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Research paper

Dialkyl imidazolium acetate ionosilica as efficient and recyclable organocatalyst for cyanosilylation reactions of ketones

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Abstract

We report new heterogeneous organocatalyst based on silica hybrid supported N-heterocyclic carbene (NHC-) species. The organocatalyst is formed from an imidazolium iodide based ionosilica material, followed by iodide/acetate anion exchange. The imidazolium acetate generates the organocatalytic carbene *via* partial deprotonation of the imidazolium ring *in situ*. As monitored *via* EDX, solid state NMR and ion chromatography measurements, the iodide/acetate exchange involving the imidazolium ionosilica material took place only in small extent. Despite the fact that the exchanged material contains only a very small amount of acetate, we observed good catalytic activity and recyclability in cyanosilylation reactions of ketones with trimethylsilyl cyanide. The versatility of the catalyst was highlighted *via* reaction with several substrates, yielding the corresponding cyanohydrins in good yields. In recycling experiments, the material showed decreasing catalytic activity starting from the third reaction cycle, but high catalytic activity can be regenerated *via* another acetate treatment. Our work is important as it highlights the possibility to combine carbene chemistry and silica, which are antagonistic at a first glance. We show that imidazolium acetate based ionosilicas are therefore heterogeneous 'proto-carbenes', and that there is no need to form strongly basic silica supported NHCs to obtain heterogeneous NHC-organocatalysts. This work therefore opens the route towards heterogeneous and re-usable NHC-organocatalysts from supported ionic liquid imidazolium acetates.

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Keywords: N-heterocyclic carbenes; Ionosilica; Heterogeneous organocatalysis; Cyanosilylation; Ionic liquids

1. Introduction

Organocatalysis is considered the third pillar of catalysis, alongside metal catalysis and biocatalysis. Organocatalysis allows bypassing the use of polluting and often toxic organometallic catalytic complexes, as it involves predominantly C, H, O, N, S and P based small molecules to increase chemical reaction rates. Additionally, organocatalysts are often insensitive to moisture and oxygen, present low toxicity and are often readily available and cheap. All these aspects represent huge benefit in comparison to metal catalysts, in particular for the synthesis of pharmaceuticals and drugs.

Among the different types of organocatalysts reported in literature, N-heterocyclic carbenes (NHCs) have an outstanding position due to their polyvalence and versatility [1–6]. A long time considered as highly reactive intermediates, several carbenes are in fact stable and can be isolated, as shown by the pioneering work of Arduengo [7]. NHCs offer large possibilities for organocatalytic transformations such as Benzoin condensations, Stetter Reaction or Umpolung reactions. NHCs are easily formed by the deprotonation of heterocyclic azolium cations, and imidazolium based ionic liquids have been shown to be versatile precursors for the formation of NHC species *via* deprotonation of the C2 proton from the imidazolium ring. Besides their huge potential in organocatalysis, carbene chemistry opened also the route towards a large variety of metallic NHC complexes with huge potential in organometallic catalysis.

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The immobilization of catalytic species on heterogeneous support is highly desirable in view of easy catalyst separation, recycling and efficient re-use. The immobilization of highly polyvalent NHC based organocatalysts may therefore open new routes in green catalyst engineering. In this respect, the immobilization of ionic liquids as a reservoir for the formation of NHC species has already thoroughly been studied and has recently been reviewed [8–11].

Silica displays some interesting features that makes it particularly interesting as support for heterogeneous catalysis. Silica is a moderately hydrophilic support, which offers the possibility of control its texture and architectures. These features allow designing objects with controlled morphologies, allowing good diffusion of reactants through the silica support. The high and tunable porosity allows for high accessibility of the immobilized function, *i.e.* catalytic sites. However, the low resistance against bases limits the use of silica as support for catalytic species. For this reason, the formation of NHCs on silica support appears to be particularly challenging, as carbenes are highly basic species. Examples of silica supported NHC organocatalysts are therefore extremely scarce [12]. However, we believe that chemists have valuable strategies to combine NHC chemistry and silica support in one system:

- 1) The basicity of NHC species can be tuned [13]. The basicity depends on the acidity of the corresponding azolium salt. Imidazoliums are generally the least acidic ($pK_a \sim 20\text{--}24$ in water), while thiazoliums and triazoliums are more acidic ($pK_a \sim 16\text{--}19$ in water) [14–16]. Substituents on the azolium cations can have a drastic effect on the acidity. Stable NHC species often show further increased basicity [14].
- 2) The silica scaffold can be stabilized, *e.g.* *via* surface hydrophobization/trimethylsilylation of residual surface located silanol groups.
- 3) Finally, carbenes can be formed '*in situ*'. The presence of a very small amount of NHC species often results in sufficient catalytic performance. This approach can be carried out under relatively soft conditions. For example, the basicity of the acetate anion is sufficient to promote a partial deprotonation of imidazolium species. In this way, imidazolium acetates appear as a reservoir for NHC species [17]. Although the presence of free NHC in imidazolium acetate ILs is currently a matter of debate, it has been reported that these salts are efficient organocatalysts to promote *e.g.* the benzoin condensations [18] or cyanosilylation reactions [19]. These examples show that it is not necessary to apply strongly basic reaction conditions to obtain catalytically active 'free' NHC catalysts. The possibility to form catalytic amounts of NHC species *in situ* (Scheme 1) appears as an interesting strategy to circumvent the sensitivity of carbenes and their potential incompatibility with silica.



Scheme 1. Deprotonation of butylmethylimidazolium (BMIM) cation with acetate anions and formation of a N-heterocyclic carbene (*right*).

Due to our expertise in the field of ionosilicas [20] and in particular of imidazolium based periodic mesoporous organosilicas [21–23], we focused on silica supported NHC organocatalysts *via* the synthesis of imidazolium acetate containing ionosilica. The evaluation of the organocatalytic properties of these materials was addressed in cyanosilylation reactions. In fact, cyanosilylations are of high importance in organic chemistry. The formed cyanohydrins are key intermediates in organic synthesis that allow accessing a wide range of products such as β -amino alcohols, α -hydroxy acids or α -amino acids [24]. In this paper, we show that imidazolium acetate containing ionosilicas are active and re-usable heterogeneous organocatalysts for cyanosilylation reactions of ketones.

2. Experimental section

2.1. Methods and materials

Tetrabutylammonium fluoride (2 mL of a 1 M solution in THF), ammonium acetate, trimethylsilyl cyanide, acetophenone, cyclohexanone, 4-hydroxyacetophenone, 2-acetonaphthone and sodium hydride (60% dispersion in mineral oil) were purchased from Sigma-Aldrich. 3-Chloropropyl trimethoxysilane and hexamethyldisilazane were purchased at ABCR. Butylmethylimidazolium acetate (BMIM [OAc]) was purchased at IoLiTec. All reagents were used as received. 3-Iodopropyl trimethoxysilane was synthesized as reported in the literature [25].

The solvents THF, diethylether and toluene were purchased from Sigma-Aldrich. For experiments requiring anhydrous conditions, the solvents were filtered over appropriate desiccant columns.

Solid state ^{13}C and ^{29}Si CP MAS NMR experiments were recorded on a Varian VNMRs 300 MHz solid spectrometer using a two-channel probe with 7.5 mm ZrO_2 rotors. The ^{29}Si solid state NMR spectra were recorded using both CP MAS and one pulse (OP) sequences with samples spinning at 6 kHz. CP MAS was used to get a high signal-to-noise ratio with 5 ms contact time and 5 s recycling delay. For OP experiments, $\pi/6$ pulse and 60 s recycling delay were used to obtain quantitative information on the silane-silanol condensation degree. The ^{13}C CP MAS spectra were obtained using 3 ms contact time, 5 s recycling delay and 5 kHz spinning rate. The number of scans was in the range of 1000–3000 for ^{29}Si OP MAS spectra and of 2000–4000 for ^{13}C CP MAS spectra.

The specific surface area and pore structure parameters of the materials studied in the present work were inferred from the measurements of adsorption–desorption of gaseous nitrogen at 77 K with the use of a Micromeritics Tristar unit (USA). Prior to the experiment, each sample was degassed down to about 2 Pa at 373 K for 10 h. BET plots were constructed below a relative pressure of 0.3 from the adsorption

branches and employed to evaluate the BET specific surface (taking a cross-sectional area of 0.162 nm^2 per nitrogen molecule).

Scanning electronic microscopy (SEM) images and Energy Dispersive X-ray (EDX) analyses were obtained with a Hitachi S-4800 apparatus.

2.2. Synthesis of precursors and materials

2.2.1. Synthesis of 3-iodopropyl triethoxysilane

Under argon atmosphere, sodium iodide (25.0 g/166 mmol) and 3-chloropropyl triethoxysilane (35 mL/138 mmol) were dissolved in acetone (200 mL). The resulting homogeneous solution was stirred under reflux for 72 h. A white precipitate of sodium chloride formed progressively. After cooling down to room temperature, the white precipitate was filtered off and washed with a small quantity of acetone. The crude product was distilled under reduced pressure. The resulting 3-iodopropyl triethoxysilane was obtained as a colorless liquid. Yield: 30.6 g/66%.

$^1\text{H-NMR}$ (CDCl_3 , 400 MHz): 3.80 ppm (q, $3 \times 2\text{H}$, $J = 7.0 \text{ Hz}$, $\text{O-CH}_2\text{-CH}_3$), 3.20 ppm (m, 2H, CH_2), 1.87 ppm (m, 2H, CH_2), 1.20 ppm (t, $3 \times 3\text{H}$, $J = 7.0 \text{ Hz}$, $\text{O-CH}_2\text{-CH}_3$), 0.71 ppm (m, 2H, Si- CH_2). $^{13}\text{C-NMR}$ (CDCl_3 , 400 MHz): 10.7, 12.2, 18.3, 27.5, 58.4. IR (ATR) ν (cm^{-1}): 2972, 2884, 1073, 784, 629.

2.2.2. Synthesis of *N*-(3-(triethoxysilyl)propyl)imidazole **1**

Under argon, sodium hydride (2.9 g, 0.120 mol) was suspended in anhydrous THF (30 mL). The mixture was cooled to 0°C in an ice bath, and a solution of imidazole (8.2 g, 0.120 mol) in 100 mL of anhydrous THF was added dropwise under stirring. Upon addition of imidazole to the suspension of NaH in THF, hydrogen gas evolved. After complete addition of the imidazole solution, the ice bath was removed and the mixture was kept under stirring at room temperature for 2 h. Then, 3-iodopropyl triethoxysilane (26.12 g, 0.090 mol) was added. The mixture was heated under reflux for 16 h. The orange suspension was filtered off and the volatiles were pumped off. The resulting heterogeneous reaction product was extracted with $3 \times 50 \text{ mL}$ of dichloromethane under argon atmosphere. After evaporation of the solvent, the crude product was purified by distillation (bp $140^\circ\text{C}/1 \text{ mbar}$). *N*-(3-Propyltrimethoxysilane)imidazole was isolated as a colorless liquid. Yield: 15.5 g/63%.

$^1\text{H-NMR}$ (200 MHz, CDCl_3): 0.56 (m, 2 H), 1.21 (t, $J = 7.0 \text{ Hz}$, 9 H), 1.91 (m, 2 H), 3.81 (q, $J = 7.0 \text{ Hz}$, 6 H), 3.93 (t, $J = 7.0 \text{ Hz}$, 2 H), 6.96 (s, 1 H), 7.11 (s, 1 H), 7.71 (s, 1 H). $^{13}\text{C-NMR}$ (50 MHz, CDCl_3): 7.2, 18.1, 24.7, 49.0, 58.2, 118.6, 129.0, 137.0. IR (ATR) ν (cm^{-1}): 3110, 2974, 2929, 2888, 1506, 1391, 1228, 1104, 957, 783, 664. HRMS (FAB+): Calcd for $\text{C}_{12}\text{H}_{25}\text{O}_3\text{N}_2\text{Si}$ [$\text{M} + \text{H}$] $^+$ 273.1634; found, 273.1631.

2.2.3. Synthesis of 1,3-bis(3-(triethoxysilyl)propyl)imidazolium iodide **2**

Under argon atmosphere, a mixture of *N*-(3-(triethoxysilyl)propyl)imidazole **1** (1.19 g, 4.37 mmol) and 3-iodopropyl

triethoxysilane (1.59 g, 4.8 mmol) was heated to 110°C overnight. The product was washed with toluene, and dried under vacuum. The compound **2** was obtained as highly viscous yellow oil. Yield: 2.64 g/95%.

$^1\text{H-NMR}$ (200 MHz, CDCl_3): 0.63 (m, 4 H), 1.04 (t, $J = 7.0 \text{ Hz}$, 18 H), 1.98 (m, 4 H), 3.71 (q, $J = 7.0 \text{ Hz}$, 12 H), 4.27 (m, 4H), 7.46 (s, 2 H), 9.85 (s, 1 H). $^{13}\text{C-NMR}$ (50 MHz, CDCl_3): 6.9, 18.2, 24.3, 51.7, 58.5, 122.4, 136.0. IR (ATR) ν (cm^{-1}): 3070, 2972, 2923, 2886, 1562, 1445, 1391, 1163, 1076, 957, 783. HRMS (FAB+): Calcd for $\text{C}_{21}\text{H}_{45}\text{O}_6\text{N}_2\text{Si}_2$ [M] $^+$ 477.2816; found 477.2824.

2.2.4. Materials' syntheses

Synthesis of material **A**. A solution of the imidazolium precursor **2** (1 g, 1.65 mmol) in absolute EtOH (2 mL), were added water (2 mL, 180 μL , 10 mmol, 6 eq) and tetrabutylammonium fluoride (TBAF) (10 μL of a 1 M solution in THF) under vigorous stirring. After complete addition, the homogeneous solution was allowed to stand at room temperature for 1 h. The formed gel was crushed into a fine powder and heated to 80°C under air overnight. The powder was dried under vacuum at 80°C to give 0.51 g (80%) of a yellowish powder.

Surface passivation of the material **A**. Material **A** (1.00 g) was dried under vacuum at room temperature for 2 h. A solution of HMDS (0.54 g) in toluene (12 mL) was added to the silica material. The mixture was stirred at reflux for 1 h. The solid was filtered, washed 3 times with toluene and ethanol and finally dried at 80°C overnight to give material **B**. Material **D** was obtained by a similar procedure starting from material **C** (*vide infra*).

Iodide-acetate anion exchange procedure. Material **A** (1.42 g) was suspended in a saturated ammonium acetate solution in methanol (60 mL). The suspension was gently stirred, kept without stirring for 15 min and then filtered. The procedure was repeated three times. After the three treatments with a saturated methanolic ammonium acetate solution, the material was washed with absolute EtOH, filtered, and dried under vacuum at 80°C for 2 h. We obtained 1.08 g of material **C** as a white powder.

2.3. Catalytic tests

The reaction was carried out by mixing ketone (1 mmol) and trimethylsilyl cyanide (TMSCN) (1.2 mmol) in neat condition with 5 mol-% of the catalyst at room temperature for 20 min. The conversion was determined by $^1\text{H-NMR}$.

3. Results and discussion

3.1. Precursor and materials' synthesis and characterization

The disilylated imidazolium precursor was synthesized following a well-established two step sequence involving the formation of the monosilylated imidazole intermediate **1** and finally the ionic imidazolium iodide precursor **2** (Scheme 2) [21,22]. The latter precursor was directly used for the

formation of the imidazolium based ionosilica following classical sol-gel reactions [26,27]. We performed the hydrolysis-polycondensation reactions under nucleophilic catalysis, promoted by catalytic amount of fluoride ions, as this procedure is a particularly mild and straightforward method for the formation of silica hybrid materials and in particular ionosilicas, avoiding the use of strong acids or bases, or other types of additives. The formed ionosilica material **A** bearing imidazolium iodide species was then used for the formation of the passivated material **B**, obtained *via* trimethylsilylation using hexamethyldisilazane (HMDS). Finally, both materials **A** and **B** were treated with ammonium acetate in order to obtain imidazolium acetate containing phases **C** and **D**. The synthesis strategy of the materials is illustrated in Scheme 3.

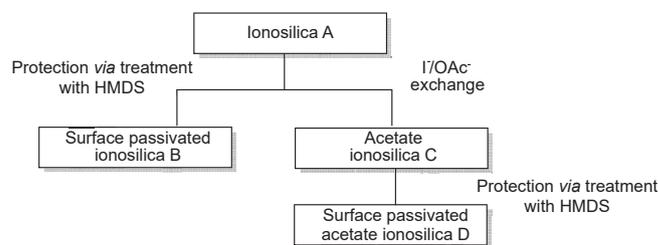
It is noteworthy to mention that attempts to access the disilylated dialkylimidazolium acetate precursor *via* a silver acetate treatment of the iodide precursor **2** were unsuccessful. Despite the fact that yellow silver iodide spontaneously precipitated from the solution, the disilylated dialkylimidazolium cation degraded under the anion exchange conditions as shown by ^1H NMR spectroscopy. We could not isolate the acetate precursor with sufficient purity *via* this anion exchange strategy.

3.2. Materials characterization - chemical

The materials were characterized in order to determine their chemical composition and their surface properties.

We firstly studied the evolution of the materials in the course of the various synthesis steps *via* solid state NMR spectroscopy. ^{13}C CP-MAS and ^{29}Si OP-MAS solid state NMR spectra of the materials **A**, **B** and **D** are given in Fig. 1.

^{13}C CP-MAS solid state NMR spectroscopy allows getting information about the changes of the organo-ionic substructure or the presence of new organic groups within the materials. The spectrum of material **A** shows the characteristic peaks of the imidazolium ring (123.3, 136.7 ppm) together with the propyl bridges of the precursor **2** (10.4, 25.1, 52.3 ppm). After surface passivation, the spectrum of material **B** shows the additional peaks characteristic for trimethylsilyl groups at 3.5 and -0.4 ppm, whereas the other signals are nearly unchanged. Finally, material **D**, after iodide/acetate exchange, displays an additional peak at 178.4 ppm which can be attributed to acetate anions. Hence, the characterization of the materials *via* ^{13}C CP-MAS solid state NMR spectroscopy clearly monitors the evolution of the materials during the passivation and anion exchange steps. As ^{13}C CP-MAS solid state NMR spectroscopy is not a quantitative method, it does not allow quantifying the exact amount of the different carbon



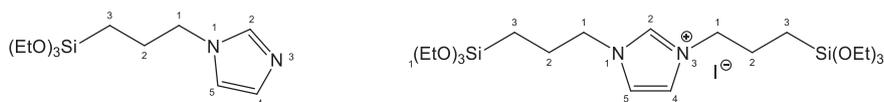
Scheme 3. Synthesis scheme of the materials used in this study.

species within the materials. However, the low intensity of the signal relative to the acetate anions compared to the signals of the imidazolium entity in the spectrum of material **D** suggests a rather low extent of iodide/acetate exchange.

^{29}Si OP-MAS solid state NMR spectroscopy allows detecting the evolution and changes of the silica scaffold during the various experimental steps. All three spectra of the materials **A**, **B** and **D** clearly show the T signals of the ionosilica scaffold. In all materials, the T³ species (-67.7 ppm) corresponding the silicon in a $\text{RSi}(\text{OSi})_3$ environment, is the predominant one. The signal of the T² species that can be seen at -59 ppm, is of significantly lower intensity. These results indicate a relatively high condensation degree of the materials, and show that nucleophilic catalysis *via* fluoride ions is an efficient way to promote hydrolysis-polycondensation reactions of precursor **2** to yield ionosilica materials. We notice that the spectra of materials **B** and **D** show the additional peaks of the trimethylsilyl ($\text{Si}-\text{OSiMe}_3$) groups at ~ 10 ppm, which originate from the surface passivation reaction with HMDS.

The evolution of the chemical composition of the materials was then addressed *via* energy-dispersive X-ray spectroscopic (EDX) measurements. We focused in particular on the determination of the silicon/iodine (Si/I) ratio of the materials in view of the determination of the iodide/acetate exchange degree. Furthermore, the determination of heavy elements such as silicon and iodine provides more accurate results compared to lighter elements such as carbon, nitrogen or oxygen. The given values are calculated from average values obtained from four different analyses. The results of this study are given in Table 1.

The parent material **A** shows a Si/I ratio of 1.77, which is slightly lower than the expected value of 2 (entry 1). Surface passivation leads to an increase of the silicon content as monitored by the increase of the Si/I ratio from material **A** to material **B** (1.77–1.93) and from material **C** to material **D** (2.05–2.31). Finally, the Si/I ratio only slightly increases during the iodide/acetate exchange from material **A** to material **C** (1.77–2.05), indicating *i*) that the material **D** still contains a



Scheme 2. Structures of the silylated precursors **1** (left) and **2** (right).

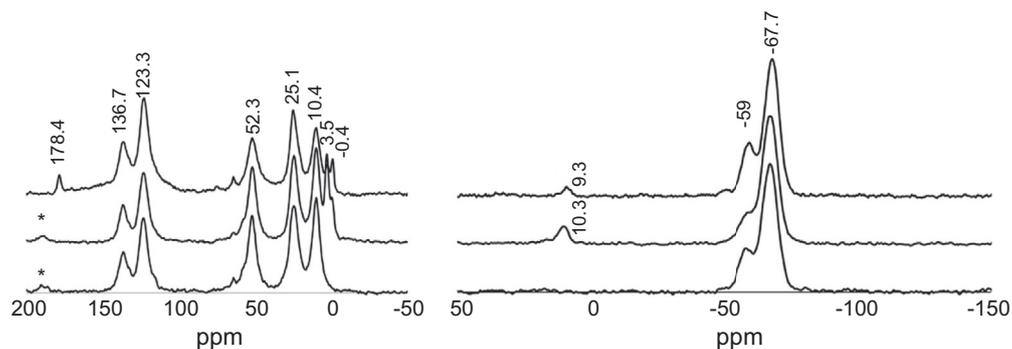


Fig. 1. *Left*: ^{13}C CP-MAS solid state NMR spectra of materials **A**, **B** and **D** (bottom to top); rotational bands are marked by asterisks; *right*: ^{29}Si OP-MAS solid state NMR spectra of materials **A**, **B** and **D** (bottom to top).

high amount of iodide and *ii*) that the anion exchange only took place to a very low extent. Although EDX is a method with high uncertainty, this confirms the results obtained *via* ^{13}C CP-MAS solid state NMR spectroscopy.

Solid state NMR and EDX therefore give concordant results and qualitatively indicate a low degree of the iodide/acetate exchange, but do not allow a quantitative determination of the acetate content in the materials. In order to determine quantitatively the exchange degree, we followed the iodide/acetate exchange *via* ion chromatography. We determined in particular the iodide content of the supernatant solution after anion exchange. Specifically, we suspended 50 mg of the material **A** in 10 mL of methanol. This quantity corresponds to a molar amount of 13.1 μmol of iodide. After a first treatment of this material with sodium acetate, we measured a total quantity of 0.2 μmol of iodide in the supernatant, corresponding to approx. 1–2% of exchanged iodide. In a second and third exchange cycle with the same material, we observed similar results. In total, we can therefore assume that approx. 5% of iodide was exchanged against acetate in three successive exchange steps.

All these chemical analyses give a clear and concordant image regarding the chemical composition of the materials and their evolution during the various modification steps. The sol-gel process, promoted by nucleophilic catalysis involving fluoride ions, smoothly gives the corresponding imidazolium based ionosilicas with a rather high condensation degree. Solid-state NMR spectroscopy clearly shows that the organo-ionic entity of the precursor remains intact and that no Si–C bond cleavage occurred during the hydrolysis-polycondensation reaction. Secondly, the passivation reaction with HMDS allows the transformation of silanol groups *via* trimethylsilylation, as seen by the characteristic signals of trimethylsilyl groups in both the ^{13}C CP-MAS and the ^{29}Si -

OP-MAS solid-state NMR spectra. Finally, the iodide/acetate exchange occurred only to a very low extent, as indicated by EDX and ^{13}C CP-MAS solid-state NMR spectroscopy. Ion chromatographic analyses indicated that the exchange degree was of approx. 5%.

3.3. Materials characterization—surface properties and morphology

We also followed the evolution of the surface properties of the materials **A**–**D** during the successive modification steps. We used in particular nitrogen sorption measurements in order to elucidate the surface properties of the materials in terms of specific surface area, pore size and pore size distribution. The obtained values are summarized in Table 2. The morphology of the materials was also addressed *via* scanning electron microscopy.

The characterization of the materials shows that all solids are moderately porous systems with specific surface areas in the range of 85–160 $\text{m}^2 \text{g}^{-1}$. The parent ionosilica **A**, obtained *via* sol-gel transformation of precursor **2**, exhibits a specific surface area of 160 $\text{m}^2 \text{g}^{-1}$, with an average pore diameter of approx. 15 nm. Both anion exchange and surface passivation have a certain influence on the surface properties of the formed materials **B** and **C**. Upon surface passivation *via* trimethylsilylation reaction with HMDS, the specific surface area remains nearly unchanged, but the average pore size decreases to 5 nm (Table 2, entry 2). On the other side, the anion exchange process with ammonium acetate leads to a significant decrease of the specific surface area to 85 $\text{m}^2 \text{g}^{-1}$, whereas the average pore diameter only slightly changes (Table 2, entry 3). The surface passivation reaction of this material **C** to yield material **D** results only in slight textural changes of the material (Table 2, entries 3/4).

Table 1
Atomic Si/I ratio of the materials **A**–**D** from EDX measurements.

Entry	Material	atomic Si/I ratio
1	A	1.77
2	B	1.93
3	C	2.05
4	D	2.31

Table 2
Surface properties of the materials **A**–**D**.

Entry	Material	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Average pore diameter (nm)	Mesopore volume ($\text{m}^3 \text{g}^{-1}$)
1	A	160	15.4	0.61
2	B	152	5.5	0.21
3	C	85	21.9	0.27
4	D	99	16.3	0.48

The morphology of the materials was addressed *via* scanning electron microscopy (SEM). The SEM images of the materials **A–D** are shown in Fig. 2. All materials show similar morphological features. The materials are relatively dense solids without specific features. No significant morphological evolution during the different passivation or anion exchange steps was detected.

3.4. Catalytic tests: cyanosilylation reactions of ketones

Cyanosilylation reactions of carbonyl compounds (aldehydes/ketones) lead to the formation of cyanohydrins (Scheme 4) that are versatile intermediates in organic synthesis. The formation of these compounds using organocatalytic approaches prevents metal contamination of the products and is therefore of interest for sustainable synthesis strategies, and in particular the preparation of drugs. Mechanistic considerations suggest a nucleophilic catalysis pathway, involving the formation of a pentavalent silicon species *via* the addition of TMSCN to the carbene, followed by the transfer of the cyano group to the carbonyl compound. Finally, this intermediate fragments to give the cyanohydrin and the carbene organo-catalyst [25].

Here, we investigated in particular cyanosilylation reactions of ketones. These reactions are more challenging compared to similar reactions of aldehydes, as the high electrophilicity of aldehydes allows the reaction to take place even under catalyst-free conditions [28]. On the contrary, the conversion of ketones necessitates the use of catalysts, as no product formation took place in the absence of catalyst (Table 3, entry 1). Furthermore, we observed that the reaction occurred smoothly in the presence of imidazolium acetate in

homogeneous solution, due to the formation of *N*-heterocyclic carbenes *in situ* (Table 3, entry 3). This supposition is supported by the fact that only low conversion rates were observed in the presence of ammonium acetate (Table 3, entry 2), highlighting that the presence of imidazolium ions as a reservoir for the formation of NHCs is crucial for the generation of catalytic activity in cyanosilylation reactions.

In a second time, we investigated the catalytic properties of the imidazolium based ionosilica materials **A–D** as heterogeneous organocatalysts in cyanosilylation reactions. We investigated different aspects related to this initial question: *i*) Which material shows the highest catalytic activity among the synthesized ionosilicas? *ii*) Can we use different ketones as substrates in heterogeneous organocatalytic cyanosilylation reactions? and finally *iii*) Can the heterogeneous catalysts be re-used?

Regarding the use of the four materials **A–D** as heterogeneous cyanosilylation catalysts, we observed that no product was detected in the presence of materials **A**, **B** and **C**. Only material **D** led to the formation of the cyanohydrin, however with a lower catalytic activity compared to the pure ionic liquid (Table 3, entries 3 and 7). This result can be explained by the low acetate content of the material, as demonstrated by various characterization techniques (*vide supra*), and hindered accessibility of the immobilized imidazolium centers. In this regard, the conversion rate of 75% observed with the material **D** appears as a highly interesting result, as it clearly indicates the formation of a material with significant catalytic activity in cyanosilylation reactions, whereas immobilized imidazolium iodide based materials do not show any catalytic activity. Due to the low acetate content of the material, the TON value of the material is considerably higher compared to the pure acetate

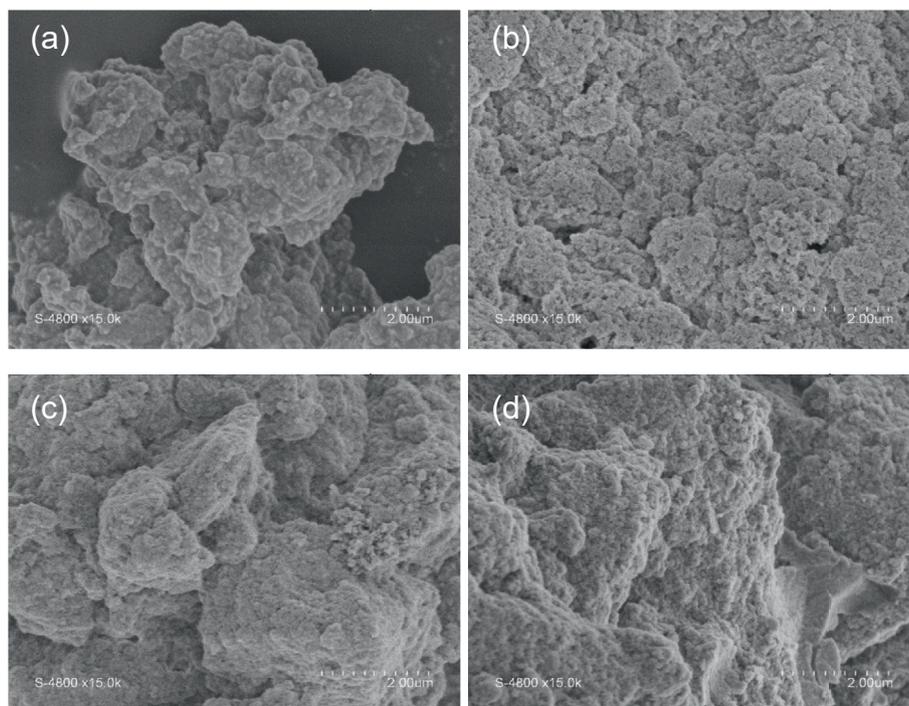
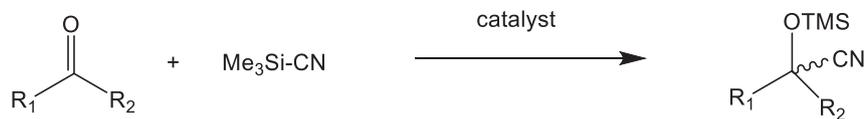


Fig. 2. SEM images of materials (a)–(d).



Scheme 4. Cyanosilylation reactions of ketones with trimethylsilyl cyanide.

Table 3
Cyanosilylation reaction of acetophenone with trimethylsilyl cyanide in the presence of various catalysts and materials.

Entry	Material/catalyst	Conversion (%)	TON
1	None	0	x
2	ammonium acetate	trace	x
3	butylmethylimidazolium acetate	100	20
4	A	0	x
5	B	0	x
6	C	0	x
7	D	75	300
8 ^a	D	100	80

Reaction conditions: ketone (1 mol%), TMSCN (1.2 mol%), catalyst (5 mol %), rt, 20 min.

^a Reaction was performed with 25 mol% of catalyst. The conversion was determined by ¹H NMR measurements.

ionic liquid. Finally, our results show that the surface passivation *via* trimethylsilylation of residual silanol groups is necessary in order to generate catalytically active materials. We believe that the presence of acidic silanol groups impedes the formation of NHC species due to protonation. Finally, the complete conversion in cyanosilylation reaction was observed when a five times higher quantity of ionosilica organocatalyst was used (Table 1, entry 8).

After having ascertained the catalytic activity of the material **D**, we investigated the scope of the reaction *via* the use of different ketones as electrophiles in the cyanosilylation reaction. The results are summarized in Table 4. Whereas cyclohexanone gave the corresponding cyanohydrin in quantitative yield (Table 4, entry 2), sterically more hindered ketone (4-hydroxyacetophenone, Table 4, entry 3) or substituted ketone (2-acetonaphthone, Table 4, entry 4) led to lower conversions compared to acetophenone. However, these results show that the imidazolium acetate material **D** is a versatile catalyst allowing activating a variety of electrophiles in cyanosilylation reactions, despite its low content of acetate anions. The TON values are in the range of 200–400.

Finally, we focused on the re-use of the heterogeneous organocatalytic material **D** in the cyanosilylation reaction. We

Table 4
Cyanosilylation reaction of various ketones with trimethylsilyl cyanide in the presence of materials **D**.

Entry	Material	Ketone	Conversion (%)	TON
1	D	acetophenone	75	300
2	D	cyclohexanone	100	400
3	D	4-hydroxyacetophenone	62	250
4	D	2-acetonaphthone	51	200

Reaction conditions: ketone (1 mol%), TMSCN (1.2 mol%), catalyst (5 mol %), rt, 20 min. The conversion was determined by ¹H NMR measurements.

Table 5
Recycling experiments of material **D** in the cyanosilylation reaction of acetophenone with trimethylsilyl cyanide.

Entry	Amount of material (mg)	Conversion (%)	Recovery (mg) (%)	TON
1	100	100	96.7 (97)	80
2	96.7	100	88.1 (91)	<i>n.a.</i>
3	88.1	84	83.9 (95)	<i>n.a.</i>
4	83.9	65	76.7 (91)	<i>n.a.</i>
5	76.7	97	<i>n. d.</i>	<i>n.a.</i>

Reaction conditions: ketone (1 mol%), TMSCN (1.2 mol%), catalyst, rt, 20 min. The conversion was determined by ¹H NMR measurements.

chose as test reaction the cyanosilylation of acetophenone with trimethylsilyl cyanide. In our study, we used the same material in four successive catalytic cycles. In order to minimize the influence of materials' loss during the catalytic cycles, we increased notably the amount of used catalytic material. Due to the four times higher amount of catalyst, we observed quantitative conversion in the first and the second catalytic cycles (Table 5, entries 1 and 2). Starting with the third cycle, the conversion rate decreased to reach values of 84% and 65% in the third and fourth reaction cycle, respectively (Table 5, entries 3 and 4). We believe that this decrease is due to the loss of acetate anions during the subsequent catalytic cycles. As the materials only contains a very low amount of acetate, crucial for the generation of the catalytically active NHC species, the loss of even small amounts of acetate results in a reduced catalytic activity of the material. This hypothesis is supported by the fact the catalytic activity almost reaches the initial level *via* a new treatment of the material with ammonium acetate (Table 5, entry 5). Due to the unknown exact content of acetate anions in the recycled materials, it is not possible to determine accurately the TON values of the catalysts in the various catalytic cycles (entries 2–5).

4. Conclusions

Our results show that silica supported dialkylimidazolium acetate containing materials display interesting organocatalytic properties in cyanosilylation reactions. The reaction is promoted by N-heterocyclic carbene species that are formed *in situ* by deprotonation of the imidazolium rings by acetate anions. Despite the very small amount of adsorbed acetate anion, the material shows high catalytic activity in the first two catalytic cycles. The decrease of the catalytic activity can be explained by the elimination of the acetate anion. Interestingly, the catalytic activity can be re-established *via* a new acetate treatment of the materials.

Our approach is therefore interesting for the elaboration of novel heterogeneous NHC organocatalysts. It indicates that

only very small amounts of acetate are necessary to generate a sufficient amount of catalytically active NHC species. Our approach may therefore open the route toward a new class of highly versatile and polyvalent recyclable heterogeneous organocatalysts. In particular, this work shows that silica can be a suitable support for the immobilization of NHC species, due to the *in situ* formation of carbenes. This approach is of particular interest for the elaboration of other types of heterogeneous organocatalytic systems, e.g. for asymmetric heterogeneous organocatalysis.

Conflict of interest

The authors declare no conflict of interest.

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References

- [1] D. Enders, O. Niemeier, A. Henseler, *Chem. Rev.* 107 (2007) 5606–5655.
- [2] D.M. Flanigan, F. Romanov-Michaïlidis, N.A. White, T. Rovis, *Chem. Rev.* 115 (2015) 9307–9387.
- [3] H.W. Wanzlick, H. Schonherr, *Angew. Chem. Int. Ed.* 7 (1968) 141–142.
- [4] K. Öfele, *J. Organomet. Chem.* 12 (1968) 42–43.
- [5] D. Bourissou, O. Guerret, F.P. Gabbai, G. Bertrand, *Chem. Rev.* 100 (2000) 39–91.
- [6] N. Marion, S. Diez-Gonzalez, S.P. Nolan, *Angew. Chem. Int. Ed.* 46 (2007) 2988–3000.
- [7] A.J. Arduengo, R.L. Harlow, M. Kline, *J. Am. Chem. Soc.* 113 (1991) 361–363.
- [8] R. Zhong, A.C. Lindhorst, F.J. Groche, F.E. Kuehn, *Chem. Rev.* 117 (2017) 1970–2058.
- [9] R. Lambert, P. Coupillaud, A.L. Wirotius, J. Vignolle, D. Taton, *Macromol. Rapid Commun.* 37 (2016) 1143–1149.
- [10] S. Garmendia, R. Lambert, A.-L. Wirotius, J. Vignolle, A.P. Dove, R.K. O'Reilly, D. Taton, *Eur. Polym. J.* 107 (2018) 82–88.
- [11] B.W. Xin, J.C. Hao, *Chem. Soc. Rev.* 43 (2014) 7171–7187.
- [12] L. Wang, E.Y.X. Chen, *ACS Catal.* 5 (2015) 6907–6917.
- [13] T. Droge, F. Glorius, *Angew. Chem. Int. Ed.* 49 (2010) 6940–6952.
- [14] E.M. Higgins, J.A. Sherwood, A.G. Lindsay, J. Armstrong, R.S. Massey, R.W. Alder, A.C. O'Donoghue, *Chem. Commun.* 47 (2011) 1559–1561.
- [15] T.L. Amyes, S.T. Diver, J.P. Richard, F.M. Rivas, K. Toth, *J. Am. Chem. Soc.* 126 (2004) 4366–4374.
- [16] Z. Li, X. Li, J.-P. Cheng, *J. Org. Chem.* 82 (2017) 9675–9681.
- [17] I. Chiarotto, L. Mattiello, F. Pandolfi, D. Rocco, M. Feroci, *Front. Chem.* 6 (2018) 355.
- [18] Z. Kelemen, O. Holloczki, J. Nagy, L. Nyulaszi, *Org. Biomol. Chem.* 9 (2011) 5362–5364.
- [19] B. Ullah, J. Chen, Z. Zhang, H. Xing, Q. Yang, Z. Bao, Q. Ren, *Sci. Rep.* 7 (2017) 42699.
- [20] S. El Hankari, B. Motos-Perez, P. Hesemann, A. Bouhaouss, J.J.E. Moreau, *J. Mater. Chem.* 21 (2011) 6948–6955.
- [21] V. Polshettiwar, P. Hesemann, J.J.E. Moreau, *Tetrahedron Lett.* 48 (2007) 5363–5366.
- [22] N. Thy Phuong, P. Hesemann, J.J.E. Moreau, *Micropor. Mesopor. Mater.* 142 (2011) 292–300.
- [23] B. Motos-Perez, J. Roeser, A. Thomas, P. Hesemann, *Appl. Organomet. Chem.* 27 (2013) 290–299.
- [24] M. North, D.L. Usanov, C. Young, *Chem. Rev.* 108 (2008) 5146–5226.
- [25] M. Kronstein, J. Akbarzadeh, C. Drechsel, H. Peterlik, M.-A. Neouze, *Chem-Eur J.* 20 (2014) 10763–10774.
- [26] R.J.P. Corriu, J.J.E. Moreau, P. Thepot, M.W.C. Man, *Chem. Mater.* 4 (1992) 1217–1224.
- [27] A. Brethon, P. Hesemann, L. Rejaud, J.J.E. Moreau, M.W.C. Man, *J. Organomet. Chem.* 627 (2001) 239–248.
- [28] W.F. Wang, M. Luo, W.W. Yao, M.T. Ma, S.A. Pullarkat, L. Xu, P.H. Leung, *ACS Sustain. Chem. Eng.* 7 (2019) 1718–1722.