

## Environmentally benign and effective syntheses of N-substituted carbamates via alcoholysis of disubstituted ureas over TiO<sub>2</sub>/SiO<sub>2</sub> catalyst\*

Liguo Wang<sup>1,2</sup>, Jianpeng Shang<sup>1,2</sup>, Shimin Liu<sup>1,2</sup>, Lequan Liu<sup>1</sup>, Shiguo Zhang<sup>1</sup>, and Youquan Deng<sup>1,‡</sup>

<sup>1</sup>Centre for Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China; <sup>2</sup>Graduate University of Chinese Academy of Sciences, Beijing 100039, China

**Abstract:** Catalytic syntheses of cyclohexyl carbamates via alcoholysis of dicyclohexyl urea (DCU), which can be synthesized from CO<sub>2</sub> and amines, were first investigated with low-molecular-weight alcohols, i.e., methanol, ethanol, butan-1-ol. TiO<sub>2</sub>/SiO<sub>2</sub> catalyst was prepared by wet impregnation method using tetrabutyl titanate as titanium source. The catalyst was characterized by inductively coupled plasma/atomic emission spectroscopy (ICP/AES), N<sub>2</sub> adsorption, X-ray diffraction (XRD), field emission/scanning electron microscopy (FE/SEM), transmission electron microscopy (TEM), and NH<sub>3</sub>/temperature-programmed desorption (TPD) in detail. TiO<sub>2</sub>/SiO<sub>2</sub> with 5 wt % loadings and calcination at 600 °C exhibited better catalytic activity, and excellent yields of >95 % with 98 % selectivities for desired carbamates were achieved. Accordingly, the strong acidity was considered to be responsible for its superior activity. Moreover, the catalytic activity can essentially be preserved during the recycling tests. The scope was also expanded to synthesize other alkyl or aryl carbamates via alcoholysis of the corresponding disubstituted ureas, and 94 % yields with 96 % selectivities can be achieved. It provided a good candidate for the organic carbamates syntheses via a phosgene/halogen-free and effective route.

**Keywords:** alcoholysis; disubstituted ureas; N-substituted carbamates; TiO<sub>2</sub>/SiO<sub>2</sub>; phosgene-free.

### INTRODUCTION

Organic carbamates have wide applications in the polymer industry (e.g., polyurethane), the agrochemical chemicals (pesticides, herbicides, etc.), or the pharmaceutical industry as drug intermediates [1]. They have also been shown to be a powerful tool to serve as protecting groups for amines as well as excellent templates for the formation of C–C and carbon–hetero atom bonds [2]. The conventional processes for carbamate production were mainly via the route of alcoholysis of isocyanate, which was synthesized by a primary amine and phosgene, or aminolysis of chloroformates [3]. The major drawbacks of the former route were that the raw material of phosgene was highly toxic, corrosive, and stoichiometric quantity of sodium chloride was also co-produced. Analogously, the waste salt was also unavoidably produced in the chloroformates process. Alternative phosgene-free routes were reported

\**Pure Appl. Chem.* **84**, 411–860 (2012). A collection of invited papers for the IUPAC project 2008-016-1-300 “Chlorine-free Synthesis for Green Chemistry”.

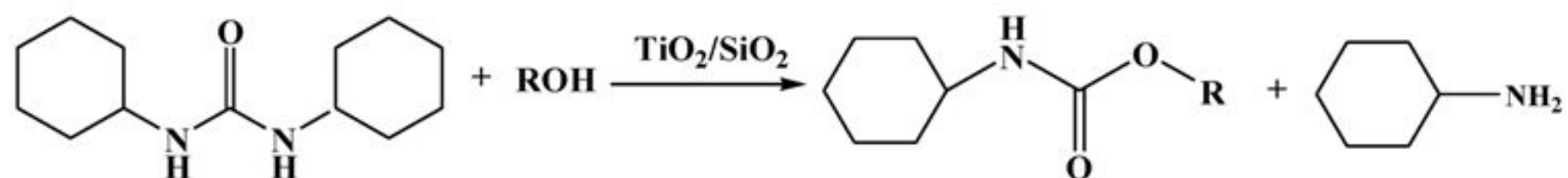
‡Corresponding author: E-mail: ydeng@licp.cas.cn

previously based on carbon monoxide as carbonyl source, including reductive carbonylation of nitro aromatics and oxidative carbonylation of amines [4]. However, the drawbacks, such as the involvement of noble metal catalysts, e.g., Pt, Ru, Au, or potential explosion due to the mixture of carbon monoxide and oxygen, made these routes neither economical nor safe. Dimethyl carbonate (DMC) was also reported as a carbonyl source in the syntheses of carbamates [5]. The main disadvantage to restricting this route was that the separation of the methanol-DMC azeotrope in the post-treatment increases the cost of manufacture.

The utilization of CO<sub>2</sub> as a carbonyl source in producing carbamates is currently a hot topic [6]. However, the direct utilization of CO<sub>2</sub> in carbamate synthesis required special conditions owing to the chemical inertness of CO<sub>2</sub>, e.g., alkyl halide as alkylation reagent [7], or dehydration reagent [8], which weakened the significance of the chemical fixation of CO<sub>2</sub> in view of environmental protection. The direct syntheses of carbamates from CO<sub>2</sub>, amines and alcohols were found to exhibit relatively low yields of <44 % with <79 % selectivities for desired carbamate products without dehydration agents [9]. A process was also reported for the synthesis of alkyl *N*-alkyl carbamates from symmetrically disubstituted ureas catalyzed by organotin catalyst [10]. It is worth mentioning that disubstituted ureas were successively synthesized from amines and CO<sub>2</sub> using hydrophilic ionic liquids as reaction medium in our previous report [11]. Therefore, the effective syntheses of carbamates are now depending on the way to transfer the carbonyl group in disubstituted ureas into *N*-substituted carbamates.

Titania supported on silica support have attracted much attention as versatile catalytic materials for a variety of reactions, e.g., epoxidation of olefins [12], selective oxidation [13], and transesterification [14]. The supported titania were considered to be superior to bulk TiO<sub>2</sub> owing to the improved mechanical strength, thermal stability, and high dispersion of TiO<sub>2</sub> [15]. Several preparation methods were reported previously, such as chemical vapor deposition [16], atomic layer deposition [17], and liquid-phase grafting [18]. Additionally, TiCl<sub>4</sub> containing chlorine was usually involved as titanium source [19]. In comparison with the methods aforementioned, the wet impregnation using tetrabutyl titanate as an alternative precursor has the merits of facile synthesis and halogen-free and easy scale-up.

In this work, varied loadings of TiO<sub>2</sub>/SiO<sub>2</sub> catalysts were prepared via hydrolysis of tetrabutyl titanate firstly in the presence of diluted nitric acid, followed by wet impregnation and calcined at different temperatures (denoted as *x*TiO<sub>2</sub>/SiO<sub>2</sub>-*T*, where *x* is the titania loadings and *T* represents the calcination temperature). The catalyst was characterized by inductively coupled plasma/atomic emission spectroscopy (ICP/AES), N<sub>2</sub> adsorption, X-ray diffraction (XRD), field emission/scanning electron microscopy (FE/SEM), transmission electron microscopy (TEM), and NH<sub>3</sub>/temperature-programmed desorption (TPD) in detail. Among the catalysts tested, the TiO<sub>2</sub>/SiO<sub>2</sub> with 5 wt % TiO<sub>2</sub> loadings and calcined at 600 °C exhibited better catalytic activity in alcoholysis of dicyclohexyl urea (DCU) with low-molecular-weight alcohols, e.g., methanol, ethanol, and butan-1-ol, as shown in Scheme 1. The desired product could be obtained with >95 % yields and >98 % selectivities. The reusability of the catalyst and scope of substrates were also investigated, and the syntheses of *N*-substituted carbamates via a phosgene/halogen-free, eco-friendly and effective route were realized.



**Scheme 1** Cyclohexyl carbamate synthesis via alcoholysis of DCU with low-molecular-weight alcohols over TiO<sub>2</sub>/SiO<sub>2</sub>.

## RESULTS AND DISCUSSION

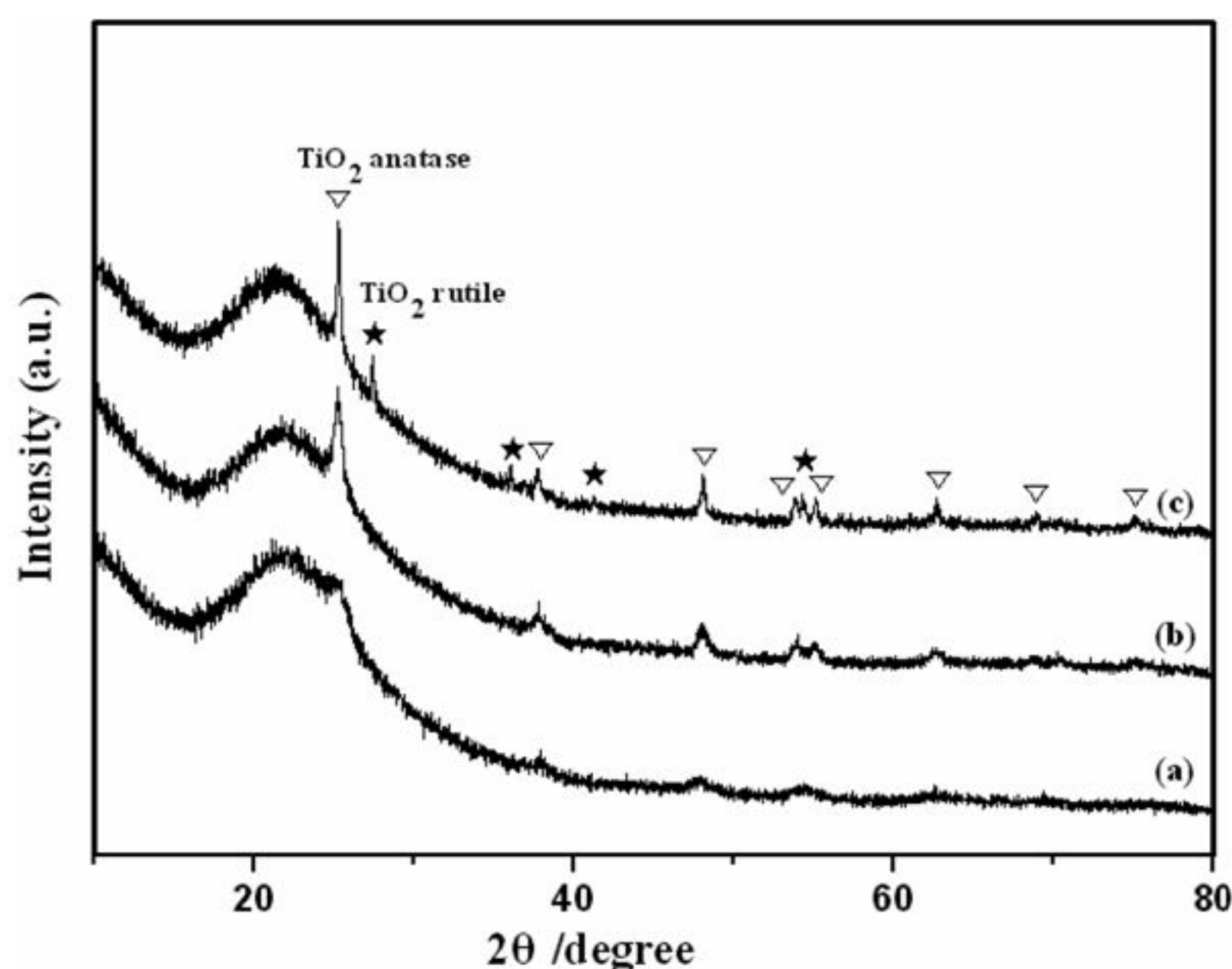
### Catalyst characterization

Table 1 shows the textural properties of pure amorphous SiO<sub>2</sub> or 5 wt % TiO<sub>2</sub>/SiO<sub>2</sub>-*T* samples as estimated from the adsorption/desorption isotherms of nitrogen at 77 K. The SiO<sub>2</sub> support possesses Brunauer–Emmett–Teller (BET) surface as large as 601 m<sup>2</sup>/g, as well as pore size 5.0 nm and pore volume 0.74 cm<sup>3</sup>/g. The isotherm of SiO<sub>2</sub> is type VI (not shown here), suggesting the presence of mesoporous structure according to the IUPAC classification [20]. As expected, the decrease of BET surface area and pore volume was observed when titania was loaded, especially pronounced at a higher calcination temperature. By contrast, the pore diameter was retained at ca. 5.0 nm without remarkable decline. The relatively large BET surface area and pore diameter was considered to facilitate the mass transfer during the reaction process and was especially favorable for the reactant molecule with big size, e.g., DCU.

**Table 1** BET surface area ( $S_{\text{BET}}$ ), average pore diameter ( $d_p$ ), pore volume ( $V_p$ ) of pure SiO<sub>2</sub> or 5 wt % TiO<sub>2</sub>/SiO<sub>2</sub>-*T* samples as a function of the calcination temperature.

Sample	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$d_p$ (nm)	$V_p$ (cm <sup>3</sup> /g)
SiO <sub>2</sub>	601	5.0	0.74
5 wt % TiO <sub>2</sub> /SiO <sub>2</sub> -400	509	5.2	0.69
5 wt %TiO <sub>2</sub> /SiO <sub>2</sub> -600	511	5.1	0.68
5 wt %TiO <sub>2</sub> /SiO <sub>2</sub> -800	463	5.0	0.61

The XRD patterns of 5 wt % TiO<sub>2</sub>/SiO<sub>2</sub> samples calcined at varied temperatures are shown in Fig. 1. For the sample calcined at 400 °C, the wide peaks and low signal-to-noise ratios indicated that TiO<sub>2</sub> particles were highly dispersed on the catalyst surface. The peak intensities became stronger when the calcination temperature increased to 600 °C, and anatase crystalline phase can be identified. The



**Fig. 1** XRD patterns of 5 wt % TiO<sub>2</sub>/SiO<sub>2</sub> calcined at 400 °C (a), 600 °C (b), 800 °C (c).

average crystalline size estimated by the Scherrer equation was 17 nm according to the crystallographic plane of anatase (101), suggesting the nano-sized  $\text{TiO}_2$  crystallites were formed. In association with the result reported in the previous literature [21], the transformation of anatase  $\text{TiO}_2$  to rutile phase would occur at the calcination temperature of 600 °C for pure  $\text{TiO}_2$ . Therefore, it is reasonable to deduce that the  $\text{TiO}_2$  particles may be stabilized by the  $\text{SiO}_2$  support and the phase transformation at high temperature was inhibited to some extent. When the temperature was further increased to 800 °C, the intensity of reflections related to anatase crystalline phase became sharper, suggesting the crystallite size increased along with the calcination temperature. Moreover, besides the dominant phase of anatase, the additional diffractions ascribed to rutile  $\text{TiO}_2$  were also present, indicating the partial transformation of anatase to rutile phase occurred.

Representative curves from the TPD of ammonia are plotted in Fig. 2, and the acidity distribution is shown in Table 2. The pure  $\text{SiO}_2$  exhibited total acidity of 139  $\mu\text{mol/g}$ , which was dominated by weak acidity (128  $\mu\text{mol/g}$ ), entry 1. It can be seen that the total acidity increased when titania was supported onto the  $\text{SiO}_2$ , irrespective of the calcination temperature, entries 2–4. Evidently, the acid amount in the strong strength region increased remarkably as compared to pure  $\text{SiO}_2$ . The acid amount in the strong strength region reached the highest for  $\text{TiO}_2/\text{SiO}_2$ -600, and further increasing the calcination temperature to 800 °C has a detrimental effect on the amount of acid sites, especially in the weak strength region. Based on these results, it can be concluded that the introduction of titania to silica matrix enhanced the acidity remarkably in the strong strength region, which is in agreement with the result reported in the literature [14].

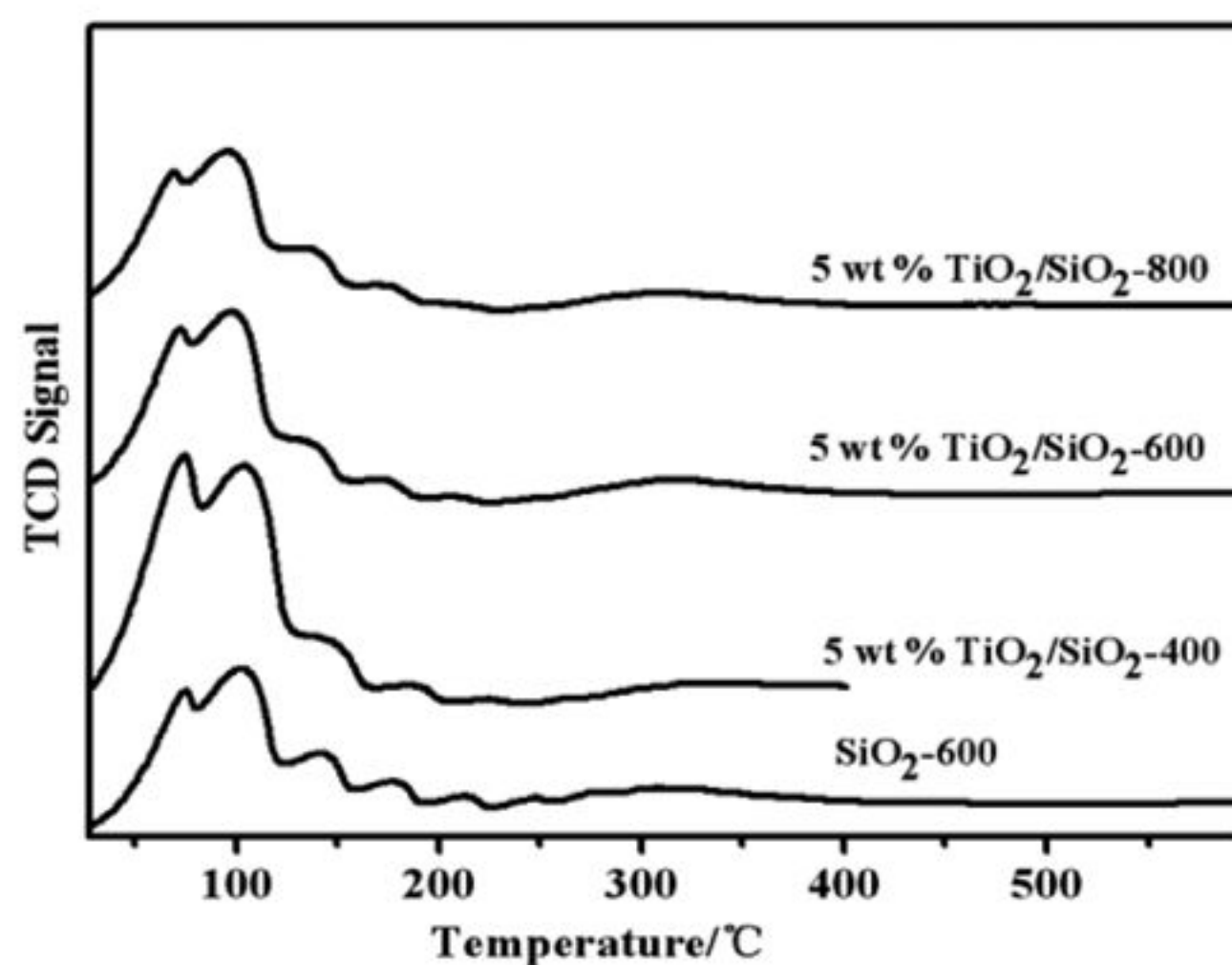


Fig. 2  $\text{NH}_3$ -TPD study for pure  $\text{SiO}_2$  and 5 wt %  $\text{TiO}_2/\text{SiO}_2$ - $T$  samples.

Table 2 Acidity distribution measured by  $\text{NH}_3$ -TPD for pure  $\text{SiO}_2$  and 5 wt %  $\text{TiO}_2/\text{SiO}_2$ - $T$ .

Entry	Sample	Weak acidity (mmol/g)	Strong acidity (mmol/g)	Total acidity (mmol/g)
1	$\text{SiO}_2$	128	11	139
2	5 wt % $\text{TiO}_2/\text{SiO}_2$ -400	198	22	220
3	5 wt % $\text{TiO}_2/\text{SiO}_2$ -600	157	30	187
4	5 wt % $\text{TiO}_2/\text{SiO}_2$ -800	114	27	141

Figure 3 shows FE-SEM (a) and TEM (b) images of 5 wt %  $\text{TiO}_2/\text{SiO}_2$ -600. From the FE-SEM image, it can be seen that the catalytic material consists of spherical particles with size in the 50–100 nm range. The TEM bright field image confirmed the crystallite sizes were in the range of 10–15 nm, which is slightly smaller than that obtained from the Scherrer equation. Well-resolved crystalline plane with d spacing of 0.35 nm can be ascribed to the crystallographic plane of anatase (101), which is consistent with the result of XRD characterization. It indicated that  $\text{TiO}_2$  was well dispersed on the surface of  $\text{SiO}_2$ , and the nano-sized anatase  $\text{TiO}_2$  particles were formed.

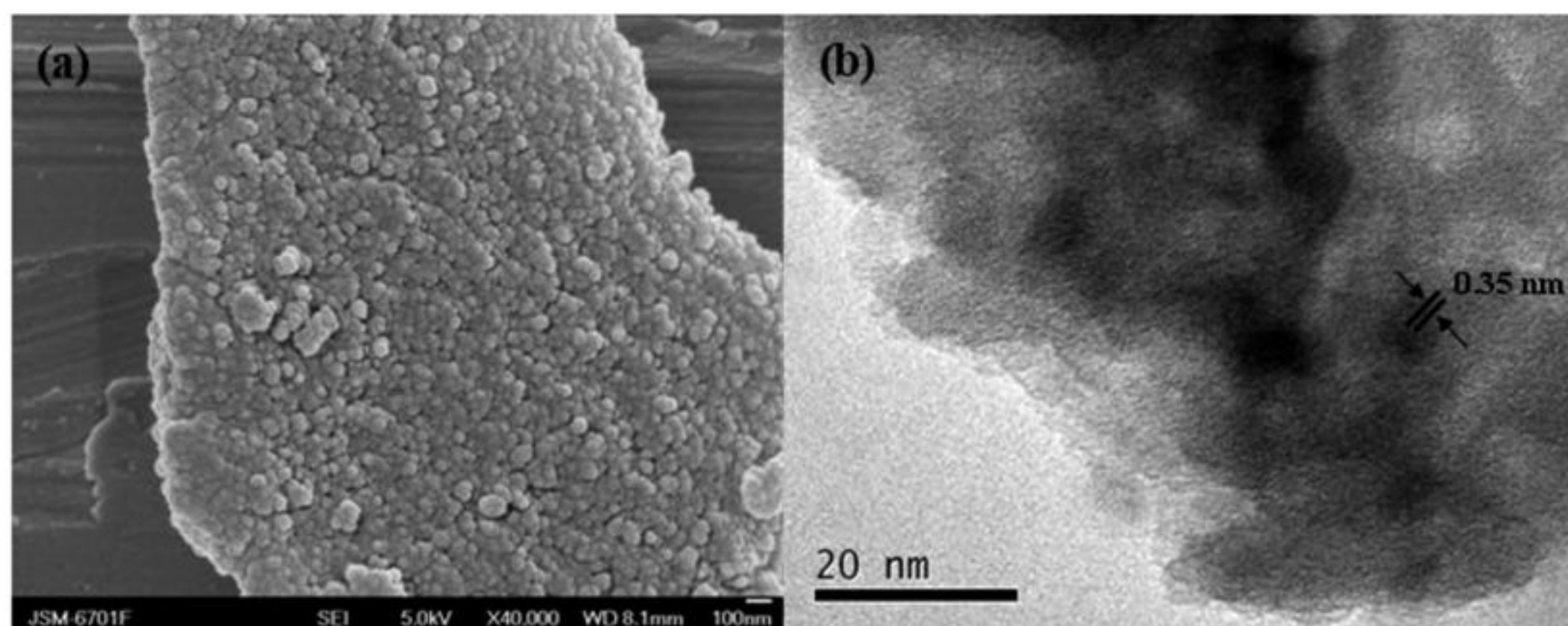


Fig. 3 FE-SEM image (a) and TEM image (b) of 5 wt %  $\text{TiO}_2/\text{SiO}_2$ -600.

### Catalytic testing

#### *Catalytic syntheses of methyl, ethyl, or butyl cyclohexyl carbamate*

Firstly, the synthesis of butyl cyclohexyl carbamate (BCC) via alcoholysis of DCU with butan-1-ol was surveyed without catalyst, entry 1, Table 3. Low conversion of 30 % for DCU was obtained. Compared with the result in a blank test, the DCU conversion was slightly increased to 38 % in the presence of pure  $\text{SiO}_2$ . In association with the characterization result, it probably indicated that the acidity originated from silanol catalyzed the reaction to some extent. The catalytic activity was greatly enhanced when titania was supported on  $\text{SiO}_2$ , entries 3–5. Among the catalysts calcined at different temperatures, the one calcined at 600 °C exhibited relatively higher catalytic activity (77 % of DCU conversion), entry 4, corresponding to a turnover number (TON) of 35 mmol/ $\text{g}_{\text{cat}}$ . It suggested the calcination temperature influenced the catalytic activity remarkably. It is worth mentioning that the catalytic results obtained were in agreement with the trend of strong acidity as determined by  $\text{NH}_3$ -TPD, indicating the strong acidity probably plays an important role in its superior catalytic activity. In association with the XRD and TEM results for catalyst of 5 wt %  $\text{TiO}_2/\text{SiO}_2$ , the nano-sized anatase  $\text{TiO}_2$  species may be the active sites. Varied loadings of titania were also prepared and tested, entries 6–7. When the loading amount was as low as 1 wt %, 66 % of DCU conversion was obtained, suggesting the too low loading may be not enough to obtain better activity. When the loading increased to 11 wt %, however, decreased DCU conversion of 57 % was obtained in comparison with that of 5 wt % loading. Therefore, 5 wt % loading may be the better choice for obtaining higher catalytic activity. For the result obtained over pure  $\text{TiO}_2$ , 44 % DCU conversion was obtained, entry 8, suggesting the dispersion of active species to the support was necessary to obtain high catalytic activity. Moreover,  $\text{TiO}_2$  supported on different supports, i.e., SAPO-11 or MCM-41 molecular sieves, were also investigated for BCC synthesis, entries 9–10. In comparison with the active species supported on amorphous  $\text{SiO}_2$ , the SAPO-11 or MCM-41 used as support exhibited relatively lower catalytic activity, especially for the SAPO-11 with smaller pore size.

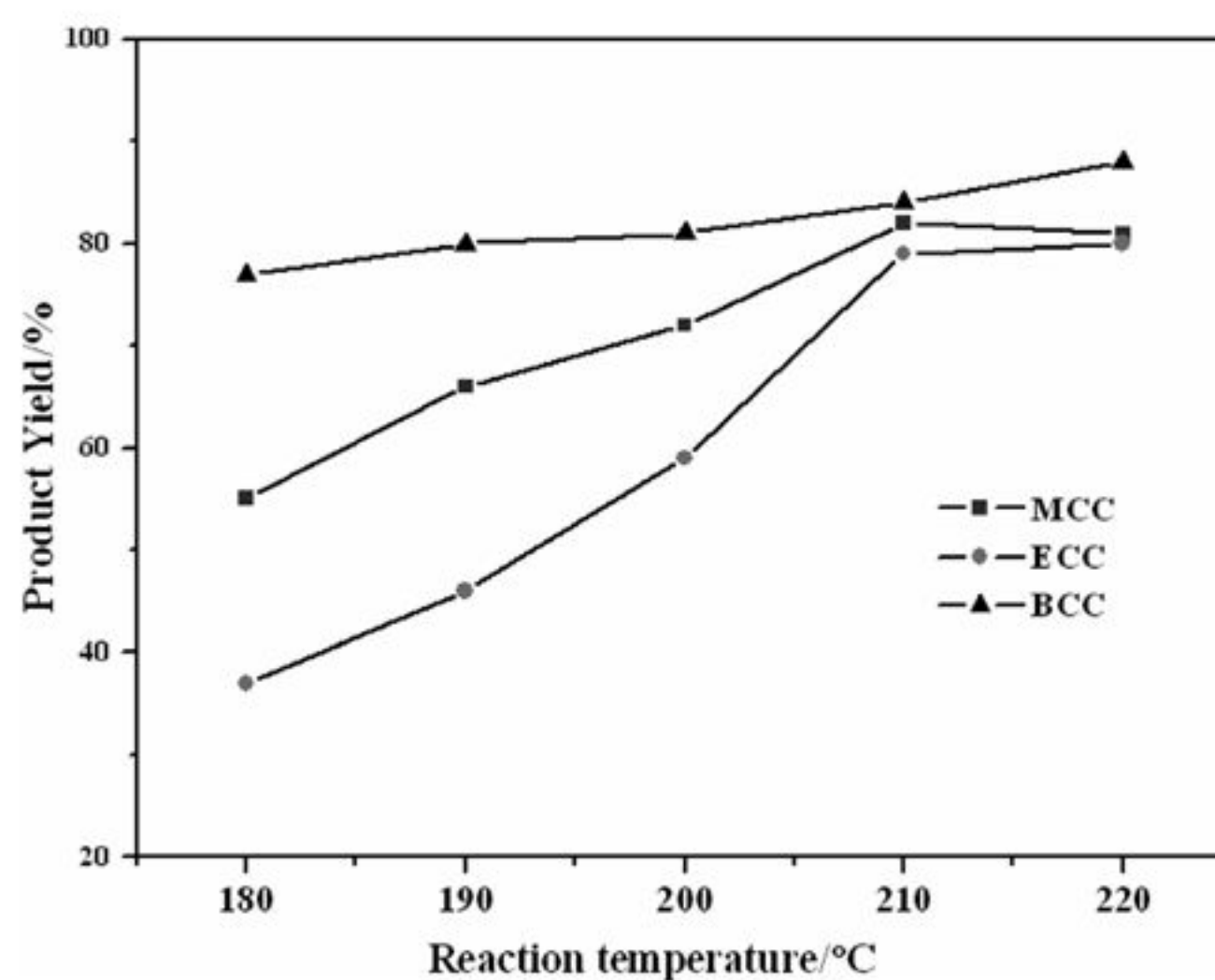
**Table 3** Results of BCC synthesis from DCU and butan-1-ol.

Entry	Catalyst	DCU con./%	BCC sel./%	TON <sup>a</sup> (mmol/g <sub>cat</sub> )
1	–	30	>99	–
2	SiO <sub>2</sub>	38	>99	–
3	5 wt % TiO <sub>2</sub> /SiO <sub>2</sub> -400	51	>99	23
4	5 wt % TiO <sub>2</sub> /SiO <sub>2</sub> -600	77	>99	35
5	5 wt % TiO <sub>2</sub> /SiO <sub>2</sub> -800	64	>99	29
6	1 wt % TiO <sub>2</sub> /SiO <sub>2</sub> -600	66	>99	30
7	11 wt % TiO <sub>2</sub> /SiO <sub>2</sub> -600	57	>99	25
8	TiO <sub>2</sub> -600	44	>99	20
9	5 wt % TiO <sub>2</sub> /SAPO-11-600	43	>99	20
10	5 wt % TiO <sub>2</sub> /MCM-41-600	59	96	27

Reaction conditions: 1.0 g DCU, 0.1 g 5 wt % TiO<sub>2</sub>/SiO<sub>2</sub>-600, 20 ml butan-1-ol, 180 °C, 2 h.

<sup>a</sup>TON was calculated based on mole of DCU converted per gram of catalyst.

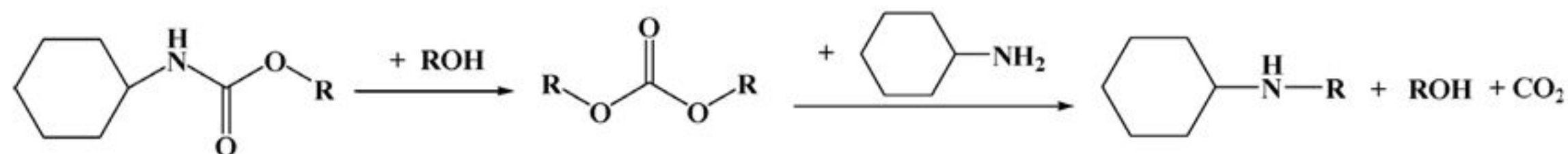
The influence of reaction temperature on the syntheses of methyl cyclohexyl carbamate (MCC), ethyl cyclohexyl carbamate (ECC), and BCC via alcoholysis of DCU was investigated in the range of 180–220 °C, as shown in Fig. 4. The desired product yield increased monotonically with elevating the reaction temperature. The product yields of 78–83 % were obtained with >98 % selectivities at 210 °C, further increasing the reaction temperature to 220 °C deteriorated the product selectivities to <97 % (not shown here). Therefore, comprehensively speaking, 210 °C was considered as the appropriate reaction temperature. The main by-product was the corresponding alkylated cyclohexyl amine and slight amount of cyclohexyl isocyanate (<0.5 %).



**Fig. 4** Influence of reaction temperature on the syntheses of MCC, ECC, and BCC. Reaction conditions: 1.0 g DCU, 20 ml alcohol (methanol, ethanol, butan-1-ol), 0.1 g 5 wt % TiO<sub>2</sub>/SiO<sub>2</sub>-600, 2 h.

To give insights of the origin the by-product, two possible pathways were taken into account. One way was the resultant carbamate further reacted with alcohol to form dialkyl carbonate, followed by reaction with amine along with releasing one molecule CO<sub>2</sub>, as shown in Scheme 2. To identify this conjecture, the reaction for BCC synthesis was performed with the atmosphere in autoclave replaced by nitrogen several times prior to reaction in order to ensure the carbon dioxide excluded from the reac-

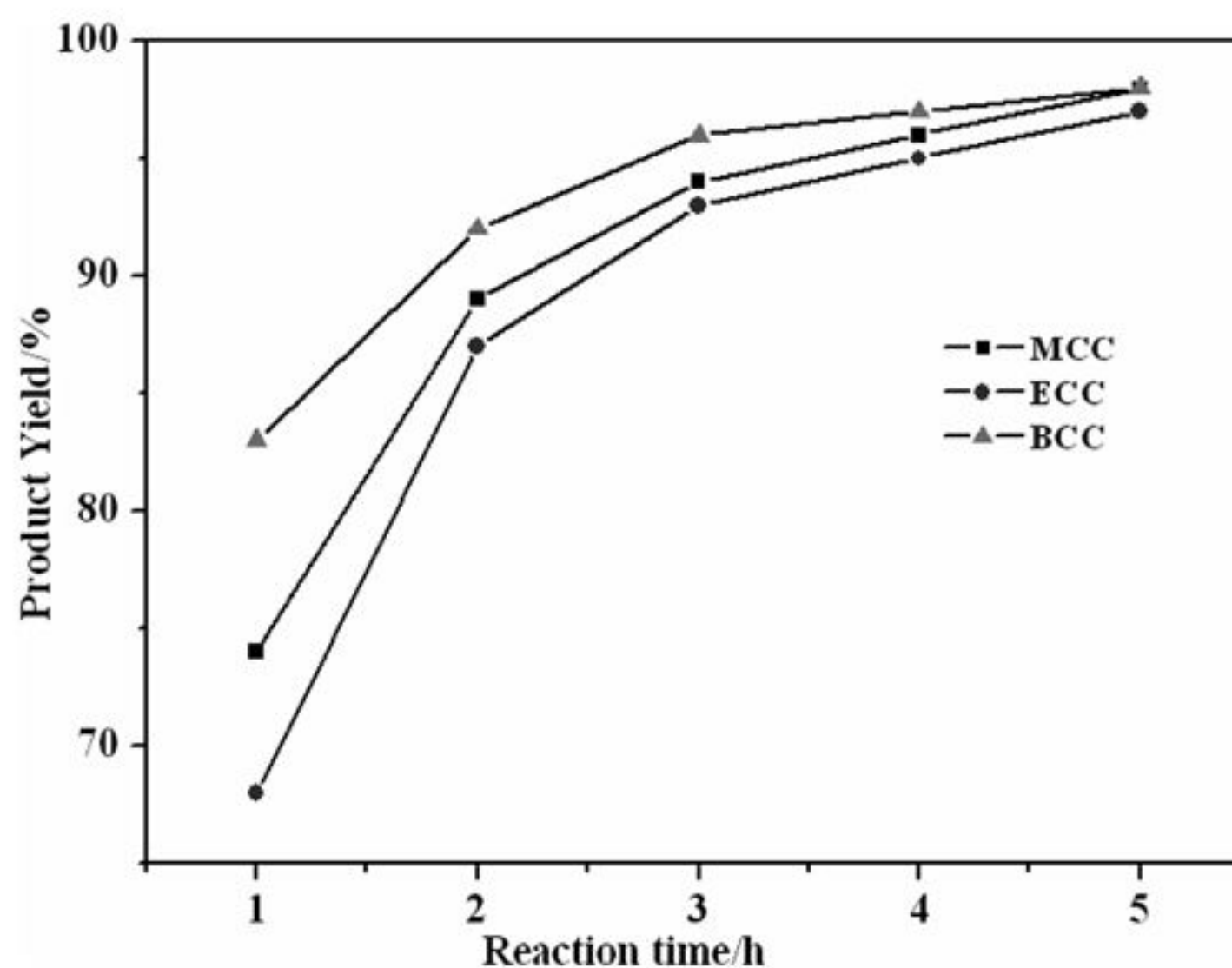
tion system. The appearance of  $\text{CO}_2$  in the reactor was confirmed by GC with TCD detector after reaction. Therefore, the formation of alkylated product probably occurred via the pathway shown in Scheme 2. This suggestion is also similar to the view in ref. [22].



**Scheme 2** The plausible way for the formation of alkylated by-product.

Another possibility was the direct reaction between the amine and alcohol. The test using amine and ethanol as reactants was carried out, unfortunately, no alkylated by-product was observed. So, the possibility for alkylated by-product via direct reaction between the amine and alcohol can be excluded. On the basis of these results, it can be deduced that the by-product of alkylated amine probably occurred via the intermediate of dialkyl carbonate.

The influence of reaction time on the syntheses of carbamates was investigated to obtain higher product yields, as shown in Fig. 5. The desired product yields increased rapidly at initial 2 h, and gradually reached the equilibrium with prolonged reaction time. Among the different reactions, BCC was formed at the highest reaction speed, while ECC was the lowest. 97–98 % of desired product yields could be obtained with selectivities >98 %, and the main by-product was same as that aforementioned.



**Fig. 5** Influence of reaction time on the syntheses of MCC, ECC, and BCC. Reaction conditions: 1 g DCU, 20 ml alcohol (methanol, ethanol, butan-1-ol), 0.1 g 5 wt %  $\text{TiO}_2/\text{SiO}_2$ -600.

The results for catalytic syntheses of MCC, ECC, and BCC under optimized reaction conditions are summarized in Table 4. Excellent yields of 95–96 % for MCC, ECC, and BCC with 98 % selectivities could be obtained with isolated yields of 89–92 %, entries 1–3. The  $\text{TiO}_2/\text{SiO}_2$  catalyst can be recycled easily by filtration. When it was reused 6 times for BCC synthesis, entry 4, 94 % DCU conversion with 98% BCC selectivity still can be obtained, suggesting the catalyst was stable and the cat-

alytic activity can be essentially preserved. It realized the synthesis of cyclohexyl carbamate in an effective and practical pathway.

**Table 4** Results for the syntheses of MCC, ECC, or BCC from DCU with methanol, ethanol, or butan-1-ol at optimized reaction conditions over 5 wt % TiO<sub>2</sub>/SiO<sub>2</sub>-600.

Entry	Alcohol	DCU con./%	Product sel./%	Yield/%	Isolated yield/%
1 <sup>a</sup>	methanol	98	98	96	89
2 <sup>a</sup>	ethanol	97	98	95	90
3 <sup>b</sup>	butan-1-ol	98	98	96	92
4 <sup>b,c</sup>	butan-1-ol	94	98	92	88

Reaction conditions: a: 1.2 g DCU; b: 1.5 g DCU, 0.1 g catalyst, 20 ml alcohol, 6 h, c: reused for six times.

#### *Expansion of the substrate scope for the syntheses of N-substituted carbamates*

The scope of substrate was expanded to other *N*-alkyl or aryl (containing electron-donating or electron-withdrawing groups on benzene ring) disubstituted ureas for alcoholysis over 5 wt % TiO<sub>2</sub>/SiO<sub>2</sub>-600, the reaction formula is shown in Scheme 3, and the results are listed in Table 5. Product yield of 94 % with >98 % selectivity can be obtained for *N*-alkyl carbamate (butyl dodecylcarbamate) at 200 °C within 4 h, entry 1. For the butyl benzyl carbamate synthesis, >99 % of dibenzyl urea conversion with 96% selectivity for the desired product can be obtained at 190 °C within 2 h, entry 2. On the contrast, lower reaction temperature of 180°C and reaction time of 1–2 h were enough for syntheses of *N*-aryl carbamates, entries 3–7. Meanwhile, aryl isocyanate was found to be the main by-product and responsible for the lower selectivity. One possible reason for the relatively higher catalytic activity towards aryl carbamates can be ascribed to the good leaving ability of aryl amine moieties appended on the aryl substrates, thus facilitating the nucleophilic attack of alcohol in comparison with the aliphatic substrates. Moreover, the conjugate effect between the phenyl amine and the adjacent carbonyl group could contribute to stabilize the resulted aryl carbamate. The success in expansion of substrates provided the feasibility to the green process and an effective catalyst for the syntheses of carbamates from disubstituted ureas.



**Scheme 3** Carbamate syntheses via alcoholysis of disubstituted ureas with low-molecular-weight alcohols.



**Table 5** Scope and limitations for the alcoholysis of disubstituted ureas with butan-1-ol.

Entry	Substrate	Product	Temperature/ °C	Time/ h	Con./ %	Sel./ %
1			200	4	94	>98
2 <sup>a</sup>			190	2	>99	96
3			180	1	>99	98
4			180	2	>99	97
5			180	1	>99	99
6			180	1	>99	99
7			180	1	>99	98

Reaction conditions: 2 g disubstituted urea, 20 ml butan-1-ol, 0.1 g 5 wt % TiO<sub>2</sub>/SiO<sub>2</sub>-600 catalyst.

<sup>a</sup>By-product was *N*-benzylidene(phenyl)methane amine.

## CONCLUSIONS

In summary, carbamate synthesis via alcoholysis of DCU, which can be synthesized from CO<sub>2</sub> and amines, was firstly demonstrated over TiO<sub>2</sub>/SiO<sub>2</sub>, and >95 % of desired carbamate yields with 98 % selectivities can be achieved. Thus, the utilization of CO<sub>2</sub> as a carbonyl source for carbamate synthesis was realized, to some extent, via an efficient and environmentally route. The catalyst is active, stable, and easy to scale up in industrial scale. The detailed characterization of the catalyst revealed that the strong acidity was considered to play an important role for its superior activity. Moreover, the catalytic activity can be preserved during the recycling tests, which exhibited potential application in industrial manufacture. It also provided an effective catalyst that can yield other alkyl or aryl carbamates via alcoholysis of disubstituted ureas. Therefore, N-substituted carbamates syntheses via alcoholysis of disubstituted ureas can be realized in a green and effective way.

## EXPERIMENTAL SECTION

### Materials and methods for the preparation of catalyst

A titanium precursor solution was prepared by adding tetrabutyl titanate ( $\geq 98.0\%$ , Shanghai Shanpu Chemical Co., Ltd.) to diluted nitric acid solution slowly under vigorous stirring. Subsequently, upper butan-1-ol formed during the hydrolysis of tetrabutyl titanate was carefully separated by a separatory funnel. A solution containing titanium acid was obtained and used for the subsequent process. Then  $\text{SiO}_2$  powder (purchased from Qingdao Hai Yang Chemical Co., Ltd.), which was pretreated at  $600\text{ }^\circ\text{C}$  for 4 h, was used for wet impregnation with the solution aforementioned, dried, and calcined at the temperature ranges of  $400\text{--}800\text{ }^\circ\text{C}$ . Finally, white powders were obtained, denoted as  $x\text{TiO}_2/\text{SiO}_2\text{-}T$ , and defined as aforementioned. The catalyst was pretreated in refluxing ethanol to remove the titanium species attached weakly on the catalyst surface before use.  $\text{TiO}_2\text{-}600$  was prepared according to the similar procedure aforementioned in absence of the  $\text{SiO}_2$  support. Similar procedure was used for preparation of 5 wt %  $\text{TiO}_2/\text{SAPO-11-}600$  or 5 wt %  $\text{TiO}_2/\text{MCM-41-}600$ . Among them, SAPO-11 molecular sieve (average pore diameter of 1 nm, pore volume of  $0.15\text{ cm}^3/\text{g}$ ,  $S_{\text{BET}}$  of  $230\text{ m}^2/\text{g}$ ), and MCM-41 molecular sieve (average pore diameter of 3.5 nm, pore volume of  $0.7\text{ cm}^3/\text{g}$ ,  $S_{\text{BET}}$  of  $800\text{ m}^2/\text{g}$ ) were purchased from Tianjin Chemist Scientific, Ltd.

### Characterization of the $\text{TiO}_2/\text{SiO}_2$ catalyst

The weight percentage of titania in the catalyst was measured by an IRIS Advantage ER/S ICP emission spectrometer (TJA, USA). The BET surface area, pore volume, and pore diameter distribution were obtained by physisorption of  $\text{N}_2$  at 77 K on a Micrometrics ASAP 2010 with the samples outgassed at  $200\text{ }^\circ\text{C}$  prior to the adsorption/desorption measurements. XRD was measured on a Siemens D/max-RB powder X-ray diffract meter. Diffraction patterns were recorded with  $\text{Cu K}\alpha$  radiation (40 mA, 40 kV) over a  $2\theta$  range of  $10$  to  $80^\circ$  and a position-sensitive detector. The morphological structures were examined by FE-SEM, JSM-6701F. TEM observations were performed on a JROL JEM-2010 electron microscopy operated at an acceleration voltage of 120 KV. The surface acid/base properties of the catalysts were measured by TPD of  $\text{NH}_3$  and carried out on TPD flow system equipped with a TCD detector. The TPD diagrams were recorded under the following conditions: nitrogen flow rate:  $50\text{ ml min}^{-1}$ ; heating rate:  $10\text{ }^\circ\text{C min}^{-1}$ ; amount of sample: 80 mg. The strengths of the acidity were defined according to desorption temperature ( $T_d$ ), i.e., weak ( $T_d < 200\text{ }^\circ\text{C}$ ) and strong ( $T_d > 200\text{ }^\circ\text{C}$ ).

### Catalytic reaction for the preparation of N-substituted carbamates

In a typical experiment, 1.0 g DCU, 20 ml alcohols, and 0.1 g  $\text{TiO}_2/\text{SiO}_2$  were introduced into a 45-ml autoclave with a magnetic stirrer and sealed. The reaction system was heated to the desired reaction temperature. After completion of the reaction, the autoclave was cooled to room temperature. The catalyst could be recycled simply by filtration. The alcohol and cyclohexyl amine were easily separated by distillation under reduced pressure from product mixture, and subsequently the alkyl carbamates were dissolved in diethyl ether, resulting in insoluble substrate of DCU. The DCU conversion was determined by measuring the weight that unreacted. Product yield was determined by gas chromatography (GC) with a flame ionization detector (FID). A similar procedure was used for the syntheses of other N-substituted carbamates except of minor modification in the separation of carbamate and amine with relatively higher boiling point ( $>200\text{ }^\circ\text{C}$ ), i.e., naphthyl amine, dodecanamine, *p*-chloroaniline, or *p*-hydroxyaniline. After the distillation of alcohol, hot water was added to the mixture of amine and carbamate to remove the amine, simultaneously the insoluble carbamate was easily recycled by filtration.

### Recycling experiments for 5 wt % TiO<sub>2</sub>/SiO<sub>2</sub> catalyst

For the recycling tests, the catalyst of 5 wt % TiO<sub>2</sub>/SiO<sub>2</sub>-600 was separated by filtration, washed with acetone (2 × 3 ml), and dried at 80 °C. A new charge of reactants with the recycled catalyst was added to the autoclave, sealed, and submitted for the next run.

### SUPPLEMENTARY INFORMATION

Supplementary Information is available online (doi:10.1351/PAC-CON-11-05-06).

### ACKNOWLEDGMENT

Partial financial support from Bayer MaterialScience is gratefully acknowledged.

### REFERENCES

1. (a) J. Barthelemy. *Lyon Pharm.* **37**, 297 (1986); (b) D. B. Dell'Amico, F. Calderazzo, L. Labella, F. Marchetti, G. Pampaloni. *Chem. Rev.* **103**, 269 (2003); (c) F. Paul. *Coord. Chem. Rev.* **203**, 269 (2000); (d) R. Srivastava, M. D. Manju, D. Srinivas, P. Ratnasamy. *Catal. Lett.* **97**, 41 (2004).
2. D. Chaturvedi, N. Mishra, V. Mishra. *Curr. Org. Syn.* **4**, 308 (2007).
3. *Ullmann's Encyclopedia of Industrial Chemistry*, 6<sup>th</sup> ed., electronic version, Wiley-VCH (2000).
4. (a) F. Shi, Y. Deng. *Chem. Commun.* 443 (2001); (b) B. Chen, S. S. C. Chuang. *J. Mol. Catal., A: Chem.* **195**, 37 (2003); (c) F. Shi, Y. Deng, T. Sima, H. Yang. *J. Catal.* **203**, 525 (2001); (d) F. Ragaini, S. Cenini, F. Demartin. *J. Chem. Soc., Chem. Commun.* 1467 (1992).
5. M. Distaso, E. Quaranta. *J. Catal.* **253**, 278 (2008).
6. M. Aresta, A. Dibenedetto. *Dalton Trans.* **28**, 2975 (2007).
7. R. Salvatore, S. Shin, A. Nagle, K. Jung. *J. Org. Chem.* **66**, 1035 (2001).
8. M. Abla, J. Choi, T. Sakakura. *Chem. Commun.* **21**, 2238 (2001).
9. A. Ion, C. V. Doorslaer, V. Parvulescu, P. Jacobs, D. D. Vos. *Green Chem.* **10**, 111 (2008).
10. S. N. Mantrov, A. A. Orlova, A. L. Chimishkyan. Russ. RU 2359958 C2 20090627 (2009).
11. F. Shi, Y. Deng, T. Sima, J. Peng, Y. Gu, B. Qiao. *Angew. Chem., Int. Ed.* **42**, 3257 (2003).
12. C. B. Khouw, C. B. Dartt, J. A. Labinger, M. E. Davis. *J. Catal.* **149**, 195 (1994).
13. S. Klein, J. A. Martens, R. Parton, K. Vercruysse, P. Jacobs, W. F. Maier. *Catal. Lett.* **38**, 209 (1996).
14. W. Kim, J. S. Lee. *J. Catal.* **185**, 307 (1999).
15. B. Bonelli, M. Cozzolino, R. Tesser, M. Di Serio, M. Piumetti, E. Garrone, E. Santacesaria. *J. Catal.* **246**, 293 (2007).
16. H. Kanai, H. Kobayashi. *Catal. Lett.* **20**, 125 (1993).
17. J. Lu, K. M. Kosuda, R. P. Van Duyne, P. C. Stair. *J. Phys. Chem. C* **113**, 12412 (2009).
18. E. Santacesaria, M. Cozzolino, M. Di Serio, A. M. Venezia, R. Tesser. *Appl. Catal., A* **270**, 177 (2004).
19. S. Wang, X. Ma, H. Guo, J. Gong, X. Yang, G. Xu. *J. Mol. Catal., A: Chem.* **214**, 273 (2004).
20. S. Brunauer, L. Deming, W. E. Deming, E. Teller. *J. Am. Chem. Soc.* **62**, 1723 (1940).
21. G. Tian, H. Fu, L. Jing, B. Xin, K. Pan. *J. Phys. Chem. C* **112**, 3083 (2008).
22. P. Tundo, S. Bressanello, A. Loris, G. Sathicq. *Pure Appl. Chem.* **77**, 1719 (2005).