Oxidative Homocoupling of Alkynes Using Supported Ionic Liquid Phase (SILP) Catalysts – Systematic Investigation of the Support Influence

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Abstract: Supported Ionic Liquid Phase (SILP) catalysts have been prepared by effective immobilization of [Cu(TMEDA)(OH)]Cl in a nano-metric film of an ionic liquid on various oxidic support materials. The catalysts were tested for the oxidative homocoupling of 1-alkynes to the corresponding diynes in in a combined high throughput and conventional batch reaction approach. Among the screened support materials silica based materials performed best. The results indicate that for the specific reaction the thickness of the ionic liquids layer and therefore the mobility of the homogeneous copper complex within the ionic liquid layer as deduced from solid state nmr measurements have major impact on the catalytic performance. The optimized catalysts could be recycled up to four times without any loss of activity.

Keywords: Catalysis, glaser-hay coupling, high throughput experimentation, ionic liquids, SILP.

1. INTRODUCTION

Ionic liquids (ILs) are known for almost a century, in the beginning being the exclusive domain of electrochemists. However since the 1990s, there is a steadily growing interest in Ionic Liquids in almost all aspects of science and technology among the broad field of catalysis [1].

Although this is only an arbitrary divide, Ionic Liquids are generally defined as salts that melt at or below 100°C to afford liquids that are entirely composed of ions [2]. Ionic Liquids with a melting point near ambient temperature are called *room-temperature Ionic liquids*. The low melting point is often accompanied by a lower viscosity which certainly has a clear advantage in terms of handling. Generally, the properties of Ionic Liquids such as the melting point, viscosity, thermal stability, liquidus range and solvent properties can be varied or tailored in a broad range by the choice of the anion/cation combination of the IL [3].

In the past few years several reviews were published covering the application of Ionic Liquids in the broad field of catalysis [4]. In the earlier years of research much of this interest was centered on the possible use of ILs as “green solvent”. In those cases the Ionic Liquid was used as an alternative solvent for the commonly used organic solvents. Chosen examples of application are the hydroformylation [5], hydrogenation [6] or oxidation reactions [7]. In this context the low volatility of the Ionic Liquid and the possibility to reuse the Ionic Liquid catalyst solution brought about the attribute “green”. Moreover, Ionic Liquids were used in the field of catalysis as

- catalysts themselves, e.g. for alkylation [8] or acylation reactions [9]
- as co-catalytic systems, the most prominent application being the olefin dimerization [10]
- as a ligand source [11]
- as organocatalyst [12] and more.

In spite of the fact that 85% of the industrially relevant processes being heterogeneously catalyzed much less attention has been paid to the use of Ionic Liquids in heterogeneous catalysis [13]. In recent years two new concepts were introduced that preserve the advantages that Ionic Liquids may offer for several applications and at the same time minimize the main drawbacks like their high costs, diffusion limitations connected with the high viscosity and uncertainties connected with toxicity and disposal issues. For SCILL (*Solid Catalyst with an Ionic Liquid Layer*) catalysts a small amount of an Ionic Liquid is used to modify the properties of a conventional – ready-to-use – heterogeneous catalyst [14]. In a SILP (*Supported Ionic liquid Phase*) catalyst a homogeneous catalyst or catalyst precursor is immobilized in a thin film of an ionic liquid on the surface of a porous carrier material by physisorption, ionic or covalent anchoring [15]. The application of both concepts results in a very efficient use of the employed Ionic Liquid and in negligible diffusion distances for the reactants compared to the conventional biphasic systems. The immobilization of the molecular-defined catalysts on a solid support in SILP systems is highly desirable in view of economical demands as well as for practical reasons. This concept has already successfully been applied to several important reactions like the hydroformylation [16], hydrogenation [17], hydroamination [18], water-gas shift-[19] as well as the Heck reaction [20] and more.

In most of the published work the primary focus was to transfer the existing knowledge from the homogeneous mode of operation to the heterogenized counterpart. Like for the biphasic systems the influence of the type of Ionic liquid, the loading of the ionic liquid and of course the interplay

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between Ionic Liquid and transition metal catalyst were investigated in detail. In most cases standard support materials like silica or alumina carriers were used. The influence of the solid support on the performance of the resulting catalyst was only examined to a minor degree. For the hydroformylation of propene it was found that the calcination of the silica support and thus the reduction of Brönsted-acid sites has a positive effect on both activity and life-time of the catalyst [16]. For the water-gas shift reaction it was found that in accordance with the generally accepted mechanism proposed for the homogeneous water-gas shift reaction carriers with basic sites are superior to slightly acidic ones [19].

The limited number (or lack) of systematic investigation on the carrier influence is probably not very surprising since porous solids are complex systems with quite a large number of properties which can be varied. The most important properties to describe such solid supports are the chemical composition, the crystallographic phase if applicable, surface functionalities, the surface area (often expressed as BET surface area), the pore volume as well as the type and size of pores. To cover such a broad range of independent variables conventional laboratory techniques, such as single batch reactions, are not adequate. The vast experimental space spanned by the physico-chemical properties of the carrier calls for a high throughput approach. In this account we present our results on combined high throughput and conventional batch reaction experimentation for the first systematic investigation of the influence of the support material on the performance of Supported Ionic Liquid catalysts.

2. EXPERIMENTAL METHODS

2.1. Materials

Unless stated otherwise all chemicals and solvents were used as received from commercial suppliers.

Support materials: Süd-Chemie, Merck, SASOL, NorPro Saint-Gobain, Sigma-Aldrich.

Ionic Liquids (Solvent Innovation, Sigma Aldrich, Merck): BMMIM[OTf] = 1-butyl-2,3-dimethydimidazolium trifluoromethansulfonate; BMIM[$C_8H_{17}SO_4$] = 1-butyl-3-methylimidazolium octylsulfate; BMPyrr[NTf_2] = 1-butyl-3-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide; BMP [OTf] = 1-butyl-3-methylpyridinium trifluoromethan- sulfonate; EMP[NTf_2] = 1-ethyl-3-methylpyridinium bis(tri-fluoromethyl-sulfonyl); BMIM[Cl] = 1-butyl-3-methylimida-zolium chloride; EMP[$C_2H_5SO_4$] = 1-ethyl-3-methylpyridinium ethylsulfate; EMIM[$C_2H_5SO_4$] = 1-ethyl-3-methylimidazolium ethylsulfate; BMIM[CH_3SO_4] = 1-butyl-3-methylimidazolium methylsulfate; BMMIM[Cl] = 1-butyl-3-methylimidazolium chloride; BMIM [CH_3SO_3] = 1-butyl-3-methylimidazolium methylsulfonate; Bu_4N[Cl] = tetrabutylammonium chloride; BMIM[CH_3PO_3] = 1-butyl-3-methylimidazolium methyl-phosphonate; BMIM[FAP] = 1-butyl-3-methylimidazolium tris(pentafluoroethyl)trifluoro-phosphate; BMIM[PF_6] = 1-butyl-3-methylimidazolium hexa-fluorophosphate; BMIM[BF_4] = 1-butyl-3-methylimidazolium tetrafluoroborate. All other reagents were purchased from Sigma-Aldrich.

2.2. Preparation of [CuCl(OH).TMEDA]

The copper complex [CuCl(OH).TMEDA] was prepared according to a method described in the literature [21] with slight modifications. A mixture of anhydrous CuCl (8.20 g; 0.083 mol) and *N,N,N',N'*-tetramethylethylene diamine (TMEDA, 19.00 g; 0.16 mol) in 250 ml of 95% methanol was stirred at ambient temperature for 1h. The resulting deeply colored solution is poured onto 250 ml of Et_2O. The precipitate is collected by filtration, washed with acetone and dried in vacuum to give 19.0 g (98%) of the title compound as a purple powder.

2.3. General Procedure for the Preparation of SILP Catalysts

The SILP catalysts are prepared according to the method published in the literature with slight modifications [22]. The homogeneous copper catalyst [CuCl(OH)*TMEDA] is prepared in-situ and subjected without further purification to the impregnation of the solid support.

2.4. Catalyst Screening

2.4.1. General Method for the Oxidative Coupling of Terminal Alkynes

To a solution of the corresponding alkynes in the appropriate solvent is added the calculated amount of the as-prepared SILP catalyst. The resulting suspension is stirred at air (for the high throughput reactions synthetic air was used) under ambient conditions for the specified time. The progress of the reaction is followed by GC-MS, aliquots of the solutions were taken at fixed time intervals. For the bench scale reactions the catalyst was filtered after the specified time and washed twice with the solvent. The solvent of the combined organic extracts were then removed in vacuum to yield the products as white to off-white solids. The recovered catalysts can be re-used after thorough drying in vacuum.

2.4.2. Bench Scale Equipment

The bench scale reactions were conducted in conventional 1 L double jacketed glass reactors from hws - Mainz. To ensure isotherm throughout the reaction the vessels were thermostated with a Julabo F12-EH refrigerated/heating circulator. Samples were taken *via* a syringe, solid particle were immediately filtered off with the aid of a syringe filter and the solution was analyzed *via* GC-MS (internal standard n-dodecane).

2.4.3. High Throughput Screening

The high throughput experiments were conducted in a 4 × 10 batch reactor set-up with a volume of 100 ml per vessel which is commercially available from ILS (Fig. **1**). Four reactor arrays each array equipped with individual heating zones as well as individual stirring zones (magneti-cally stirring) allow for 10 reactions at the same time.

2.4.4. Analytics

For **^{1}H MAS NMR** measurements the samples were finely ground and packed into 4 mm ZrO_2 rotors. A Bruker MSL 300 spectrometer (B_0 = 7.5 T) was used. The spinning

Fig. (1). Reactor set-up used for the high throughput experiments. Courtesy of ILS.

rate was 10 kHz. 64 scans were recorded with a recycle of 2 s. The spectra were calibrated against an external standard of adamantane. **Elemental analysis** (CHN) of reagents and catalysts were determined on a Heraeus Elementar Vario EI (CHN). The copper content of the catalysts was determined by ICO on a Spectra Modula spectrometer. **N_2 physisorption** isotherms were obtained on a Micromeritics Gemini instrument. Samples were degassed at 150°C for 2 h prior to measurement. Surface areas were measured using the BET method, pore size distributions were calculated from the BJH method and the total pore volumes were calculated from the nitrogen adsorption/desorption data (single point volume at $p/p_0 = 0.995$). The **GC-MS** data were obtained on a Shimadzu GCMS-QP2010.

3. RESULTS

The oxidative coupling of terminal alkynes was chosen as a model reaction for this investigation as the reaction is well understood, active catalysts are readily available (Glaser-Hay system; Scheme **1**) and the reaction is usually highly selective [23]. This allows for a systematic investigation of the “pure” carrier influence independent from secondary effects.

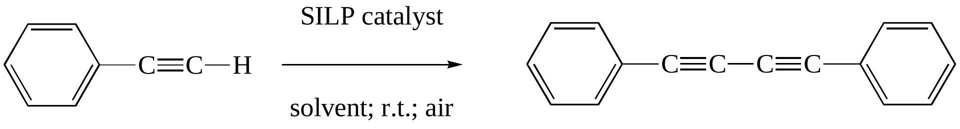
The SILP catalysts are prepared according to the method published in the literature with slight modifications [22]. In a first step an appropriate amount of the homogeneous catalyst, [CuCl(OH)*TMEDA], is dissolved in acetone. To this strongly colored (deep green) solution is then added the calculated amount of an Ionic Liquid and the appropriate support material, in the given order. In order to achieve a uniform distribution of the IL and the homogeneous catalyst on the support the solvent is reduced at moderate vacuum and a constant temperature of 25°C. When the solvent is evaporated too fast the copper complex precipitates from the solution as violet crystals. Finally the catalyst is dried thoroughly in vacuum to produce the SILP catalyst as deep green to deep blue free-flowing powders. The synthesis workflow can be easily automated by resorting to liquid dispensing robots. The 4-dimensional parameter space to be screened is spanned by the combinations of catalyst amount x type of IL x amount of IL x carrier. Typically libraries were designed using orthogonal linear gradients of two independent parameters to be optimized, e.g. amounts of catalyst and IL for a given type of IL and carrier.

To evaluate the activity of the resulting SILP catalysts, the copper content is an important issue. The theoretical copper concentration (Cu%) of the resulting solid catalysts can be calculated according to the following equations:

$$\mathrm{Cu\%} = m_{\mathrm{Cu}}/m_{\mathrm{SILP\text{-}catalyst}} \times 100\%$$

$$m_{\mathrm{SILP\text{-}catalyst}} = m_{[\mathrm{CuCl(OH).TMEDA}]} + m_{\mathrm{IL}} + m_{\mathrm{support}}$$

$$m_{\mathrm{CuCl(OH).TMEDA}} = m_{\mathrm{CuCl}} \times M_{\mathrm{CuCl(OH).TMEDA}}/M_{\mathrm{CuCl}}$$



SILP catalyst = carrier / Ionic Liquid / [CuCl(OH)*TMEDA]

Scheme 1. Oxidation coupling of phenylacetylene with a copper based SILP catalyst; TMEDA = Tetramethylethylenediamine.

$m_{Cu} = m_{CuCl} \times M_{Cu}/M_{CuCl}$

For exemplary catalysts the actual copper content was determined by ICP. As can be seen from Table **1** the deviations from the calculated concentrations are almost negligible. Thus, for the further discussion the theoretical copper content is used.

Table 1. Calculated *vs* Determined Copper Content of SILP-Catalysts ([1] Ionic Liquid: BMMIM[OTf], 1.0 g = 8.1 w%; Support: [2] Silica-365; [3] Alumina-200; [4] Titania-345; [5] Zirconia-210; [6] Activated Carbon-1050; the Denotation of the Support Materials Corresponds to their Surface Area)

Catalyst	CuCl [g/mmol]	Support [g]	Ionic Liquid1 [g]	Cu Calculated [w%]	Cu Determined [w%]
SILP 1	0.60/6.06	10.0^2	1.0	3.12	3.11
SILP 2	0.60/6.06	10.0^3	1.0	3.12	3.12
SILP 3	0.60/6.06	10.0^4	1.0	3.12	3.10
SILP 4	0.60/6.06	10.0^5	1.0	3.12	3.13
SILP 5	0.60/6.06	10.0^6	1.0	3.12	3.12

3.1. General Reaction Conditions

The first step of the investigation was to determine the general reaction conditions which are suitable to discriminate the performance of a large number of different catalysts. The solvent, reaction temperature and reaction time were varied for the five different base catalysts SILP1 – SILP5. The loading of the homogeneous catalyst was kept constant at a value of 3.12 weight% Cu, that of the Ionic Liquid BMMIM[OTf] at 8.1 weight%.

In a typical experiment for the coupling reaction, 10 mmol of phenyl acetylene are dissolved in an appropriate solvent and 1.0 g of the solid catalyst (this corresponds to 5 mol%) is added at the specified temperature. The course of the reaction can be followed by GC-MS. After a specified time, the catalyst is filtered from the crude reaction mixture and washed with additional solvent. The solvent of the combined organic phases is reduced in vacuum and the product is obtained as a colorless to slightly yellow colored solid (pure by HPLC and nmr). Based on the chemical equation, the yield of the reaction can be calculated according to the following formula:

$$\text{Yield\%} = 2 \times n_{alkyne}/n_{diyne} \times 100\%$$

When polar solvents such as THF, acetone or CH_2Cl_2 were used, the ionic catalyst solution (ionic liquid and copper catalyst) is, at least to some extent, removed from the support material. Therefore, we decided to use more non polar solvents which are not miscible with the ionic liquid. Among the non polar solvents *n*-hexane gave the best results. Surprisingly, the yield of the reaction decreased with increasing reaction temperature (Fig. **2**) which is probably due to the high volatility of the starting material phenyl acetylene. Thus, for the further composition studies of the SILP-catalysts we have chosen to conduct the reaction in n-hexane at ambient temperature.

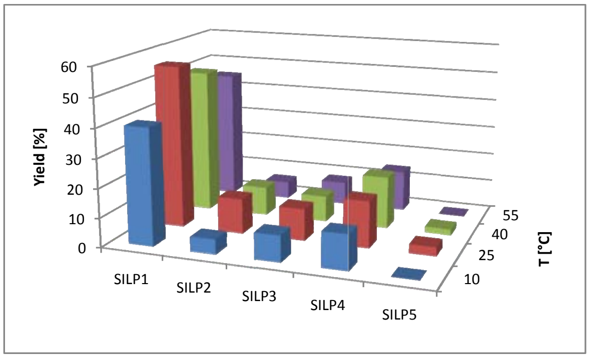


Fig. (2). Yield of 1,4-Diphenylbutadiyne in n-hexane at different temperatures (after 72 h in *n*-hexane).

In order to assure that neither the Ionic Liquid nor a small portion of the copper complex is leached into the organic solvent and this leached (homogeneous) catalyst is responsible for the catalytic activity a filtration experiment was conducted. Two identical experiments were started and at about 50% conversion the solid catalyst of one experiment was removed by filtration, the other was left unchanged (Fig. **3**). After filtration of the solid catalyst no significant change in conversion was observed. In addition, the copper content of the resulting clear solution was determined by ICP and AAS and the copper content was below the detection limit (< 0.1 ppm). This serves as a proof that only the immobilized SILP catalyst is responsible for the catalytic activity.

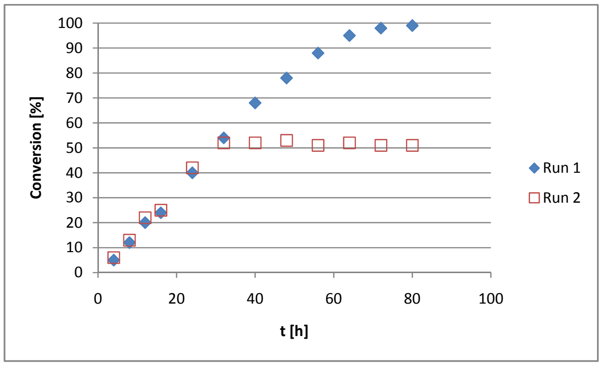


Fig. (3). Filtration experiment.

3.2. Screening of Support Materials

The further screening of the support materials was conducted under adopted conditions in a high throughput reactor under the following standard conditions: 50 ml *n*-hexane; 10 mmol phenylacetylene; 1.0 g SILP catalyst (5 mol% Cu); r.t.; 72h; synthetic air. The support materials are standard materials from commercial suppliers and were used after drying at 120°C for 16h, or in the case of SILP10 (MCF) [24] and SILP11 (MCM-41) [25] synthesized according to literature procedures and dried at 120°C for 16h. The textural properties of the applied supports are summarized in Table **2**. The results of the first screening experiments are depicted in Fig. (**4**).

As can be seen from Fig. (**4**) the activity of the tested catalysts increases gradually with decreasing surface area of the parent support material and reaches a maximum for medium surface areas from 80 – 180 m^2/g. For lower surface areas the activity of the resulting catalysts decreases again. This trend is most pronounced for the silica carriers but can also be found for alumina, titania and zirconia. No correlation can be found for the pore volume or the pore size of the carrier materials. It is noteworthy that selected examples of the high throughput runs were also conducted in conventional batch reactors and the same trends were observed thus validating the scalability of the high throughput approach.

Table 2. Characterization by Hg Porosimetry of Support Materials Used for SILP1 – SILP32

Catalyst	Support	BET Surface Area [m^2/g]	Pore Volume [ml/g]	Medium Pore Size [nm]
SILP 1	silica-365	365	1.01	10.9
SILP 2	alumina-200	200	0.52	9.7
SILP 3	titania-345	345	0.37	4.3
SILP 4	zirconia-210	210	0.31	3.9
SILP 5	activated carbon-1050	1050	0.98	1.7
SILP 6	silica-520	520	0.75	5.5
SILP 7	silica-100	100	0.43	15.5
SILP 8	silica-170	170	0.48	10.9
SILP 9	silica-160	160	0.43	10.1
SILP 10	silica-570	570	2.20	15.4
SILP 11	silica-1185	1185	0.90	2.6
SILP 12	silica-200	200	0.52	10.3
SILP 13	silica-70	70	0.32	36.0
SILP 14	silica-530	530	0.93	6.9
SILP 15	silica-30	30	0.52	
SILP 16	alumina-175	175	0.54	7.5
SILP 17	alumina-150	150	0.53	8.3
SILP 18	alumina-350	350	0.70	3.5
SILP 19	alumina-100	100	0.67	11.2
SILP 20	alumina-35	35	0.42	
SILP 21	titania-55	55	0.39	13.2
SILP 22	titania-32	32	0.26	19.8
SILP 23	titania-110	110	0.43	6.1
SILP 24	titania-150	150	0.44	5.5
SILP 25	zirconia-150	150	0.42	4.9
SILP 26	zirconia-80	80	0.34	8.9
SILP 27	zirconia-60	60	0.50	13.2
SILP 28	zirconia-35	35	0.32	
SILP 29	activated carbon-1000	1000	1.10	1.9
SILP 30	activated carbon-1300	1300	1.32	1.6
SILP 31	activated carbon-900	900	0.89	2.8
SILP 32	activated carbon-500	500	0.75	3.5

The results may be explained as follows: The loading of the Ionic Liquids on various supports was identical in all cases (8.1 weight%). Thus, a higher surface area of the support leads to a reduced thickness of the Ionic Liquid layer and therefore to a restricted mobility of the copper complex. The restricted mobility of transition metal complexes in IL solvent cages has already been reported [26]. The average thickness of the Ionic Liquid layer was calculated to 0.06 nm for silica-1185, 0.13 nm for silica 570 and 0.49 nm for silica-160, respectively. For lower surface areas of the support consequently, the interfacial surface area between Ionic Liquid and organic solvent is also reduced, thus leading to lower overall activity. This is additionally supported by the fact that under identical conditions but without a solid support (liquid-liquid biphasic reaction) the system was virtually inactive.

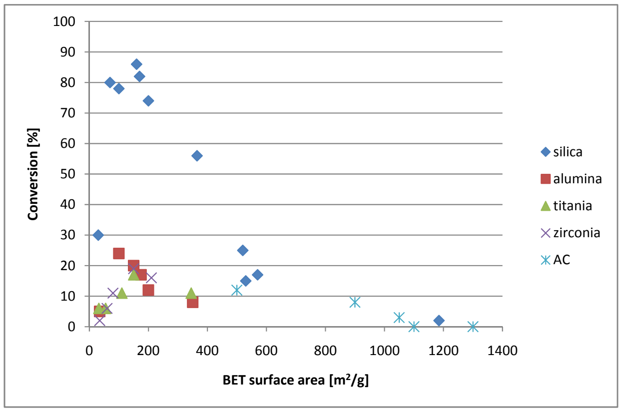


Fig. (4). Screening of various support materials. Conversion *vs* BET surface area.

In order to test this hypothesis further two set of experiments were conducted i) variation of IL loading for a given support (Fig. **5**) and ii) variation of the surface area of a given support by post-calcination while keeping the IL loading constant (Fig. **6**).

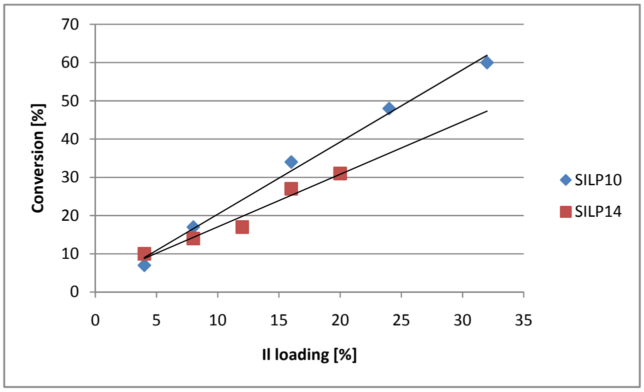


Fig. (5). Screening of SILP10 and SILP14 with different IL loading.

Both sets of experiments corroborate the above mentioned hypothesis. With increasing thickness of the Ionic Liquid layer (higher IL loading or lower surface area) the activity of the resulting SILP catalyst increases. For the SILP12 series also the decrease of activity for very low surface areas was found.

To further underline those findings ^{1}H NMR MAS spectra of SILP10 with 8% IL and 24% IL, respectively, were conducted (Fig. **7**).

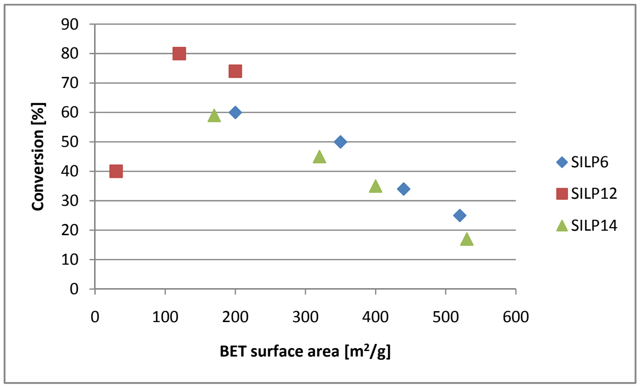


Fig. (6). Screening of post-calcined silica-200, silica-520 and silica-530 with constant IL loading.

Both spectra are badly resolved with very broad signals for the individual nuclei. The broadening of the signals is very likely due to the restricted rotation of the ionic liquid as well as the copper complex on the surface of the support. The formation of quasi ordered solvent cages has already been reported for similar palladium SILP catalysts [26]. However, in both cases the signals at 6.3 and 6.4 ppm, respectively, can be assigned to the protons bound to C4 and C5 of the imidazolium ring. The signals between 0.8 and 3.0 ppm stem from the methylene- or methyl-groups of the ionic liquid or the TMEDA ligand. The spectrum of SILP10-24% IL is much better resolved with only slight broadening of the resonances. The spectrum is dominated by the signals of ionic liquid cation. This confirms the above suggestions of restricted mobility at low IL loadings and the "true" homogeneous nature of the catalyst in such SILP-catalysts.

3.3. Screening of Ionic Liquids

The properties of ionic liquids can be easily tuned by the choice of the anion/cation combination. ILs can be hydrophobic (BMIM[$C_8H_{17}SO_4$]; EMP[NTf_2]), hydrophilic (BMIM[Cl]; EMIM[$C_2H_5OSO_3$]), coordinating (BMIM[CH_3OSO_3]; BMIM[Cl]) or non-coordinating (BMPyrr[NTf_2]; BMMIM[OTf]). These properties may affect the performance of SILP-catalysts. Therefore, several SILP-catalysts were prepared with unmodified silica-365 as the support, 8.1 weight% of an ionic liquid and 3 weight% of copper. All new catalysts were tested under the standard reaction conditions. The results are depicted in Table **3**.

Table 3 Performance of SILP Catalysts Prepared with Various Ionic Liquids

Catalyst	Ionic liquid	Conversion [%]
SILP1	BMMIM[OTf]	79
SILP33	BMIM[$C_8H_{17}SO_4$]	56
SILP34	BMPyrr[NTf_2]	83
SILP35	BMP[OTf]	83
SILP36	1-EMP[NTf_2]	87
SILP37	BMIM[Cl]	84
SILP38	EMP[$C_2H_5SO_4$]	85
SILP39	EMIM[$C_2H_5SO_4$]	89
SILP40	BMIM[CH_3SO_4]	76
SILP41	BMMIM[Cl]	82
SILP42	BMIM[CH_3SO_3]	74
SILP43	Bu_4N[Cl]	79
SILP44	BMIM[CH_3PO_3]	84
SILP45	BMIM[FAP]	88
SILP46	BMIM[PF_6]	81
SILP47	BMIM[BF_4]	84

Except for SILP19, prepared with BMIM[$C_8H_{17}OSO_3$], which gave moderate results all tested catalysts gave good

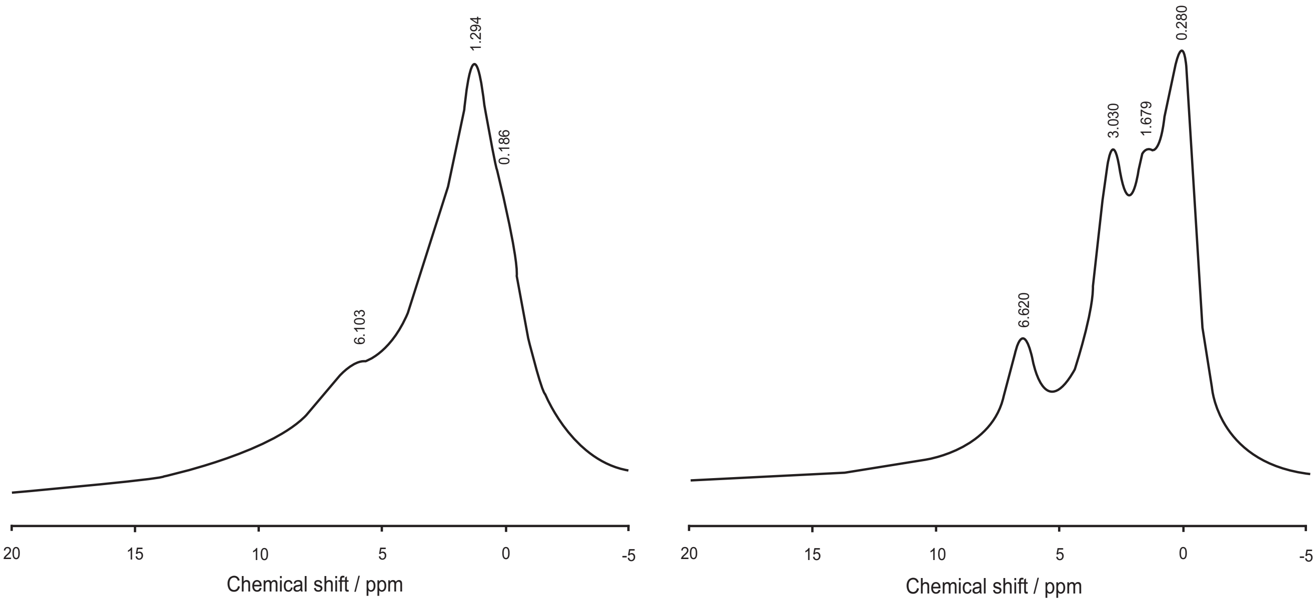


Fig. (7). ^{1}H nmr mas spectra of SILP10 with 8% IL (left) and 24% IL (right).

results with conversions between 74 and 89 %. Thus, the type of IL influences the overall performance of the SILP-catalysts only to a minor degree.

3.4. Catalyst Recycling

As already described, one major advantage of SILP catalysts is the possibility to separate them from the reaction mixture by a simple filtration procedure. In view of economics it is highly desirable to reuse the recovered catalyst for further transformations.

The recyclability of the prepared SILP-catalysts was investigated by employing the recovered catalysts in successive runs. The tests were conducted under identical (standard) conditions with about 5 mol% of the copper SILP catalyst. After a catalytic run, the recovered catalyst was thoroughly dried in vacuum in order to remove all volatiles.

In the first step, the influence of the support material on the recyclability of the SILP-catalysts ([CuCl(OH). TMEDA]/support/BMMIM[TfO]) was investigated (Table **4**).

Table 4. Recyclability of Cu/Silica-100/BMMIM[OTf] SILP-Catalysts

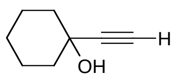
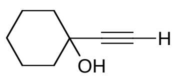
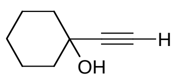
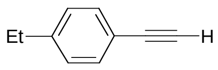
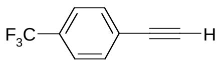
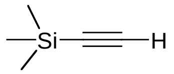
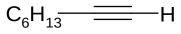
Catalyst	Support	Ionic Liquid	Run	Conversion [%]
SILP1	silica-365	BMMIM[OTf]	1	58
	silica-365	BMMIM[OTf]	2	43
	silica-365	BMMIM[OTf]	3	37
	silica-365	BMMIM[OTf]	4	12
SILP7	silica-100	BMMIM[OTf]	1	83
	silica-100	BMMIM[OTf]	2	85
	silica-100	BMMIM[OTf]	3	89
	silica-100	BMMIM[OTf]	4	85
	silica-100	BMMIM[OTf]	5	87
SILP9	silica-160	BMMIM[OTf]	1	93
	silica-160	BMMIM[OTf]	2	88
	silica-160	BMMIM[OTf]	3	86
	silica-160	BMMIM[OTf]	4	95
	silica-160	BMMIM[OTf]	5	93

The yield of the reaction with the SILP catalyst based on the silica-365 support gradually decreases from 58% in the first run to about 12% in the 4th run. In contrast, both catalytic systems based on silica-100 as well as silica-160 as support can be recovered for at least 4 times with virtually no loss in activity. Similar observations were made with BMIM[BF_4] and BMIM[CH_3SO_4] as ionic liquids.

3.5. Scope

The scope of the new SILP-catalyst was checked by screening various terminal alkynes as starting materials in parallel under standard reaction conditions. Due to the low solubility of some alkynes in *n*-hexane, the reaction was also conducted in diethyl ether as the solvent. The activity ranking found is summarized in Table **5**.

Table 5. Oxidative Homocoupling of Terminal Alkynes

Alkyne	Catalyst	Solvent	Yield (%)
	SILP7	diethyl ether	81.3
	SILP9	diethyl ether	89.7
	SILP39	n-hexane	74.9
	SILP7	n-hexane	84.5
	SILP7	n-hexane	79.8
	SILP7	n-hexane	94.3
	SILP7	n-hexane	86.1

For all tested terminal alkynes the tested SILP catalysts gave good to excellent conversions underlining the generality of the catalyst concept for the oxidative coupling of terminal alkynes.

4. CONCLUSION

By resorting to a high throughput synthesis and screening workflow for the SILP-catalyzed homocoupling of alkynes it was possible to efficiently map out the parameter space consisting of substrate, type and amount of IL, as well as the carrier and it was discovered that for the given reaction system the thickness of the Ionic Liquid phase on the solid support is the most dominating factor for the performance of the resulting catalyst.

At a constant IL loading of the SILP catalyst the maximum of activity was found for solid supports with medium surface. For both, a higher and a lower surface area of the support the activity drastically decreases. This result may be rationalized by the necessity for an optimum Ionic Liquid layer thickness: on the one hand a reasonably high IL loading is mandatory to preserve the homogeneous nature of the catalyst complex, whereas even higher loadings lead to substantial pore filling and thus to a low liquid-liquid reaction interface.

The optimized SILP catalysts could be reused several times without loss of activity and could be applied to the oxidative coupling of a variety of terminal alkynes.

REFERENCES

[1] (a) P. Wasserscheid, T. Welton (Eds.), *Ionic Liquids in Synthesis*, Wiley-VCH: Weinheim, **2003**; (b) Plechkova, N.V.; Seddon, K.R.

Applications of ionic liquids in the chemical industry. *Chem. Soc. Rev*., **2008**, *37*, 123-150.

[2] (a) Seddon, K.R. Ionic liquids for clean technology. *J. Chem. Technol. Biotech*., **1997**, *68*, 351-356; (b) Rogers, R. D.; Voth, G. A. Ionic liquids. *Acc. Chem. Res.*, **2007**, *40*, 1077-1078.

[3] Chiappe, C.; Pieraccini, D. Ionic liquids: solvent properties and organic reactivity *J. Phys. Chem. Soc*., **2005**, *18*, 275-297.

[4] (a) Welton, T. Ionic liquids in catalysis. *Coord. Chem. Rev*., **2004**, *248*, 2459-2477; (b) Welton, T. Room-temperature ionic liquids. Solvents for synthesis and catalysis. *Chem. Rev*., **1999**, *99*, 2071-2083; (c) Holbrey, J.D.; Seddon, K.R. Ionic liquids. *Clean Prod. Proc*., **1999**, *11*, 223-236; (d) Earle, M.J.; Seddon, R. Ionic liquids. Green solvents for the future. *Pure Appl. Chem*., **2000**, *72*, 1391-1398; (e) Wilkes, J.S. Properties of ionic liquids for catalysis. *J. Mol. Catal. A: Chem*., **2004**, *214*, 11-17; (f) Keskin, S.; Kayrak-Talay, D.; Akman, U.; Hortacsu, Ö. A review of ionic liquids towards supercritical fluids. *J. Supercr. Fluids*, **2007**, *43*, 150-180; (g) Olivier-Bourbigou, H.; Magna, L.; Morvan, D. Ionic liquids and catalysis: Recent progress from knowledge to application. *Appl. Catal. A: Gen*., **2010**, *373*, 1-56; (h) Werner, S.; Haumann, M.; Wasserscheid, P. Ionic liquids in chemical engineering. *Ann. Rev. Chem. Biomol. Eng*., **2010**, *1*, 203-230.

[5] (a) Kottsieper, K.W.; Stelzer, O.; Wasserscheid, P. 1-Vinylimidazole - a versatile building block for the synthesis of cationic phosphines useful in ionic liquid biphasic catalysis. *J. Mol. Catal. A Chem*., **2001**, *175*, 285-288; (b) Brauer, D.J.; Kottsieper, K.W.; Liek, C.; Stelzer, H.; Waffenschmidt, H.; Wasserscheid, P. Phosphines with 2-imidazolium and *para*-phenyl-2-imidazolium moieties - synthesis and application in two-phase catalysis. *J. Organomet. Chem*., **2001**, *630*, 177-184; (c) Favre, F.; Olivier-Bourbigou, H.; Commereuc, D.; Saussine, L. Hydroformylation of 1-hexene with rhodium in non-aqueous ionic liquids : how to design the solvent and the ligand to the reaction. *Chem. Commun.*, **2001**, 1360-1361; (d) Knifton, J.F. Syngas reactions : Part XI. The ruthenium 'melt' catalyzed oxonation of internal olefins. *J. Mol. Catal*., **1987**, *43*, 65-77; (f) Knifton, J.F. Syngas reactions : Part XIII. The ruthenium 'melt'-catalyzed oxonation of terminal olefins. *J. Mol. Catal.*, **1988**, *47*, 99-116.

[6] (a) Chauvin, Y.; Mussmann, L.; Olivier, H. A novel class of versatile solvents for two-phase catalysis: Hydrogenation, isomerization, and hydroformylation of alkenes catalyzed by Rhodium complexes in liquid 1,3-dialkylimidazolium salts. *Angew. Chem., Int. Ed. Engl*., **1995**, *34*, 2698-2700; (b) Suarez, P.A.Z.; Dullius, J.E.L.; Einloft, S.; de Souza, R.F.; Dupont, J. The use of new ionic liquids in two-phase catalytic hydrogenation reaction by rhodium complexes. *Polyhedron,* **1996**, *75*, 1217-1219; (c) MacLeod, S.; Rosso, R.J. Hydrogenation of low molecular weight polymers in ionic liquids and the effects of added salt. *Adv. Synth. Catal.,* **2003**, *345*, 568-571; (d) Widegren, J.A.; Finke, R.G. A review of the problem of distinguishing true homogeneous catalysis from soluble or other metal-particle heterogeneous catalysis under reducing conditions. *J. Mol. Catal. A Chem*., **2003**, *198*, 317-341; (e) Baudequin, C.; Baudoux, J.; Levillain, J.; Cahard, D.; Gaumont, A.C.; Plaquevent, J.C. Ionic liquids and chirality: opportunities and challenges. *Tetrahedron: Asymmetry,* **2003**, *14*, 3081-3093; (f) Anthony, J.L.; Magninn, E.J.; Brenneke, J.F. Solubilities and thermodynamic properties of gases in the ionic liquid 1-*n*-butyl-3-methylimidazolium hexafluorophosphate. *J. Phys. Chem. B,* **2002**, *706*, 7315-7320; (g) Guernik, S.; Wolfson, A.; Herskowitz, M.; Greenspoon, N.; Shimona, G. A novel system consisting of Rh–DuPHOS and ionic liquid for asymmetric hydrogenations. *Chem. Commun.,* **2001**, 2314-2315; (h) Monteiro, A.L.; Zinn, F.K.; de Souza, R.F.; Dupont, J. Asymmetric hydrogenation of 2-arylacrylic acids catalyzed by immobilized Ru-BINAP complex in 1-*n*-butyl-3-methylimidazolium tetrafluoroborate molten salt. *Tetrahedron: Asymmetry* **1997**, *8*, 177-179; (i) Sun, Y.; Landau, R.N.; Wang, J.; LeBlond, C.; Blackmond, D.G. A re-examination of pressure effects on enantioselectivity in asymmetric catalytic hydrogenation. *J. Am. Chem. Soc.*, **1996**, *118*, 1348-1353; (j) Ngo, H.L.; Hu, A.; Lin, W. Highly enantioselective catalytic asymmetric hydrogenation of β-keto esters in room temperature ionic liquids. *Chem. Commun*., **2003**, 1912-1913; (k) Lee, S.; Zhang, Y.J.; Piao, J.Y.; Yoon, H.; Song, C.E.; Choi, J.H.; Hong, J. Catalytic asymmetric hydrogenation in a room temperature ionic liquid using chiral Rh-complex of ionic liquid grafted 1,4-bisphosphine ligand. *Chem. Commun*., **2003**, 2624-2625; (l) Yinghuai, Z.; Carpenter, K.; Bun, C.C.; Bahnmueller, S.; Ke, C.P.; Srid, V.S.; Kee, L.W.; Hawthorne, M.F. (*R*)-Binap-mediated asymmetric hydrogenation with a rhodacarborane catalyst in ionic-liquid media. *Angew. Chem. Int. Ed*., **2003**, *42*, 3792-3795; (m) Brown, R.A.; Pollet, P.; McKoon, E.; Eckert, C.A.; Liotta, C.L.; Jessop, P.G. Asymmetric hydrogenation and catalyst recycling using ionic liquid and supercritical carbon dioxide. *J. Am. Chem. Soc*., **2001**, *123*, 1254-1255; (n) Dyson, P.J.; Laurenczy, G.; Ohlin, C.A.; Vallance, J.; Welton, T. Determination of hydrogen concentration in ionic liquids and the effect (or lack of) on rates of hydrogenation. *Chem. Commun*., **2003**, 2418-2419; (o) Dyson, P.J.; Ellis, D.J.; Welton, T. A temperature-controlled reversible ionic liquid - water two phase - single phase protocol for hydrogenation catalysis. *Can. J. Chem*., **2001**, *79*, 705-708.

[7] Muzart, J. Ionic liquids as solvents for catalyzed oxidations of organic compounds. *Adv. Synth. Catal*., **2006**, *348*, 275-295.

[8] (a) Boon, J.A.; Levisky, J.A.; Pflug, J.L.; Wilkes, J.S. Friedel-Crafts reactions in ambient-temperature molten salts. *J. Org. Chem*., **1986**, *57*, 480-483; (b) Koch, V.R.; Miller, L.L.; Osteryoung, R.A. Electroinitiated Friedel-Crafts transalkylations in a room-temperature molten-salt medium. *J. Am. Chem. Soc.*, **1976**, *98*, 5277-5284; (c) Kim, D.S.; Ahn, W.S. Diphenylmethane synthesis using ionic liquids as lewis acid catalyst. Korean *J. Chem. Eng.,* **2003**, *20*, 39-43; (d) Newman, D.S.; Winans, R.E.; McBeth, R.L. Reactions of coal and model coal compounds in room temperature molten salt mixtures. *J. Electrochem. Soc*., **1984**, *131*, 1079-1083; (e) Chauvin, Y.; Hirschauer, A.; Olivier, H. Alkylation of isobutane with 2-butene using 1-butyl-3-methylimidazolium chloride-aluminium chloride molten salts as catalysts. *J. Mol. Catal*., **1994**, *92*, 155-165; (f) Ladnak, V.; Hofmann, N.; Brausch, N.; Wasserscheid, P. Continuous, ionic liquid-catalysed propylation of toluene in a liquid-liquid biphasic reaction mode using a loop reactor concept. *Adv. Synth. Catal*., **2007**, *349*, 719-726; (g) Bui, T. L. T.; Korth, W.; Aschauer, S.; Jess, A. Alkylation of isobutane with 2-butene using ionic liquids as catalyst. *Green Chem*., **2009**, *11*, 1961-1967.

[9] (a) Adams, C.J.; Earle, M.J.; Roberts, G.; Seddon, K.R. Friedel–Crafts reactions in room temperature ionic liquids. *Chem. Commun*., **1998**, 2097-2098; (b) Yeung, K.-S.; Farkas, M.E.; Qiu, Z.; Yang, Z. Friedel–Crafts acylation of indoles in acidic imidazolium chloroaluminate ionic liquid at room temperature. *Tetrahedron Lett*., **2002**, *43*, 5193-5195; (c) Luer, G.D.; Bartak, D.E. Electrochemistry of carbonium ions in acidic media. 1. Triphenylmethyl ion in aluminum chloride containing melts. *J. Org. Chem*., **1982**, *47*, 1238-1243; (d) Csihony, S.; Mehdi, H.; Horvath, I.T. *In situ* infrared spectroscopic studies of the Friedel–Crafts acetylation of benzene in ionic liquids using $AlCl_3$ and $FeCl_3$. *Green Chem*., **2001**, *3*, 307-309; (e) Qiao, K.; Deng, Y. Alkylations of benzene in room temperature ionic liquids modified with HCl. *J. Mol. Catal. A Chem.*, **2001**, *171*, 81-84; (f) Smith, G.P.; Dworkin, A.S.; Pagni, R.M.; Zingg, S.P. Broensted superacidity of hydrochloric acid in a liquid chloroaluminate. Aluminum chloride - 1-ethyl-3-methyl-1H-imidazolium chloride. *J. Am. Chem. Soc*., **1989**, *111*, 525-530; (g) Trulove, P.C.; Osteryoung, R.A. Proton speciation in ambient-temperature chloroaluminate ionic liquids. *Inorg. Chem*., **1992**, *31*, 3980-3985; (h) Campbell, J.L.E.; Johnson, K.E. The chemistry of protons in ambient-temperature ionic liquids: Solubility and electrochemical profiles of HCl in HCl:ImCl:AlCl3 ionic liquids as a function of pressure (295 K). *J. Am. Chem. Soc.*, **1995**, *117*, 7791-7800; (i) Elaiwi, A.; Hitchcock, P.B.; Seddon, K.R.; Srinivasan, N.; Tan, Y.-M.; Welton, T.; Zora, J.A. Hydrogen bonding in imidazolium salts and its implications for ambient-temperature halogenoaluminate (III) ionic liquids. *J. Chem. Soc, Dalton Trans*., **1995**, 3467-3472.

[10] (a) Chauvin, Y.; Gilbert, B.; Guibard, I. Catalytic dimerization of alkenes by nickel complexes in organochloroaluminate molten salts. *J. Chem. Soc, Chem. Commun*., **1990**, 1715-1716; (b) Chauvin, Y.; Einloft, S.; Olivier, H. Catalytic dimerization of propene by nickel-phosphine complexes in 1-Butyl-3-methylimidazolium chloride/$AlEt_xCl3_{-x}$ (x = 0, 1) ionic liquids. *Ind. Eng. Chem. Res.*, **1995**, *34*, 1149-1155; (c) Chauvin, Y.; Olivier, H.; Wyrvalski, C.N.; Simon, L.C.; de Souza, R.F. Oligomerization of *n*-Butenes catalyzed by nickel complexes dissolved in organochloroaluminate ionic liquids. *J. Catal*., **1997**, *165*, 275-278; (d) Simon, L.C.; Dupont, J.; de Souza, R.F. Two-phase *n*-butenes dimerization by nickel complexes in molten salt media. *Appl.*

Catal. A: Gen., **1998**, *175*, 215-220; (e) Einloft, S.; Dietrich, F.K.; de Souza, R.F.; Dupont, *J.* Selective two-phase catalytic ethylene dimerization by Ni^{II} complexes/$AlEtCl_2$ dissolved in organoaluminate ionic liquids *Polyhedron*, **1996**, *75*, 3257-3259; (f) Robinson, J.; Osteryoung, R.A. An electrochemical and spectroscopic study of some aromatic hydrocarbons in the room temperature molten salt system aluminum chloride-n-butylpyridinium chloride. *J. Am. Chem. Soc*., **1979**, *707*, 323-327.

[11] (a) Xu, L.; Chen, W.; Xiao, J. Heck reaction in ionic liquids and the *in situ* identification of *N*-heterocyclic carbene complexes of palladium. *Organometallics,* **2000**, *19*, 1123-1127; (b) Hamill, N.; Hardacre, C.; McMath, S.E.J. *In situ* XAFS investigation of palladium species present during the Heck reaction in room temperature ionic liquids. *Green Chem*., **2002**, *4*, 139-142; (c) Chen, W.; Xu, L.; Chatterton, C.; Xiao, Palladium catalysed allylation reactions in ionic liquids. *J. Chem. Commun*., **1999**, 1247-1248; (d) Ross, J.; Chen, W.; Xu, L.; Xiao, J. Ligand effects in palladium-catalyzed allylic alkylation in ionic liquids. *Organometallics,* **2001**, *20*, 138-142; (e) Rajagopal, R.; Jarikote, D.V.; Srinivasan, K.V. Ultrasound promoted Suzuki cross-coupling reactions in ionic liquid at ambient conditions. *Chem. Commun*., **2002**, 616-617.

[12] (a) Dalko, P.I.; Moisan, L. Enantioselective organocatalysis. *Angew. Chem. Int. Ed*., **2001**, *40*, 3726-3748; (b) Schreiner, P.R. Metal-free organocatalysis through explicit hydrogen bonding interactions. *Chem. Soc. Rev*., **2003**, *32*, 289-296; (c) Fischer, T.; Sethi, A.; Welton, T.; Woolf, J. Diels-Alder reactions in room-temperature ionic liquids. *Tetrahedron Lett*., **1999**, *40*, 793-796; (d) Earle, M.J.; McCormac, P.B.; Seddon, K.R. Diels–Alder reactions in ionic liquids. A safe recyclable alternative to lithium perchlorate–diethyl ether mixtures. *Green Chem*., **1999**, *1*, 23-25; (e) Ludley, P.; Karodia, N. Phosphonium tosylates as solvents for the Diels–Alder reaction. *Tetrahedron Lett*., **2001**, *42*, 2011-2014; (f) Dzyuba, S.V.; Bartsch, R.A. Expanding the polarity range of ionic liquids. *Tetrahedron Lett*., **2002**, *43*, 4657-4659; (g) Dubreuil, J.F.; Bazureau, J.P. Rate accelerations of 1,3-dipolar cycloaddition reactions in ionic liquids. *Tetrahedron Lett*., **2000**, *41*, 7351-7355; (h) Aggarwal, A.; Lancaster, N.L.; Sethi, A.R.; Welton, T. The role of hydrogen bonding in controlling the selectivity of Diels–Alder reactions in room-temperature ionic liquids. *Green Chem*., **2002**, *4*, 517-520; (i) Gholap, A.R.; Venkatesan, K.; Daniel, T.; Lahoti, R.J.; Srinivasan, K.V. Ultrasound promoted acetylation of alcohols in room temperature ionic liquid under ambient conditions. *Green Chem*., **2003**, *5*, 693-696; (j) Forsyth, S.A.; MacFarlane, D.R.; Thompson, R.J.; von Itzstein, M. Rapid, clean, and mild *O*-acetylation of alcohols and carbohydrates in an ionic liquid. *Chem. Commun*., **2002**, 714-715; (k) Dere, R.T.; Pal, R.R.; Patil, P.S.; Salunkhe, M.M. Influence of ionic liquids on the phase transfer-catalysed enantioselective Michael reaction. *Tetrahedron Lett*., **2003**, *44*, 5351-5353; (l) Yadav, J.S.; Reddy, B.V.S.; Baishya, G. Green protocol for conjugate addition of Thiols to α,β-unsaturated ketones using a $[Bmim]PF_6/H_2O$ system. *J. Org. Chem*., **2003**, *68*, 7098-7100.

[13] (a) Gu, Y.; Li, G. Ionic liquids-based catalysis with solids: State of the art. *Adv. Synth. Catal.*, **2009**, *351*, 817-847; (b) Van Doorslaer, C.; Wahlen, J.; Mertens, P.; Binnemans, K.; De Vos, D. Immobilization of molecular catalysts in supported ionic liquid phases. *Dalton Trans*., **2010**, *39*, 8377-8390.

[14] (a) Gu, Y; Ogawa, C.; Kobayashi, J.; Mori, Y.; Kobayashi, S. A heterogeneous silica-supported scandium/ionic liquid catalyst system for organic reactions in water. *Angew. Chem. Int. Ed.*, **2006**, *45*, 7217-7220; (b) Kernchen, U.; Etzold, B.; Korth, W.; Jess, A. Solid catalyst with ionic liquid layer (SCILL) – A new concept to improve selectivity illustrated by hydrogenation of cyclooctadiene. *Chem. Eng. Techn*., **2007**, *30*, 985-994; (c) Arras, J.; Steffan, M.; Shayeghi, Y.; Ruppert, D.; Claus, P. Regioselective catalytic hydrogenation of citral with ionic liquids as reaction modifiers. *Green Chem*., **2009**, *11*, 716-723; (d) Arras, J.; Steffan, M.; Shayeghi, Y.; Claus, P. The promoting effect of a dicyanamide based ionic liquid in the selective hydrogenation of citral. *Chem. Commun*., **2008**, 4058-4060; (e) Arras, J.; Paki, E.; Roth, C.; Radnik, J.; Lucas, M.; Claus, P. How a supported metal is influenced by an ionic liquid: In-depth characterization of SCILL-type palladium catalysts and their hydrogen adsorption. *J. Phys. Chem*., **2010**, *114*, 10520-10526.

[15] (a) Riisager, A.; Fehrmann, R.; Haumann, M.; Wasserscheid, P. Catalytic SILP materials. *Top. Organomet. Chem*., **2008**, *23*, 149-161; (b) Wasserscheid, P. Continous reactions using ionic liquids as catalytic phase. *J. Ind. Eng. Chem*., **2007**, *13*, 325-338; (c) Riisager, A.; Fehrmann, R.; Haumann, M.; Wasserscheid, P. Supported ionic liquid phase (SILP) catalysis: An innovative concept for homogeneous catalysis in continuous fixed-bed reactors. *Eur. J. Inorg. Chem*., **2006**, 695-706.

[16] (a) Riisager, A.; Wasserscheid, P.; van Hal, R.; Fehrmann, R. Continuous fixed-bed gas-phase hydroformylation using supported ionic liquid-phase (SILP) R catalysts. *J. Catal*., **2003**, *219*, 452-455; (b) Panda, A.G.; Jagtap, S.R.; Nandurkar, N.S.; Bhanage, B.M. Regioselective hydroformylation of allylic alcohols using Rh/PPh_3 supported ionic liquid-phase catalyst, followed by hydrogenation to 1,4-butanediol using Ru/PPh_3 supported ionic liquid-phase catalyst. *Ind. Eng. Chem. Res*., **2008**, *47*, 969-972; (c) Hamza, K.; Blum, J. Highly selective hydroformylation of vinylarenes to branched aldehydes by $[Rh(cod)Cl]_2$ entrapped in ionic liquid modified silica sol-gel. *Eur. J. Org. Chem*., **2007**, 4706-4710.

[17] (a) Mehnert, C.P.; Mozeleski, E.; Cook, R.A. Supported ionic liquids catalysis investigated for hydrogenation reactions. *Chem. Commun*., **2002**, 3010-3011; (b) Wolfson, A.; Vankelecom, I.F.J.; Jacobs, P.A. Co-immobilization of transition-metal complexes and ionic liquids in a polymeric support for liquid-phase hydrogenations. *Tetrahedron Lett*., **2003**, *44*, 11951198; (c) Huang, J.; Jiang, T.; Gao, H.; Han, B.; Liu, Z.; Wu, W.; Chang, Y.; Zhao, G. Pd nanoparticles immobilized on molecular sieves by ionic liquids: Heterogeneous catalysts for solvent-free hydrogenation. *Angew. Chem., Int. Ed*., **2004**, *43*, 1397-1399; (d) Fujita, S.-I.; Sano, Y.; Bhanage, B.M.; Arai, M. Supported liquid-phase catalyst containing ruthenium complexes for selective hydrogenation of α,β-unsaturated aldehyde: importance of interfaces between liquid film, solvent, and support for the control of product selectivity. *J. Catal*., **2004**, *225*, 95-104; (e) Huang, J.; Jiang, T.; Han, B.; Wu, W., Liu, Z.; Xie, Z.; Zhang, J. A novel method to immobilize Ru nanoparticles on SBA-15 firmly by ionic liquid and hydrogenation of arene. *Catal. Lett*., **2005**, *103*, 59-62; (f) Miao, S.; Liu, Z.; Han, B.; Huang, J.; Sun, Z.; Zhang, J.; Jiang, T. Ru nanoparticles immobilized on montmorillonite by ionic liquids: A highly efficient heterogeneous catalyst for the hydrogenation of benzene. *Angew. Chem., Int. Ed*., **2006**, *45*, 266-269; (g) Gelesky, M.A.; Chiaro, S.S.X.; Pavan, F.A.; dos Santos, J.H.Z.; Dupont, J. Supported ionic liquid phase rhodium nanoparticle hydrogenation catalysts. *Dalton Trans*., **2007**, 5549-5553; (h) Virtanen, P.; Mikkola, J.-P-; Salmi, T. Kinetics of citral hydrogenation by supported ionic liquid catalysts (SILCA) for fine chemicals. *Ind. Eng. Chem. Res.*, **2007**, *46*, 9022-9031.

[18] (a) Valkenberg, M.H.; de Castro, C.; Hölderich, W.F. Immobilisation of ionic liquids on solid supports. *Green Chem*., **2002**, *4*, 88-93; (b) Valkenberg, M.H.; de Castro, C.; Hölderich, W.F. Friedl-Crafts acylation of aromatics catalysed by supported ionic liquids. *Appl. Catal. A*, **2001**, *215*, 185-190; (c) Valkenberg, M.H.; de Castro, C.; Hölderich, W.F. Immobilisation of chloroaluminate ionic liquids on silica materials. *Top. Catal*., **2001**, *14*, 139-144.

[19] (a) Werner, S.; Szesni, N.; Fischer, R.W.; Haumann, M.; Wasserscheid P. Homogeneous ruthenium-based water-gas shift catalysts *via* supported ionic liquid phase (SILP) technology at low temperature and ambient pressure. *Phys. Chem. Chem. Phys.*, **2009**, *11*, 10817-10819; (b) Werner, S.; Szesni, N.; Kaiser, M.; Fischer, R.W.; Haumann, M.; Wasserscheid P. Ultra-low-temperature water-gas shift catalysis using supported ionic liquid phase (SILP) materials. *ChemCatChem.*, **2010**, *2*, 1399-1402; (c) Werner, S.; Szesni, N.; Bittermann, A.; Schneider, M.J.; Härter, P.; Haumann, M.; Wasserscheid P. Screening of supported ionic liquid phase (SILP) catalysts for the very low temperature water-gas-shift reaction. *Appl. Catal. A: Gen*., **2010**, *377*, 70-75.

[20] (a) Hagiwara, H.; Shimizu, Y.; Hoshi, T.; Suzuki, T.; Ando, M.; Ohkubo, K.; Yokoyama, C. Heterogeneous Heck reaction catalyzed by Pd/C in ionic liquid. *Tetrahedron Lett*., **2001**, *42*, 4349-4351; (b) Okubo, K.; Shirai, M.; Yokoyama, C. Heck reactions in a non-aqueous ionic liquid using silica supported palladium complex catalysts. *Tetrahedron Lett*., **2002**, *43*, 7115-7118; (c) Hagiwara, H.; Sugawara, Y.; Isobe, K.; Hoshi, T.; Suzuki, T. Immobilization of $Pd(OAc)_2$ in ionic liquid on silica: Application to sustainable

Mizoroki-Heck reaction. *Org. Lett.*, **2004**, *6*, 2325-2328; (d) Ma, X.; Zhou, Y.; Zhang, J.; Zhu, A.; Jiang, T., Han, B. Solvent-free Heck rection catalyzed by a recyclable Pd catalyst supported on SBA-15 *via* an ionic liquid. *Green Chem.*, **2008**, *10*, 59-66.

[21] Nakajima, M.; Miyoshi, I.; Kanayama, K.; Hashimoto, S.-I. Enantioselective synthesis of binaphthol derivatives by oxidative coupling of naphthol derivatives catalyzed by chiral diamine·copper complexes. *J. Org. Chem.*, **1999**, *64*, 2264-2271.

[22] Mehnert, C.P.; Cook, R.A.; Dispenziere, N.C.; Afeworki, M. Supported ionic liquid catalysis - A new concept for homogeneous hydroformylation catalysts. *J. Am. Chem. Soc.*, **2002**, *124*, 12932-12933.

[23] Hay, A. Oxidative coupling of acetylenes. II. *J. Org. Chem.*, **1962**, *27*, 3320-3321.

[24] Lee, S.S.; Hadinoto, S.; Ying, J.Y. Improved enantioselectivity of immobilized chiral bisoxazolines by partial precapping of the Siliceous Mesocellular Foam Support with Trimethylsilyl Groups. *Adv. Synth. Catal.*, **2006**, *348*, 1248-1254.

[25] Angloher, S.; Kecht, J.; Bein, T. Optimization of reaction conditions for the metalorganic modification of MCM-41. T. *Chem. Mat.*, **2007**, *19*, 3568-3574.

[26] Fow, K.L.; Jaenicke, S.; Müller, T.E.; Sievers, C. Enhanced enantioselectivity of chiral hydrogenation catalysts after immobilisation in thin films of ionic liquid. *J. Mol. Catal. A: Chem.*, **2008**, *279*, 239-247.

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