Atom-economy Synthesis of N-Substituted Carbamate from Urea Derivative and Dimethyl Carbonate Catalyzed by La/SiO₂: **Characterization and Activity**

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A series of silica gel immobilized lanthanum catalysts were prepared for the atom-economy synthesis of N-substituted carbamates from urea derivatives and dimethyl carbonate. The La/SiO₂ catalysts with lanthanum loadings varied from 1.3 wt% to 8.5 wt% were characterized by AES, BET, XRD, TEM, FT-IR, XPS and TPD. According to the characterization, lanthanum species with particle sizes of 5-10 nm on the surface of silica gel were formed. The catalysts were all amorphous and the surface areas were 336.5-530.2 m²/g. NH₃-TPD analysis showed that all samples exhibited similar acid strength with different acid amounts. FT-IR measurement indicated that the component of lanthanum species on the catalyst surface were La(OH)₃, LaOOH and hydrated La₂O₃. Also, the peak value of the absolute amount of LaOOH was obtained with 4.3 wt% lanthanum loading. The BET surface area decreased dramatically when the lanthanum loading was above 4.3 wt%. In consideration of the results obtained from the catalytic reactions, it could be concluded that LaOOH was the possible active species and high surface area was important for the high catalytic activity.

Keywords *N*-substituted carbamate, urea derivative, dimethyl carbonate, lanthanum, green chemistry

Introduction

Organic carbamates are key intermediates for the synthesis of pharmaceuticals, pesticides, fungicides and herbicides.¹⁻⁸ Moreover, it has become the potential compound for the non-phosgene synthesis of isocyanate via thermal decomposition. Unfortunately, till today, the most convenient method for the synthesis of these products is the aminolysis of chloroformate, which is produced from phosgene and alcohols.^{9,10} Although it is a versatile technique for carbamate synthesis, the toxicity and corrosion properties of phosgene and hydrogen chloride have caused severe environmental problems.¹¹ In the last decades, great efforts have been made in order to explore an environmentally benign method for carbamate synthesis. The classical research work in this area is the carbonylation of nitroaromatics and amines catalyzed by various transitional metal complexes.¹²⁻¹⁷ Also, dimethyl carbonate as a green carbonylation reagent has attracted extensive attention.¹⁸⁻²¹ Apart from carbon monoxide and dimethyl carbonate, carbon dioxide should be an ideal carbonyl source in chemical industry. In addition to its nontoxic character, the release of "green house" gas could be reduced if carbon dioxide as carbonyl source can be realized. The difficulty in realization of this target is the inert property of carbon dioxide. It has been reported that carbamates could be synthesized with amine and alkyl halide as starting materials and carbon dioxide as carbonyl source.^{22,23} Unfortunately, the use of alkyl halide would produce a large amount of inorganic waste. It has been reported that disubstituted ureas could be synthesized from amine and carbon dioxide.²⁴⁻²⁶ As it is known, organic carbamate could be obtained through the alcoholysis of urea derivatives and the amine byproduct from the disubstituted urea could be recycled for the next run.^{27,28} Undoubtedly, it is gratifying if all the fractions inside disubstituted urea could be transferred into a carbamate molecule. The synthesis of N-substituted carbamate using urea and dimethyl carbonate as starting materials offered a nice method to solve this problem.²⁹⁻³¹ The indirect employment of carbon dioxide as carbonyl source therefore is also realized. Here we present the new results about N-substituted carbamate synthesis from urea and dimethyl carbonate using silica gel immobilized nano lanthanum as catalyst, as shown in Scheme 1.

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Scheme 1 Indirect use of carbon dioxide in organic *N*-substituted carbamate synthesis



Experimental

Catalyst preparation

Lanthanum nitrate $[La(NO_3)_3 \circ 6H_2O, ca. 0.66 g]$ and urea (*ca.* 0.15 g) were dissolved in *ca.* 25 mL of distilled water. The molar ratio of lanthanum to urea was *ca.* 1 : 1.7. 5.0 g of silica gel (200—300 mesh, BET surface area=601.1 m²/g, pore volume=0.74 cm³/g, average pore diameter=4.93 nm. It was pretreated at 600 °C for 4 h before use) was dropped into the solution under ultrasound irradiation. The suspension was further magnetically stirred at 90 °C for 3 h and the final pH value of the system was *ca.* 8. Then it was filtrated and dried in air at 100 °C for 4 h. It was further calcined at 600 °C for 4 h and *ca.* 5.2 g of 4.3 wt% La/SiO₂ catalyst was obtained. By varying the quantity of La(NO₃)₃•6H₂O added, catalysts with different lanthanum loadings were obtained with the same procedure.

Characterization of the catalysts

The loadings of La were determined on an inductively coupled plasma-atomic emission spectrometer (ICP-AES) (ThermoElemental Company in the USA) by dissolving the samples in aqueous nitric acid.

The BET surface area, pore volume and average pore diameter of catalyst were measured by physisorption of N₂ at 76 K using a Micromeritics ASAP 2010 instrument. Before the measurement, the samples were degassed at 200 $^{\circ}$ C for 12 h to remove adsorbed gases from the catalyst surface. The isotherms were elaborated according to the BET method for surface area calculation, with the Horwarth-Kavazoe and BJH methods used for micropore and mesopore evaluation, respectively.

TPD analysis with NH₃ was carried out on an improved GC112 instrument to study the acidity of the catalyst surface. In a typical experiment, 250 mg of dried sample (dried at 120 °C for 5 h) was taken in a U-shaped quartz sample tube. The sample was pretreated under argon flow (50 mL/min) at 500 °C for 1 h. After pretreatment, the sample was cooled to ambient temperature under argon and then treated by a 10% NH₃-Ar mixture (75 mL/min) for 1 h at 40 °C. After being flushed with pure argon (50 mL/min) at 100 °C for 1 h to remove physisorbed NH₃, TPD analysis was carried out from 100 to 500 $^{\circ}$ C at a heating rate of 10 $^{\circ}$ C/min under argon flow of 50 mL/min.

X-ray photoelectron spectroscopy (XPS) was performed with a VG ESCALAB 210 instrument. Mg K α radiation was used with a pass energy of 150 eV at an energy scale calibrated versus C 1s peak at 285.00 eV arising from adventitious carbon.

X-ray diffraction (XRD) was measured on a Siemens D/max-RB powder X-ray diffractometer. Diffraction patterns were recorded with Cu K α radiation (30 mA, 40 kV) over a 2 θ range of 10° to 50° with a position-sentient detector using a step size of 0.017°.

High resolution transmission electron microscopic (HR-TEM) investigations were carried out using a JEOL JEM-2010 Electron Microscope. The powder of catalysts was suspended in ethanol by ultrasonic dispersion for 5—10 min and then the resulting solution was dropped on a carbon film supported by a 300 mesh copper grid.

FT-IR analysis was conducted with a Nicolet 910 FT-IR spectrometer. Samples with different lanthanum loadings were loaded on the sample holder (KBr) to form a uniform thin layer.

Qualitative and quantitative analyse were carried out with GC-MS (HP 6890/5973), GC-FID (Agilent 6820, biphenyl was used as an internal standard), ¹H NMR (Bruker AMX FT 400-MHz) and ¹³C NMR (Bruker AMX FT 100-MHz).

General procedure

All reactions were conducted in a 90 mL stainless steel autoclave with a glass tube inside equipped with magnetic stirring. In each reaction, urea derivative (5 mmol), dimethyl carbonate (15-75 mmol) and 50 mg of La/SiO₂ catalyst were charged respectively into the autoclave. After being flushed with N₂, it was heated up to 150 $^{\circ}$ C and reacted for 6–12 h. Then, the autoclave was cooled to room temperature and opened to air. The catalyst was separated by centrifugation and filtration. The pure compounds were obtained with different procedures. For compound 1, the solvent was removed and pure product could be obtained after the solid was further washed by hexane/diethyl ether and then vacuum dried. For compounds 2, 3 and 4, the products were purified by column chromatography [silica gel, V(petroleum ether) : V(methylene dichloride) = 7.5 : 2.5]. For compounds 5 and 6, the solvent and DMC were removed and pure products could be obtained after the solids were further washed by hexane/acetone and vacuum dried. For compounds 7, 8 and 9, the solvent and DMC were removed and the carbamates could be achieved after the solid was further washed by ethanol/diethyl ether or ethanol/hexane and vacuum dried.

Results and discussion

Characterization of catalysts

BET analyse of pure silica gel and the silica gel im-

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mobilized La samples are given in Table 1. Clearly, the BET surface area and pore volume decreased after the immobilization of lanthanum. For the average pore diameter, it kept constant at the initial stage but dropped dramatically when the lanthanum loading was higher than 4.3 wt%. This turning point was also observed on the surface area and pore volume measurement. The BET surface area was *ca*. 500 m²/g and the pore volume was between 0.59—0.74 cm³/g when lanthanum loadings were lower than 4.3 wt%. However, the BET surface area was only 336.5 m²/g and the pore volume was 0.44 cm³/g when the lanthanum loading reached 8.5 wt%. Therefore, 4.3 wt% La/SiO₂ might be a good composition for this catalyst based on the BET measurement.

Table 1 BET parameters of the catalysts

Entry	Catalyst	Area ^a /	Vol. ^b /	$d^{c}/$
		$(m^2 \bullet g^{-1})$	$(cm^3 \cdot g^{-1})$	nm
1	SiO ₂	601.1	0.74	4.9
2	1.3 wt% La/SiO ₂	530.2	0.67	5.0
3	3 wt% La/SiO ₂	496.9	0.63	4.8
4	4.3 wt% La/SiO ₂	447.3	0.59	5.3
5	6.4 wt% La/SiO ₂	388.5	0.47	4.1
6	8.5 wt% La/SiO ₂	336.5	0.44	3.8

^{*a*} BET surface area. ^{*b*} Volume of pore. ^{*c*} Average pore diameter.

Through the NH₃-TPD measurement, similar acid strength with different acid amounts was observed in all samples (Figure 1). The acidity of the catalysts is possibly originated from the silica gel surface. The incorporation of lanthanum species caused slight weakness of the surface acidity. Furthermore, the acid amount was decreased dramatically when the lanthanum loading was above 4.3 wt%. This is consistent with the observation of the BET analysis. The remarkable decreasing in surface area leads to less acid amount.



Figure 1 NH₃-TPD profile of La/SiO₂ sample. The loadings are 0 wt%, 1.3 wt%, 4.3 wt%, 6.4 wt% and 8.5 wt% respectively from the topside.

XPS analysis has been performed in order to understand the surface structure of silica gel immobilized lanthanum catalysts well (Figure 2). The spectrum of Si 2s was served as the preferable choice to reduce the disturbance of electron binding energy between La 4d and Si 2p. The La 3d signals consist of the $3d_{3/2}$ and $3d_{5/2}$ spin-orbit doublets, and the La $3d_{5/2}$ peaks are centered at 835.8, 835.8, 835.9 and 836.0 eV for catalysts with different lanthanum loadings. The binding energy (B.E.) value for current La features is in agreement with the standard XPS data, *i.e.* La³⁺ ion.³² So the chemical state of the surface lanthanum species is La³⁺.



Meantime, the atom ratio of La 3d/Si 2s of 4.3 wt% La/SiO₂ is 0.48. The theoretical value for a monolayer dispersion according to models proposed in former reports is 0.49.^{33,34} So it can be assumed that the lanthanum species is monolayer dispersed on the silica gel surface.

Typical XRD patterns obtained from pure SiO₂, 4.3 wt% La/SiO₂ and 8.5 wt% La/SiO₂ were presented in Figure 3. Clearly, pure silica gel, 4.3 wt% La/SiO₂ and 8.5 wt% La/SiO₂ exhibited similar patterns. The immobilization of La on silica gel has resulted in negligible effect on the crystal structure of catalyst samples. The silica gel itself is amorphous and highly dispersed lanthanum is formed. According to the XRD measurement, it could be concluded that the increment of lanthanum loading did not cause aggregation and crystallization of lanthanum.



Figure 3 XRD patterns of pure SiO₂, 4.3 wt% and 8.5 wt% La/SiO₂ samples.

Typical HR-TEM pictures of samples 4.3 wt% La/SiO_2 and 8.5 wt% La/SiO_2 are shown in Figure 4,

which confirmed the suggestions of XRD measurement. Similar lanthanum species particle size was observed over different samples. The particle size of lanthanum species is ca. 5—10 nm in all the samples. Also, from the TEM analysis, all the samples showed uniform structures.



Figure 4 HR-TEM images of the 4.3 wt% (left) and 8.5 wt% (right) La/SiO₂ samples.

To further investigate the composition of lanthanum, a series of catalysts with varied lanthanum loadings, *i.e.*

3 wt%, 4.3 wt% and 8.5 wt%, were investigated by FT-IR (Figure 5). From the IR spectra, the most significant change for different loading catalyst occurs in the region of OH vibrations. As it can be seen from Figure 5a, sample of lanthanum oxide under air included four typical peaks (3608, 3449, 1636 and 641 cm^{-1}). For the FT-IR spectra of immobilized lanthanum catalysts, the peak at 641 cm⁻¹ disappeared completely, and the peak at 3608 cm^{-1} [La(OH)₃], 3449 cm⁻¹ (LaOOH) and 1636 cm^{-1} (possibly absorbed water) still existed.³⁵⁻³⁷ The results showed that there was no lanthanum oxide maintained in the La/SiO₂ catalysts. Samples of 3-8.5 wt% La/SiO₂ catalysts presented a broad band from 3700 to 3200 cm^{-1} , and it was further fitted with three peaks $(3608, 3449 \text{ and } 3246 \text{ cm}^{-1})$, which could originate from three different types of surface OH groups [*i.e.* La(OH)₃ (I), LaOOH (II) and hydrated La_2O_3 (III)]³⁵ (Figure 5b— 5d).

Additionally, the relative contents of $La(OH)_3$, La-OOH and hydrated La_2O_3 for 3–8.5 wt% La/SiO₂ catalyst were listed in Table 2. With increasing the



Figure 5 FT-IR spectra of La/SiO₂ catalysts. (a) 1: La₂O₃, 2: 3 wt% La/SiO₂, 3: 4.3 wt% La/SiO₂, 4: 8.5 wt% La/SiO₂; (b) 1: OH group of La₂O₃, 2: OH group of 3 wt% La/SiO₂; (c) OH group of 4.3 wt% La/SiO₂; (d) OH group of 8.5 wt% La/SiO₂; all the samples were calcined at 600 $^{\circ}$ C under air for 5 h. The peaks in b, c and d were fitted with the I, II and III peaks.

Cable 2 Relative content of OH compound on differently loaded catalysts su	.rface ^a
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Loading	La(OH) ₃	LaOOH	Hydrated La ₂ O ₃	Absolute amount of LaOOH ^b
3 wt%	8.2%	79.4%	12.4%	2.8%
4.3 wt%	8.7%	77.1%	14.2%	3.9%
8.5 wt%	20.2%	33.5%	46.3%	3.4%

^{*a*} Each peak area was calculate by integrating the fitted Gaussian equation, and then using a normalization method, the relative contents were obtained. ^{*b*} The content of LaOOH on SiO₂ surface=Loading × Relative content of LaOOH.

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lanthanum loadings, the relative contents of $La(OH)_3$ and hydrated La_2O_3 increased correspondingly. However, the relative content of LaOOH increased initially and reached a maximum (absolute amount *ca.* 3.9 wt%) with 4.3 wt% lanthanum loading, and then decreased.

Results for reaction condition optimization and discussion

The catalyst screening and reaction condition optimization were carried out over the reaction of N,N'-dicyclohexyl urea (DCU) and dimethyl carbonate (DMC) (Table 3). The blank reaction was tested in the absence of catalyst and the yield to methyl N-cyclohexyl carbamate (MCC) was <1% (Entry 1). As it can be imagined, 28% MCC formed if silica gel itself was used as catalyst (Entry 2). According to the NH₃-TPD analysis, there was a large amount of acid upon silica gel surface. This is helpful for this transesterification. Excellent yield could be obtained when silica gel immobilized lanthanum was used as catalyst (Entries 3-7). According to the isolated yield, the optimal composition of the catalyst was 4.3 wt% La/SiO2. The isolated yield to MCC reached 90% together with 94% selectivity. Higher or lower lanthanum loading led to lower conversion of starting material and lower yield of the desired product, which means both the activity and selectivity of the catalyst decreased.

The characterization of the catalyst samples gives a good explanation to this phenomenon. By the HR-TEM measurement we can know that the particle size is

unchanged with increasing the lanthanum loading, which suggests that the lower activity is not due to the aggregation of catalytically active species. The XRD characterization showed there was no crystallization occurring with increasing the lanthanum loading. Similar information was obtained from XPS analysis. However, the surface area, pore volume and average pore diameter all decreased severely based on the BET analysis when the loading was higher than 4.3 wt%. FT-IR measurement revealed the highest LaOOH absolute amount in 4.3 wt% La/SiO₂ catalyst. Therefore, the possible active catalyst species is LaOOH and high surface area is also important.

Although a good result was obtained under reaction conditions as mentioned above, the usage of a large excess of DMC made the practical application difficult. Other organic solvent was therefore chosen to improve the reaction with less DMC as reactant. Three typical organic solvents, i.e. DMF, THF and toluene, were used to explore the possibility (Entries 8-11). Interestingly, the non-polar toluene exhibited a more positive result than the polar DMF and THF. The yield to MCC reached 74% with 85% conversion of DCU when the molar ratio of DCU to DMC was 1:3. If the molar ratio of DCU to DMC was increased to 1:5, the yield to MCC was 88%. This result was better than the self-solvent system, in which the molar ratio of DCU to DMC was 1:15. Undoubtedly, the application of solvent to this reaction can efficiently promote the formation of carbamate.

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	DCU [DMC		
Entry	Catalyst	Conv. ^b /%	Sel. ^{<i>c</i>} /%	Yield ^d /%
1	None	<5%	—	—
2^e	SiO_2	41	82	28
3	1.3 wt% La/SiO ₂	70	92	59
4	3 wt% La/SiO ₂	88	92	75
5	4.3 wt% La/SiO ₂	>99	94	90
6	6.4 wt% La/SiO ₂	98	91	85
7	$8.5 \text{ wt\% La/SiO}_2$	96	91	83
8 ^{f1}	4.3 wt% La/SiO ₂	35	60	15
9 ^{f2}	4.3 wt% La/SiO ₂	68	80	50
10 ^{f3}	4.3 wt% La/SiO ₂	85	92	74
11^g	4.3 wt% La/SiO ₂	97	94	88

 Table 3
 Catalyst screening and reaction condition optimization^a

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^{*a*} 5 mmol (1.12 g) of DCU, 75 mmol (8 mL) of DMC, 50 mg of (0.1—0.5 mol% La) catalyst, 150 °C, 6 h. ^{*b*} Conversion of DCU determined by GC-FID. ^{*c*} Chemoselectivity to methyl *N*-cyclohexyl carbamate determined by GC-FID. ^{*d*} Isolated yield. All the compounds were characterized by ¹H NMR, ¹³C NMR and MS analysis. ^{*e*} Commercial compound (200—300 mesh, BET surface area=601.1 m²/g, pore volume=0.74 cm³/g, average pore diameter=4.93 nm). It was pretreated at 600 °C for 4 h and then cooled in a drier before use. ^{*f*1-*f*3} 5 mmol (1.12 g) of DCU, 15 mmol (1.6 mL) of DMC, 5 mL of solvent, 50 mg of 4.3 wt% La/SiO₂, 150 °C, 6 h. The solvents were DMF, THF and toluene from *f*1 to *f*3, respectively. ^{*g*} 5 mmol (1.12 g) of DCU, 25 mmol (2.7 mL) of DMC, 5 mL of toluene, 50 mg of 4.3 wt% La/SiO₂, 150 °C, 6 h.

Generality investigation

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By applying the optimized reaction condition, the generality of the silica gel immobilized lanthanum in carbamate synthesis from urea derivatives and dimethyl carbonate was investigated (Table 4). Aliphatic urea derivatives with different structures were firstly studied. The isolated yields to corresponding carbamates were 81%—90% (Entries 1—5). The structure of side chains of the urea derivatives has less effect on the formation of carbamates although the presence of benzyl group needs a little bit longer reaction time. Excellent yields were also obtained when aromatic urea derivatives were used as starting materials (Entries 6-9). The isolated yields were 72%-85% for three typical aromatic urea derivatives, i.e. N,N'-diphenyl urea, N,N'-di-4-tolyl urea and N,N'-di-4-chlorophenyl urea.

To our delight, a 78% isolated yield to methyl N-tosylcarbamate was achieved when N,N'-carbonylbis-(4-toluenesulfonamide) was employed as starting material (Entry 9).

Table 4 Scope and limitation of 4.3 wt% La/SiO₂ catalyzed carbamate synthesis from urea and dimethyl carbonate^a

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	$N_{R} + O_{O}$.0 <u> </u>	a/SiO ₂ ► R	
Entry	R	t/h	Conv. ^b /%	Yield ^c /%
1	C Str	6	97	88
2^d	()35,	6	94	81
3	() ³ / ₆	6	96	86
4	()35 11	8	>99	90
5	and the second s	12	95	82
6	C Sol	12	92	79
7		12	95	85
8	CI	12	88	72
9	O S S S S S S S S S S S S S S S S S S S	12	90	78

^a 5 mmol of disubstituted ureas, 25 mmol of dimethyl carbonate, 5 mL of toluene, 50 mg of La/SiO₂ (0.3 mol% La), 150 °C.^b Conversion of urea. ^c Isolated yield. ^d 120 °C.

Conclusion

In conclusion, a series of silica gel immobilized lanthanum catalysts were successfully prepared for the syntheses of N-substituted carbamates from urea derivatives and dimethyl carbonate. This method is simple, easily operable and general. And different methyl carbamates with various structures were synthesized with high isolated yields.

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