# Calcined Mg-Al Layered Double Hydroxide as a Heterogeneous Catalyst for the Synthesis of Urea Derivatives from Amines and CO<sub>2</sub><sup>†</sup>

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The calcined Mg-Al layered double hydroxides (LDHs) with a Mg/Al molar ratio of 3: 1 were synthesized and characterized thoroughly by X-ray diffraction (XRD), temperature-programmed desorption (TPD) of CO<sub>2</sub>, and thermogravimetric analysis (TGA). Thus the calcined Mg-Al LDHs were used as catalyst for the catalytic synthesis of disubstituted ureas from amines and CO<sub>2</sub>. The effects of reaction time, reaction temperature, pressure, solvent and calcined temperature on activity have been investigated. The results indicated that aliphatic amines, cyclohexylamine and benzylamine can be converted to the corresponding ureas selectively over the calcined Mg-Al LDHs catalysts with *N*-methyl-2-pyrrolidone (NMP) as solvent without using any dehydrating regent. The catalyst can be recycled several times with only slight loss of activity.

**Keywords** carbon dioxide, 1,3-disubstituted urea, hydrotalcites, layered double hydroxide, heterogeneous catalysis

## Introduction

There is currently necessary for alternatives to chemical feedstocks for the fine chemicals industry that is independent of oil. Carbon dioxide has emerged as a renewable candidate for its abundance, non-toxicity and non-inflammability. However, its use as a C-1 reagent poses big challenges for its thermodynamic and kinetical stability. On the other hand, as we have known, N-containing compounds such as isocyanates, carbamates and 1,3-disubstituted urea derivatives are important chemicals. 1,3-Disubstituted urea derivatives are good chemical intermediates in the synthesis of agricultural chemicals, pharmaceuticals, and also widely used as antioxidants in gasoline and additives as well as in dye chemistry.<sup>[1,2]</sup>

Highly toxic phosgene is used as raw material in the traditional synthetic process of 1,3-disubstituted urea derivatives. Because of the high toxicity of phosgene, some alternative routes have been developed. Oxidative carbonylations of amines with CO as carbonyl resource are studied by using Au/polymer,<sup>[3]</sup> metallomacrocyclic compounds,<sup>[4]</sup> Ru(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>,<sup>[5]</sup> W(CO)<sub>6</sub>,<sup>[6]</sup> *etc.* as catalysts. However, CO is toxic and the mixture of carbon monoxide and air is dangerous. Thus expensive methylating reagent like dimethyl carbonate has also been used as alternative carbon source.<sup>[7]</sup> Because car-

bon dioxide is environmentally benign and conveniently available, therefore more and more concerns have been received to use carbon dioxide as direct carbon source to synthesize 1,3-disubstituted urea derivatives. Recently, the direct synthesis of 1,3-disubstituted urea derivatives from amines and CO<sub>2</sub> has been reported. Several types of catalysts, including strong inorganic bases  $Cs_2CO_3$ ,<sup>[8]</sup> homogeneous catalysts such as  $RuCl_3 \cdot H_2O/Bu_3P^{[9]}$  and titanium imido complexes,<sup>[10]</sup> the ionic liquid [Bmim]OH,<sup>[2]</sup> and supported base catalysts such as  $CsOH/IL^{[11]}$  and KOH/ PEG1000<sup>[12]</sup> have been utilized for this reaction. Although 1,3-disubstituted urea can also be synthesized from carbonylation of amines with  $CO_2$  in absence of any solvent and catalyst under optimal conditions,<sup>[13]</sup> the reaction conditions were harsh and remained to be improved.

The previously reported catalysts are normally expensive and difficult to be recycled. Clearly, to develop an efficient, cheaper and reusable catalytic system which can transform carbon dioxide and a series of organic amines into 1,3-disubstituted urea directly still remains challenges.

It was reported that solid base catalysts like LDHs could show an excellent performance in various basecatalyzed organic transformations and also be used as adsorbents for carbon dioxide or other acidic gases.<sup>[14,15]</sup>

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Received November 18, 2012; accepted January 31, 2013; published online March 14, 2013.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cjoc.201201143 or from the author.

<sup>&</sup>lt;sup>†</sup> Dedicated to the 60th Anniversary of East China University of Science and Technology.

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They can be seen as possessing a pair of strong basic sites ( $O^{2-}$  ions) and weak Lewis acid sites (co-ordinatively unsaturated  $Al^{3+}$  ions).<sup>[16,17]</sup> Inspired by the previous work,<sup>[18,19]</sup> we prepared a series of the calcined Mg-Al LDHs with Mg-Al LDH as precursor and then attempted to use the calcined Mg-Al LDHs as the catalyst for carbonylation of amine with CO<sub>2</sub>. Herewith, the LDH materials have been characterized and then applied in the synthesis of 1,3-disubstituted urea derivatives from direct carbonylation of various amines and CO<sub>2</sub> with 1-methyl-2-pyrrolidinone (NMP) as solvent. The reaction conditions have been optimized to achieve high catalytic performance.

## Experimental

## General

All chemicals were analytical grade and commercially available. They were used without further purification, unless otherwise stated.  $CO_2$  was supplied by Shanghai Shangnong Gas Factory with a purity of >99.95%.

### Synthesis of Mg-Al LDH

The Mg-Al LDHs used in this work were prepared via a co-precipitation technique. Briefly, 0.09 mol  $Mg(NO_3)_2 \cdot 6H_2O$  and 0.03 mol  $Al(NO_3)_3 \cdot 9H_2O$  were dissolved in 120 mL deionized water. The solution was then added, dropwise with vigorous stirring, to a 120 mL solution containing 0.24 mol NaOH and 0.03 mol Na<sub>2</sub>CO<sub>3</sub>. The mixture was then refluxed at 70 °C for 1 h with continuous stirring and the pH was maintained at 10. The resultant mixture was then aged at 70 °C for 18 h. The resulting precipitate was separated by vacuum filtration, washed with deionized water repeatedly and then dried at 80 °C in a vacuum drying oven overnight. Similarly, Zn-Al LDH was also prepared and characterized by XRD (Figure 1S).

#### Synthesis of the calcined Mg-Al LDHs

The Mg-Al LDHs were placed in a ceramic crucible with a lid and heated in muffle furnace at a ramp-rate of 5 °C/min to a specified temperature such as 550 °C. The material was held at this temperature for 6 h before being allowed to cool to room temperature at a rate of *ca.* 10 °C/min. The material obtained was stored ready for use in a dessicator filled with activated molecular sieve and color silica gel so as to minimise the uptake of atmospheric water. The material was recorded as Mg-Al LDH550. In the same way, a series of the calcined Mg-Al LDHs were prepared by calcining Mg-Al LDH at 450, 650, 750 and 850 °C, which were denoted as Mg-Al LDH450, Mg-Al LDH650, Mg-Al LDH750 and Mg-Al LDH850, respectively.

#### Procedure for the carbonylation reactions

Reactions were performed in 50 mL stainless steel autoclaves (32 mL with PTFE liner), equipped with pressure gauge and thermocouple. The desired amounts of amine, catalyst, and the organic solvent were loaded into autoclave, successively. Then the reactor was closed and purged three times with dry CO<sub>2</sub>. The reaction was magnetically stirred and heated in a temperature-controlled heating jacket. After reaction, the reactor was cooled under ice bath condition, and then carefully depressurized. The product was recovered by adding CH<sub>3</sub>OH to reaction mixture, and the catalyst was separated from the organic liquid phase by centrifuging. The liquid phase was analyzed by gas chromatograph (Shimadzu GC-2014, KB-50 capillary column, 30 m×0.32 mm×0.50 µm) and GC-MS (Agilent-6890GC-5973MS, HP-5MS, 30 m×0.25 mm×0.25 µm). Conversion and selectivity of products were then both obtained.

For the recycling of catalysts, the recovered Mg-Al LDH was regenerated by a thermal regeneration as reported in the previous literature.<sup>[20,21]</sup> After each run, the catalyst was recovered and then calcined according to the previous procedure.

### **Catalyst characterization**

The LDH structure and its evolution were identified by X-ray diffraction (XRD). The XRD patterns were recorded using a Rigaku D/max 2550VB/PC X-ray diffractometer (with a variable slit width). Graphite monochromator, Cu K $\alpha$  target ( $\lambda$ =0.15056 nm), tube voltage 40 kV, tube current 40 mA, emission slit (1/6)°, scan rate 6 (°)/min, scan area  $10-80^{\circ}$ . The samples were also characterized by thermogravimetric analysis (TGA) and N2 adsorption-desorption method. Thermal decomposition diagrams of the raw LDH and calcined samples were investigated through TGA instrument. All samples were heated at a constant heating rate of 10 °C/min in flowing anhydrous air (20 mL/min) from room temperature to 800 °C. The specific surface area (BET) was calculated by the N<sub>2</sub> adsorption-desorption method at 77 K using a Quantachrome Instrument. Prior to the experiments the catalysts were outgassed at 200  $^{\circ}$ C for 12 h under vacuum. Surface concentrations of the basic centers were determined by temperature-programmed desorption of carbon dioxide (CO2-TPD). CO2-TPD was carried under argon as carrier gas with flowing rate 20 mL/min. Prior to CO<sub>2</sub> adsorption, all prepared catalysts were pretreated at 100  $\,^{\circ}$ C for 1 h and exposed to a flow of CO<sub>2</sub> for 2 h. Desorption proceeded by heating (10  $^{\circ}C/$ min) up to the final temperature of 650  $^{\circ}$ C.

## **Results and Discussion**

#### The solvent effect

At first, we chose the direct carbonylation of butylamine (BA) and  $CO_2$  as a model reaction to examine the effect of solvents on the reaction (Scheme 1).

It was found that the butylamine conversion was only 10.1% (Table 1, entry 1) when the reaction was carried out in the absence of any solvent and catalyst under the present conditions. The activity was improved Scheme 1 Carbonylation of butylamine with CO<sub>2</sub>

$$CO_2 + n-Bu-NH_2 \longrightarrow n-Bu-N H H^0 - n-Bu + H_2O$$

slightly but still was relatively low if Mg-Al LDH550 was used as catalyst without any solvent (Table 1, entry 2). In the next step, the different solvents such as tertiary butanol, acetonitrile and NMP have been screened for the reaction. It was observed that the moderate conversion was afforded with NMP as solvent in the absence of catalyst (25.0%, Table 1, entry 3). While (CH<sub>3</sub>)<sub>3</sub>COH was used as reaction solvent very low butylamine conversion was obtained (Table 1, entry 4). Although CH<sub>3</sub>CN could afford higher butylamine conversion, the selectivity was too low (Table 1, entry 5). In contrast, good conversion and excellent selectivity can be achieved when NMP was used as solvent (Table 1, entry 6). The results above showed that different solvents affected the conversion considerably. Acetonitrile reacted with the substrate and thus the selectivity was poor. The basic solvent NMP gave best results. In contrast, tertiary butanol seemed to inhibit the reaction (Table 1, entries 2 and 4) due to its very weak solvation. It was reported that NMP experienced a volume expansion of ~30% when exposed to 2.5 MPa of  $CO_2$  at 25 °C.<sup>[8,22]</sup> which indicated that CO<sub>2</sub> can be dissolved in NMP considerably. In addition, NMP could also stabilize the ionic intermediates by the deprotonation,<sup>[23]</sup> which was favorable to the reaction. Thus NMP as solvent afforded the highest reaction activity.

**Table 1** Effect of different solvents on the carbonylation ofbutylamine with  $CO_2^a$ 

Entry	Catalyst	Solvent	Conv./%	Sel. <sup>b</sup> /%
1	None	None	10.1	≥99
2	Mg-Al LDH550	None	30.2	≥99
3	None	NMP	25.0	≥99
4	Mg-Al LDH550	(CH <sub>3</sub> ) <sub>3</sub> COH	5.2	≥99
5	Mg-Al LDH550	CH <sub>3</sub> CN	92.0	35.0 <sup>c</sup>
6	Mg-Al LDH550	NMP	67.0	≥99

<sup>*a*</sup> Reaction conditions: BA 32 mmol, pressure 3.0 MPa, temperature 170 °C, reaction time 6 h, NMP: 2 mL. 0.300 g Mg-Al LDH550 catalyst was charged if needed. <sup>*b*</sup> Selectivity to 1,3-disubstituted urea. <sup>*c*</sup> By-product was detected as *N*-butylacetamide.

For the sake of comparison, the different catalysts have been used with NMP as solvent for the reaction. As shown in Table 2, MgO,  $Al_2O_3$  and Zn-Al LDH gave only 5.7%, 36.8%, and 29.2% of butylamine conversion, respectively (Table 2, entries 1, 2 and 4). TiO<sub>2</sub> and Mg-Al LDH catalysts afforded moderate conversion as

44.5% and 48.2%, respectively (Table 2, entries 3 and 5), which demonstrated that Mg-Al LDH has an obvious advantage for this reaction. It has been reported that the basicity of the catalysts can play an important role in the reaction.<sup>[8]</sup> Therefore, the CO<sub>2</sub>-TPD was carried out to investigate further the distribution of the surface basic centers. Figure 1 showed the CO<sub>2</sub>-desorption curves of different catalysts. When considering the desorption temperature of CO<sub>2</sub>, it appeared that only weak basic centers existed on surfaces of Al<sub>2</sub>O<sub>3</sub> and MgO, while Mg-Al LDH and TiO<sub>2</sub> showed weak basic centers and some moderately strong basic centers. It should be noticed that Zn-Al LDH showed more amounts of very strong basic centers, in comparison with Mg-Al LDH. Combined with the catalytic performance shown above, it can be concluded that weak and moderate strong basic centers are critical to the reaction, while too strong basic centers are unfavorable to the reaction.

 Table 2
 Synthesis of 1,3-disubstituted urea in presence of different catalysts<sup>a</sup>

Entry	Catalyst	Conv./%	Sel. <sup>b</sup> /%
1	MgO	5.7	≥99
2	$Al_2O_3$	36.8	≥99
3	TiO <sub>2</sub>	44.5	≥99
4	Zn-Al LDH	29.2	≥99
5	Mg-Al LDH	48.2	≥99

<sup>*a*</sup> Reaction conditions: BA 32 mmol, pressure 4.0 MPa, temperature 170 °C, time 4 h, catalyst 0.300 g, NMP 2 mL. <sup>*b*</sup> A trace of dibutylamine was detected.



**Figure 1** Temperature-programmed desorption of CO<sub>2</sub> for indicated samples. (a) Al<sub>2</sub>O<sub>3</sub>; (b) TiO<sub>2</sub>; (c) MgO; (d) Mg-Al LDH; (e) Zn-Al LDH.

#### Effect of calcination temperature

The Mg-Al LDH samples calcined at different temperatures were characterized by XRD. As shown in Figure 2, the Mg-Al LDH exhibited some common features of layered materials (*e.g.* narrow, symmetric, strong lines at low  $2\theta$  values and weaker, less symmetric lines at high  $2\theta$  values) (Figure 2a). The LDHs samples cal-

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cined at 450 °C (Figure 2b) caused the crystallinity decreasing with no any other significant changes in the structures. On the other hand, a calcination temperature of 550 °C destroyed the LDH structure and led to the formation of a periclase MgO phase in addition to amorphous aluminium oxides (Figure 2c). These results are consistent with previous findings that periclase MgO is the sole crystalline phase expected to occur at this calcination temperature.<sup>[24,25]</sup> Raising the calcination temperature to 650 and 750 °C (Figure 2d and 2e) resulted in no change in the phases and only a slowly sharpening of the MgO reflections in the samples. There occurred reflections for spinel MgAl<sub>2</sub>O<sub>4</sub> when calcined at 850 °C (Figure 2f). Obviously, the structure calcined at 550 °C was transient state from layered double hydroxides to layered double oxides, and some amorphous phases occurred.

The distribution of the surface basic centers was also monitored by CO<sub>2</sub>-TPD (Figure 3). As shown in Figure 3, there mainly existed weak basic centers in Mg-Al LDH precursor (Figure 3a) or its products calcined at either 450 °C (Figure 3b) or 850 °C (Figure 3f). In contrast, a large amount of basic centers appeared at calcination temperature ranged from 550 to 750 °C (Figure 3c, 3d and 3e). It can be seen that the material calcined at 550 °C harbored the largest amount of moderately strong base.



Figure 2 XRD patterns of Mg-Al LDH and its products calcined at different temperatures. (a) Mg-Al LDH; (b) Mg-Al LDH450; (c) Mg-Al LDH550; (d) Mg-Al LDH650; (e) Mg-Al LDH750; (f) Mg-Al LDH850. The phases were indicated by the different symbols: ● hydrotalcite, ■ periclase, ▼ spinel.

The pattern of typical TG also substantiated the formation of Mg-Al LDHs (Figure 2S). The mass loss in the range from the room temperature to around 200  $^{\circ}$ C can be attributed to the removal of interlayered water, the gradual mass loss from 200 to 600  $^{\circ}$ C can be attributed to the decomposition of hydroxyl groups from the inorganic layers. These phenomena were consistent with structure evolution as shown in Figure 2.

Figure 4 showed the effect of calcination temperature on the reaction activity. We can see that a maximum can be observed when Mg-Al LDH550 catalyst



**Figure 3** Temperature-programmed desorption of CO<sub>2</sub> for indicated samples. All samples were calcined for 6 h. (a) no calcination; (b) Mg-Al LDH450; (c) Mg-Al LDH550; (d) Mg-Al LDH650; (e) Mg-Al LDH750; (f) Mg-Al LDH850.

was used and afforded 67.0% conversion of butylamine, which is higher than 59.0% conversion reported with [Bmim]OH as catalyst.<sup>[2]</sup> The catalytic activity was consistent with the special structure of Mg-Al LDH550 as shown in Figure 2c, where low crystalline phase formed along with structure transition from layered double hydroxides to layered double oxides compared with other samples. Perhaps it is just the amorphous phase with more exposed defects that promotes the reaction. In addition, the CO<sub>2</sub>-TPD in Figure 3c has illustrated that Mg-Al LDH550 possessed broad distribution of moderately strong basic centers, which can also contribute to the relatively higher catalytic activity. The Mg-Al LDH 550 and Mg-Al LDH 650 showed higher specific surface area (Table 1S), as comparison with those samples calcined at other temperatures, resulting in higher catalytic activity (Figure 4).



Figure 4 Influence of calcination temperature on the reaction activity. BA 32 mmol, pressure 3.0 MPa, time 6 h, temperature 170  $^{\circ}$ C, Mg-Al LDH550 0.300 g, NMP 2 mL. All samples were calcined for 6 h. The selectivity to 1,3-disubstituted urea was more than 99% in all cases.

#### Effect of reaction conditions

It was observed that a suitable reaction temperature was crucial for the reaction to reach a reasonable con-

version (Figure 5). The conversion reached a maximum at 170 °C, *i.e.* 67.0%. This reaction is exothermic and reversible.<sup>[8]</sup> If the reaction temperature is too low, reaction activation energy cannot be achieved, resulting in low activity. When the temperature was increased up too high, the reaction equilibrium was not favored to shift towards the right and the conversion decreased. Thus a maximum occurred as the temperature increased.



**Figure 5** Effect of reaction temperature on the activity. BA 32 mmol, pressure 3.0 MPa, time 6 h, Mg-Al LDH550 0.300 g, NMP 2 mL. The selectivity to 1,3-disubstituted urea was more than 99% in all cases.

Figure 6 showed the reaction kinetics curve over Mg-Al LDH550 catalyst. The carbonylation reaction between amines and  $CO_2$  can be performed smoothly without any dehydrating agents. With the increasing reaction time, the butylamine conversion first sharply increased and then kept constant after reaction for 6 h.



Figure 6 Effect of reaction time on the activity. BA 32 mmol, pressure 3.0 MPa, temperature 170  $^{\circ}$ C, Mg-Al LDH550 0.300 g, NMP 2 mL. The selectivity to 1,3-disubstituted urea was more than 99% in all cases.

The reaction pressures also have a significant influence on the reaction. As shown in Figure 7, the butylamine conversion firstly increased with the reaction pressure and then started to decrease when pressure is above 3.0 MPa. At pressures below 3.0 MPa, with pressure increasing, more compressed  $CO_2$  could be dissolved in the liquid phase and fully contacted with the substrate, facilitating the reaction.<sup>[13]</sup> On the other hand, too high CO<sub>2</sub> pressure could cause a dilution effect and also make the surface of the Mg-Al LDH550 to be adsorbed with an excess of carbon dioxide and there were few and even no active centers accessible to substrate molecules.<sup>[26]</sup> Thus a maximum occurred with the changes of CO<sub>2</sub> pressure.



Figure 7 The dependence of the conversion of butylamine on the reaction pressure. BA 32 mmol, temperature 170  $^{\circ}$ C, time 6 h, Mg-Al LDH550 0.300 g, NMP 2 mL. The selectivity to 1,3-di-substituted urea was more than 99% in all cases.

#### **Recycling of Mg-Al LDH550 catalyst**

Table 3 showed that Mg-Al LDH550 can be recycled at least 4 times with only slight loss of catalytic activity, which might result form the mechanical loss of catalyst for each catalytic run (Table 3, entries 1-4). This can be clarified that if the ratio of substrate to the recovered catalyst was kept constant for the consecutive recycles, the catalytic activity can be restored (Table 3, entry 5).

**Table 3** Recyling of catalyst in the carbonylation of amine with  $CO_2^{a}$ 

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Run	$m_{\text{catalyst}}^{b}/g$	Conv./%	Sel./%
1	0.300	68.7	≥99
2	0.291	65.7	≥99
3	0.249	62.0	$\geq 99$
4	0.219	58.8	$\geq 99$
5 <sup>c</sup>	0.204	65.8	≥99

<sup>*a*</sup> Reaction condition: BA 32 mmol, time 6 h, temperature 170 °C, pressure 3.0 MPa, NMP 2 mL. <sup>*b*</sup> Catalyst was regenerated after every run through calcining at 550 °C for 6 h. <sup>*c*</sup> Less substrate (22.4 mmol) was used.

As reported previously, DMSO can make LDH form a transparent or semi-transparent colloidal system and allowed the partial exfoliation of LDHs,<sup>[27]</sup> which followed a similar mechanism to that of formamide,<sup>[28]</sup> presumably because of their strong hydrogen-bonding interaction with the hydroxyl groups of the LDH layers.

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Interestingly, in our work we observed that NMP phase became semi-transparent colloidal and viscous after reaction. Observed from X-ray diffraction patterns in Figure 8b, the structure of Mg-Al LDH550 disappeared after reaction and there occurred three new peaks at low angles with one sharp peak and two broad peaks. It has been known that the evolution of an amorphous-like halo in a  $2\theta$  range of  $3^{\circ}-20^{\circ}$  is the characteristics of exfoliation.<sup>[29-32]</sup> The broad halo at  $2\theta = 7.5^{\circ}$  (arrow position) in Figure 8b is due to scattering from an aggregate of partially exfoliated LDH sheets, and the sharp diffraction was perhaps arisen from structure fracture in the reaction-induced exfoliation. Interestingly, adding amounts of water restored its structure and further identified its exfoliation (Figure 8c). The catalyst after reaction was calcined at 550 °C for 6 h, the structure of Mg-Al LDHs was regenerated unambiguously (Figure 8d).



Figure 8 XRD patterns of Mg-Al LDH550 catalyst. (a) before reaction; (b) after reaction; (c) adding water after reaction; (d) after one catalytic recycle and calcined at 550  $^{\circ}$ C for 6 h. Arrow position: broad halo.

According to the characterization of XRD (Figure 8), NMP and the bulky product molecular could intercalate into the layers and partial exfoliation of LDH emerged in the course of reaction. It has been observed that the exfoliated catalyst afforded low butylamine conversion (38.4%) because some water was present in exfoliated samples, and also strong interaction between the intercalated molecules and basic centers, which could hinder the adsorption and activation of substrate molecules on the catalyst. However, the calcined materials can restore the catalytic activity perfectly (Table 3). This implied that although the exfoliation might destroy to some extent the structure of Mg-Al LDHs, the layered double hydroxide structure can be recovered easily and afforded the almost same catalytic activity as the fresh calcined LDH catalyst.

Finally, the scope of the substrates was examined and the results were displayed in Table 4. It can be seen that although the present Mg-Al LDH catalyst still afforded low activity with the branch chain aliphatic amine as a substrate (Table 4, entry 1), it indeed exhibited comparable activity with that of homogenous catalyst as reported when long chain aliphatic amine, benzylamine and cyclohexylamine were used as substrates (Table 4, entries 2-4).<sup>[8]</sup>

**Table 4**Carbonylation of other organic amines with  $CO_2^a$ 

Entry	Substrate	Product	Conv./%
1	i-Pr−−NH <sub>2</sub> 1a	i-Pr-N N-i-Pr <b>2a</b>	22.7
2	<i>n-</i> HeNH <sub>2</sub> 1b	∩-He−N N− <i>n</i> -He H H 2b	51.8
3	Cy-NH <sub>2</sub> 1c	Cy-N N-Cy 2c	58.9
4	Bn-NH <sub>2</sub> 1d	Bn-N N-Bn H H 2d	70.2

<sup>*a*</sup> Reaction condition: amine 32 mmol, pressure 3.0 MPa, time 10 h, temperature 170 °C, Mg-Al LDH550 0.300 g, NMP 2 mL. The selectivity to 1,3-disubstituted urea was more than 99% in all cases.

### Conclusions

In summary, the calcined Mg-Al layered double hydroxide (Mg-Al LDH550) is an efficient heterogeneous catalyst for the synthesis of 1,3-disubstituted urea from different amines and  $CO_2$  in NMP without any dehydrating agents. This catalytic process is cost-effective because the catalyst is cheap, easily available and reusable. In addition, NMP played an important role in the reaction. Although the calcined Mg-Al LDH was exfoliated in the course of reaction, the structure of LDH can be regenerated only thorough simple calcination, which offered the good recyclability for present catalytic system.

## Acknowledgement

The authors are grateful for the support from the National Natural Science Foundation of China (No. 21073058), the Research Fund for the Doctoral Program of Higher Education of China (20100074110014), and the Fundamental Research Funds for the Central Universities.

### References

- [1] Bigi, F.; Maggi, R.; Sartori, G. Green Chem. 2000, 2, 140.
- [2] Jiang, T.; Ma, X. M.; Zhou, Y. X.; Liang, S. G.; Zhang, J. C.; Han, B.

X. Green Chem. 2008, 10, 465.

- [3] Shi, F.; Deng, Y. Q. J. Catal. 2002, 211, 548.
- [4] Leung, T. W.; Dombek, B. D. J. Chem. Soc., Chem. Commun. 1992, 3, 205.
- [5] Cenini, S.; Pizzotti, M.; Crotti, C.; Porta, F.; La Monica, G. J. Chem. Soc., Chem. Commun. 1984, 19, 1286.
- [6] McCusker, J. E.; Main, A. D.; Johnson, K. S.; Grasso, C. A.; McElwee-White, L. J. Org. Chem. 2000, 65, 5216.
- [7] Nagaraju, N.; Kuriakose, G. Green Chem. 2002, 4, 269.
- [8] Ion, A.; Parvulescu, V.; Jacobs, P.; De Vos, D. Green Chem. 2007, 9, 158.
- [9] Fournier, J.; Bruneau, C.; Dixneuf, P. H.; Lécolier, S. L. J. Org. Chem. 1991, 56, 4456.
- [10] James, C.; Anderson; Rafael, B. M. Org. Biomol. Chem. 2012, 10, 1334.
- [11] Shi, F.; Deng, Y. Q.; SiMa, T. L.; Peng, J. J.; Gu, Y. L.; Qiao, B. T. Angew. Chem., Int. Ed. 2003, 42, 3257.
- [12] Kong, D. L.; He, L. N.; Wang, J. Q. Synlett 2010, 8, 1276.
- [13] Wu, C. Y.; Cheng, H. Y.; Liu, R. X.; Wang, Q.; Hao, Y. F.; Yua, Y. C.; Zhao, F. Y. *Green Chem.* **2010**, *12*, 1811.
- [14] (a) Kagunya, W.; Hassan, Z.; Jones, W. Inorg. Chem. 1996, 35, 5970;
  (b) Carlino, S.; Hudson, M. J.; Husain, S. W.; Knowles, J. A. Solid State Ionics 1996, 84, 117; (c) Kaneda, K.; Ueno, S.; Ebitani, K. Curr. Top. Catal. 1997, 1, 91; (d) Velu, S.; Swamy, C. S. React. Kinet. Catal. Lett. 1997, 62, 339; (e) Othman, M. R.; Rasid, N. M.; Fernando, W. J. N. Chem. Eng. Sci. 2006, 61, 1555.
- [15] (a) Ram Reddy, M. K.; Xu, Z. P.; Lu, G. Q.; Diniz da Costa, J. C. Ind. Eng. Chem. Res. 2006, 45, 7504; (b) Hutson, N. D.; Attwood, B. C. Adsorption 2008, 14, 781; (c) Horiuchi, T.; Hidaka, H.; Fukui, T.; Kubo, Y.; Horio, M.; Suzuki, K.; Mori, T. Appl. Catal., A: General 1998, 167, 195; (d) Meis, N. N. A. H.; Bitter, J. H.; de Jong, K. P. Ind. Eng. Chem. Res. 2010, 49, 8086; (e) Yavuz, C. T.; Shinall, B. D.; Iretskii, A. V.; White, M. G.; Golden, T.; Atilhan, M.; Ford, P. C.; Stucky, G. D. Chem. Mater. 2009, 21, 3473; (f) Zou, Y.; Mata, V.; Rodrigues, A. E. Purif. Technol. 2002, 26, 195; (g) Dadwhal, M.;

Kim, T. W.; Sahimi, M.; Tsotsis, T. T. *Ind. Eng. Chem. Res.* **2008**, *47*, 6150; (h) Wang, X. P.; Yu, J. X.; Cheng, J.; Hao, Z. P.; Xu, Z. P. *Environ. Sci. Technol.* **2008**, *42*, 614.

- [16] Shen, J. Y.; Kobe, J. M.; Chen, Y.; Dumesic, J. A. Langmuir 1994, 10, 3902.
- [17] Tichit, D.; Bennani, M. N.; Figueras, F.; Ruiz, J. R. Langmuir 1998, 14, 2086.
- [18] Talawar, M. B.; Jyothi, T. M.; Sawant, P. D.; Rajab, T.; Rao, B. S. Green Chem. 2000, 2, 266.
- [19] Climent, M. J.; Corma, A. S.; Iborra, S.; Primo, J. J. Catal. 1995, 151, 60.
- [20] Zhang, F.; Ni, Z.; Xia, S. J.; Liu, X. M.; Wang, Q. Q. Chin. J. Chem. 2009, 27, 1767.
- [21] Crepaldi, E.; Tronto, J.; Cardoso, L. P.; Valim, J. B. Colloids Surf., A: Physicochem. Eng. Aspects 2002, 211, 103.
- [22] Rajasingam, R.; Lioe, L.; Pham, Q. T.; Lucien, F. P. J. Supercrit. Fluids 2004, 31, 227.
- [23] Vaidya, P. D.; Mahajani, V. V. Ind. Eng. Chem. Res. 2005, 44, 1868.
- [24] Reichle, W. T.; Kang, S. Y.; Everhardt, D. S. J. Catal. 1986, 101, 352.
- [25] Aramendía, M. A.; Avilés, Y.; Borau, V.; Luque, J. M.; Marinas, J. M.; Ruiz, J. J. Mater. Chem. 1999, 9, 1603.
- [26] Zhao, F. Y.; Fujita, S.; Akihara, S. J.; Arai, M. J. Phys. Chem., A 2005, 109, 4419.
- [27] Zhao, Y.; Yang, W. D.; Xue, Y. H.; Wang, X. G; Lin, T. J. Mater. Chem. 2011, 21, 4869.
- [28] Gordijo, C. R.; Constantino, V. R. L.; Silva, D. D. J. Solid State Chem. 2007, 180, 1967.
- [29] Sasaki, T.; Watanabe, M. J. Am. Chem. Soc. 1998, 120, 4682.
- [30] Wu, Q. L.; Sjåstad, A. O.; Ørnulv, B.; Knudsen, K. D.; Roots, J.; Pedersen, J. S.; Norby, P. J. Mater. Chem. 2007, 17, 965.
- [31] Ma, R. Z.; Liu, Z. P.; Li, L.; Iyi, N.; Sasaki, T. J. Mater. Chem. 2006, 16, 3809.
- [32] Román, M. S. S.; Holgado, M. J.; Jaubertie, C.; Rives, V. Solid State Sci. 2008, 10, 1333.

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