Article

Environmental-Friendly Synthesis of Alkyl Carbamates from Urea and Alcohols with Silica Gel Supported Catalysts

Yubo Ma ^{1,2} , Lei Wang ^{1,3,*}, Xiaodong Yang ^{4,*} and Ronghui Zhang ⁵

¹ School of Chemical Engineering, Chongqing Chemical Industry Vocational College, Chongqing 401220, China; myb3210@126.com

² Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

³ Department of Chemistry and Chemical Engineering, Xinjiang University, Urumqi 830011, China

⁴ Institute of Resources and Environment Science, Xinjiang University, Urumqi 830011, China

⁵ Guangdong Key Laboratory of Intelligent Transportation System, School of Engineering, Sun Yat-sen University, Guangzhou 510275, China; zhangrh25@sysu.edu.cn

* Correspondence: myb32103210@163.com (L.W.); mking@163.com (X.Y.)

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Abstract: $\text{TiO}_2/\text{SiO}_2$, $\text{Cr}_2\text{O}_3\text{-NiO}/\text{SiO}_2$, and $\text{TiO}_2\text{-Cr}_2\text{O}_3/\text{SiO}_2$ were prepared by the impregnation method for alkyl carbamate synthesis using urea as the carbonyl source. Up to 97.5% methyl carbamate yield, 97% ethyl carbamate yield, and 96% butyl carbamate yield could be achieved, respectively. The catalysts were characterized by ICP-AES, BET, XRD, XPS, NH_3 -TPD, and EPMA. Catalytic activity investigation revealed that $\text{TiO}_2/\text{SiO}_2$, $\text{Cr}_2\text{O}_3\text{-NiO}/\text{SiO}_2$, and $\text{TiO}_2\text{-Cr}_2\text{O}_3/\text{SiO}_2$ were effective catalysts for methyl carbamate (MC), ethyl carbamate (EC), and butyl carbamate (BC), respectively. The recycling tests suggested that these silica gel supported catalyst system is active, stable, and reusable. A total of 96–97% alkyl carbamate (methyl, ethyl, and butyl) could be obtained in a 2 L autoclave, and these data suggested that our catalyst system is relatively easy to scale up.

Keywords: alkyl carbamate; $\text{TiO}_2/\text{SiO}_2$; $\text{TiO}_2\text{-Cr}_2\text{O}_3/\text{SiO}_2$; $\text{Cr}_2\text{O}_3\text{-NiO}/\text{SiO}_2$; urea; alcohol

1. Introduction

Alkyl carbamates are important intermediates and end products in the synthesis of a variety of organic compounds [1–3]. For example, it is extensively used for the synthesis of melamine derivatives, polyethylene amine, alkanediol dicarbamates, textile crease-proofing agents [4–8], and itself is also a promising “tranquilizing” drug [9–12]. In the meantime, alkyl carbamates could be used as feedstocks for the synthesis of corresponding organic carbonates such as dimethyl carbonate, diethyl carbonate, dibutyl carbonate, and so on. Significantly, the alkyl carbamate could be used as carbonyl source to replace phosgene for the synthesis of isocyanates [13–16]. Since more than 85% phosgene was consumed in isocyanate industry, this could be the promising usage of carbamates in the future [17].

Various systems have been reported for carbamate synthesis [18–28]. One of the typical methods was the reaction of alcohol and phosgene; however, large amounts of chloroformate ester would be formed during the reaction.

Recently, the reaction of alcohol with urea has been more attractive because the ammonia emitted in this process could be easily recycled for synthesis of urea. As well known, urea production is the only way for large scale chemical fixation of carbon dioxide. Thus, carbon dioxide is indirectly used as carbonyl source in the whole process for carbamates synthesis with urea as the carbonyl sources. So, the green and cheap carbonyl source, carbon dioxide, could be successfully used for large-scale industrial process and the green-house gas emission could be reduced.

Since the end of the last century, different kinds of solid acidic and basic catalysts such as ZnO, MgO, CaO, and transition metal oxides have been used for the synthesis of carbamates [4,5,21–28]. Unfortunately, the low yield towards the desired products and the reusability of the catalyst have been significant problems until now. In view of the practical application, the development of catalysts, which should be simple, active, and easily reusable, for the synthesis of alkyl carbamates from urea is highly desirable.

Higher than 80% O-substituted carbamate could be achieved. Moreover, a 10% difference of yield was observed in different autoclaves in our lab, which motivated us to study the possible reason for this reaction; the composites of autoclave were 1Cr9Ni18Ti, which may be played a key for urea conversion and alkyl carbamate yield. Therefore, a series of catalysts containing Ti, Cr, Ni was prepared by the impregnation method and used for synthesis of alkyl carbamates. The catalytic performance of catalyst for MC synthesis is little effect, while an obviously effect were observed for BC and EC synthesis. Three different catalysts were selected by screening the catalysts containing Ti, Cr, and Ni. Three different catalysts were obtained for MC, EC, and BC synthesis, respectively.

More than 98.7% MC yield could be achieved in Ref. [27], EC and BC was not studied; the catalyst of [28] was a nano metal oxide and R₃N, which was a mixed catalyst, and R₃N was dissolved in the reaction system.

Therefore, this kind of reaction was studied in this work over supported catalysts containing Ti, Cr, and Ni. Here, we report our results about the preparation, characterization and usage of TiO₂/SiO₂, Cr₂O₃-NiO/SiO₂, and TiO₂-Cr₂O₃/SiO₂ catalysts for synthesis of methyl carbamate (MC), ethyl carbamate (EC), and butyl carbamate (BC) (Scheme 1).

Scheme 1. Synthesis of methyl, ethyl, butyl carbamate/dimethyl, diethyl, and dibutyl carbonate.

2. Results and Discussion

2.1. Characterization of Catalysts

The catalysts were characterized by ICP-AES, BET, XPS, XRD, TPR, and EPMA. All the catalysts prepared and characterized in this work are shown in Table 1.

Table 1. Typical physicochemical properties of TiO₂/SiO₂, Cr₂O₃-NiO/SiO₂, and TiO₂-Cr₂O₃/SiO₂ catalysts with different composition.

Catalyst	M/Si atom% Bulk	Surface Area/m ² /g	Pore volume /cm ³ /g	B. E. /eV	M/Si atm% Surface
SiO ₂		601	0.74		
2.2 wt% TiO ₂ /SiO ₂ -500	Ti/Si 3.8	554	0.69	Ti 2p _{3/2} 459.1	Ti/Si 3.0
2.9 wt% TiO ₂ /SiO ₂ -500					
3.6 wt% TiO ₂ /SiO ₂ -500					
3.5 wt% Cr ₂ O ₃ -8.0 wt% NiO/SiO ₂ -500	Cr/Si 10 Ni/Si 7.9	370	0.47	Cr 2p _{3/2} 577.6 Ni 2p _{3/2} 856.6	Cr /Si 12.6 Ni/Si 7.8
7.1 wt% Cr ₂ O ₃ -6.3 wt% NiO/SiO ₂ -500					

Table 1. Cont.

Catalyst	M/Si atom% Bulk	Surface Area/m ² /g	Pore volume /cm ³ /g	B. E. /eV	M/Si atm% Surface
9.0 wt% Cr ₂ O ₃ -3.6 wt% NiO/SiO ₂ -500					
1.7 wt% TiO ₂ -4.9 wt% Cr ₂ O ₃ /SiO ₂ -500					
1.4 wt% TiO ₂ -6.1 wt% Cr ₂ O ₃ /SiO ₂ -500	Ti/Si 2.0 Cr/Si 7.9	434	0.49	Ti 2p _{3/2} 458.7 Cr 2p _{3/2} 577.2	Ti/Si 2.4 Cr/Si 8.6
1.0 wt% TiO ₂ -8.5 wt% Cr ₂ O ₃ /SiO ₂ -500					

BET surface areas and pore volumes of the catalysts are lower than that of pure SiO₂. The BET surface areas decreased with the increasing of the loadings of oxides of transition metal and the surface area of the catalysts were in the range of 350–540 m²/g, Table 1.

The XPS analysis confirmed that the bond valence of titanium on the surface of 2.9 wt% TiO₂/SiO₂-500 was Ti⁴⁺ (BE of Ti 2p_{3/2} = 459.1 eV) (Figure 1a and Table 1). The binding energies of Ti 2p_{3/2} and Cr 2p_{3/2} are 458.7 eV and 577.2 eV, respectively, in 1.4 wt% TiO₂-6.1 wt% Cr₂O₃/SiO₂-500 (Figure 1b and Table 1). The binding energies of Cr 2p_{3/2} and Ni 2p_{3/2} are 577.6 eV and 856.6 eV, respectively, in 7.1 wt% Cr₂O₃-6.3 wt% NiO/SiO₂-500 (Figure 1c and Table 1). Thus, the corresponding chemical states of these surface Ti, Cr, and Ni species are Ti⁴⁺, Cr³⁺, and Ni²⁺.

Figure 1. Cont.

Figure 1. XPS patterns of (a) 2.9 wt% $\text{TiO}_2/\text{SiO}_2$ -500; (b) 7.1 wt% Cr_2O_3 -6.3 wt% NiO/SiO_2 -500; (c) 1.4 wt% TiO_2 -6.1 wt% $\text{Cr}_2\text{O}_3/\text{SiO}_2$ -500.

XRD showed that only weak diffraction peaks of body-centered tetragonal TiO_2 (anatase) could be observed in 2.9 wt% $\text{TiO}_2/\text{SiO}_2$ -500 (Figure 2a), which suggests that TiO_2 in the 2.9 wt% $\text{TiO}_2/\text{SiO}_2$ -500 is poorly crystallized. Surprisingly, although the Cr_2O_3 content reaches 7.1 wt%, no diffraction peaks of Cr_2O_3 are observable in 7.1 wt% Cr_2O_3 -6.3 wt% NiO/SiO_2 -500 and only weak diffraction peaks of face-centered cubic NiO appeared (Figure 2b). In reverse, only weak diffraction peaks of rhomb-centered rhombohedral Cr_2O_3 was observed and no diffraction peaks of TiO_2 appeared for 1.4 wt% TiO_2 -6.1 wt% $\text{Cr}_2\text{O}_3/\text{SiO}_2$ -500 (Figure 2c). All these results indicated that Cr_2O_3 and TiO_2 species are highly dispersed.

Figure 2. Cont.

Figure 2. XPS patterns of (a) 2.9 wt% $\text{TiO}_2/\text{SiO}_2$ -500; (b) 7.1 wt% Cr_2O_3 -6.3 wt% NiO/SiO_2 -500; and (c) 1.4 wt% TiO_2 -6.1 wt% $\text{Cr}_2\text{O}_3/\text{SiO}_2$ -500.

Pure silica gel, 2.9 wt% $\text{TiO}_2/\text{SiO}_2$ -500, 1.4 wt% TiO_2 -6.1 wt% $\text{Cr}_2\text{O}_3/\text{SiO}_2$ -500 and 7.1 wt% Cr_2O_3 -6.3 wt% NiO/SiO_2 -500 were further characterized by TPD- NH_3 . It indicated significant difference in acidities among the catalysts, Figure 3. Only one NH_3 adsorption peak in the weak acid site region, i.e., T_{max} 423–523 K, appeared. The temperatures at which NH_3 adsorption reached the maximum are 473K for 2.9 wt% $\text{TiO}_2/\text{SiO}_2$ -500, 443K for SiO_2 , 453K for 1.4 wt% TiO_2 -6.1 wt% $\text{Cr}_2\text{O}_3/\text{SiO}_2$ -500 and 463K for 1.4 wt% TiO_2 -6.1 wt% $\text{Cr}_2\text{O}_3/\text{SiO}_2$ -500, respectively. Thus the 2.9 wt% $\text{TiO}_2/\text{SiO}_2$ -500 exhibited the strongest acidic strength. The TPD analysis also suggested that 500 °C is a suitable temperature in order to achieve more acidic sites, Figures 4–6.

Figure 3. NH_3 -TPD profiles of (a) SiO_2 (pretreated at 600 °C for 2 h); (b) 2.9 wt% $\text{TiO}_2/\text{SiO}_2$ -500; (c) 7.1 wt% Cr_2O_3 -6.3 wt% NiO/SiO_2 -500; and (d) 1.4 wt% TiO_2 -6.1 wt% $\text{Cr}_2\text{O}_3/\text{SiO}_2$ -500.

Figure 4. NH_3 -TPD profiles of (a) 2.9 wt% $\text{TiO}_2/\text{SiO}_2$ -400, (b) 2.9 wt% $\text{TiO}_2/\text{SiO}_2$ -500; and (c) 2.9 wt% $\text{TiO}_2/\text{SiO}_2$ -600.

Figure 5. NH_3 -TPD profiles of (a) 7.1 wt% Cr_2O_3 -6.3 wt% NiO/SiO_2 -400; (b) 7.1 wt% Cr_2O_3 -6.3 wt% NiO/SiO_2 -500; and (c) 7.1 wt% Cr_2O_3 -6.3 wt% NiO/SiO_2 -600.

Figure 6. NH_3 -TPD profiles of (a) 1.4 wt% TiO_2 -6.1 wt% $\text{Cr}_2\text{O}_3/\text{SiO}_2$ -400; (b) 1.4 wt% TiO_2 -6.1 wt% $\text{Cr}_2\text{O}_3/\text{SiO}_2$ -500; and (c) 1.4 wt% TiO_2 -6.1 wt% $\text{Cr}_2\text{O}_3/\text{SiO}_2$ -600.

The distributions of Ti, Cr, and Ni of 2.9 wt% $\text{TiO}_2/\text{SiO}_2$ -500, 1.4 wt% TiO_2 -6.1 wt% $\text{Cr}_2\text{O}_3/\text{SiO}_2$ -500, and 7.1 wt% Cr_2O_3 -6.3 wt% NiO/SiO_2 -500 inside the SiO_2 pellet were analyzed with electron probe microanalysis (EPMA), Figure 7. It was very clear that distributions of Ti, Cr, and Ni inside SiO_2 pellets were relatively uniform in all three catalysts and almost synchronous distributions of Cr-Ni and Ti-Cr were formed in 7.1 wt% Cr_2O_3 -6.3 wt% NiO/SiO_2 -500 and 1.4 wt% TiO_2 -6.1 wt% $\text{Cr}_2\text{O}_3/\text{SiO}_2$ -500. This means that strong interaction between Cr and Ni or Ti and Cr may occur, and relatively uniform distributions of Ti, Cr, and Ni in support maybe favorable to get highly stable catalysts.

Figure 7. The distributions of Ti, Cr and Ni in the cross section of catalyst pellets: 2.9 wt% $\text{TiO}_2/\text{SiO}_2$ -500, 7.1 wt% Cr_2O_3 -6.3 wt% NiO/SiO_2 -500, and 1.4 wt% TiO_2 -6.1 wt% $\text{Cr}_2\text{O}_3/\text{SiO}_2$ -500 from edge to center.

2.2. Catalytic Activity Test

2.2.1. Effect of Active Metal Loading on Synthesis of Alkyl Carbamate

As shown in Table 2, almost same urea conversion, 1–6 yields could be obtained in the absence of catalyst or SiO₂ as the catalyst.

The effect of amount of Ti loading on the synthesis of **1** and **2** was then examined. The results were shown in Table 2. The conversion of urea increases from 94% to 100% and remains unchanged with the increasing of Ti loading (entries 1–5). The highest yield, 97.5%, was obtained with 2.9 wt% of titanium loading.

Table 2. Effect of catalyst loading on synthesis of alkyl carbamate *.

Entry	Catalyst	Con./%	Y. Carbamate%	Y. Dialkyl Carbonate/%
1		94	MC 89	DMC 0.3
2	SiO ₂	94	MC 90	DMC 0.4
3	2.2 wt% TiO ₂ /SiO ₂ -500	>99	MC 94	DMC 0.4
4	2.9 wt% TiO ₂ /SiO ₂ -500	>99	MC 97.5	DMC 0.6
5	3.6 wt% TiO ₂ /SiO ₂ -500	>99	MC 96	DMC 0.7
6		85	EC 80	DEC 0.2
7	SiO ₂	85	EC 80	DEC 0.2
8	3.5 wt% Cr ₂ O ₃ -8.5 wt% NiO/SiO ₂ -500	>99	EC 94	DEC 0.3
9	7.1 wt% Cr ₂ O ₃ -6.3 wt% NiO/SiO ₂ -500	>99	EC 97	DEC 0.5
10	9.0 wt% Cr ₂ O ₃ -3.6 wt% NiO/SiO ₂ -500	>99	EC 96	DEC 0.55
11		92	BC 88	DBC 0.4
12	SiO ₂	92	BC 88	DBC 0.4
13	1.0 wt% TiO ₂ -8.5 wt% Cr ₂ O ₃ /SiO ₂ -500	>99	BC 95	DBC 0.2
14	1.4 wt% TiO ₂ -6.1 wt% Cr ₂ O ₃ /SiO ₂ -500	>99	BC 96	DBC 0.5
15	1.7 wt% TiO ₂ -4.9 wt% Cr ₂ O ₃ /SiO ₂ -500	>99	BC 94	DBC 0.65

* Catalysts 0.1 g, urea 1 g, reaction temperature 170 °C. For MC synthesis, 13.5 mL methanol, 6 h. For EC synthesis, 15 mL ethanol, 4 h. For BC synthesis, 20 mL butanol, 4 h.

The effect of loadings of Cr and Ni, Ti, and Cr on the synthesis of EC, BC was also examined by the reaction of urea (1 g) with ethanol (15 mL) and butanol (20 mL) with catalyst (0.1 g) at 170 °C for 4 h, Table 2.

The yield of **3**, **4**, **5**, and **6** is also found to be strongly dependent on the amount of transitional metal loadings. The yield of **3** is only 80% with pure SiO₂ as catalyst and 97% yield was achieved in the presence of catalyst with 7.1 wt% Cr loading and 6.3 wt% Ni loading (entry 9). The yield of **5** is 88% with pure SiO₂ as catalyst and 96% yield was obtained with catalyst containing 1.4 wt% Ti and 6.1 wt% Cr (entry 14).

2.2.2. Performances of Different Catalysts for Synthesis of MC, EC, and BC

Interestingly, quite different catalytic activity exhibited by these three silica gel supported catalysts on synthesis of MC, EC, and BC. As shown in Table 2, the catalyst 2.9 wt% TiO₂/SiO₂-500, 7.1 wt% Cr₂O₃-6.3 wt% NiO/SiO₂-500, and 1.4 wt% TiO₂-6.1 wt% Cr₂O₃/SiO₂-500 gave MC (**1**), EC (**3**), and BC (**5**) in high yields together with the corresponding lower yields of dialkyl carbonates as by-products, respectively. In the reaction of synthesizing alkyl carbamate, the yield for MC, EC, and BC were 97.5%, 97%, and 96%, respectively. These indicate that supported transition metal oxides have good catalytic activity for alkyl carbamate synthesis from urea and alcohols.

2.2.3. Effect of Calcination Temperature

The effect of calcined temperature on the yield of **1**, **3** and **5** was shown in Table 3. The yield of **1** increased from 95% to 97.5 % with the increasing of calcination temperature from 400 °C to 500 °C. A further increase in the calcination temperature led to the decrease of the yield of **1**. Similar trends

were also observed in synthesis of **3** and **5**. One of the possible reasons may be that, more acidic positions could be produced at such a temperature, as suggested by TPD-NH₃ characterization results.

Table 3. Effect of calcinations temperature on the catalytic activity *.

Entry	Catalyst	Time	GC Yield of Alkyl Carbamate
1	2.9 wt% TiO ₂ /SiO ₂ -400	6 h	MC 95%
2	2.9 wt% TiO ₂ /SiO ₂ -500	6 h	MC 97.5%
3	2.9 wt% TiO ₂ /SiO ₂ -600	6 h	MC 94%
4	7.1 wt% Cr ₂ O ₃ -6.3 wt% NiO/SiO ₂ -400	4 h	EC 95%
5	7.1 wt% Cr ₂ O ₃ -6.3 wt% NiO/SiO ₂ -500	4 h	EC 97%
6	7.1 wt% Cr ₂ O ₃ -6.3 wt% NiO/SiO ₂ -600	4 h	EC 96%
7	1.4 wt% TiO ₂ -6.1 wt% Cr ₂ O ₃ /SiO ₂ -400	4 h	BC 95%
8	1.4 wt% TiO ₂ -6.1 wt% Cr ₂ O ₃ /SiO ₂ -500	4 h	BC 96%
9	1.4 wt% TiO ₂ -6.1 wt% Cr ₂ O ₃ /SiO ₂ -600	4 h	BC 95%

* Catalysts 0.1 g, urea 1 g, reaction temperature 170 °C. For MC synthesis, 13.5 mL methanol, 6 h. For EC synthesis, 15 mL ethanol, 4 h. For BC synthesis, 20 mL butanol, 4 h.

2.2.4. Effect of Alcohol/Urea Molar Ratio

The effect of the methanol/urea molar ratio on the yields of **1** and by-product **2** is examined by changing the amounts of methanol while maintaining constant initial amounts of urea (0.017 mol) and 2.9 wt% TiO₂/SiO₂-500 (0.1 g). The results were shown in Figure 8. The conversion of urea remains unchanged and it is normally 100%. The yields of **1** and by-product **2** are found to be strongly dependent on the amounts of methanol (methanol/urea molar ratio). The yield of **1** reached a maximum with a methanol/urea molar ratio of 20. Further increase of the amount of methanol caused the more production of **2**. Thus, the reasonable methanol/urea molar ratio is ~20.

Figure 8. Effect of methanol/urea molar ratio on yield and selectivity of **1** and **2**. Reaction conditions: 1 g urea, 0.1 g TiO₂/SiO₂, 170 °C, and 6 h.

In the synthesis of **3** and **5**, the results with varied ethanol or butanol/urea molar ratio were shown in Table 4. It was found that the suitable ethanol/urea molar ratio is 15.7 and the butanol/urea molar ratio is 13 for the synthesis of EC and BC, respectively.

Table 4. Effect of molar ratio of ethanol/urea or butanol/urea on synthesis of EC or BC *.

Catalyst	Alcohol/Urea	Urea Con./%	Y. Carbamate/%	Y. Dialkyl Carbonate/%
7.1 wt% Cr ₂ O ₃ -6.3 wt% NiO/SiO ₂ -500	10.4	>99	EC 91	DEC 0.8
7.1 wt% Cr ₂ O ₃ -6.3 wt% NiO/SiO ₂ -500	15.7	>99	EC 97	DEC 0.5
7.1 wt% Cr ₂ O ₃ -6.3 wt% NiO/SiO ₂ -500	21	>99	EC 93	DEC 0.3
1.4 wt% TiO ₂ -6.1 wt% Cr ₂ O ₃ /SiO ₂ -500	9.7	>99	BC 92	DBC 2.5
1.4 wt% TiO ₂ -6.1 wt% Cr ₂ O ₃ /SiO ₂ -500	13	>99	BC 96	DBC 0.5
1.4 wt% TiO ₂ -6.1 wt% Cr ₂ O ₃ /SiO ₂ -500	16.2	>99	BC 94	DBC 0.3

* Catalysts 0.1 g, urea 1 g, reaction temperature 170 °C, reaction time 4 h.

2.2.5. Effect of Catalyst Loadings

The effect of the loading of catalyst 2.9 wt% TiO₂/SiO₂-500 on the yields of **1** and by-product **2** is examined at 170 °C using a methanol/urea molar ratio of 20. The results were given in Figure 9. The conversion of urea without catalyst is 94% with 90% yield of **1** and 0.4% of **2**. The conversion of urea increases to more than 99% when 0.05 g catalyst was used and the corresponding yield was 97.5%. When the catalyst loading increased to 0.1 g, more byproduct **2** would be generated and the yield of **1** decreased to 95%.

Figure 9. Effect of amount of 2.9 wt% TiO₂/SiO₂-500 on urea conversion, yields of **1** and **2**, and selectivity for **1**. Urea 1 g, methanol 13.5 mL, 170 °C, and 6 h.

As above mentioned in Table 2, almost same urea conversion, 1–6 yields could be obtained in the absence of catalyst or SiO₂ as the catalyst. Therefore, there was no catalyst was used for blank test for the effect of amount on synthesis of MC, EC, and BC.

The results for the optimization of the reaction of urea with ethanol or butanol were shown in Table 5. The conversion of urea without catalyst is 85% or 92%, respectively, and the yield of **3** is

80%, **4** is 0.2%, **5** is 88% and **6** is 0.4%. The conversion of urea increases to more than 99% with the employment of 5 wt% catalyst. At the same time, the yield of **3** or **5** increased to 97% and 96% if 10 wt% catalysts were applied. With further increase of the amount of catalyst, the yield of **3** or **5** will decrease to 94% or 90%, respectively.

Table 5. Effect of catalyst amount on synthesis of EC and BC *.

Entry	Catalyst/%	Alcohol	Con./%	Y. Carbamate/%	Y. Dialkyl Carbonate/%
1 ^a	0	Ethanol	85	EC 80	DEC 0.2
2 ^a	5	Ethanol	>99	EC 90	DEC 0.4
3 ^a	10	Ethanol	>99	EC 97	DEC 0.5
4 ^a	15	Ethanol	>99	EC 94	DEC 0.55
5 ^b	0	Butanol	92	BC 88	DBC 0.4
6 ^b	5	Butanol	>99	BC 92	DBC 2.5
7 ^b	10	Butanol	>99	BC 96	DBC 0.6
8 ^b	15	Butanol	>99	BC 90	DBC 2.5

* Ethanol 15 mL, butanol 20 mL, urea 1 g, reaction temperature 170 °C, reaction time 4 h. a: Catalyst, 7.1 wt% Cr₂O₃-6.3wt% NiO/SiO₂-500; b: Catalyst, 1.4 wt% TiO₂-6.1wt% Cr₂O₃/SiO₂-500.

2.2.6. Effect of Reaction Temperature

The effect of reaction temperature on reaction behavior is examined by the reaction of urea (1 g) with methanol (13.5 mL) at temperatures from 150 °C to 180 °C by using 2.9 wt% TiO₂/SiO₂-500 (0.1 g) as catalyst. The results are shown in Figure 10. The yield of **1** increased from 75 to 97.5% with the increase of reaction temperature from 150 °C to 170 °C. However, it decreases again if the reaction temperature is above 170 °C. Obviously, more production of **2**, 1%, was obtained at 180 °C.

Figure 10. Effect of reaction temperature on urea conversion; yields of **1** and **2**, and selectivity for **1**. Urea 1 g, methanol 13.5 mL, 0.1 g 2.9 wt% TiO₂/SiO₂-500, reaction time: 6 h.

In the reaction of urea with ethanol or butanol, it was also very sensitive to the reaction temperature, Table 6. At 150 °C, 3 and 5 are the only product with yields of 70% and 78%. Then the yields of 3 and 5 were sharply enhanced to 97% and 96% from 70% and 78% when the reaction temperature was increased to 170 °C from 150 °C.

The formation of by-product 4 or 6 is observed at reaction temperatures higher than 160 °C. The yield of 4 and 6, 2% and 2.5%, was obtained at 180 °C. Therefore, the optimum reaction temperature is determined to be 170 °C.

Table 6. Effect of reaction temperature on synthesis of EC and BC *.

Catalyst	T/°C	Con./%	Y. Carbamate/%	Y. Dialkyl Carbonate/%
7.1 wt% Cr ₂ O ₃ -6.3 wt% NiO/SiO ₂ -500	150	72	EC 70	DEC 0
7.1 wt% Cr ₂ O ₃ -6.3 wt% NiO/SiO ₂ -500	160	80	EC 78	DEC 0.3
7.1 wt% Cr ₂ O ₃ -6.3 wt% NiO/SiO ₂ -500	170	>99	EC 97	DEC 0.5
7.1 wt% Cr ₂ O ₃ -6.3 wt% NiO/SiO ₂ -500	180	>99	EC 94	DEC 2
1.4 wt% TiO ₂ -6.1 wt% Cr ₂ O ₃ /SiO ₂ -500	150	80	BC 78	DBC 0
1.4 wt% TiO ₂ -6.1 wt% Cr ₂ O ₃ /SiO ₂ -500	160	92	BC 90	DBC 0.4
1.4 wt% TiO ₂ -6.1 wt% Cr ₂ O ₃ /SiO ₂ -500	170	>99	BC 96	DBC 0.6
1.4 wt% TiO ₂ -6.1 wt% Cr ₂ O ₃ /SiO ₂ -500	180	>99	BC 92	DBC 2.5

* Catalyst 0.1 g, urea 1 g, 4 h, 15 mL ethanol or 20 mL butanol.

2.2.7. Effect of Reaction Time

The results for the synthesis of MC with varied reaction time were shown in Figure 11. The yield of 1 increased from 94.5 to 97.5% with the increasing of reaction time from 4 h to 6 h. However, it would decrease if longer reaction time was applied.

Figure 11. Effect of reaction time on urea conversion, yields of 1 and 2, and selectivity for 1. Urea 1 g, methanol 13.5 mL, 0.1 g 2.9 wt% TiO₂/SiO₂-500, 170 °C.

In the reaction of urea and ethanol or butanol, the similar results were observed, Table 7. The yield of **3** and **5** increased from 93% to 97% and 94% to 96% if prolonged the reaction time to 4 h from 3 h. If the reaction time was longer than 4 hours, more by-product **4** or **6** would be produced.

Table 7. Effect of reaction time on synthesis of EC and BC *.

Catalyst	T/h	Con./%	Y. Carbamate/%	Y. Dialkyl Carbonate/%
7.1 wt% Cr ₂ O ₃ -6.3 wt% NiO/SiO ₂ -500	3	96	EC 93	DEC 0.2
7.1 wt% Cr ₂ O ₃ -6.3 wt% NiO/SiO ₂ -500	4	>99	EC 97	DEC 0.5
7.1 wt% Cr ₂ O ₃ -6.3 wt% NiO/SiO ₂ -500	5	>99	EC 94	DEC 1.3
1.4 wt% TiO ₂ -6.1 wt% Cr ₂ O ₃ /SiO ₂ -500	3	97	BC 94	DBC 0.4
1.4 wt% TiO ₂ -6.1 wt% Cr ₂ O ₃ /SiO ₂ -500	4	>99	BC 96	DBC 0.6
1.4 wt% TiO ₂ -6.1 wt% Cr ₂ O ₃ /SiO ₂ -500	5	>99	BC 95	DBC 1

* Catalyst 0.1 g, urea 1 g, 170 °C, 15 mL ethanol or 20 mL butanol.

2.2.8. Recyclability Test

As a potential reaction process in industry, the reusability of the catalyst some time was more important than the initial catalytic activity. The reusability performance for methyl carbamate synthesis was firstly performed at 170 °C for 6 h with 0.1 g of 2.9 wt% TiO₂/SiO₂-500 catalyst. As shown in Figure 12, MC, EC, and BC yields higher than 95.8%, 94%, and 94% were still remained even after 10 runs, 20 runs, and 10 runs for the three different catalysts, and MC, EC, and BC yield decreased 1.7%, 2%, and 2% after 10 runs. It is to say these silica gel supported catalyst system is active and reusable.

But based on the blank test, there are about 10% MC, 18% EC and 8% BC yields due to the catalyst. MC, EC and BC yield decrease after 10 runs were actually corresponds to a 17%, 11%, and 25% for the catalytic performance, possible reason was that some mass loss of catalysts during the reaction because of mechanical wear. There should be a lot of work need to be done for avoiding mechanical wear in our future work.

Figure 12. Reusability testing of catalysts 2.9 wt% TiO₂/SiO₂-500 for synthesis of MC, 7.1 wt% Cr₂O₃-6.3 wt% NiO/SiO₂-500 for synthesis of EC and 1.4 wt% TiO₂-6.1 wt% Cr₂O₃/SiO₂-500 for synthesis of BC.

2.2.9. Scaling Up in the 2 L Autoclave

Based on the optimized reaction conditions obtained from the results in 90 mL autoclave, synthesis of MC, EC, and BC with urea and methanol (or ethanol and butanol) over 2.9 wt% TiO₂/SiO₂-500, 7.1 wt% Cr₂O₃-6.3 wt% NiO/SiO₂-500, and 1.4 wt% TiO₂-6.1 wt% Cr₂O₃/SiO₂-500 as catalysts were further tested in a 2 L autoclave. It was shown that 96–97% isolated yields were achieved. In comparison with the results obtained from 90 mL autoclave, almost the same catalytic performance was achieved in 2 L autoclave. That means our catalyst system is relatively easy to be scaled up.

3. Experimental

3.1. Materials

All the chemicals were of A.R. degree and were directly used without further treatment. Silica gel pellets: pore volume = 0.60–0.85 mL/g, pore diameter = 4.5–7 nm, BET surface area = 450–650 m²/g, average diameter of the beads = 3 mm).

3.2. Preparation of Catalysts

TiO₂/SiO₂: 10 mL 26–27 wt% HNO₃ aqueous solution was added into a 100 mL beaker containing 3 mL tetrabutyl titanate (Ti(OC₄H₉)₄) to get a homogeneous solution (pH value ~1–2). Then 10 g silica gel pellets was added after being calcined at 600 °C for 2 h and impregnated at room temperature for ~4 h. The silica gel pellets with complete absorption of the aqueous solution were dried at 90 °C for 4 h and then calcined at 500 °C for 4 h. The raw catalyst and 50 mL methanol were introduced into a 250 mL flask and refluxed at 80 °C for 8 h. Then it was filtrated and dried at 100 °C for 4 h in air. The resulted catalyst was denoted as 2.2 wt% TiO₂/SiO₂-500. Catalysts 2.9 wt% TiO₂/SiO₂-500 and 3.6 wt% TiO₂/SiO₂-500 were prepared with the same procedure. 2.9 wt% TiO₂/SiO₂-400 and 2.9 wt% TiO₂/SiO₂-600 were achieved by variation of calcination temperature.

TiO₂-Cr₂O₃/SiO₂: 10 mL 26–27 wt% HNO₃ aqueous solution was added into a 100 mL beaker containing 4 mL Ti(OC₄H₉)₄ to get a homogeneous solution (pH value ~1–2). Then 3.85 g Cr(NO₃)₃·9H₂O was further added (pH value ~2–3). Then 10 g silica gel pellets was added after being calcined at 600 °C for 2 h and impregnated at room temperature for ~4 h. The resulted catalyst precursor was dried at 90 °C for 4 h and then calcined at 500 °C for 4 h. The raw catalyst and 50 mL butanol were introduced into a 250 mL flask and refluxed at 120 °C for 8 h. Then it was filtrated and dried at 100 °C for 4 h in air. The resulted catalyst was denoted as 1.7 wt% TiO₂-4.9 wt% Cr₂O₃/SiO₂-500. Catalysts 1.4 wt% TiO₂-6.3 wt% Cr₂O₃/SiO₂-500 and 1.0 wt% TiO₂-8.5 wt% Cr₂O₃/SiO₂-500 were prepared by variation of the mass of Cr(NO₃)₃·9H₂O with the same procedure. 1.4 wt% TiO₂-6.3 wt% Cr₂O₃/SiO₂-400 and 1.4 wt% TiO₂-6.3 wt% Cr₂O₃/SiO₂-600 were achieved by variation of calcination temperature.

Cr₂O₃-NiO/SiO₂: 7.69 g Cr(NO₃)₃·9H₂O and 4.0 g Ni(NO₃)₂·6H₂O were respectively added into a 100 mL beaker containing 10 mL H₂O. After complete dissolution, the pH value of the solution was 3–3.5. Then 10 g silica gel pellets was added after being calcined at 600 °C for 2 h and then impregnated in the above solutions at room temperature for 4 h. The resulted catalyst precursor was dried at 90 °C for 4 h and then calcined at 500 °C for 4 h. The raw catalyst and 50 mL ethanol were introduced into a 250 mL flask and refluxed at 100 °C for 8 h. Then it was filtrated and dried at 100 °C for 4 h in air. The resulted catalyst was denoted as 3.5 wt% Cr₂O₃-8.0 wt% NiO/SiO₂-500. Catalysts 7.1 wt% Cr₂O₃-6.3 wt% NiO/SiO₂-500 and 9.0 wt% Cr₂O₃-3.6 wt% NiO/SiO₂-500 were prepared by variation of the mass of Cr(NO₃)₃·9H₂O with the same procedure. 7.1 wt% Cr₂O₃-6.3 wt% NiO/SiO₂-400, and 7.1 wt% Cr₂O₃-6.3 wt% NiO/SiO₂-600 were achieved by variation of calcinations temperature.

3.3. Characterization of Catalysts

3.3.1. Elemental Analysis (EA)

The loadings of Ti, Cr, and Ni were determined on an inductively coupled plasma-atomic emission spectrometry (ICP-AES) (ThermoElemental Company Madison, WI, USA) by dissolving the samples in aqueous nitric acid.

3.3.2. BET Analysis

The BET surface area, pore volume and average pore diameter of the catalysts were measured by physisorption of N₂ at 76 K using a Micromeritics ASAP 2010 (San Francisco, CA, USA). Before the measurement, the samples were degassed at 200 °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.

3.3.3. X-ray Photoelectron Spectroscopy (XPS) Measurement

The surface composition was analyzed with a VG ESCALAB 210 instrument (Madison, WI, USA) with an Mg anode and a multi-channel detector. Charge referencing was measured against adventitious carbon (C 1s, 285.0 eV). The surface atomic-distributions were determined from the peak areas of the corresponding lines using a Shirley-type background and empirical cross-section factors for XPS.

3.3.4. X-ray Diffraction XRD Analysis

X-ray diffraction (XRD) patterns were performed on a Siemens D/max-RB powder X-ray Diffractometer (Karlsruhe, Germany). Diffraction patterns recorded with Cu K α radiation (40 mA, 40 kV) over a 2θ range of 15–70° in steps of 0.04° with a count time of 1 s.

3.3.5. Temperature-Programmed Desorption (TPD) Study

TPD analysis with NH₃ was carried out on an improved GC112 instrument (Shanghai, China) to study the acidity of the catalyst surface. In a typical experiment, 250 mg of dried sample (dried at 393 K for 5 h) was taken in a U-shaped quartz sample tube. The sample was pretreated by passing argon over the catalysts at a flow of 50 mL/min at 773 K for 1 h. After pretreatment, the sample was cooled to ambient temperature and treated in a flow of 10% NH₃-Ar mixture (75 mL/min) for 1 h at 313 K. After being flushed with pure argon (50 mL/min) at 373 K for 1 h to remove physisorbed NH₃, TPD analysis was carried out from 373 K to 773 K with a heating rate of 10 °C/min in an argon flow of 50 mL/min.

3.3.6. EPMA Analysis

Ti, Cr, and Ni distributions inside the silica gel pellets were analyzed with a JCXA-733 Super Probe Analyzer (Tokyo, Japan).

3.4. Reaction Conditions for Carbamates Synthesis

3.4.1. General Precedure for Synthesis of Alkyl Carbamate in a 90 mL Autoclave

A total of 13.5 mL methanol (or 15 mL ethanol, or 20 mL butanol), 1 g urea, and 0.1 g of catalyst were successively introduced into a 90 mL autoclave inside a glass tube. After reacting at 170 °C for 4–6 h, the autoclave was cooled to room temperature for qualitative and quantitative analyses. In order to achieve higher yield for desired product, ammonia gas produced during the reaction was released 2–3 times.

Ammonia produced in the MC (EC, BC) synthesis was vented as followed: firstly, the autoclave was heated to 170 °C within 20 min, after reacted 1.5 h (1 h, 1 h), the reaction was stopped and cooled to the room temperature by cool water; the pressure of the headspace was 0.2 MPa, the valve was opened. Then, the autoclave was heated to 170 °C within 20 min, after reacted 2.5 h (1.5 h, 1.5 h), the reaction was stopped again and cooled to the room temperature by cool water; the pressure of the headspace was 0.2 MPa, the valve was opened. Then, the autoclave was heated to 170 °C within 20 min, after reacted 1.5 h, the reaction was stopped again and cooled to the room temperature by cool water. After each reaction, the catalyst was separated by filtration and washed by methanol (3 × 20 mL). After it was dried in air, it was directly reused for the next run without any other treatment. The reaction temperature was measured with a thermometer.

3.4.2. A Demonstration for the Scaling up of the Synthesis of Carbamates

A total of 1000 mL methanol (or ethanol, or butanol), 50–70 g urea and 5–7 g catalysts were successively introduced into a 2 L autoclave with a mechanical stirrer and then sealed. After reacted at 170 °C for 4 h, the autoclave was cooled to room temperature for qualitative and quantitative analyses. During the reaction, the autoclave was opened 2–3 times to release the ammonia produced. After it was cooled to room temperature, the catalyst was removed by filtration and the desired product, i.e., raw MC, EC, or BC, could be obtained after the alcohol was removed by distillation. The main impurity inside the product is unreacted urea. After dissolving the crude product in diethyl ether, the urea could be removed by filtration easily. Then, white solid MC, EC, or BC with GC purity > 98% could be obtained.

Qualitative analyses were conducted with a HP 6890/5973 GC-MS (Santa Clara, CA, USA) with a 30 m × 0.25 mm × 0.33 µm capillary column with chemstation containing a NIST mass spectral database. Quantitative analysis was conducted with an Agilent 6820 GC (Santa Clara, CA, USA) with a 30 m × 0.25 mm × 0.33 µm capillary column (FID detector) using an external-standard method.

3.5. Recyclability of the Catalyst

The solid catalyst was recovered by simple filtration, being washed with methanol and dried in air, and then directly reused for the next run without any other treatment.

4. Conclusions

In conclusion, a series of silica gel supported catalysts were successfully prepared, characterized, and employed in the synthesis of alkyl carbamates using urea as the carbonyl source. Up to 96–98% GC yield was achieved for the synthesis of MC, EC, and BC. Reusability testing showed that these catalysts were enough stable and without obvious deactivation even after being reused for 10 times. Reaction investigation in 2 L autoclave suggested that this system is easily to be scaled up. Therefore, it should be helpful to develop industrially applicable catalysts for the synthesis of alkyl carbamate from urea and alcohol.

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