SYNTHESIS OF ALKYL CARBAMATES IN THE PRESENCE

OF AN ALUMINOSILICATE CATALYST

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The interesting properties of alkyl carbamates as selective solvents for aromatic hydrocarbons [1-3] determine the importance of developing a simple method for their preparation.

Alkyl carbamates are obtained by reaction of urea with the corresponding alcohols:

$ROH + (NH_2)_2CO \longrightarrow NH_2COOR + NH_3$

The synthesis is carried out in the presence of various catalysts: BF_3 [4], metal salts and oxides [5, 1], zinc oxide with mineral acids [6, 7], etc. All of these catalysts have a series of disadvantages: in their presence the reaction occurs insufficiently rapidly, a high yield of side products is obtained, the catalysts themselves submit with difficulty to regeneration, and so on.

The authors developed a method of preparing alkyl carbamates in the presence of an aluminosilicate catalyst designated for catalytic cracking (VTU, 367-54). Urea (All-Union State Standard 2081-57) and methyl, ethyl, propyl, and butyl alcohols were used as raw materials. Experiments were carried out on a laboratory flow-type apparatus (Fig. 1). The initial raw material (solution of urea in alcohol) was passed from storage tank 1, heated to 50 °C to dissolve urea completely and to prevent its precipitation from solution, with pump 3 into preheater 4. The temperature in the preheater was maintained at 10-20°C below the reaction temperature. All connecting tubes of the system were heated. From the preheater the mixture was directed into reactor 5, $\frac{3}{4}$ filled with catalyst. From the reactor the reaction mixture entered cooler 7, from which it was directed into a cooled receiver 9. The ammonia liberated in the reaction process was absorbed with an acid solution.

At the end of reaction the unreacted alcohol was distilled from the reaction mixture, and the residue was treated with dichloroethane at 40-45 °C for 15 min to remove unreacted urea, which was separated by filtration; the solvent was distilled from the filtrate, and the residue was subjected to vacuum distillation to isolate the desired product.

The Box-Wilson method [8], based on the use of mathematical statistics with systematization of experiments, was used to find the optimal conditions of occurrence of the reaction.

Enstern	Levels		
	-1	+2	
Temperature, ^o C Molar ratio of urea and	140	180	
methanol Space velocity of	1:6	1:12	
introduction, h ⁻¹ Pressure, atm	0,5 40	1,5 80	

TABLE 1. Levels of Varied Factors

To find the limits of the possible optimal region of methyl carbamate sythesis, preliminary experiments were carried out at various pressures in the system, and by changing the temperature from 100 to 180 °C, the molar ratio of urea and methanol from 1:3 to 1:16, and the space velocity of initial-reagent introduction from 0.5 to 2.0 h⁻¹. The outside regions in which the set experiment should be carried out were found during the experiment. The desired product could not be isolated at temperatures of 100 and 120 °C, a molar ratio of urea and methanol of 1:3,

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Experimental conditions			Yield of methyl carbamate, wt. %					
temperature •C	molar ratio of urea and methanol	space velo- city of raw- material in- troduction,h	pressure, atm	of theore- tical	on initial urea	on unreacted urea	Selectivity of the pro- cess, wt.%	Conversion of urea after a pass, wt. %
160 140 180 180 140 140 180 140 140 140 180 180	$\left \begin{array}{c}1:9\\1:12\\1:12\\1:12\\1:6\\1:6\\1:6\\1:6\\1:12\\1:12$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c} 32,7\\25,2\\12,4\\30,8\\22,3\\5,9\\7,3\\1,2\\12,5\\26,3\\14,0\\31,7\\25\\0\end{array}$	41,0 31,4 19,6 38,5 27,8 7,45 9,1 1,49 15,7 32,9 17,5 32,9 17,5 39,6 21,2	49,2 33,0 17,1 58,2 40,6 9,2 61,4 3,31 29,5 34,0 52,1 57,7 42,4	39,3 23,9 39,4 46,5 32,1 7,6 48,0 2,6 23,6 27,2 41,0 46,1 246,1	$\begin{array}{c} 83,3\\96,0\\31,5\\66,2\\70,0\\7,7\\14,8\\45,5\\53,2\\96,7\\34,2\\68,8\\72,0\end{array}$
140 140 180 180 140	1:6 1:6 1:6 1:6	0,5 0,5 1,5	80 80 80 80 80	6,3 8,5 1,9 14,2	7,88 10,62 2,38 17,8	9,7 65,4 5,4 31,2	$ \begin{array}{c c} 34,7 \\ 9,77 \\ 52,2 \\ 4,07 \\ 25,0 \end{array} $	81,0 16,3 46,7 57,0

TABLE 2. Experimental Results on the Synthesis of Methyl Carbamate Used for Mathematical Calculation



Fig. 1. Scheme of the continuous flow-type laboratory apparatus for preparing alkyl carbamates: 1) dosing apparatus; 2) glass for measuring the level; 3) dosing pump; 4) preheater; 5) reactor; 6) regulating valve; 7) cooler; 8) gas meter; 9) receiver.

Fig. 2. Effect of molar ratio of urea and methanol on the yield of methyl carbamate (t = 160 °C; ν = 1.6 h⁻¹, P = 40 atm): A) conversion of urea, wt. %; B) yield of methyl carbamate; C) selectivity of the process, wt %.

and a pressure of 20 Atm; therefore, the experiment having the following levels was chosen as the zero experiment: temperature 160°C, space velocity of raw-material introduction 1.0 h⁻¹, molar ratio of urea and methanol 1:9, pressure 50 atm; under these conditions the desired product was obtained in acceptable yields.

The levels at which the variables were varied – experimental temperature, molar ratio of urea and methanol, space velocity of raw-material introduction, and pressure – are presented in Table 1. Experimental results of the synthesis of methyl carbamate used for mathematical calculation are presented in Table 2.

Equations of response functions for the following values were separated during the mathematical calculation: y_1 is the yield of methyl carbamate based on the theoretical; y_2 is the selectivity of the process; y_3 is the conversion of urea. Equations were presented in a polynomial form:

 $\eta = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_{1,2} x_1 x_2 \ \beta_{1,3} x_1 x_3 + \beta_{1,4} x_1 x_4 + \beta_{2,3} x_2 x_3 + \beta_{2,4} x_2 x_4 + \beta_{3,4} x_3 x_4,$

i.e., both coefficients of linear effects β_1 , β_2 , β_3 , β_4 , and coefficients of effects of linear-linear interaction $\beta_{1,2}$, $\beta_{1,3}$, $\beta_{2,4}$, $\beta_{3,4}$ were calculated.



Fig. 3. Effect of reaction temperature on yield of methyl carbamate (P= 40 atm, $\nu = 1.6 \text{ h}^{-1}$, molar ratio of urea and methanol 1:14): A) conversion of urea, wt. %; B) yield of methyl carbamate, % of theoretical; C) selectivity of the process, wt. %.

Fig. 4. Effect of space velocity of raw-material introduction on yield of methyl carbamate (t = 160 °C, P = 40 atm, molar ratio of urea and methanol 1:14); A) conversion of urea, wt. %; B) yield of methyl carbamate, % of theoretical; C) selectivity of the process, wt. %.

Calculated values of coefficients for y_1 showed that to increase the yield of methyl carbamate it is necessary to increase the space velocity and molar ratio of the initial materials. Increase of temperature is not required.

Calculation of coefficients for y_2 showed that it is necessary to increase the temperature and molar ratio of methanol and urea, and also to decrease significantly the space velocity of raw-material introduction to increase the selectivity of the process.

Carrying out analogous calculations of response functions for conversion of urea we found that it is necessary to decrease the molar ratio of initial reagents and the space velocity, and also to decrease the temperature insignificantly.

As a result of carrying out the mathematical calculation the optimal regions of methyl carbamate synthesis on a continuous appratus and the direction in which further experiments should be carried out were determined. Examining the general conditions necessary for increasing the selectivity of the process, conversion of urea, and yield of methyl carbamate based on the theoretical, it can be concluded that the optimal region of methyl carbamate synthesis is in the temperature intervals close to 160 °C; it is necessary to increase the space velocity of raw-material introduction and the molar ratio of urea and methanol and to decrease the pressure in the system in comparison with the levels of the zero experiment.

Further experiments were carried out to find conditions at which a maximum yield of methyl carbamate is reached and to clarify the effect of various levels of the reaction on the yield of methyl carbamate.

The effect of the ratio of initial reagents, reaction temperature, and space velocity of raw-material introduction on the yield of methyl carbamate were studied.

To expose the effect of the ratio of initial reagents on the yield of methyl carbamate, a series of experiments was carried out at molar ratios of methanol and urea from 9:1 to 16:1 at the constant conditions: temperature 160 °C, pressure 40 atm, and a space velocity of raw-material introduction of 1.6 h⁻¹ (Fig. 2). As is seen from Fig. 2, an increase in the molar ratio of methanol and urea from 9:1 to 14:1 gives an increase in yield of methyl carbamate from 17.8 to 42% of the theoretical, while conversion of urea increases after passing through selectivity of the process. A further increase in amount of methanol used in the experiment does not affect the yield of the desired product.

The increase in all indices of the process with an increase in the amount of methanol used in the reaction is probably explained by the production in this case of less concentrated solutions of ammonia (liberated in the reaction process) which shifts the chemical equilibrium in the direction of formation of the desired product. In this case the solubility of urea in methanol also improves, and the yield of side products decreases.

The effect of reaction temperature on yield of methyl carbamate was studied in the temperature interval from 140 to 180 °C at the constants: molar ratio of methanol and urea 14:1, pressure 40 atm, space velocity of raw-material introduction 1.6 h^{-1} (Fig. 3).

TABLE 3. Synthesis of Alkyl Carbamates in the Presence of an Aluminosilicate Catalyst (t = 160 °C, Molar Ratio of Urea and Alcohol 1:14; $\nu = 1.6$ h⁻¹, P=40 atm)

Formula of synthesized alkyl carbamate, %	Conver- sion of urea, %	Yield of carbama of theore- tical	alkyl ate, % on used urea
$\begin{array}{c} C_2H_5COONH_2 \\ n-C_3H_7COONH_2 \\ n-C_4H_9COONH_2 \\ n-C_5H_{11}COONH_2 \\ n-C_5H_{11}COONH_2 \\ \end{array}$	76,9	75,0	111,0
	80,0	78,9	138,0
	72,5	71,0	194,0
	79,4	79,0	199,2

Maximum yield of 42% methyl carbamate is obtained at 160 °C. An increase in temperature decreases the yield of methyl carbamate probably due to formation of side products.

An increase in space velocity from 0.5 to 1.6 h^{-1} at constants: molar ratio of methanol and urea 14: 1, temperature 160 °C, pressure 40 atm, led to an increase in yield of methyl carbamate from 20.3 to 42% based on the theoretical (Fig. 4). A further increase of space velocity of raw-material introduction to 2.0 h^{-1} decreased the yield of methyl carbamate to 23% of the theoretical. Conversion of urea decreased in this case from 64.5 to 59%.

Thus, the maximum yield of methyl carbamate was obtained at a temperature of 160 °C, a molar ratio of methanol and urea of 14:1, a space velocity of raw-material introduction of 1.6 h^{-1} , and a pressure of 40 atm.

For the purpose of investigating the possibility of a repeated use of urea and methanol a series of experiments was carried out, the starting materials for which were returned methanol and returned urea.

Experiments were carried out at the optimum conditions found earlier. Use of returned methanol and fresh urea as initial reagents virtually does not lead to a decrease in yield of methyl carbamate: using returned urea as the initial raw material shows a more significant decrease in yield of methyl carbamate: from 42 to 34% of the theoretical, while the selectivity of the process decreases sharply. Experimental data indicate that, in the case of recycling the initial components, side reactions increase and the main reaction is slowed down; to increase the yield of methyl carbamate an additional washing of urea is necessary.

To clarify the length of operation of the catalyst the same portion of aluminosilicate catalyst was used to carry out reactions for more than 520 h at the optimal conditions.

The effectiveness of the catalyst was determined from the yield of methyl carbamate and conversion of urea and also from the value of the specific surface of the catalyst in the process of its operation. The yield of methyl carbamate increased slightly upon increasing the length of operation of the catalyst to 48 h; upon further increasing the length of operation of the catalyst to 520 h the yield of methyl carbamate and conversion of urea virtually did not change.

These data agree with results of determination of the specific surface of the aluminosilicate catalyst. The specific surface of the catalyst increased from 313 to 362 m^2/g upon increasing the length of its operation to 50 h, which indicates that the catalyst is developed in the course of all this time. The specific surface of the catalyst remains virtually constant upon increasing the length of operation of the catalyst to 520 h.

Side reaction products were isolated in the synthesis of methyl carbamate. A white finely crystalline product was isolated in an insignificant amount upon distillation of alcohol from the reaction mixture which, according to analyses, was ammonium carbamate.

Judging from molecular weight and elementary composition, the residues after distillation of methyl carbamate were condensation products of methyl carbamate, dimers and trimers, formed by the reaction:

$$\mathrm{NH}_{2}\mathrm{COOCH}_{3} + \mathrm{NH}_{2}\mathrm{COOCH}_{3} \xrightarrow{-\mathrm{CH}_{3}\mathrm{OH}} \mathrm{NH}_{2}\mathrm{CONHCOOCH}_{3} \xrightarrow{\mathrm{NH}_{2}\mathrm{COOCH}_{3}} \mathrm{NH}_{2}\mathrm{CONHCONHCOOCH}_{3}$$

Yield of oligomers amount to about 1 wt. % based on initial raw material.

 C_2-C_4 alkyl carbamates in a yield of 75-79% of the theoretical were obtained under the optimal conditions found for methyl carbamate while conversion of urea amounted to 72.5-80.0% (Table 3).

CONCLUSIONS

1. A process was developed for obtaining alkyl carbametes from urea and the corresponding alcohols in the presence of an aluminosilicate catalyst.

2. Optimal regions for synthesis of methyl carbamate were determined by the Box-Wilson method of multifactor systematization. 3. The effect of various factors (temperature and length of reaction, ratio of initial reagents, space velocity of raw-material introduction, quality of the initial raw material, and length of operation of the catalyst) on the yield of methyl carbamate were studied.

4. C_2-C_5 alkyl carbamates were obtained in yields of 75-79% of the theoretical under the optimal conditions found for methyl carbamate.

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