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Immobilization of Imidazolium Ionic liquids to Hydrotalcites Using Silane Linkers: Retardation of Memory Effect

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We report a new covalent surface immobilization of silane-modified imidazolium ionic liquids on hydrotalcite-like materials (HTs) and provide detailed characterization of the resulting surface chemistry using PXRD, CP-MAS, TGA and FT-IR. We show that this immobilization interferes with the "memory effect" of HTs and explore the stability of the resulting complexes to hydrolysis.

Hydrotalcite like materials (HTs) are naturally occurring layered double hydroxides (LDH) with general formula $[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$, where A^- are anions, such as CO_3^{2-}, OH^-, Cl^-, or SO_4^{2-}.[1] These materials are structurally similar to brucite, $Mg(OH)_2$, where M^{2+} and M^{3+} cations form stacked sheets, and water molecules and anions (A^-) fill the interlayers.[1] Naturally occurring HTs consist of Mg^{2+} and Al^{3+}, while synthetic HTs can be prepared with varying concentrations of a number of transition metal cations.[2] The HTs that result have similar morphology but different basicity, which makes them particularly interesting as catalytic supports. The basicity can also be modulated by calcination at 400-500°C, which causes the LDH to expel the anions and water from the interlayers and form mixed metal oxides.[3] Upon rehydration, these mixed oxides can recover the original lamellar structure, leading to meixnerite (magnesium aluminum hydroxide hydrate), which contains intercalated hydroxyls as compensating anions in the interlayers. This phenomenon is known as the "memory effect". Up to three cycles of calcination and rehydration have been reported without observed decomposition.[3]

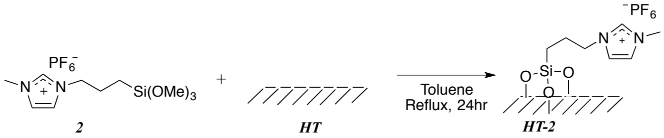
HTs have found an increasing number of applications in recent years, not just as heterogeneous catalysts and catalyst supports,[4] but also as anion exchangers,[5] CO_2 adsorbants[6] and waste water treatment agents.[7, 8] Their catalytic utility stems from the fact that the number and strength of the basic sites can be finely tuned by varying the composition.[5] As a result, many HTs have been shown to be active heterogeneous catalysts for organic transformations, such as transesterification,[9] Michael addition,[10] alcohol oxidation[11] and epoxidation,[12] and the synthesis of amides.[13]

As catalyst supports, HTs have been used to immobilize transition metal nanoparticles (np's)[14] and homogeneous catalysts.[15] HT-supported Pd np's have shown high activity for Suzuki cross-coupling,[16] hydroformylation,[17] oxidation of alcohols and deoxygenation of epoxides.[18, 19]

HTs are highly tunable catalyst supports that are increasingly being used to immobilize highly active heterogeneous catalysts. In order to study them as supports for single-site homogeneous catalysts, (SSHCs) and dye-sensitized solar cells, the surface immobilization by different types of organic linkers must characterized. Although HTs have been used to immobilize homogeneous catalysts via intercalation in the interlayers, their stability limits recyclability.[15] Strong surface immobilization is likely to overcome this challenge and would offer higher catalyst accessibility. Whereas the surface chemistry of commonly used supports for SSHCs (e.g. silica, alumina and titania) have been extensively characterized,[20, 21] hydrotalcite has not.

One of the most commonly used functional groups for immobilizing homogeneous catalysts on oxide supports is alkoxysilane.[22] While the surface chemistry of alkoxysilane condensation on silica and alumina has been extensively studied,[23, 24] analogous surface binding on LDHs, such as HT, is still not reported. Several reports have described the intercalation of organosilanes into the interlayers of HTs via calcination-rehydration,[25] induced hydrolysis,[26] and the use of surfactants.[27-30] While interlayer silylation results in materials with interesting novel properties, the immobilization of homogeneous catalysts via surface coordination is a more promising strategy for synthesis of supported homogeneous catalysts that are robust enough to withstand recycling.

Here we report the covalent surface immobilization of trimethoxysilane-modified imidazolium salts on HTs, and show that this modification impedes the memory effect, i.e. the ability of the mixed metal oxide to revert to a lamellar HT structure. The retardation of the memory effect likely results from cross-linking of surface sites by silane groups, thus preventing reconstitution of the brucite structure upon hydration. We further describe the surface chemistry and water stability based on characterization by PXRD, CP-MAS, TGA and FT-IR.



Scheme 1. Attachment of ***2*** to surface of HT gives HT-***2***

Synthetic HT was prepared via co-precipitation of $Mg(NO_3)_2$ and $Al(NO_3)_3$ under basic conditions. The precipitates were dried at 110 °C and, where necessary, calcined at 450 °C for 24 hours. *N*-3-(3-trimethoxysilyl propyl)-3-methyl imidazolium chloride (***1***) was synthesized via microwave heating using a modified previously reported procedure.[31] Replacement of chloride anion for the hexafluorophosphate anion gave ***2***.

Surface functionalization of HT by ***2*** was achieved by refluxing the HT and ***2*** in toluene for 24 hours, followed by removal of weakly adsorbed ***2*** using Soxhlet extraction. The resulting solid was dried *in vacuo* at 80 °C to give HT-***2*** and HTc-***2*** for uncalcined and calcined samples respectively.

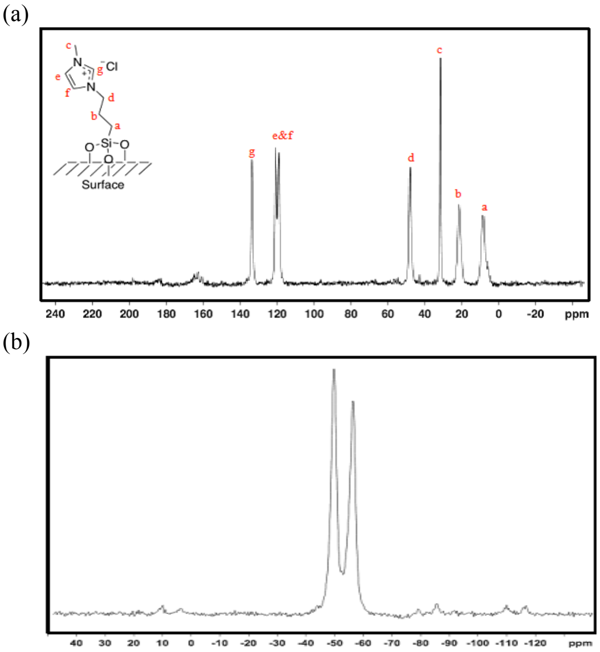


Fig 1. (a)^{13}C and (b) ^{29}Si CP/MAS NMR of ionic liquid attached to surface of hydrotalcite (HT-***1***).

Solid state CP/MAS NMR has been shown to be an excellent tool for elucidating surface structure.[22] ^{13}C and ^{27}Si CP/MAS spectra for HT-***1*** (chloride analog) were used to confirm the structure and bonding of the ionic liquid to the HT, as shown in Figure 1. The ^{13}C NMR spectrum of the unbound and bound ionic liquid shows that ***1*** is immobilized intact on the support, consistent with the spectra reported for immobilization of ***1*** on SiO_2 by Wang et.al.[32] The peak corresponding to methoxy-CH_3 groups of the trimethoxysilane is not present, indicating that all three methoxy groups have been lost upon immobilization (i.e. T^3 (tripodal) attachment to the surface[33]). The ^{29}Si NMR provides insight into the nature of the M-O-Si bonds on the surface (Figure 1b). Hydrotalcites with a surface Mg:Al ratio of 3:1 have hydroxyl groups in two distinct surface environments, Mg_3-OH and $AlMg_2$-OH.[14] Given that at least the majority of immobilized species have tripodal (T^3) attachment (according to the ^{13}C MAS spectrum), the presence of two distinct peaks in the Si spectrum likely indicates attachment of the silane groups to the Mg_3-OH and $AlMg_2$-OH environments respectively. Although the spectra for HT-***2*** are not presented here, the anion is not expected to have a major impact on the structure of the bound ionic liquid, as suggested by the similarity of all remaining characterizations that were carried out for both materials.

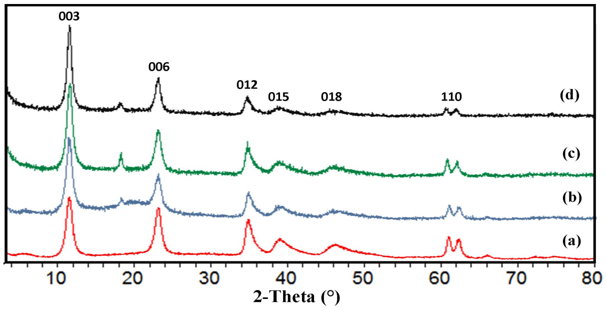


Fig 2. PXRD patterns of (a) HT (b) HT-***2*** (c) HT-***2*** hydrolysis test (d) HT hydrolysis test

PXRD patterns were used to determine whether the immobilization of ***2*** altered the HT structure (Figure 2). Pattern **a** shows the characteristic reflection pattern of HT.[2] Upon immobilization of ***2*** no distinct changes in the reflection pattern are observed, except for a small artifact at18°, which was also found in the control reaction (HT refluxed in toluene with no ionic liquid). More notably, we do not observe a change in the interlayer spacing after silylation, which would be reflected by a shift in d_{003} to lower 2θ values.[15] In fact, the interlayer distances for **a** and **b** are 2.99Å and 3.07Å respectively, which is within the normal range for hydrotalcite.[1] Changes in interlayer spacing would thus reflect intercalation of the organic ligand between the layers, as opposed to surface binding. No change in the interlayer spacing is consistent with surface attachment of the ionic liquid to HT. This result contrasts the change in interlayer spacing observed by Parida *et al* when immobilizing *N*-[3-(trimethoxysilyl)-propyl] ethylenediamine TPED (a molecule of comparable size to ***2***) in the interlayers of Zn:Al HT.[33]

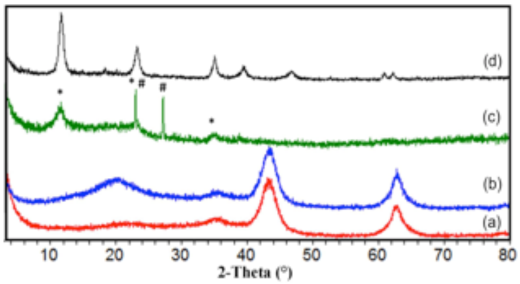


Fig 3. PXRD patterns of (a) calcined hydrotalcite (HTc) (b) HTc-***2*** (c) HTc-***2*** after hydrolysis (d) HTc after hydrolysis.

PXRD was also used to study the immobilization of the ionic liquid to the surface of calcined hydrotalcite (Figure 3). Upon calcination the layered structure of hydrotalcite collapses to a Mg:Al mixed metal oxide (HTc),[14] which is reflected in the PXRD pattern by broad reflections at 43° and 63° associated with MgO (Figure 3**a**). The alumina is amorphous, and thus does not show distinct reflections. Upon immobilization of ***2*** we observe that the mixed metal oxide structure persists, as the reflections at 43° and 63° are still present (Figure 3**b**). However, we also observe the appearance new broad reflection at 20°, which could be attributed to increasingly crystalline Al_2O_3 phases.[34]

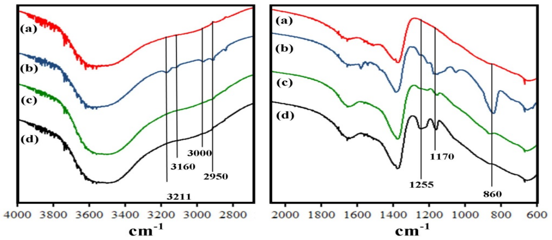


Fig 4. FT-IR Spectra of (a) HT (b) HT-***2*** (c) HT-*2* hydrolysis test (d) HT hydrolysis test

The attachment of the ionic liquid to both non-calcined and calcined HTs was also studied with FT-IR spectroscopy. Figure 4**a** shows the stretches characteristic of HT at 3600, 1600, and 1400 cm^{-1}, corresponding to normal modes of –OH, H_2O, and CO_3^- respectively.[1] In the FT-IR spectrum of HTc (ESI Figure S1) these stretches are absent due to loss of interlayer water and carbonate ions. Upon addition of ***2***, new peaks appear at 3200-2900 cm^{-1} (C-H stretches of ***2***), at ~850 cm^{-1} (C-C bending of ***2***) and at 1600 cm^{-1} (C=C stretches of ***2***). These new peaks are consistent with the IR pattern of unsupported ***2*** (ESI Figure S6) and match well with reported spectra of ***2*** immobilized in SiO_2.[32] The peak at 1020 cm^{-1} was identified as a Mg-O-Si stretch using theoretical modeling by DFT (B3LYP 6-31G*).[35] This further supports the assertion that covalent attachment of ***2*** to the HT through condensation of silane groups has taken place.

The thermal stability of the attached ligand was studied by TGA/FTIR. Figure 5 shows the TGA/DTA curves of HT and HT-***2*** and the FT-IR spectra of HT-***2*** after heating at 100 °C, 200 °C and 300 °C. DTA curves for HT show two main weight loss peaks, the first at 235 °C, corresponding to the loss of interlayer water and partial dehydroxylation, and a second at 440°C, corresponding to loss of interlayer carbonate.[1] HT-***2*** shows an additional weight loss at 340°C, most likely due to the loss of the organic ligand from the surface. This weight loss is consistent with the thermal stability of ***1*** immobilized on SiO_2 (stable below 280°C) as reported by Karimi et.al.[36]

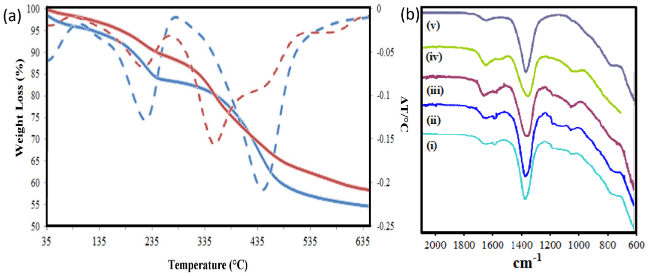


Fig 5. TGA/DTA curves for HT(blue) and HT-***2***(red). FTIR taken (a) unheated HT-***2*** (b) HT-***2*** at 100°C (c) HT-***2*** at 200°C (d) HT-***2*** at 300°C (e) unheated HT

FT-IR spectra taken at 100 °C intervals are shown in Figure 5b. Due to the loss of interlayer carbonates, the intensity of the peak at 1360 cm^{-1} slowly decreases as temperature increases. The peaks attributed to ***2*** at 1600 and 1020 cm^{-1} are still present after heating at 300 °C (although decreasing in intensity due to gradual loss of organic moiety), confirming there some ***2*** is still present at 300 °C. The elemental composition of the HTs before and after immobilization were determined by Atomic Absorption Spectroscopy (AAS) and Energy Dispersive X-Ray Spectroscopy (EDX) (Table 1). Due to matrix effects in the EDX, AAS was used to confirm the Mg and Al content of the samples. The Si content was reflective of the loading of ***2***, and was found to be comparable for uncalcined and calcined HT (10.3% and 14.8% respectively. A substantial drop in BET surface area was observed after ***2*** was immobilized on uncalcined HT (111 vs. 24.8 m^2/g) as well as calcined HT (118 vs. 10.1 m^2/g), both with corresponding drops in pore volumes.

Table 1. Elemental analysis and BET surface area of HT and ILs supported on HTs.

Sample	Mg %[b]	Al %[b]	Si %	BET SA (m^2/g)	PV[c](c m^3/g)
HT	26.4	12.0	-	111	0.34
HT-2	19.9	7.8	10.3	24.8	0.08
HT-2[a]	25.4	7.8	-	94.3	0.22
HTc	36.3	11.1	-	118	0.38
HTc-2	36.3	12.0	14.8	10.1	0.04
HTc-2[a]	37.8	10.9	-	11.5	0.03

[a] Hydrothermal stability test: Samples refluxed in water before testing. [b] Determined using AAS; [c] Single point pore volume measured at P/P_0=0.97 on absorption isotherm.

To test the water stability of the immobilized ionic liquid, HT-***2*** and HTc-***2*** were refluxed in deionized water for 2 hours and dried under reduced pressure at 80 °C. The FT-IR spectra of both samples after hydrolysis show the loss of all peaks attributed to the ionic liquid (***2***). Thus, the immobilization ***2*** on HT and HTc is not water stable. This is confirmed with EDX data, where Si drops below the detection limit after hydrolysis. It is notable that after hydrolysis of HT-***2*** its surface area reverts close to that of HT (111 vs. 94.3 m^2/g); however, the same is not true for the calcined samples – the drop in surface area persists (118 vs 11.5 m^2/g). Although not stable in aqueous media, HT-***2*** and HTc-***2*** are stable in refluxing organic solvents, such as toluene and dichloromethane.

We observed a retardation of the memory effect of HTs upon immobilization of ***2***. In a control reaction where HTc is refluxed in water, the reformation of the layered structure is evident by PXRD (Figure 3**d**).[3] However, when HTc-***2*** is treated under the same conditions, the layered structure is not reformed, Figure 3**c**). It should be noted that although two new sharp reflections are present in pattern **c** (denoted by #), they are likely due to salts deposited on the surface from ***2***, while the new broader reflections (labeled with *) are attributed to magnesium aluminum hydroxide phases.

Refluxing in water thus hydrates the mixed metal oxide but does not allow it to regain a recognizable and crystalline HT structure based on PXRD data (Fig 3c). What we observe instead is consistent with either meixenrite (a layered structure with hydroxyl groups in the interlayer)[37, 38] or a very poorly crystalline HT phase. The lack of high angle reflections in PXRD patterns (Fig 3c) are consistent with a meixenrite phase, but could also be due to very poor crystallinity of a hydrotlcite phase. The FT-IR spectrum does not distinguish well between these two, as the stretches at ~ 1400 cm^{-1} could be due to interlayer carbonate of hydrotalcite or interlayer water of meixenrite (Figure 3).[1, 39] Immobilization of 2 thus impedes the reformation of a recognizable and crystalline HT structure. According to our working definition of "memory effect" as the reversion to a recognizable HT phase by PXRD, we can conclude that the immobilization of 2 retards the memory effect upon rehydration. As a result, after hydrolysis HTc-2 does not regain its original surface area (Table 1 entry 6).

Here we reported the first surface modification of hydrotalcite (HT) via covalent attachment of immidizolium-based ionic liquids through silane linkers. The characterization performed shows evidence of strong covalent binding to the HT surface analogous to immobilization of similar moieties to silica and other supports.[20, 40, 41] Although attachment is not water stable, the applicability of these materials for supported catalysis is not sacrificed, as they are stable in organic solvents. It should be noted that most silica-immobilized species are also not hydrolytically stable,[42] but are still successfully used as catalysts in non-aqueous media. Furthermore, this result does not preclude that the use of other linkers will lead to hydrolytically stable moieties immobilized on HTs. We hope the surface chemistry elucidated here will enable further exploration of HTs as supports for single-site heterogeneous catalysts.

Notes and references

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