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# A new and efficient catalytic method for synthesizing isocyanates from carbamates

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**Abstract**—Operationally simple, recyclable and environmentally friendly montmorillonite efficiently catalyses dealcoholysis of a wide range of mono- and dicarbamates to isocyanates. © 2002 Elsevier Science Ltd. All rights reserved.

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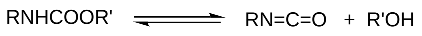
Isocyanates are produced on the billions of pounds scale annually, mainly for the synthesis of polyurethanes.[1] Nowadays, there is a greater awareness of the need for new chemical processes to manufacture isocyanates without using or generating toxic and environment-threatening materials.

Eliminating alcohol from urethane is a simple and convenient way to produce isocyanates (Scheme 1). The most common methods include thermal decomposition reactions[2] carried out at high temperatures in the presence of powdered boron or bismuth,[2a] germanium oxide,[2b] or the more recently developed manganese, molybdenum, tungsten, zinc[2c] or zirconium[2d] catalysts. However, under these reaction conditions, significant amounts of high-temperature boiler byproducts are formed. Also, the resulting isocyanate may recombine with alcohol, which would make longer reaction times necessary.

The interception of alcohol to prevent this recombination with isocyanates has recently been accomplished with chlorocatecholborane and borohalides with triethylamine.[3,4] Despite the effectiveness of this simple and highly selective method, it may not succeed commercially on a large scale because it is difficult to recover and reuse the stoichiometric amounts of boron derivatives and triethylamine. Silanes have also been used extensively to promote the conversion of carbamates into isocyanates. However, the usual thermal conditions required for the silane-induced reaction lead to extensive decomposition of the substrate and reaction product.[5] More recently, diiodosilanes have therefore been considered as useful reagents for this transformations, however the isocyanates were not isolated but rather trapped in situ with amines to afford ureas in good to excellent yields.[6]



$$\mathrm{RNHCOOR'} \rightleftharpoons \mathrm{RN{=}C{=}O} + \mathrm{R'OH}$$

**Scheme 1.**

On the other hand, there have been a number of important advances in the practical aspects of organic synthesis during the last years, namely due to the concept of utilizing reagents or reactants absorbed on inorganic supports. Of the attractive new approaches to organic chemistry using surface-active inorganic reagents,[7,8] the smectite clay montmorillonite K-10 had already proved to be a good acid catalyst in several heterogeneous catalytic processes.[9–12] In our ongoing research in this area, we found that the smectite clay montmorillonite K-10 catalyzes the dealcoholysis of carbamates towards isocyanates. We have first examined the dealcoholysis of several monocarbamates with montmorillonite K-10.[13] It must be pointed out that working at the reflux temperature of 1,2-dichlorobenzene, 183°C, *N*-carbomethoxyaniline is extensively converted to phenylisocyanate in 5 h, (entry 1, Table 1). Almost quantitative conversions to the monoisocyanate were achieved when the substituents R on the substrate RNHCOOR′ had electron-withdrawing properties, even with lower reaction times, (entries 2 and 3, Table 1). On the contrary, monocarbamates with electron-donor substituents were transformed into the corresponding monoisocyanates with only moderate conversions, (entries 4–6, Table 1).

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*Keywords*: carbamates; isocynates; clays; dealcoholysis.

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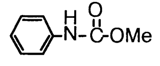
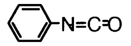
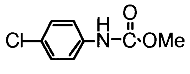
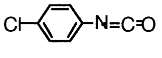
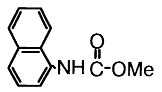
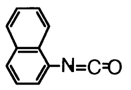
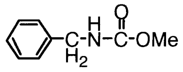
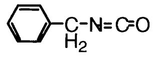
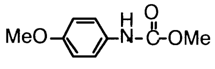
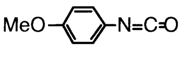
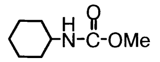
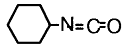
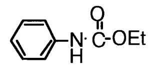
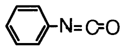
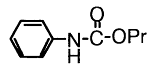
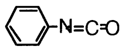
**Table 1.** Synthesis of isocyanates from carbamates using montmorillonite K-10 as catalyst[a]

| Entry | Substrate | Product[b] | Conv. [%][c] |
|---|---|---|---|
| 1 |  |  | 96 |
| 2 |  |  | 99 |
| 3 |  |  | 93[d] |
| 4 |  |  | 67 |
| 5 |  |  | 86 |
| 6 |  |  | 12 |
| 7 |  |  | 73 |
| 8 |  |  | 25 |

[a] Reaction conditions: carbamate / montmorillonite K-10 = 0.6 mmol / 100mg, 1,2-dichlorobenzene (8 mL), 183°C, 5h.

[b] Products were characterized by comparison of spectral data (IR, NMR, MS) and retention times (G.C.) with the commercially available monoisocyanates.

[c] Conversion of the isocyanates or their propylcarbamates derivatives were analysed by G.C.

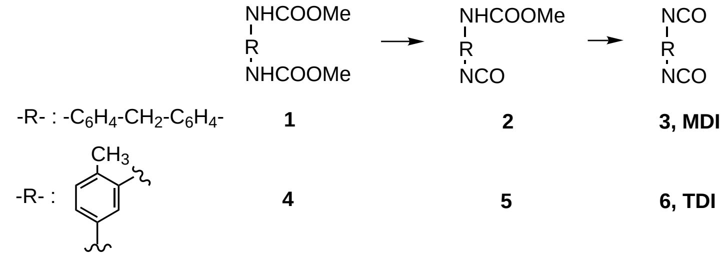
[d] Reaction time: 1h.

The dealcoholysis process in the presence of montmorillonite K-10 is not a purely thermal reaction because in similar reactions carried out in the absence of montmorillonite K-10 and under the same reaction conditions, isocyanate was not formed. So montmorillonite K-10 was assumed to catalyze the dealcoholysis process, probably initiated by the interaction of the Brönsted acid centers of the clay and the carbamates. The methoxy and proton moieties from the substrate could be adsorbed onto the surface of montmorillonite K-10, which prevents the reversible recombination of isocyanate with methanol. We studied the desorption with the TPD technique which has shown that MeOH is mainly adsorbed on the weak acid centers of the montmorillonite K-10 surface. The refluxing reaction conditions promote the elimination of MeOH from montmorillonite K-10, and thus regenerate the active surface, and significant amounts of MeOH have been recovered by distillation during the dealcoholysis process.

While *N*-carbomethoxyaniline can be extensively converted to phenylisocyanate in the presence of montmorillonite K-10, the conversion under the same reaction conditions for the analogues *N*-carboethoxyaniline and *N*-carbopropoxyaniline decreases from R′ = OMe>OEt>OPr, (entries 1, 7 and 8, Table 1). We also carried out desorption studies with the TPD technique which has shown that bulkier alcohols are more strongly bonded to montmorillonite K-10, so that a higher temperature is required to desorb them. A similar slow-down effect was also reported in the literature for the dealcoholysis of *N*-Boc carbamates with silane reagents.[6]

We have assessed the generality of this method by converting dicarbamates into diisocyanates of industrial interest. These are large scale raw materials for manufacturing polyurethanes foams[14] such as 4,4′-methylenebis(phenylisocyanate), MDI, and 2,4-toluene-bis(isocyanate), TDI, (Scheme 2).

Table 2 shows the conversion of the dealcoholysis of 4,4′-methylenebis-(*N*-carbomethoxyaniline), selectivity on diisocyanate **3** versus monoisocyanate **2**, and isolated



**Scheme 2.**

**Table 2.** Synthesis of MDI from 4,4′-methylenebis-(*N*-carbomethoxianiline) using montmorillonite K-10 as catalyst[a]

| Entry | Substrate/Mont K-10 | Solvent (mL) | Time (h) | Conv. (%)[b] | Selectivity **2**/**3**[b] | Yield **3** (%) |
|---|---|---|---|---|---|---|
| 1 | 1 g/1 g | 80 | 5 | 100 | 25/75 | 32 |
| 2 | 1 g/1 g | 80 | 24 | 100 | 2/98 | 40 |
| 3 | 1 g/0.25 g | 80 | 24 | 100 | 17/83 | 68 |
| 4 | 1 g/0.25 g | 40 | 24 | 100 | 3/97 | 75 |

[a] *Reaction conditions*: decaline, 190°C.

[b] Isocyanate product was isolated by vacuum distillation under $N_2$ atmosphere and characterized by comparison of spectral data (IR, NMR, MS) with the commercially available 4,4′-methylenebis-(phenylisocyanate).

yield of **3**, when working on a 1 g scale and substituting chlorinated solvents for decaline (bp = 190°C) to avoid environment-threatening solvents. Reaction times longer than in the dealcoholysis of monocarbamates were required (24 h) for both complete conversion and high selectivity on **3**, (entries 1 and 2, Table 2), but isolated yields were only moderate. Similarly high conversions and selectivities, as well as enhanced isolated yields of up to 68%, were achieved when we decreased the percentage of montmorillonite K-10 in the reaction media, (entry 3, Table 2) to minimize the possible retention of isocyanate product on the surface of the montmorillonite K-10. However, results were best when the reaction was performed with the minimum amount of solvent. This guarantees that the reactive diffusion is efficient and increases the reaction rate (entry 4, Table 2).

The influence of the amount of solvent on the synthesis of diisocyanates has also been observed in the conversion of 2,4-toluene-bis(*N*-carbomethoxyurethane) towards 2,4-toluene-bis(isocyanate), TDI, in the presence of montmorillonite K-10. We then carried out the dealcoholysis of 2,4-toluene-bis(*N*-carbomethoxyurethane) under the same reaction conditions used in the MDI synthesis, (80 mL of decaline as solvent and 24 h of reaction time), and although the conversion in isocyanate product **5**+**6** was high, the selectivity in diisocyanate **6** was only moderate, (entry 1, Table 3). The more hindered position of one of the carbamate functional groups in 2,4-toluene-bis(*N*-carbomethoxyurethane) could be the reason for the low selectivity on the diisocyanate. The highest selectivity in **6** was achieved when the amount of solvent was reduced to 40 mL, in the presence of both montmorillonite K-10 Fluka and Aldrich, (entries 2–4, Table 3), although longer reaction times were required (48 h).

To determine whether the number of Brönsted acid centers of the solid affects the conversion, selectivity and isolated yield of the product, we explored the catalytic behavior of a wide range of acid solids. Although both montmorillonite K-10 and bentonite are in fact the same smectite clay material, (montmorillonite), they are significantly different because montmorillonite K-10 is the acidic form of bentonite.[15] The acid-activation process to convert bentonite into montmorillonite K-10 is severe enough to partially destroy the bentonite layer structure, so the resulting solid is characterized by both a large number of Brönsted acid centers and a large surface area. However, bentonite shows a lower conversion and selectivity on dealcoholysis of **1** to diisocyanate **3**, (entry 1, Table 4). Acidified bentonite clay with $NH_4NO_3$ ($H^+$-B) produces a solid whose acidity is intermediate between bentonite and montmorillonite K-10. It catalyzes dealcoholysis of **1** with higher conversions and selectivities on **3** than with bentonite but lower than with montmorillonite K-10, (entry 2, Table 4).

**Table 3.** Synthesis of TDI from 2,4-toluene-bis(*N*-carbomethoxyurethane) using montmorillonite K-10 as catalyst[a]

| Entry | Substrate/Mont. K-10 | Solvent (mL) | Time (h) | Conv. (%)[b] | Selectivity **5**/**6**[b] |
|---|---|---|---|---|---|
| 1 | 0.76 g/0.25 g | 80 | 24 | 95 | 46/54 |
| 2 | 0.76 g/0.25 g | 40 | 36 | 95 | 35/65 |
| 3 | 0.76 g/0.25 g[c] | 40 | 48 | 98 | 3/97 |
| 4 | 0.76 g/0.25 g[d] | 40 | 48 | 96 | 19/81 |

[a] *Reaction conditions*: decaline, temperature: 190°C.

[b] Products were characterized by comparison of spectral data (IR, NMR, MS) and retention times (GC) with the commercially available 2,4-toluene-bis-(isocyanate). Conversion and selectivity on TDI or its dipropylcarbamate derivatives were analyzed by GC.

[c] Montmorillonite K-10 (Fluka).

[d] Montmorillonite K-10 (Aldrich).

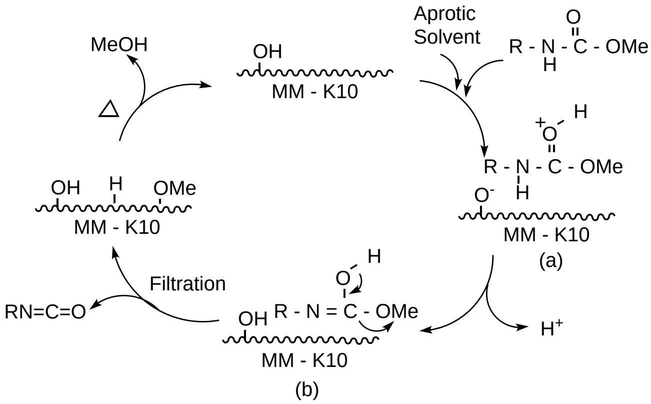
**Table 4.** Synthesis of MDI from of 4,4′-methylenebis-(*N*-carbomethoxianiline) using different clays as catalyst[a]

| Entry | Clay | BET area ($m^2$/g) | meq ($H^+/m^2$) | TPD $Et_2NH_2$[b] (°C) | Conv. (%)[c] | Selectivity **2**/**3**[c] | Yield **3** (%) |
|---|---|---|---|---|---|---|---|
| 1 | Bent. | 71 | $<1\times10^{-5}$ | 130 (w) | 71 | 44/56 | 35 |
| 2 | $H^+$-Bent. | 76 | $5.2\times10^{-5}$ | 131 (m)<br>305 (w) | 82 | 29/71 | 54 |
| 3 | MMK-10 | 221 | $1.4\times10^{-4}$ | 120 (i)<br>263 (m) | 100 | 17/83 | 68 |
| 4 | $H^+$-MMK-10 | 219 | $7.7\times10^{-4}$ | 120 (i)<br>287 (m) | 96 | 31/69 | 51 |

[a] *Reaction conditions*: decaline (80 mL), substrate/clay = 1 g/0.25 g, 190°C, 24 h. Bent.: bentonite; $H^+$-Bent.: $NH_4NO_3$–bentonite; MMK-10: montmorillonite K-10; $H^+$-MMK-10: $HNO_3$–montmorillonite K-10.

[b] (w): weak, (m): medium, (i): intense.

[c] Isocyanate product was isolated by vacuum distillation under $N_2$ atmosphere and characterized by comparison of spectral data (IR, NMR, MS) with the commercially available 4,4′-methylenebis-(phenylisocyanate).



**Scheme 3.**

In agreement with the above results, the increase of Brönsted acid centers of the clay can favor the dealcoholysis. Taking into account how the number of Brönsted acid centers affects the catalytic process, we prepared a more acidic clay than montmorillonite K-10, by acidification of montmorillonite K-10 with $HNO_3$ to provide $H^+$-M with $7.7\times10^{-4}$ meq $H^+/m^2$. However, although the conversion of dicarbamate **1** on isocyanates was still almost quantitative, the selectivity on diisocyanate **3** and the isolated yield decreased probably because more of the product was retained on the clay surface, (entry 4, Table 4). It therefore seems that montmorillonite K-10 has the optimum number of Brönsted acid centers to perform the dealcoholysis of dicarbamates efficiently.

The catalytic cycle shown in Scheme 3 is a plausible pathway for coupling this chemistry. Montmorillonite K-10 may act as an acid catalyst if its Brönsted acid centers interact with the carbamate by protonation of the carbonyl functional group of the substrate to give the ionic intermediate (a), followed by the elimination of the amidic proton (b) and subsequent formation of the isocyanate. The reaction temperature allows the elimination of MeOH from the clay, in order to regenerate the active surface.

In summary, montmorillonte K-10 is an efficient catalyst for synthesizing mono- and diisocyanates from mono- and dicarbamates, removing the alcohol efficiently since this is the driving force behind the reaction. Also its low cost, easy accessibility and reusability are additional advantages to take into consideration for large-scale production.

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