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## Synthesis of carbonates via acid-promoted alcoholysis of carbamates

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**Abstract** : Several carbonates are synthesized from carbamates either with hydrochloride as coreactant or with zeolites as catalysts under low temperature and pressure, whereas high yield is achieved through either the formation of ammonium chloride as precipitate or the adsorption of ammonia in zeolites. With hydrochloride as coreactant, the yield reaches 58% at 60 °C, while the highest yield is 19% at 140 °C with zeolites as catalysts. Carbonates are considered as environmentally compatible reagents, solvents and gasoline additives, and the new processes may be potential for the substitution of the phosgene routes of pollution hazards.

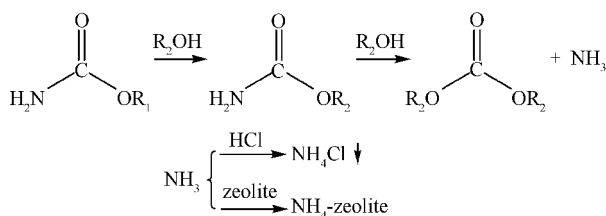
**Key words** : carbonate ; carbamate ; alcoholysis ; zeolites ; hydrochloride

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Organic carbonates are compounds of growing interest because of their versatilities as chemical reagents and solvents<sup>[1]</sup> and the non-toxic and environmentally benign properties<sup>[2]</sup>. Especially, dimethyl carbonate as gasoline additive owns excellent characteristics such as high octane, high density and reduced CO and NOx emissions. The commercial production of organic carbonates is still mainly based on the phosgene routes, which is essential to be substituted by the environmentally benign routes due to the worldwide awareness of pollution hazards of phosgene. The oxidative carbonylation of alcohols<sup>[3,4]</sup> and carbonate interchange reaction between carbonates and alcohols<sup>[5]</sup> are interesting options to replace the phosgene routes, which have attracted considerable attentions. However, both routes suffer from some problems; the former requires harsh reaction conditions and the catalyst deactivated rapidly due to the accumulation of water in the liquid phase<sup>[6]</sup>, while the latter lacks economical preponderance.

Alcoholysis of urea is also a potential route to synthesize carbonates, in which the carbonate forms in two steps. The first step of urea to carbamate is favored, but the second step of carbamate to carbonate is difficult to achieve, which demands high temperature and a proper catalyst<sup>[7]</sup>. By using boron trifluoride as a coreactant, the alcoholysis may be enhanced

through the formation of aminoboron trifluoride precipitate, which provides the thermodynamic driving force for the reaction<sup>[8]</sup>. The major drawback is that boron trifluoride is too expensive to be used as a coreactant in industry.



Scheme 1 Synthesis of carbonates via acid-promoted alcoholysis of carbamates

This approach could be more attractive if a better coreactant or catalyst was employed, allowing operation under low temperature and pressure. As shown in Scheme 1, hydrochloride as an intense acid is an ideal choice for its easy separation and economical superiority. Zeolites such as HY, H $\beta$  and HZSM-5 are well-defined solid acids, which is capable of absorbing basic molecule into their framework. The absorbed basic molecule in the zeolites can be desorbed at temperature above the characteristic temperature, as revealed in the temperature-programmed desorption (TPD)<sup>[9]</sup>. The presence of coreactants provides the thermodynamic driving force for the synthesis of car-

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bonates from carbamates through removing ammonia liberated from alcoholysis. In this work, we have successfully synthesized carbonates in high yields from two kinds of carbamates either with hydrochloride as coreactant or with three kinds of zeolites as catalysts at low temperature and pressure.

## 1 Experimental

Zeolites HY, H $\beta$  and HZSM-5 were prepared by impregnating the commercial samples with a solution of nitrate overnight, followed by drying at 120 °C for 6 h and calcination at 550 °C for 3 h.

With hydrochloride as a coreactant, the experimental procedure was: 50 mmol of carbamate and 30 mL alcohol were first added to a 250 mL 3-neck flask equipped with a magnetic agitator and a condenser. After the dissolution of carbamate, anhydrous hydrochloric acid gas was then introduced until the solution was saturated. The flask was heated at 60 °C for 1 h, and ammonium chloride was precipitated during this time. After cooling, the product was identified by GC-MS and the yield was then determined by GC.

When using zeolites as catalyst, a typical procedure was: In a stainless steel autoclave with the inner volume of 250 cm<sup>3</sup>, 3.0 g zeolites, 50 mmol carbamate and 50 mL alcohol were added. After sealing, the autoclave was then heated and kept at 140 °C for 3 h with stirring. After that, the autoclave was cooling down and the products were analyzed.

## 2 Results and discussion

**2.1 With hydrochloride as a coreactant** The carbonate interchange reaction follows the rule that the reaction of lower dialkyl carbonates with higher alcohols produce higher dialkyl carbonates. This rule can also be applied to the reactions of carbamates with alcohols utilizing hydrochloride as coreactant, i. e. the reaction of lower alkyl carbamates with higher alcohols produces higher dialkyl carbonates. The results of several carbonates synthesis were listed in Table 1.

**Table 1 HCl-promoted synthesis of carbonates**

Series	$R_1$	$R_2$	Yield $w/\%$
1	Me	Me	39
2	Me	Et	46
3	Me	<i>n</i> -Pr	24
4	Me	<i>n</i> -Bu	23
5	Et	Et	58
6	Et	<i>n</i> -Pr	34
7	Et	<i>n</i> -Bu	20

The various carbamates are different in the rate of alcoholysis reaction using hydrochloride as coreactants. It needed about 20 min for the formation of ammonium chloride precipitate in the reactions of methyl carbamate and alcohols. When it came to ethyl carbamate, the time was about 30 min. The reason for this difference may be that the substitution of methoxyl is much easier than that of ethoxyl, and the substitution of aliphatic hydroxyl is the initial step of the reaction. Moreover, the yield of carbonates is related to the quantity of ammonium chloride precipitate; the more precipitate was formed, the higher was the yield we measured. It is noteworthy that the alcoholysis with 2-propanol, 2-butanol and 2-pentanol was unsuccessful, which is presumably attributable to the steric hindrance of these alcohols.

**2.2 Using zeolites as catalyst** For the synthesis of carbonates from carbamate and alcohol ( $R_1 = R_2 = \text{Me}$  and  $R_1 = R_2 = \text{Et}$ , as shown in Scheme 1) with HY, H $\beta$  and HZSM-5 as catalysts, H $\beta$  gave the best results, though HZSM-5 exhibited the strongest acidity and HY owned the largest amounts of acid sites (Figure 1). This phenomenon may suggest that the solid acids demand proper acidity and proper pore size to be effective for the carbonate formation. Small pore size of HY and HZSM-5 may restrain reactant molecule from entering pore structure and result in poor carbamate production.

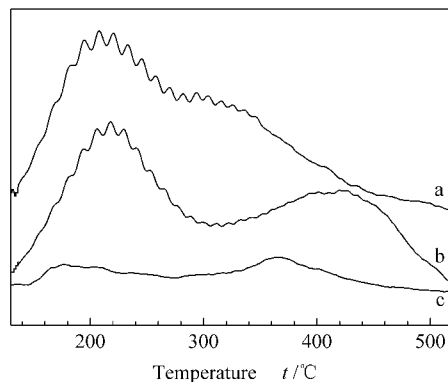


Figure 1 NH<sub>3</sub>-TPD profiles  
a HY; b HZSM-5; c H $\beta$

Figures 2 and 3 show the effects of reaction time and the amount of catalyst on the synthesis of diethyl carbonate from ethyl carbamate and ethanol with H $\beta$  as catalyst. It was observed that a maximum yield of diethyl carbonate achieved after reaction last for 3.0 h and H $\beta$  usage was 3.0 g per 50 mmol carbamate and 50 mL alcohol. Too long time and too much catalyst would lead to the decomposition of the product.

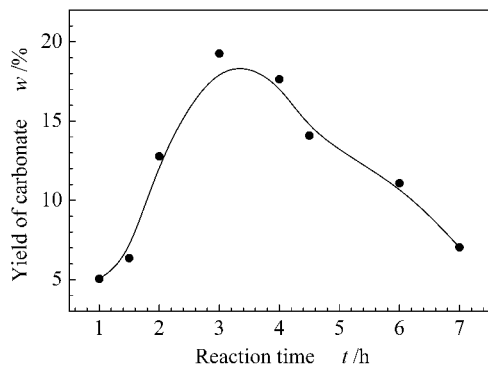


Figure 2 Effect of reaction time on the synthesis of diethyl carbonate

condition :  $H\beta$  ( 3.0 g ), ethyl carbamate ( 50 mmol ), ethanol ( 50 mL ), 140 °C , autogenous pressure

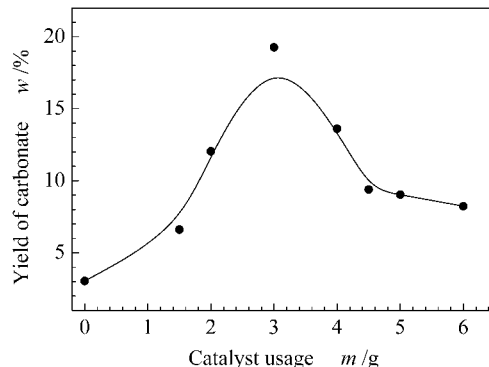


Figure 3 Effect of the catalyst (  $H\beta$  ) usage on the synthesis of diethyl carbonate

condition : ethyl carbamate ( 50 mmol ), ethanol ( 50 mL ), 140 °C , autogenous pressure , reaction last for 3.0 h

In conclusion , the carbonates can be synthesized from carbamates and alcohols with hydrochloride as a coreactants or zeolites as catalysts under low temperature and pressure , whereas high yield is achieved

through either the formation of ammonium chloride as precipitates or the adsorption of ammonia in zeolites. These new processes may be potential to substitute for the phosgene routes.

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## 酸促进的氨基甲酸酯醇解合成碳酸酯

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摘 要 : 在较低温度和压力下 , 以氯化氢为共反应物或沸石分子筛为催化剂 , 由氨基甲酸酯与醇反应合成多种碳酸酯。氯化铵沉淀的生成或沸石分子筛对氨气的吸附 , 可推动反应平衡 , 使碳酸酯的生成达到较高收率。以氯化氢为共反应物时 , 反应温度为 60 °C 最高产率达 58% 而以沸石分子筛为催化剂 , 反应温度为 140 °C 时 , 最高产率是 19%。

关键词 : 碳酸酯 ; 氨基甲酸酯 ; 醇解 ; 沸石 ; 氯化氢

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