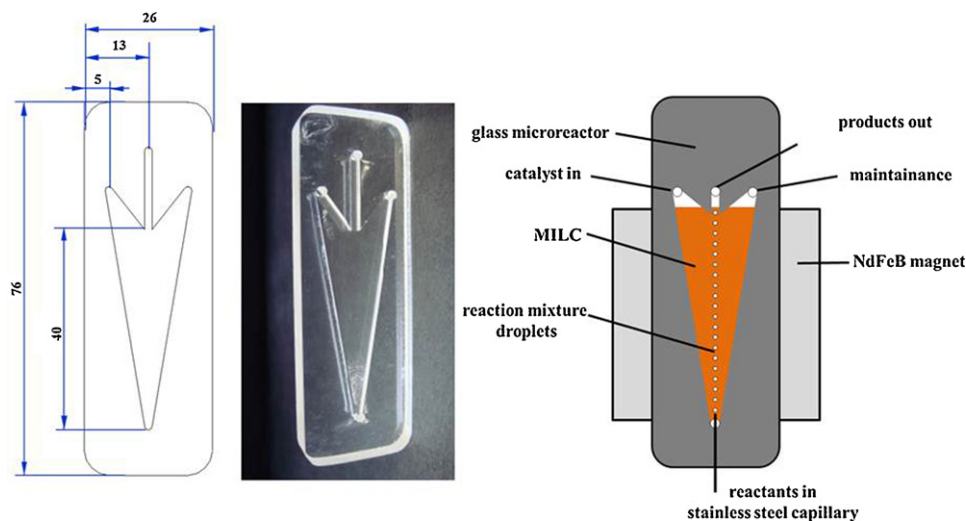


Fig. 1. Drawing of the used glass reactor (mikroglaschemtech GmbH, Mainz, Germany). All dimensions are given in mm. Cavity thickness 2.0 mm (left), image of the glass device (middle), and principle of the reactor set-up (right).

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