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Catalytic Activity of MCM-41–TBD in the Selective Preparation of Carbamates and Unsymmetrical Alkyl Carbonates from Diethyl Carbonate

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The synthesis of carbamates 3 and unsymmetrical alkyl carbonates 5 by reaction of diethyl carbonate with aliphatic amines or alcohols has been realized by using as heterogeneous catalyst a hybrid organic–inorganic material prepared by anchoring TBD to MCM-41 silica. Products are obtained in high yield and very good selectivity and the solid catalyst can be recovered simply by filtration and reused for different cycles without apparent lowering of activity. A supported *N*-carbethoxyguanidinium active intermediate is proposed, and some spectroscopic data are shown to support the mechanistic hypothesis.

Key Words: **heterogeneous basic catalyst; MCM-41; tethering; carbamates; transesterification; TBD.**

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1. INTRODUCTION

Carbamates (1) and alkyl carbonates (2) are compounds of great interest in organic chemistry because they find many important applications in pharmacology (3) as pharmaceuticals, in agriculture (4) as herbicides, fungicides, and pesticides, and in chemical industry (5) as intermediates. Their syntheses generally proceed through the condensation of amines or alcohols with toxic carbonyl compounds such as phosgene (6) or more stable and less harmful reagents, the vast majority of which are still produced from phosgene (7). Following a milder and safer approach, carbamates are prepared by reaction of amines with tetraethylammonium hydrogen carbonate (8) or carbon dioxide (9) and alkyl halides. While these reactions can be regarded as highly efficient processes utilizing clean and safe reagents, the production of a stoichiometric amount of salts brings about an increase in the *E factor* (10) and limits their large-scale applicability. More recently the synthesis of carbamates from amines and dimethyl carbonate was performed with γ-alumina as a catalyst (11). Unfortunately the reaction requires a very large amount of catalyst and no proof of the effective heterogeneity of the process was given.

The transesterification of dialkyl carbonates with alcohols or phenols represents a fundamental and safe route to different symmetrical alkyl and aryl carbonates (12). The green character of this approach is particularly evident, taking into account the fact that dimethyl carbonate is now prepared on a large scale from methanol and carbon monoxide in the presence of transition metal catalysts, which avoids the use of dangerous reagents such as phosgene (13).

In past decades metal and nonmetal catalysts bound to the surface of solid supports have attracted great interest since they combine the advantages of homogeneous catalysis with the easy recovery and reuse of heterogeneous materials (see e.g., 14). According to this approach, a few years ago some of us reported the preparation of a new solid-base catalyst obtained by immobilizing 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) on the mesoporous MCM-41 silica [MCM-41–TBD] (15). The catalytic efficiency of this material in promoting classical aldol-like and epoxidation reactions was also shown. More recently different guanidines immobilized on siliceous supports were reported as efficient epoxidation catalysts for electron deficient alkenes (16).

These results prompted us to investigate the use of silica-supported TBD as catalyst for the phosgene-free synthesis of carbamates **3** and unsymmetrical alkyl carbonates **5** by reaction of diethylcarbonate **1** with an amine or an alcohol (Scheme 1).

These reactions represent typical aminolysis or transesterification processes, where the more nucleophilic reagent displaces the less nucleophilic one, or if both reagents have similar nucleophilicity, where the less volatile compound displaces the more volatile one (see, e.g., 17). Moreover, since both reactions occur in steps, the formation of **3** or **5** can be followed by a further nucleophilic displacement of the ethoxy group by a second molecule of the amine or of the alcoholic reagent giving the corresponding urea or the

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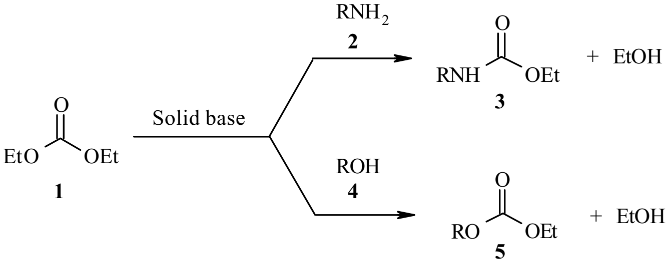


SCHEME 1

symmetric carbonate. Selective production of compounds **3** and **5** can be achieved by carefully controlling the nature of reagents and the experimental conditions.

2. EXPERIMENTAL

2.1. *Materials*

All reagents were of commercial quality and were taken from freshly opened containers.

2.2. *Catalyst Preparation*

The synthesis of KG-60–TBD and MCM-41–TBD was performed as previously reported in the literature (15).

The synthesis of 7-(2-hydroxy-3-isopropoxy-propyl)-1,5,7-triazabicyclo[4.4.0]dec-5-ene (HI–TBD) was performed as follows: A mixture of TBD (10 mmol, 1.39 g) and glycidyl isopropyl ether (12 mmol, 1.39 g, 1.52 ml) in tetrahydrofuran (10 ml) was stirred at room temperature (rt) for 15 h; the solvent was removed under reduced pressure and the product purified by distillation. Colorless oil, b.p. 175–178°C/1 mm Hg; ^{1}H NMR ($CDCl_3$): δ 3.8-3.7 (m, 1H, $\underline{CH}OH$), 3.55 (m, 1H, $J = 6.1$ Hz, $(CH_3)_2\underline{CH}$), 3.5-3.2 (m, 8H, 2 CH_2N, $N\underline{CH_2}CH(OH)$, $O\underline{CH_2}CHOH$), 3.09 (t, 2H, $J = 6.2$ Hz, CH_2N), 3.07 (t, 2H, $J = 6.2$ Hz, CH_2N), 1.92 (m, 2H, $J = 11.2$ and 1.5 Hz, $NCH_2\underline{CH_2}CH_2N$), 1.77 (m, 2H, $J = 5.8$ Hz, $NCH_2\underline{CH_2}CH_2N$), 1.12 (d, 3H, $J = 6.1$ Hz, CH_3), 1.11 (d, 3H, $J = 6.1$ Hz, CH_3); IR (NaCl) 3132, 1591 cm^{-1}; MS m/z ($M^+ + 1$) 256 (100), (M^+) 255 (15), 254 (25), 212 (18), 182 (19). *Anal.* Calcd. for $C_{13}H_{25}N_3O_2$: C, 61.15; H, 9.87; N, 16.46. Found: C, 61.29; H, 9.78; N, 16.55.

2.3. *Reaction Procedure for Carbamate Synthesis*

A mixture of the selected amine (10 mmol), diethyl carbonate (DEC; 20 ml), and MCM-41–TBD (0.100 g) was stirred at reflux (~125°C) for 15 h. After cooling to rt, the reaction mixture was filtered and the catalyst was washed with diethyl ether; the solvent and the residual DEC were removed under reduced pressure by distillation and the crude product was chromatographed on silica gel using a mixture of hexane : ethyl acetate, 80 : 20, as eluent.

2.4. *Reaction Procedure for Unsymmetrical Alkyl Carbonate Synthesis*

A mixture of the selected alcohol (10 mmol), DEC (20 ml), and MCM-41-TBD (0.100 g) was stirred at reflux (~125°C) for 15 h. After cooling to rt, the reaction mixture was filtered and the catalyst was washed with diethyl ether; the solvent and the residual DEC were removed under reduced pressure and the crude product was chromatographed on silica gel using a mixture of hexane : ethyl acetate, 80 : 20, as eluent.

2.5. *Spectroscopic Analysis*

Melting and boiling points are uncorrected. ^{1}H NMR spectra were recorded at 300 MHz. Mass spectra were obtained in EI mode at 70 eV. Microanalyses were carried out at the Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica dell'Università di Parma, Italy. Fourier transform IR (FT-IR) spectra were recorded on a Nicolet PC 5 spectrophotometer.

To the best of our knowledge, a detailed characterization of the below-reported products has never been published before and therefore it is included here.

2-(N-Ethylamino)-ethyl-carbamic acid ethyl ester (**3i**): white solid, m.p. 51.5-52.5°C; ^{1}H NMR ($CDCl_3$) δ 5.1 (br s, 1H, NHCO), 4.09 (q, 2H, $J = 7.0$ Hz, $CH_3\underline{CH_2}O$), 3.25 (br q, 2H, $J = 5.6$ Hz, $CH_2\underline{CH_2}NHCO$), 2.72 (t, 2H, $J = 5.9$ Hz, $\underline{CH_2}CH_2NHCO$), 2.63 (q, 2H, $J = 7.1$ Hz, $CH_3\underline{CH_2}NH$), 1.22 (t, 3H, $J = 7.0$ Hz, $\underline{CH_2}CH_2O$), 1.08 (t, 3H, $J = 7.1$ Hz, $\underline{CH_3}CH_2NH$); IR (NaCl) 3398, 1700 cm^{-1}; MS m/z ($M^+ + 1$) 161 (15), 115 (20), 86 (65), 84 (100). Anal. Calcd. for $C_7H_{16}N_2O_2$: C, 52.48; H, 10.07; N, 17.49. Found: C, 53.01; H, 9.88; N, 17.05.

Ethyl octyl carbonate (**5n**): colorless oil (37), b.p. 91–92°C/4 mm Hg; ^{1}H NMR ($CDCl_3$) δ 4.18 (q, 2H, $J = 7.1$ Hz, $CH_3\underline{CH_2}O$), 4.11 (t, 2H, $J = 7.0$ Hz, $CH_2\underline{CH_2}O$), 1.66 (m, 2H, $J = 7.0$ Hz, $\underline{CH_2}CH_2O$), 1.4-1.2 (m, 13H, $\underline{CH_3CH_2CH_2CH_2CH_2CH_2}CH_2$), 0.87 (t, 3H, $J = 7.0$ Hz, $\underline{CH_3}CH_2O$); IR (NaCl) 1748 cm^{-1}; MS m/z ($M^+ + 1$) 203 (12), (M^+) 202 (100), 173 (16). Anal. Calcd. for $C_{11}H_{22}O_3$: C, 65.31; H, 10.96. Found: C, 65.25; H, 10.83.

Bicyclo[2.2.1]hept-2-yl ethyl carbonate (**5o**): colorless oil, b.p. 65–68°C/0.02 mm Hg; ^{1}H NMR ($CDCl_3$) δ 4.52 (br d, 1H, $J = 7.0$ Hz, CHOCO), 4.16 (q, 2H, $J = 7.1$ Hz, $CH_3\underline{CH_2}O$), 2.38 (d, 1H, $J = 4.4$ Hz, CH), 2.28 (m, 1H, CH), 1.74 (ddd, 1H, $J = 13.5$, 7.0 and 2.5 Hz, $^1/_2$ $CH\underline{CH_2}CHOCO$), 1.6-1.4 (m, 4H, $^1/_2$ $CH\underline{CH_2}CH$, $^1/_2$ $CH\underline{CH_2CH_2}CH$, $^1/_2$ $CH\underline{CH_2}CHOCO$), 1.30 (t, 3H, $J = 7.1$ Hz, $\underline{CH_3}CH_2O$), 1.2-1.0 (m, 3H, $^1/_2$ $CH\underline{CH_2}CH$, $^1/_2$ $CH\underline{CH_2CH_2}CH$); IR (NaCl) 1739 cm^{-1}; MS m/z ($M^+ + 1$) 185 (15), 111 (14), 95 (100). Anal. Calcd. for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.28; H, 8.88.

Ethyl (1R)-menthyl carbonate (**5p**): ^{1}H NMR ($CDCl_3$) δ 4.50 (td, 1H, $J = 11.4$ and 4.4 Hz, CHOCO), 4.17 (q, 2H,

$J = 7.1$ Hz, $O\underline{CH_2}CH_3$), 2.07 (dtd, 1H, $J = 11.4$, 3.9 and 2.6 Hz, $\underline{CH}CH(CH_3)_2$), 1.96 (m, 1H, $J = 6.7$ and 2.6 Hz, $\underline{CH}(CH_3)_2$), 1.30 (t, 3H, $J = 7.1$ Hz, $OCH_2\underline{CH_3}$), 1.8-0.8 (m, 7H, $\underline{CH_2}\underline{CH_2}\underline{CH}(CH_3)\underline{CH_2}$), 0.91 (d, 3H, $J = 6.7$ Hz, $\underline{CH_3}CHCH_3$), 0.89 (d, 3H, $J = 6.7$ Hz, $CH_3CH\underline{CH_3}$), 0.78 (d, 3H, $J = 7.0$ Hz, $\underline{CH_3}CHCH_2$); IR (NaCl) 1742 cm^{-1}; MS m/z ($M^+ + 1$) 229 (3), 227 (5), 139 (100). Anal. Calcd. for $C_{13}H_{24}O_3$: C, 68.38; H, 10.60. Found: C, 68.29; H, 10.78.

1,3-Bis-ethoxycarbonyloxy-propane (**5s**): colorless oil, b.p. 80–84°C/0.02 mm Hg; ^1H NMR ($CDCl_3$) δ 4.23 (t, 4H, $J = 6.3$ Hz, 2 $CH_2\underline{CH_2}O$), 4.18 (q, 4H, $J = 7.1$ Hz, 2 $CH_3\underline{CH_2}O$), 2.04 (m, 2H, $J = 6.3$ Hz, $OCH_2\underline{CH_2}CH_2O$), 1.30 (t, 6H, $J = 7.1$ Hz, 2 CH_3); IR (NaCl) 1746 cm^{-1}; MS m/z ($M^+ + 1$) 221 (2), 131 (100). Anal. Calcd. for $C_9H_{16}O_6$: C, 49.09; H, 7.32. Found: C, 48.93; H, 7.19.

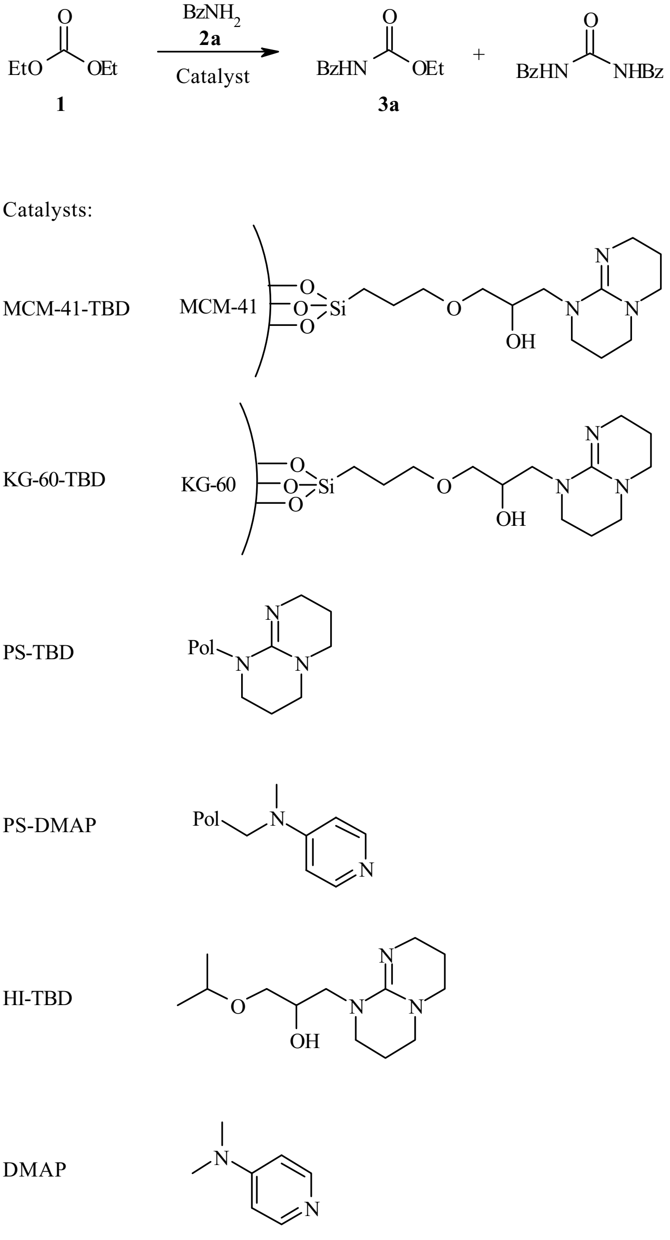
1,6-Bis-ethoxycarbonyloxy-hexane (**5t**): colorless oil, b.p. 115–120°C/0.02 mm Hg [lit. (18) b.p. 130–140°C/0.8 mm Hg]; ^1H NMR ($CDCl_3$) δ 4.18 (q, 4H, $J = 7.1$ Hz, 2 $CH_3\underline{CH_2}O$), 4.12 (t, 4H, $J = 6.6$ Hz, 2 $CH_2CH_2\underline{CH_2}O$), 1.8-1.6 (m, 4H, 2 $CH_2\underline{CH_2}CH_2O$), 1.5-1.3 (m, 4H, 2 $\underline{CH_2}CH_2CH_2O$), 1.30 (t, 6H, $J = 7.1$ Hz, 2 CH_3); IR (NaCl) 1745 cm^{-1}; MS m/z ($M^+ + 1$) 263 (100), 173 (22). Anal. Calcd. for $C_{12}H_{22}O_6$: C, 54.95; H, 8.45. Found: C, 55.11; H, 8.53.

3. RESULTS AND DISCUSSION

3.1. Catalyst Effect on Carbamate Synthesis

To check the feasibility of our approach, the model reaction between benzylamine **2a** and diethylcarbonate **1** (DEC) employed as solvent–reagent was performed in the presence of two solid catalysts prepared by immobilization of TBD on mesoporous MCM-41 silica (MCM-41–TBD) (19) or amorphous silica KG-60 (KG-60–TBD) (20) following the methodology reported in the literature (15). These prepared catalysts were compared with two commercially available basic solid catalysts usually employed in *trans*-esterification reactions, namely 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine polystyrene-bound (PS–TBD; Aldrich) and dimethylaminopyridine polystyrene-bound (PS–DMAP; Aldrich). All the reactions were carried out at 125°C for 4 h with 0.100 g of MCM-41–TBD, 0.220 g of KG-60–TBD, 0.04 g of PS–TBD, or 0.07 g of PS–DMAP, corresponding to the same amount of supported base (0.10 mmol). For comparison the reaction was performed under homogeneous conditions using 7-(2-hydroxy-3-isopropoxy-propyl)-1,5,7-triazabicyclo[4.4.0]dec-5-ene (HI–TBD) (0.10 mmol, 0.026 g) containing the same molecular framework as the supported TBD and 4-dimethylaminopyridine (DMAP) (0.10 mmol, 0.012 g) (see Scheme 2).

The preliminary results showed the total inertia of DMAP and PS–DMAP, whereas MCM-41–TBD, KG-60–TBD, PS–TBD, and HI–TBD afforded carbamate **3a** in 56, 40, 6, and 53% yield, respectively. At this point we decided to focus our attention on the activity of the three best catalysts. Yields of product **3a** *versus* time for the three reactions are shown in Fig. 1.



SCHEME 2

The activity of MCM-41–TBD strongly parallels that of the corresponding homogeneous counterpart, whereas the KG-60–TBD shows lower efficiency. These results seem to confirm that the level of structural order of the inorganic support can influence the catalyst efficiency since the supported active sites are more easily accessible in the mesoporous structure than in the amorphous material (21). In fact, diffusion of reagents and products through the

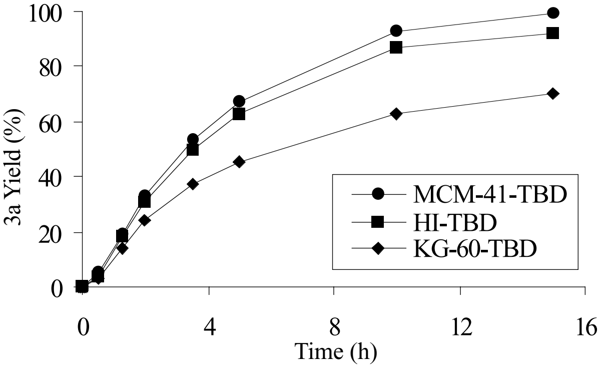


FIG. 1. Reactivity of benzylamine **2a** with diethylcarbonate **1** over different TBD-based catalysts as a function of time.

long-range ordered mesoporous material MCM-41–TBD with a surface area of 385 $m^2\ g^{-1}$ is expected to be almost completely unrestricted, while KG-60–TBD with a completely disordered pore distribution and a surface area of 155 $m^2\ g^{-1}$ can suffer from some diffusion resistance, which can render more difficult the access to the active sites. Finally, all reactions are characterized by high selectivity since the carbamate **3a** is the sole reaction product detected.

The solid catalyst could be efficiently reused for almost three further cycles after filtration, washing with diethyl ether and drying at rt under vacuum, giving product **3a** in 97, 97, and 93% yield, respectively (total TON [in mol of product (mol of catalyst)$^{-1}$] evaluated for four cycles is 385).

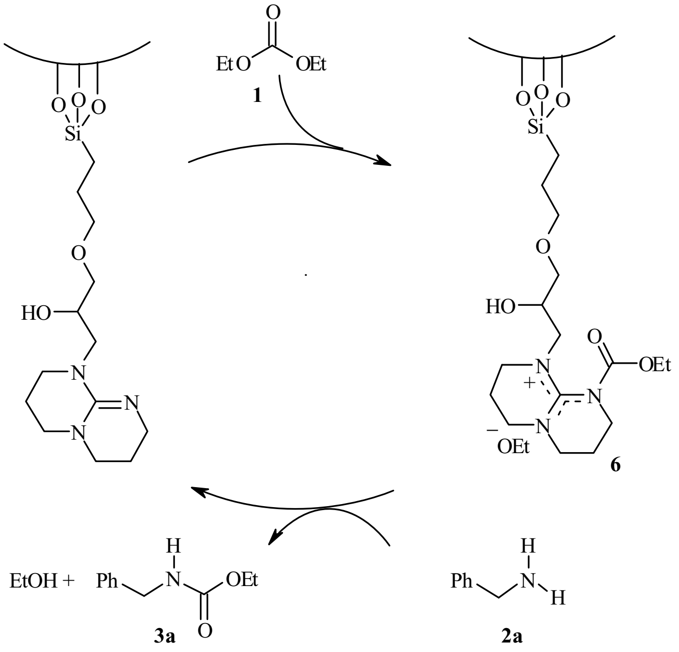
3.2. Leaching Test

To exclude the possible leaching of any active catalytic species in solution, the model reaction was examined by following the standard procedure suggested by Lempers and Sheldon (22). Thus the reaction mixture was filtered at 125°C after 4 h (when **3a** was produced in 58% yield) and the filtrate was further heated at 125°C for 12 h. Product **3a** was detected in 60% total yield (58% + 2%). In contrast, addition of both DEC (20 ml) and benzylamine **2a** (10 mmol, 1.07 g, 1.09 ml) to the recovered solid catalyst and heating at 125°C for 16 h afforded the carbamate **3a** in 95% yield. These results confirm that the reaction really occurs on the supported TBD active sites (23).

3.3. The Mechanism

Although work on mechanistic details is still in progress, it is hypothesized that the present transformation may have resulted from a catalytic cycle, depicted in Scheme 3.

As a strong base (24), the supported TBD is sufficiently nucleophilic to attack the carbonyl group of diethyl carbonate, giving the guanidinium salt **6**. Subsequent attack of the amine on the activated carbonyl group of **6** gives the product **3a** and restores the catalyst. This step is particularly favored since the positive charge, delocalized over the three nitrogens, promotes the nucleophilic attack to the carbonyl by enhancing its electrophilic character in a way similar to that observed with acylpyridinium salts (25).



SCHEME 3

Of course an EtO^- counterion may be the actual basic catalyst, and some reactions were performed to test this hypothesis. However, **3a** is only produced in traces (∼5%) in the presence of EtONa (0.10 mmol, 0.007 g) in DEC (20 ml), proving that ethoxide is not the catalyst.

To support this mechanistic hypothesis we compared the FT-IR spectra of MCM-41–TBD material before and after treatment with DEC and benzylamine at 125°C for 15 h (Fig. 2). The spectrum of the material treated with DEC (Fig. 2B) shows the appearance of a band at 1676 cm^{-1} of the C=O stretching, while the band of the C=N stretching shifts from 1636 to 1599 cm^{-1} as a consequence of the double bond weakening in the guanidinium ion **6**. The

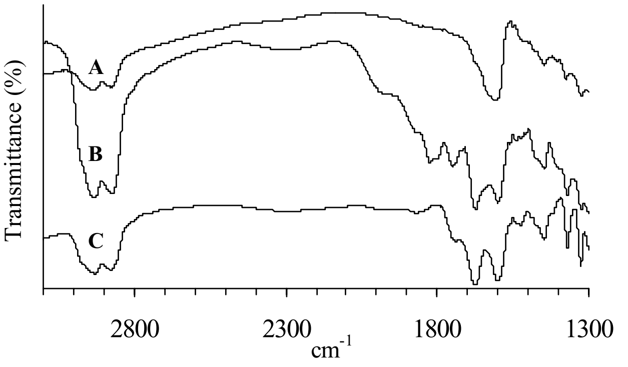


FIG. 2. FT-IR spectra of MCM-41–TBD (A), MCM-41–TBD treated with DEC (B), and MCM-41–TBD treated with DEC and benzylamine (C).

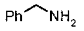
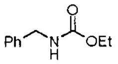
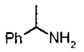
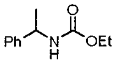
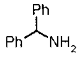
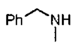
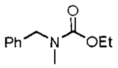
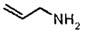
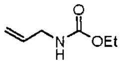
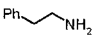
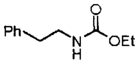
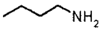
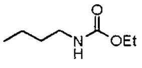
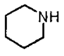
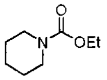
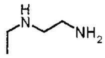
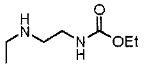
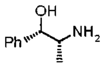
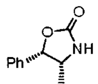
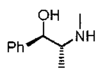
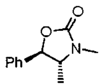
catalyst treated with DEC and washed with diethyl ether to remove physically absorbed DEC was treated with benzylamine under general reaction conditions (Fig. 2C), giving the product **3a** detected in the reaction mixture by GLC analysis. Obviously, the FT-IR spectra of the catalyst before and after treatment with benzylamine are quite similar since the reaction is carried out in DEC as solvent–reagent and consequently the catalyst is always present in the reaction mixture as *N*-carbethoxyguanidinium **6**.

3.4. Synthesis of Carbamates and Unsymmetrical Carbonates

With the reaction conditions for the model compound optimized, we sought application in the synthesis of carbamates and unsymmetrical carbonates. Accordingly, DEC was reacted with aliphatic amines in the presence of the MCM-41–TBD catalyst, affording carbamates (Table 1) (26). The reaction seems to be of general applicability with respect to the amine and proceeds efficiently and selectively at 125°C in 15 h. Only with an increased steric hindrance in the proximity of the amino group are longer reaction times and larger quantities of catalyst required (Table 1, entries b, j, and k). Similarly, the primary amine becomes the sole reaction site in a substrate containing both primary and secondary amino groups (Table 1, entry i). Finally, as expected, chiral 1,2-aminoalcohols gave the corresponding oxazolidin-2-ones with complete retention of the optical activity (Table 1, entries j and k).

TABLE 1

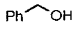
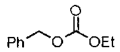
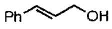
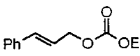
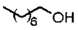
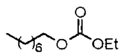
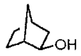
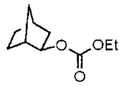
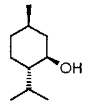
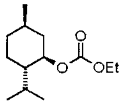
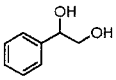
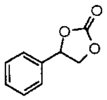
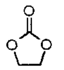
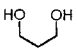
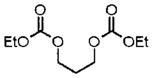
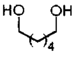
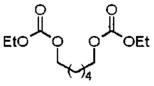
Synthesis of Carbamates 3

Entry	Reagent	Product	Yield (%)	Selectivity (%)
a			98	99
b			16 52^a	98 97
c		-	0	0
d			76	97
e			55	98
f			82	97
g			72	98
h			90	98
i			89	97
j			59^a	86
k			72^a	87

[a] Carried out for 24 h with 200 mg of MCM-41–TBD.

TABLE 2

Synthesis of Unsymmetrical Alkyl Carbonates 5

Entry	Reagent	Product	Yield (%)	Selectivity (%)
l			96	99
m			94	97
n			95	99
o			80	94
p			60 96^a	97 98
q			80	95
r			95	98
s			94	97
t			92	95

[a] Carried out for 24 h.

A quite similar behavior was observed in the reaction of DEC with alcohols to give unsymmetrical alkyl carbonates. By using benzyl alcohol as the model substrate, the reaction carried out with both HI–TBD and MCM-41–TBD was faster (96 and 93% yield, respectively, after 8 h) than the similar reaction for the preparation of carbamates (92 and 99% yield, respectively, after 15 h). However, at shorter reaction times (3 h), the homogeneous catalyst HI–TBD afforded the unsymmetrical carbonate **5l** in higher yield (72%) than did the heterogeneous MCM-41–TBD (46%).

Different unsymmetrical alkyl carbonates were synthesized in good yield and excellent selectivity (Table 2). The steric hindrance in proximity to the reactive hydroxy group represents again a limiting factor (Table 2, entries o, p, and q). It is noteworthy that whereas 1,2-diols gave the cyclic carbonates (Table 2, entries q and r), cyclic products are not formed when the number of methylene groups between the alcohol functions increases. Thus, with 1,3- and 1,6-diols, the linear biscarbonates become the sole reaction products (Table 2, entries s and t).

4. CONCLUSIONS

In conclusion, we have shown that the hybrid organic–inorganic material prepared by anchoring TBD to MCM-41 silica can be utilized as efficient heterogeneous basic catalyst for the synthesis of carbamates and unsymmetrical alkyl carbonates by reaction of DEC with aliphatic amines or alcohols. Products are obtained in high yield and selectivity and the solid catalyst can be recovered simply by filtration and reused for different cycles without apparent lowering of activity. A supported *N*-carbethoxyguanidinium active intermediate is proposed, and some spectroscopic data are shown to support the mechanistic hypothesis.

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19. The loading of MCM-41–TBD catalyst is 1.04 mmol/g, the surface area is 385 $m^2\ g^{-1}$, and the material is thermally stable up to 200°C.
20. The loading of KG-60–TBD catalyst is 0.47 mmol/g, the surface area is 155 $m^2\ g^{-1}$, and the material is thermally stable up to 200°C.
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23. For comparison the model reaction was performed using unfunctionalized MCM-41 silica under standard conditions. Recovery of all unchanged reagents confirms the inertia of the inorganic support in the present reaction.
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26. Unfortunately, under the present conditions aromatic amines showed lower reactivity and gave mixtures of carbamates and ureas: for example, the reaction carried out with aniline gave a mixture of phenyl carbamate ethyl ester (28%) and diphenylurea (24%).