# Development of a Supported Ionic Liquid Phase (SILP) Catalyst for Slurry-Phase Friedel–Crafts Alkylations of Cumene

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**Abstract:** A supported ionic liquid phase (SILP) catalyst material has been developed based on a silica support coated with an acidic chloroaluminate ionic liquid. Compared to the results in a liquid-liquid biphasic reaction these materials showed in the isopropylation of cumene a clearly different selectivity which was found to be related to a reduction of the ionic liquid's acidity by the untreated silica support. By pretreating the support with a defined amount of ionic liquid for neutralization and removal of surface hydroxy groups, a well defined, very active and also very selective SILP catalyst for slurry phase Friedel–Crafts alkylation was obtained.

**Keywords:** acidic ionic liquids; alkylation; Friedel–Crafts reaction; porous material; supported ionic liquid phase

## Introduction

The industrial scale production of alkylated arenes is mainly carried out through Friedel–Crafts alkylation reactions. Many of the existing processes utilize homogeneous alumium(III) chloride as catalyst,[1] which is decomposed in a hydrolysis step in the work-up process after reaction. During this procedure, aluminium oxide waste, toxic and corrosive HCl gas and large amounts of water contaminated with organic impurities are produced, which makes the process problematic from an environmental point of view.

As an alternative to the homogeneous $AlCl_3$-catalyzed process, zeolites and metal oxides are applied in Friedel–Crafts reactions.[2–5] These heterogeneous catalysts can be separated from the liquid reaction products very easily by filtration, allowing much simpler process schemes. However, these heterogeneous catalysts are usually less active than the homogeneous system so that longer reaction times and rather extreme reaction conditions are usually required. The latter are known to trigger undesired oligomerization[5] or even coke formation.[6–9]

Dissolving the halide-containing Lewis acid in an ionic liquid phase opens the possibility to immobilize the active acidic species in an ionic phase if the reaction mixture shows a miscibility gap with the ionic liquid in use. In this case, a recycling of the acidic, ionic catalyst phase is possible by decantation.[10,11] Another interesting point of chloroaluminate ionic liquids is their tunable acidity ranging from mildly Lewis acidity (e.g., [cation]$Cl/AlCl_3 = 1/1.1$) to very powerful Lewis acidity at the maximum solubility of $AlCl_3$. The latter is reached at a 1/2 molar ratio in the case of [cation]$Cl/AlCl_3$[12] and can reach up to 1/4.5 in the case of [cation][$NTf_2$]/$AlCl_3$ systems.[13] Numerous applications of these acidic chloroaluminate ionic liquids have been already reported.[14] Examples include various alkylation reactions of benzene and toluene with alkyl halides and alkenes as the alkylation agent,[15–17] linear alkylbenzene production for surfactant synthesis[18] and isobutene alkylation with 2-butene.[19]
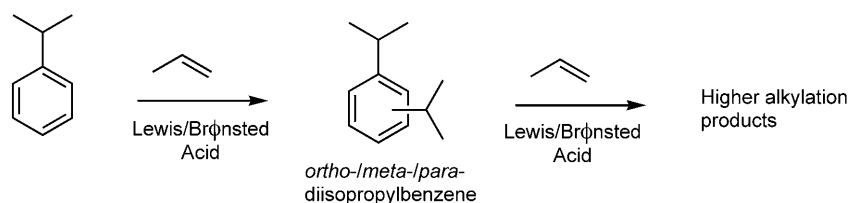
In the last five years the immobilization of catalytic ionic liquids on porous supports has become known as the so-called "supported ionic liquid phase (SILP)" concept.[20–23] Catalytic reactions in which SILP catalyst systems have been successfully applied include hydrogenations,[24–26] hydroformylations,[27–29] hydroaminations,[30] and carbonylations.[31] The attractiveness of the concept for industrial use is related to the very short diffusion distances in the supported ionic liquid films avoiding the mass transfer limitations often encountered in traditional liquid-ionic liquid catalysis[32] (due to the comparably high ionic liquid viscosity). The lack of mass transfer restrictions leads to a much more efficient utilization of the ionic liquid catalyst volume allowing for a dramatic reduction of the ionic liquid volume required for a given application. As ionic liquids are still more expensive than traditional

solvents this is an important advantage. Additionally, the supported ionic liquid phase catalyst appears macroscopically as a dry solid. Therefore, SILP catalysts can be applied in fixed-bed reactor technologies which allow continuous processing in a very simple reactor set-up.

The first example of a SILP-type catalyst based on acidic chloroaluminate ionic liquids has been reported in 2000 by Hölderich.[16,33,34] The authors added acidic chloroaluminate ionic liquids to various types of silica, alumina, TiO$_2$ and ZrO$_2$ supports. During the preparation, the formation of HCl was observed, probably due to the presence of water on the supports. The obtained solids were tested for the alkylation of benzene, toluene, naphthalene, and phenol with 1-dodecene in batch, continuous liquid-phase, and continuous gas-phase systems. The catalytic activities of the immobilized ionic liquids were found to be higher than those of the conventional H-beta zeolite under the same conditions. Leaching of AlCl$_3$ into the organic product phase was not described, but some deactivation of the catalyst was concluded from the slight loss in conversion over time in the continuous liquid-phase reaction. Later on, the same group reported in two papers the grafting of ionic liquids on the surface of a silica support by means of a chemical reaction of alkoxysilyl-functionalized cations with the support material.[33–35] In these studies, the authors use the term "novel Lewis acidic catalyst (NLAC)" for their approach.

In this paper, we report on our on-going studies to develop optimized acidic SILP catalyst materials for the application in slurry-phase alkylation reactions. Our study focuses mainly on the development of a defined and optimized pretreatment of the support material prior to the impregnation with the acidic ionic liquid in order to obtain materials with strictly reproducible catalytic performance. In contrast to the work previously reported by Hölderich[33–35] our aim was to synthesize acidic SILP materials in which the ionic liquid film remains free flowing on the support's surface while being fixed to the support by capillary force and physisorption.

As model reaction to test these SILP materials in slurry-phase reactions, we selected the isopropylation of cumene, a well known and industrially relevant transformation.

## Results and Discussion

### Cumene Isopropylation with [EMIM]Cl/AlCl$_3$ = 1/2 – SILP-Catalyzed Reaction *vs.* Liquid-Liquid Biphasic Reaction Mode

The cumene isopropylation reaction is depicted in Scheme 1. Our initial experiments aimed for a direct comparison of the liquid-liquid biphasic reaction mode and a SILP slurry-phase reaction using the identical Lewis acidic chloroaluminate ionic liquid ([EMIM]Cl/AlCl$_3$ = 1/2) under the same reaction conditions. Figure 1 shows the conversion-time plot for both catalyst systems.

As can be seen from the graphs, the catalytic reaction rate of the SILP-slurry system is significantly higher than for the liquid-liquid biphasic system. This finding can be understood from the high available catalyst phase/organic phase contact area that is provided in the SILP system by the porous support. Interestingly in SILP and liquid-liquid biphasic modes, a significantly different product distribution is observed among the diisopropylbenzenes (DIPBs). While *para*-DIPB predominates over *meta*-DIPB in the SILP-slurry system, the liquid-liquid biphasic system gives
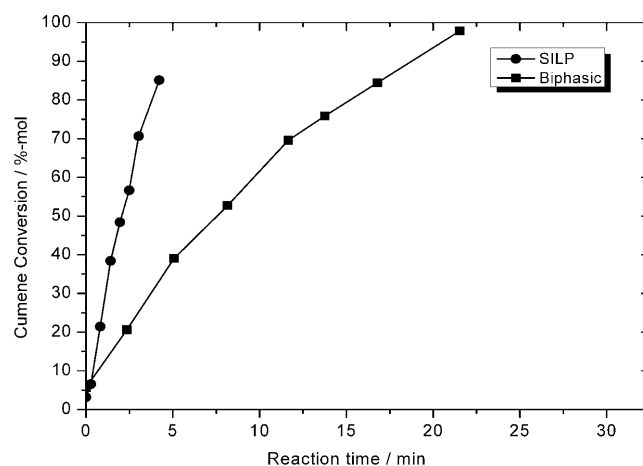


**Figure 1.** Comparison of cumene isopropylation using [EMIM]Cl/AlCl$_3$ = 1/2 as liquid-liquid biphasic system (squares) and as slurry SILP system with $\alpha = 0.2$ (circles). $p_{Tot} = 6.9$ bar; $T_{react} = 150$°C; solvent = cyclohexane; [cumene] = $3.8 \cdot 10^{-3}$ mol/mL; cumene:catalyst = 36:1.
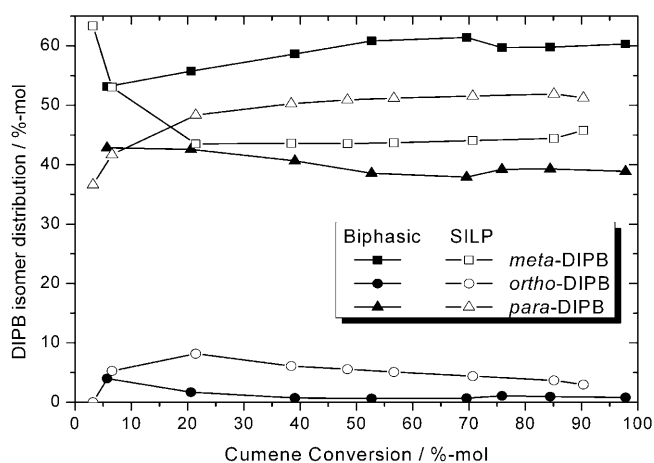


**Scheme 1.** Isopropylation of cumene with possible isomerization step.

**Figure 2.** Diisopropylbenzene isomers distribution of cumene isopropylation using [EMIM]Cl/AlCl$_3$=1/2 as liquid-liquid biphasic system and as slurry SILP system. $p_{Tot}=6.9$ bar;    $T_{react}=150\,°C$;    solvent=cyclohexane; [cumene]=3.8 10$^{-3}$ mol/mL; cumene:catalyst=36:1.

the opposite distribution (see Figure 2). Moreover. in the SILP system a significant amount of *ortho*-DIPB was observed while this was not the case for the liquid-liquid biphasic system.

An interpretation of these remarkable selectivity differences in the light of the existing literature on Friedel–Crafts alkylation reactions[36] leads to the result that in the SILP-slurry system the kinetically favoured products, *para*-DIPB and *ortho*-DIPB, are formed preferentially while in the liquid-liquid biphasic system the thermodynamically most stable product, *meta*-DIPB, is predominant (see Table 1).

Both activity and selectivity results can be understood by taking into account that the SILP-slurry system offers more active catalytic surface but at a lower Lewis acidity compared to the neat chloroaluminate-organic biphasic system. Obviously, the interaction of the acidic chloroaluminate with the untreated, dry SiO$_2$ surface (irreversible reaction of surface Si−OH groups with the acidic anions of the ionic liquid, [Al$_2$Cl$_7$]$^-$ and [Al$_3$Cl$_{10}$]$^-$) leads to this loss in acidity. The reduced acidity of the catalytic layer in case of the SILP-slurry system results in its lower ability to isomerizes the kinetic products into the thermo-

**Table 1.** Relative energy of different DIPB isomers.

| DIPB Isomer | Relative Internal Electronic Energy[a] [kJ mol$^{-1}$] |
|---|---|
| *meta*[b] | 0 |
| *ortho* | 18.05 |
| *para* | 0.25 |

[a] Estimated using DFT-B3LYP calculation.
[b] Reference isomer.

dynamic mixture. Similar findings of support reactivity *versus* components of a supported ionic liquid film have been described earlier also for non-acidic, catalytic SILP systems.[37]

## Variation of Ionic Liquid Loading (α)

Our first approach to deal with the loss of acidity towards the solid support was to increase the amount of acidic ionic liquid layer immobilized on the support. In this way, the amount of "free", acidic anions [Al$_2$Cl$_7$]$^-$ and [Al$_3$Cl$_{10}$]$^-$ is increased in the system as only the first layer of acidic ionic liquid should react with the basic surface sites of the support.

To demonstrate the effect of this variation experimentally we focused on the isomerization of a non-equilibrated mixture of diisopropylbenzenes as the rate of this transformation is more sensitive to the absolute acidity of the catalyst than the isopropylation step. The non-equilibrated mixture applied for these experiments contained 30% *meta*-DIPB, 15% *ortho*-DIPB and 55% *para*-DIPB whereas the estimated equilibrium composition using ASPEN PLUS contains approximately 70% *meta*-DIPB and 30% *para*-DIPB. Preparation of the former mixture is explained in Experimental Section.

Table 2 shows the results of these isomerization experiments using SILP-slurry systems of different ionic liquid loadings corresponding to 10–30% ($\alpha=0.1$–0.3) of the theoretical pore volume filling. Moreover, three different silica supports have been applied to study at the same time the effect of mean pore diameter and BET surface of the support on the catalytic activity (and thus on the overall acidity) of the SILP systems.

Interestingly, the results indicate the existence of a critical loading value ($\alpha_{critical}$) of the acidic ionic liquid on the support which is required to observe any isomerization activity (for SiO$_2$-100 $\alpha>0.1$, for SiO$_2$-60 $\alpha>0.2$, for SiO$_2$-30 $\alpha\gg0.3$). This finding strongly supports the idea of a kind of neutralization reaction between the basic surface sites of the support and the contact layer of the ionic liquid on the support. Consequently, the value of $\alpha_{critical}$ was found to increase with increasing BET surface area of the support. With ionic liquid loading above $\alpha_{critical}$ isomerization activity of the SILP-slurry system was indeed observed with an increasing share of *meta*-DIPB and consumption of *ortho*-DIPB towards the thermodynamic distribution. However, even the SILP system with the highest loading of ionic liquids and the smallest surface area failed to reach the acidity of the liquid-liquid biphasic system as can be seen from the corresponding comparison result in Table 2.

Attempts to enhance the SILP material's acidity by a further increase in ionic liquid loading were found

**Table 2.** Isomerization results of of non-equilibrium DIPB isomers mixture for various SILP systems.[a]

| Ionic Liquid Loading (α) $\alpha$ = Volume IL/Total Pore Volume | SiO$_2$ Support Materials | | |
|---|---|---|---|
| | $\phi_{pore}$[b] = 10 nm; $V_{pore}$ = 0.966 mL g$^{-1}$; BET = 335 m$^2$ g$^{-1}$ | $\phi_{pore}$[b] = 6 nm; $V_{pore}$ = 0.577 mL g$^{-1}$; BET = 445 m$^2$ g$^{-1}$ | $\phi_{pore}$ b) = 3 nm; $V_{pore}$ = 0.362 mL g$^{-1}$; BET = 470 m$^2$ g$^{-1}$ |
| 0.1 | 32:12:56 | 31:14:55 | 31:14:55 |
| 0.2 | 47:1:52 | 32:13:55 | 36:9:55 |
| 0.3 | 56:0:44 | 50:1:49 | 35:10:55 |
| Liquid[c] | 65:0:35 | | |
| 0.1T[d] | 60:0:40 | | |

[a] $T_{react}$ = 150 °C; solvent = decalin; [EMIM]Cl/AlCl$_3$ = 1/2; organic:acid = 10:1; reaction time = 90 min; starting DIPB feedstock composition (*meta:ortho:para*) = 30:15:55. Figures given above represent *meta*-, *ortho*- and *para*-DIPB mole fractions at the end of the experiments.

[b] Nominal mean pore diameter as supplied by provider. SiO$_2$-100, SiO$_2$-60 and SiO$_2$-30 corresponds to nominal $\phi_{pore}$ of 10, 6 and 3 nm, respectively.

[c] Liquid-liquid biphasic isomerization without SiO$_2$. All reaction conditions are identical with those of SILP experiments.

[d] SILP catalyst using pretreated SiO$_2$ ($\phi_{pore}$ = 10 nm) support. IL loading (α) = 0.1.

to be unreasonable for two distinct reasons: a) ICP-AES analyses of the organic product clearly indicated that the amount of Al leaching from the SILP material was a strong function of the ionic liquid loading with unacceptably high leaching being observed at ionic liquid loadings α greater than 0.2 (Figure 3); b) with ionic liquid loadings α ≥ 0.4 the SILP materials became a moist catalyst mass rather than a dry powder which resulted in difficult handling of the material.

Taking all these aspects into account it can be concluded that the acidity of SILP materials can be increased by higher ionic liquid loadings but increasing leaching and handling problems will limit this approach at least for potential technical application scenarios.
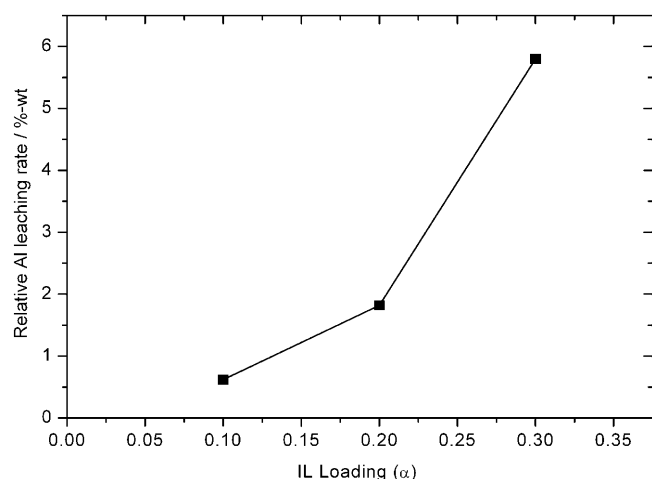
## Chemical Support Pretreatment – Comparison of Treated and Untreated Supports in SILP-Catalyzed Isomerization

From these initial results we concluded that a special pretreatment of the support material would be a very attractive alternative route to highly acidic SILP materials. The aim of this chemical support pretreatment would be to avoid all support-anion interactions detrimental for the system's acidity. Moreover, as the amount of surface Si−OH groups depends heavily on the preparation, storage and drying procedure of the support, a suitable chemical support pretreatment should also help to prepare the acidic SILP materials in a much more controlled and fully reproducible manner.

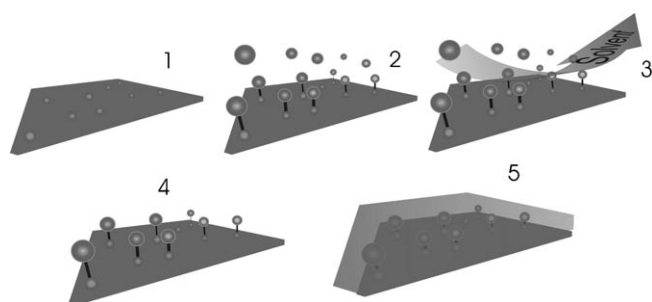To avoid the introduction of an additional chemical to the system we decided to perform the chemical



**Figure 3.** Leaching rate of acidic SILP system at different loading (α) values. $T_{react}$ = 150 °C; solvent = decalin; [EMIM]Cl/AlCl$_3$ = 1/2; organic:acid = 10:1; $\phi_{pore}$ = 10 nm; reaction time = 90 min



**Figure 4.** Schematic representation of support pretreatment process post calcination of SiO$_2$. (1) Fresh calcined SiO$_2$ containing basic surface hydroxy groups. (2) Loading of support's surface with acidic chloroaluminate ionic liquids. (3) Washing of excess and unreacted acidic species with fresh non-reacting solvent (CH$_2$Cl$_2$). (4) Evacuation of wash solvent residue giving an interacting-free support surface ready for acidic ionic liquid immobilization. (5) Reutilization of pretreated support for a more defined SILP acidity.

pretreatment procedure with exactly the same ionic liquid as later used for the SILP-coating process. The applied pretreatment procedure is schematically shown in Figure 4.

The precalcined support (Figure 4, step 1) was immersed into a solution of $[EMIM]Cl/AlCl_3 = 1/2$ (excess with respect to number of basic surface sites as estimated from the $\alpha_{critical}$ values of earlier experiments) in $CH_2Cl_2$. Dichloromethane was applied to reduce the ionic liquid's viscosity to allow quicker penetration of the ionic liquid into the pores of the support. This step was carried out under rigorous stirring for two hours in an ice bath (see Figure 4, step 2). After reaction of the ionic liquid's acidic anions with the basic surface sites, the excess of the acidic ionic liquid was removed with a large excess of continuously flowing fresh $CH_2Cl_2$. The washing process was continued to a point where no aluminium oxide precipitation was observed during addition of distilled water to a sample of the washing solution. After the washing process dichloromethane was recovered from the washing solution by simple evaporation.

The modification of the support material during this chemical pretreatment was monitored by temperature programmed desorption (TPD) of ammonia. The measurements were carried out for both the calcined $SiO_2$ and the chemically pretreated support material (see Figure 5).

The first ammonia desorption peak of the calcined silica between 50 and 120 °C can be attributed to the presence of surface hydroxy groups.[38] Obviously, these surface Si−OH groups are completely removed during the chemical pretreatment process as this desorption peak is not found for the pretreated sample. Instead, a broader peak appears at higher desorption temperature that can be linked to the fact that the
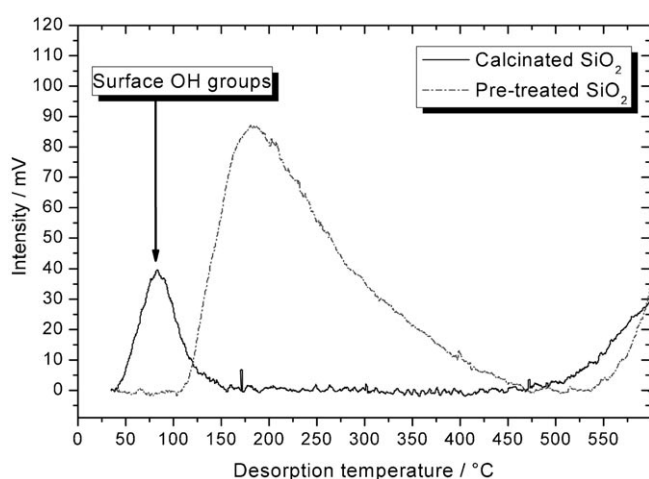
**Table 3.** Surface analysis of $SiO_2$ before and after pretreatment.

| Material | Total Pore Volume [mL g⁻¹] | BET Surface Area [m² g⁻¹] | Calculated Mean Pore Diameter $(\phi_{calc})^{[a]}$ [nm] |
|---|---|---|---|
| Calcined $SiO_2$ | 0.966 | 335 | 11.5 |
| SILP ($\alpha=0.1$) | 0.636 | 222 | 11.5 |
| Pretreated $SiO_2$ | 0.764 | 280 | 11.0 |

[a] Calculated mean pore diameter $\phi_{calc} = 4 \times$ total pore volume/BET area.

support is significantly more acidic after the pretreatment (thus more thermal energy is needed to desorb the ammonia).

BET surface, total pore volume and mean pore diameter have been determined for the chemically pretreated support and the values were compared to those for the calcined starting material and for a SILP material with an ionic liquid loading of $\alpha=0.1$ (Table 3). These data indicate that the chemically pretreated support is somewhat in-between the calcined starting material and the SILP materials with the loading $\alpha=0.1$.

Before applying the chemically pretreated supports to prepare SILP catalysts, we performed a benchmark run between the pretreated supports with an active acidic SILP ($\alpha=0.2$) on calcined $SiO_2$ in the same isomerization experiment of diisopropylbenzenes as described previously. It can be seen from the corresponding graph in Figure 6 that clearly the chemically
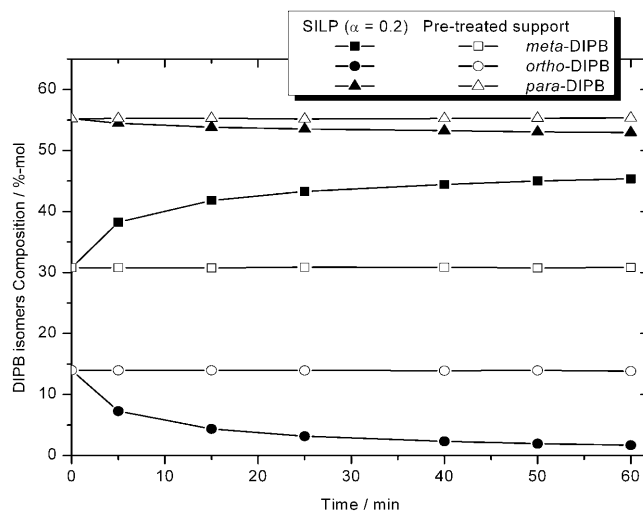
**Figure 5.** Temperature programmed desorption (TPD) of ammonia from calcined $SiO_2$ (calcination at 400 °C for 24 h) and the same support after pretreatment with the acidic chloroaluminate ionic liquid.

**Figure 6.** Comparison of pretreated support material with active SILP catalyst in the isomerization of a non-equilibrium DIPB isomer mixture. $T_{react} = 150$ °C; solvent = decalin; organic:acid = 10:1.

pretreated support alone behaves like an inert material and no isomerization reaction takes place.

In contrast, when the pretreated support was applied to prepare a SILP material of $\alpha = 0.1$, the latter showed a very attractive catalytic activity and transformed a mixture of 55% *para*-DIPB, 14% *ortho*-DIPB and 31% *meta*-DIBP to a mixture of 40% *para*-DIPB and 60% *meta*-DIPB with practically no *ortho*-DIPB within 90 min. This is very close to the selectivity of the liquid-liquid biphasic system with the same reaction time (*para*-DIPB/*meta*-DIPB = 35:65, see Table 2). It is also noteworthy that the results of the isomerization experiments were indeed very well reproducible using the SILP catalyst materials based on the chemically pretreated support.

The advantage of applying SILP materials prepared with the chemically pretreated support is even more pronounced with regard to the leaching rate of the acidic species into the organic phase. At a comparable isomerization activity (which is given for a SILP system on calcined $SiO_2$ with $\alpha = 0.3$ and for a SILP system on chemically pretreated support with $\alpha = 0.1$, see also data in Table 2) aluminium leaching is reduced from 5.8%-wt (calcined support) to 2.0%-wt (chemically pretreated support).

### Comparison of Treated and Untreated $SiO_2$ in Alkylation Reactions

Having defined through the isomerization test reactions a very promising way to chemically pretreat the silica support for highly acidic SILP catalysts, it was interesting to see whether the same materials would also show an attractive performance as catalysts in the isopropylation of cumene. The corresponding results are summarized in Table 4.

Indeed it was found that the SILP catalyst using pretreated $SiO_2$ gave in the slurry-phase isopropylation a quite similar selectivity compared to the liquid-liquid biphasic reaction with a still much higher reac-

tion rate of alkylation compared to the latter under identical reaction conditions (see Table 4).

### Recycling of the Pretreated SILP Catalyst

The experiments described above have demonstrated that the pretreatment of the support leads to catalyst of higher acidity and lowers aluminium leaching (especially when compared with the simple impregnation method of calcined support material). Since the suggested support pretreatment represents an extra step in catalyst preparation, the recyclability of the prepared systems becomes even more an issue of practical relevance. Consequently, we have investigated the recyclability of the pretreated SILP catalyst in the isopropylation of cumene (see Figure 7).

For the recycling, the SILP catalyst was isolated from the reaction products by simple decantation after 30 min settling time at ambient conditions. The residual SILP catalyst in the autoclave was loaded again with cumene and solvent. It is important to note that during the decantation process strictly inert conditions could not be realized for practical reasons of our set-up. The results of the recycling experiments are shown in Figure 7.

Only minor changes were observed in the total cumene conversion over the three recycling runs. In the third recycling it was still possible to convert 84% of cumene in only 3.5 min reaction time. While the catalytic activity stayed almost constant over recycling, selectivity to *meta*-DIPB decreased from run to run indicating a change in the nature of acidic species in the SILP system. This observation becomes understandable in the light of the short air contact of the SILP material during recycling that leads to increasing contamination of the SILP catalyst with moisture from air from run to run. Another source of small amounts of moisture is water in the applied cumene (which was approx. 80 ppm in the recycling experiments). Both moisture contact during recycling and moisture in the cumene lead to the transformation of Lewis acidic anions to acidic protons combined with a change in selectivity.

## Conclusions

In this work we have presented a convenient way to chemically pretreat silica based support materials for highly acidic chloroaluminate-based supported ionic liquid phase (SILP) catalysts. The chemical pretreatment was achieved by contacting a solution of [EMIM]Cl/$AlCl_3$ = 1/2 in dichloromethane with the calcined support, followed by a careful washing procedure that removed all acid excess from the support. The pretreated supports themselves showed no cata-

**Table 4.** Comparison of product distribution within the DIPB isomers in the isopropylation of cumene using chloroaluminate ionic liquid as biphasic and as SILP system.[a]

|  | Time[b] [min] | DIPB isomers | | |
|---|---|---|---|---|
|  |  | *meta* | *ortho* | *para* |
| Biphasic | 23 | 60 | ~0 | 40 |
| SILP ($\alpha = 0.2$) | 4 | 44 | 5 | 51 |
| SILP ($\alpha = 0.2T$)[c] | 4 | 57 | 2 | 41 |

[a] $p_{Tot} = 6.9$ bar; $T_{react} = 150\,°C$; solvent = cyclohexane; [cumene] = $3.8\ 10^{-3}$ mol/mL; cumene:catalyst = 36:1.
[b] Time required for achieving approx. 80%-mol conversion of cumene.
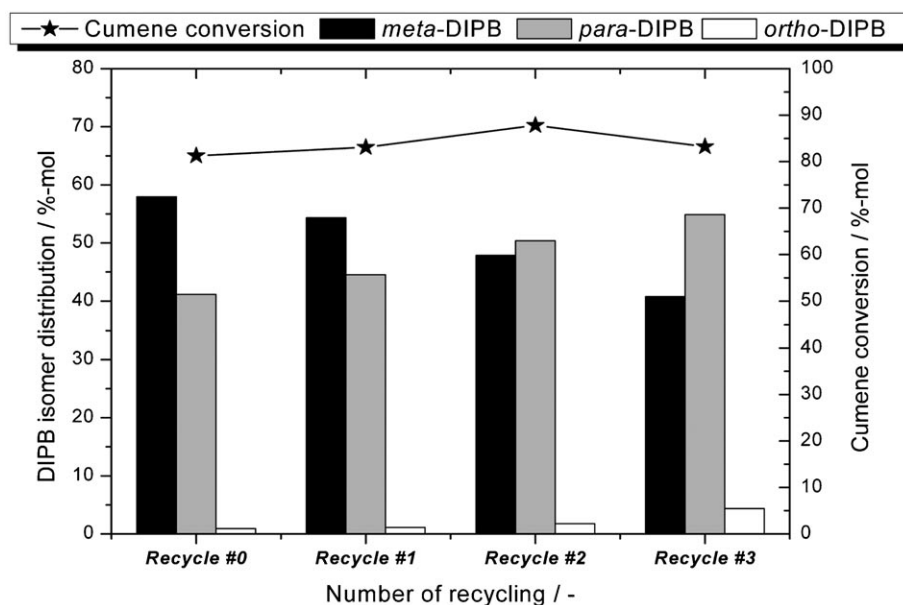[c] SILP catalyst using pretreated $SiO_2$.

**Figure 7.** Recycling esperiment of cumene isopropylation using [EMIM]Cl/AlCl$_3$=1/2 on pretreated SiO$_2$ as slurry SILP system with $\alpha$=0.2. $p_{Tot}$=7 bar; $T_{react}$=150 °C; $\tau_R$=approx. 3.5 min; solvent=cyclohexane; [cumene]=3.8 10$^{-3}$ mol/mL; cumene:catalyst per batch=approx. 36:1

lytic activity in the isomerization of diisopropylbenzenes (DIPBs) but provide a very suitable support material for the immobilization of a defined amount of acidic chloroaluminate ionic liquid. SILP materials obtained in this way proved to be highly attractive heterogeneous catalysts for the slurry-phase isomerization of DIPBs and for the isopropylation of cumene, including extremely fast reaction rates and low Al leaching into the organic product phase. Certainly, the here presented approach for optimized, acidic SILP catalysts provides distinct advantages over traditional homogeneous, zeolite based or liquid-liquid biphasic reactions. Strong points of the concept are the high reactivity of the materials, the very efficient use of the ionic liquid and the obvious opportunities for catalyst separation and recycling.

## Experimental Section

All manipulations of the acidic catalyst systems or any handling of the reactants prior to reaction were carried out under strictly inert conditions using Schlenk technique and argon (5.8, Linde) as inert gas.

### Chemicals

Cumene (99.0%) from Acros Organic was used together with propylene 2.8 (99.8%) from Linde. Cyclohexane (BASF) was used as additional extraction solvent in the catalytic isopropylation reactions after confirming its water contents to be below 20 ppm by Karl–Fischer titration. Pure

components of *meta*-DIPB (98%), *para*-DIPB (98%) and *ortho*-DIPB (97.5%) were purchased from Acros Organic. 1-Ethyl-3-methylimidazolium chloride ([EMIM]Cl) was purchased from Solvent Innovation GmbH, Cologne and used without further purification. Toluene (BASF) was applied after reactions to dilute the samples for GC analysis. Aluminium(III) chloride was purchased from Merck and used without further purification. Silica gel 100 (particle size 63–200 μm) from Merck was used as support for the preparation of the SILP catalyst.

### Catalyst Preparation

Silica gel of 10 nm mean pore diameters (silica gel 100) was calcined prior to use at 400 °C for at least 12 h in order to eliminate adsorbed moisture and surface hydroxy groups from the support. The BET surface and the total pore volume of the calcined support were determined to be 335 m$^2$g$^{-1}$ and 0.966 cm$^3$g$^{-1}$, respectively.

The acidic chloroaluminate ionic liquid was prepared by mixing a defined molar ratio of AlCl$_3$ and [EMIM]Cl at 70–80 °C in a Schlenk flask until complete dissolution of AlCl$_3$ and a clear liquid was observed. This acidic chloroaluminate ionic liquid was used directly in the liquid-liquid biphasic comparison experiments. It was also applied for the further preparation of the SILP materials.

The acidic SILP catalysts were prepared by a wet impregnation of the differently pretreated support materials with the acidic chloroaluminate ionic liquid. In this procedure, a defined ratio between the volume of the acidic chloroaluminate ionic liquid and the total pore volume of the support was adjusted. Dichloromethane was used to dilute the acidic ionic liquid during the wet impregnation process. To ensure a homogeneous penetration of the catalyst into the support's

pores, a slurry of the pretreated support and the diluted ionic liquid was stirred at 500 rpm for 1.5 h followed by evaporation of the dichloromethane at 850 mbar and 40 °C over 12 h. The so-obtained, dry SILP catalyst was stored either in a glove-box or under an argon atmosphere prior to use.

### Isopropylation Experiments

All isopropylation experiments were carried out in a 600-mL Parr autoclave equipped with a gas entrainment stirrer and a glass liner inside. Prior to the reaction, both the autoclave and the glass liner were stored in an oven at 90 °C for 24 h to avoid any moisture contamination.

The liquid organic phase consisted of cyclohexane and cumene in a 1:1 molar ratio. This organic phase was transferred into the glass liner followed by the defined amount of the acidic SILP material or the acidic ionic liquid (for the liquid-liquid biphasic comparison experiments). The filled glass liner was placed inside the autoclave and the reactor was flushed again with argon.

For reactor heating and temperature control an external heating mantle and an internal cooling coil were used to ensure isothermal conditions during reaction. Upon reaching the reaction temperature, the reactor was connected to the propylene bottle with a defined propylene pressure. The propylene pressure was set to a value that aromatic feedstock remained always in excess over propylene throughout the experiment with a typical initial ratio of cumene/propylene $= 8/1$. The reaction time was set to $t = 0$ when the gas entrainment stirrer was set to 1000 rpm and switched on. It has been verified in prior experiments that almost no reaction takes place without stirring. During the catalytic reaction, samples were taken from the autoclave. The catalytic run was stopped when one equivalent of propylene had been consumed. The amount of propylene consumption was monitored by continuously weighing the propylene reservoir with an analytical balance during the experiment.

### Isomerization Experiments

Isomerization experiments were carried out in a 50-mL Schlenk flask. The aromatic starting mixture – a non-equilibrium mixture of diisopropylbenzenes (DIPBs) – was diluted (in 1:1 volume ratios) with decalin. The initial composition of the aromatic starting mixture was set to be 30% *meta*-DIPB, 15% *ortho*-DIPB and 55% *para*-DIPB. This mixture was obtained by mixing the corresponding amount from each of the aromatic substances. Samples were taken during the isomerization experiments and analyzed by GC to follow the isomerization progress.

### GC Analysis

All samples were analyzed using a Varian CP-3900 gas chromatograph equipped with a Varian WCOT fused silica column (0.21 mm diameter and 50 m long) and flame ionization detector (FID) working at 270 °C.

The molar amount of each substance in the analyzed volume can be calculated based on the mass fraction of each substance, the mass fraction of the standard substance, the correction (CF) and the molecular weight (MW) of the analyzed substance according to Eq. (1).

$$n_i = C_F \cdot \frac{\%m_i \cdot m_{standard}}{\%m_{standard} \cdot M_{W,i}} \tag{1}$$

As the combined volume of all samples taken from the autoclave during the kinetic studies was negligible compared to the total reaction volume volumes, the amount of standard substance in the reactor was considered to be constant throughout the reaction.

### Ammonia Temperature Programmed Desorption (TPD) Analysis

Temperature programmed ammonia desorption was used to identify the acidic sites of the silica support before and after the manipulations of the support material. The analysis was carried out using a Thermo Electron TPD/R/O 1100 analyzer equipped with a thermal conductivity detector working at 120 °C. Samples of 0.1 g were heated under a continuous flow of helium at 500 °C for 30 min. Adsorption of ammonia was carried out at 80 °C for 30 min followed by flushing with helium for another 100 min. Desorption of ammonia was performed under continuous helium flow of 25 mL min$^{-1}$ at temperatures up to 600 °C with a heating rate of 10 °C min$^{-1}$.

### Induced Coupled Plasma Atom Emission Spectrospcopy (ICP-AES)

The aluminium content in the organic reaction mixture was analyzed by ICP-AES to determine the amount of acid catalyst leached into the reaction mixture. The ICP-AES analyses were carried out using a Perkin–Elmer Plasma 400 spectrometer. The latter was calibrated prior to the measurements using standard solutions of alumina plasma standard solution (1000 µg mL$^{-1}$; SpecPure® from Alfa Aesar).

### Support Characterization

Support characterization was carried out by determining the BET surface area and the total pore volume of the applied support materials prior to and after pretreatment and impregnation. The BET surface area was determined by nitrogen adsorption/desorption using a Thermo Electron Sorptomatic 1990. The total pore volume was analyzed using a Micromeritics Gemini 2360.

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## References

[1] W. Keim, M. Röper, in: *Ulmann's Encyclopedia of Industrial Chemistry*, 5<sup>th</sup> edn., Vol. A1, Wiley-VCH, Weinheim, p 267.

[2] K. Yamashita, M. Hirano, K. Okumura, M. Niwa, *Catal. Today* **2006**, *118*, 385.

[3] M. Selvaraj, S. H. Jeon, J. Han, P. K. Sinha, T. G. Lee, *App. Catal. A: General* **2005**, *286*, 44.

[4] R. Anand, R. Maheswari, K. U. Gore, S. S. Khaire, V. R. Chumbhale, *App. Catal. A: General* **2003**, *249*, 265.

[5] W. W. Kaeding, *J. Catal.* **1989**, *120*, 409.

[6] J. L. Sotelo, M. A. Uguina, J. L. Valverde, D. P. Serrano, *App. Catal. A: General* **1994**, *114*, 273.

[7] C. A. Querini, E. Roa, *App. Catal. A: General* **1997**, 163, 199.

[8] V. R. Choudhary, S. Mayadevi, D. B. Akolekar, *J. Catal.* **1993**, *144*, 16.

[9] P. A. Arroyo, C. A. Henriques, E. F. Sousa-Aguiar, A. Martinez, J. L. F. Monteiro, *Stud. Surf. Sci. Catal. 130C (International Congress on Catalysis, 2000, Pt. C)*, **2000**, 2555.

[10] M. J. Earle, U. Hakala, B. J. McAuley, M. Nieuwenhuyzen, A. Ramani, K. R. Seddon, *Chem. Commun.* **2004**, 1368.

[11] X. Mi, S. Luo, J. He, J.-P. Cheng, *Tetrahedron Lett.* **2004**, *45*, 4567.

[12] A. A. Fannin, Jr., D. A. Floreani, L. A. King, J. S. Landers, B. J. Piersma, D. J. Stech, R. L. Vaughn, J. S. Wilkes, L. Williams John, *J. Phys. Chem.* **1984**, *88*, 2614.

[13] N. Brausch, A. Metlen, P. Wasserscheid, *Chem. Commun.* **2004**, 1552.

[14] M. Earle, A. Forestier, O.-B. Helene, P. Wasserscheid, in: *Ionic Liquid in Synthesis*, 1st edn., Vol. 1, (Eds: P. Wasserscheid, T. Welton), Wiley-VCH, Weinheim, **2003**, pp 174–203.

[15] J. A. Boon, J. A. Levisky, J. L. Pflug, J. S. Wilkes, *J. Org. Chem.* **1986**, *51*, 480.

[16] C. DeCastro, E. Sauvage, M. H. Valkenberg, W. F. Hoelderich, *J. Catal.* **2000**, *196*, 86.

[17] B. J. Piersma, M. Merchant, *Proc. Int. Symp. Molten Salts 7th*, **1990**, 805.

[18] L. Xiao, K. E. Johnson, *Can. J. Chem.* **2004**, *82*, 491.

[19] K. Yoo, V. V. Namboodiri, R. S. Varma, P. G. Smirniotis, *J. Catal.* **2004**, *222*, 511.

[20] A. Riisager, R. Fehrmann, M. Haumann, P. Wasserscheid, *Eur. J. Inorg. Chem.* **2006**, *4*, 695.

[21] A. Riisager, R. Fehrmann, M. Haumann, P. Wasserscheid, *Top. Catal.* **2006**, *40*, 91.

[22] A. Riisager, R. Fehrmann, M. Haumann, P. Wasserscheid, *Top. Organomet. Chem.* **2008**, *23*, 149.

[23] A. Riisager, R. Fehrmann, P. Wasserscheid, *Supported Liquid Catalysts*, in: *Handbook of Heterogeneous Catalysis*, 2nd edn., Vol. 1, (Eds: G. Ertl, H. Knözinger, J. Weitkamp), Wiley-VCH: Weinheim, **2008**, p 631.

[24] P. Maki-Arvela, J.-P. Mikkola, P. Virtanen, H. Karhu, T. Salmi, D. Y. Murzin, *Stud. Surf. Sci. Catal.* **2006**, *162*, 87.

[25] M. A. Gelesky, S. S. X. Chiaro, F. A. Pavan, J. H. Z. dos Santos, J. Dupont, *Dalton Trans.* **2007**, 5549.

[26] M. Ruta, I. Yuranov, P. J. Dyson, G. Laurenczy, L. Kiwi-Minsker, *J. Catal.* **2007**, *247*, 269.

[27] M. Haumann, K. Dentler, J. Joni, A. Riisager, P. Wasserscheid, *Adv. Synth. Catal.* **2007**, *349*, 425.

[28] A. Riisager, R. Fehrmann, M. Haumann, P. Wasserscheid, *Proceedings of the DGMK/SCI-Conference*, **2006**, 57.

[29] A. Riisager, R. Fehrmann, M. Haumann, B. S. K. Gorle, P. Wasserscheid, *Ind. Eng. Chem. Res.* **2005**, *44*, 9853.

[30] O. Jimenez, T. E. Müller, C. Sievers, A. Spirkl, J. A. Lercher, *Chem. Commun.* **2006**, 2974.

[31] A. Riisager, B. Jorgensen, P. Wasserscheid, R. Fehrmann, *Chem. Commun.* **2006**, 994.

[32] J. Joni, D. Schmitt, P. S. Schulz, T. J. Lotz, P. Wasserscheid, *J. Catal.* **2008**, *258*, 401.

[33] M. H. Valkenberg, C. de Castro, W. F. Hoelderich, *Green Chem.* **2002**, *4*, 88.

[34] M. H. Valkenberg, C. DeCastro, W. F. Hoelderich, *Special Publication - Royal Society of Chemistry* **2001**, *266*, 242.

[35] M. H. Valkenberg, C. de Castro, W. F. Hoelderich, *Stud. Surf. Sci. Catal.* **2001**, *135*, 4629.

[36] J. March, in: *Advanced Organic Chemistry*, 4th edn., (Eds: M. J. Smith, J. March), Wiley Interscience, New York, **1992**, p 501.

[37] A. Riisager, R. Fehrmann, S. Flicker, R. van Hal, M. Haumann, P. Wasserscheid, *Angew. Chem.* **2005**, *117*, 826; *Angew. Chem. Int. Ed.* **2005**, *44*, 815.

[38] G. I. Kapustin, T. R. Brueva, A. L. Klyachko, S. Beran, B. Wichterlova, *Appl. Catal.* **1988**, *42*, 239.