Carbon dioxide uptake as ammonia and amine carbamates and their efficient conversion into urea and 1,3-disubstituted ureas

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A B S T R A C T

Solid mixtures of ammonium carbamate and bicarbonate originating from the CO$_2$ capture by NH$_3$ in water–ethanol solution were converted into urea by heating to 428 K for 60–90 min. The yield of urea was up to 53% on molar basis. An analogous technique was employed to capture CO$_2$ with 1-aminobutane, 1-amino-2-methylpropane, 2-amino-2-methylpropane, 1-aminooctane, aminocyclohexane and 1,4-diazacyclohexane, in organic solvents as amine carbamates which were separated in the solid state and thermally converted at 423 K for 15–16 h into 1,3-disubstituted ureas with 30–40% yield on molar scale. The formation of 1,3-disubstituted ureas was 100% selective. The rate of the conversion reaction was significantly improved in the presence of copper catalysts. The identification and quantification of the products in the reaction mixtures were obtained by ^{13}C NMR analysis.

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1. Introduction

The chemical absorption of CO$_2$ by aqueous alkanolamines is an efficient methodology for CO$_2$ separation in ammonia and hydrogen plants, natural gas sweetening and, in general, for CO$_2$ removing from industrial exhaust streams [1–11]. However, the critical questions facing this technology are the high energy costs of the amine regeneration and the environmental concerns because of the amine loss by thermal and oxidative degradation [12–17]. In comparison with aqueous alkanolamines, ammonia scrubbing process provides the advantage of high CO$_2$ loading capacity and absorption efficiency with no absorbent degradation [18–25]. However, this technique suffers of serious hurdles due to the ammonia loss and to the costs of NH$_3$ separation from concentrated CO$_2$ in the regeneration step.

In our laboratory we are developing a new concept of CO$_2$ capture technology which combines the CO$_2$ abatement with the production of commercially valuable products [26,27]. Even if we must admit that the conversion of CO$_2$ into commercial products does not significantly reduce the anthropogenic CO$_2$ emissions (billions of metric tons for year), nonetheless turning carbon dioxide into useful chemicals in relatively mild conditions can contribute to reduce the cost of biogas and natural gas cleaning,

hydrogen and ammonia production, and of all the processes where the separation of CO$_2$ from other gases is unavoidable.

In a previous experimental study [28] we reported that the carbon dioxide capture with ammonia in non-aqueous solvents was fast and efficient and produced pure ammonium carbamate that was subsequently converted into urea in the presence of copper(II) promoters. However, this process was unsuitable for a commercial application, due to the low rate of conversion (two–three days heating).

By going on with these studies, we present here our results focused on the fast urea production by heating mixtures of ammonium carbamate and bicarbonate to 438 K for 60–90 min. Besides the advantage of an efficient CO$_2$ capture, this unconventional process could circumvent the high energy costs of the commercial processes of urea production which is carried out in the gas phase with an excess of ammonia (NH$_3$/CO$_2$ molar ratio up to 4) and purified carbon dioxide at 450–500 K and 150–250 bar. Pure CO$_2$ is obtained by the conventional process of aqueous amine scrubbing and thermal stripping, in turn. In the commercial plants, the yield of the reaction is in the order 30–55% on NH$_3$ basis and strongly depends on reaction temperature, pressure, time and NH$_3$/CO$_2$ ratio.

We also used an analogous concept for the CO$_2$ uptake by the non-aqueous solutions of some selected amines and for the thermal conversion of the solid amine carbamates into the corresponding substituted 1,3-disubstituted ureas. The 1,3-disubstituted ureas are valuable products with a wide range of application as intermediates in agrochemical, pharmaceutical,

dye chemicals and recently as precursors of isocyanates and raw materials of polyurethanes [29–34]. Their traditional synthesis required unsafe chemicals such as phosgene or carbon oxide and Au or Pt catalysts [35–38]. In recent years the direct synthesis of substituted ureas has been accomplished with the non toxic and cheap carbon dioxide in the presence of different catalysts and dehydrating agents to increase the yield of reaction [39–42]. Ionic liquids in conjunction with a base (CsOH) or transition metal (Fe, Co, Ni, Cu, Zn) acetates were also employed as reaction medium and catalysts to obtain 1,3-disubstituted ureas in good yield [43–46]. However, most catalysts can be reused no more than 3–4 times. Carbon dioxide has been also reacted with aziridines and ionic liquids as catalysts, affording oxazolidones, which are valuable intermediates in several organic synthesis [47–50].

The unconventional technology we have devised combines the efficient CO_2 uptake from anthropogenic activities by some amines with the thermal conversion of the amine carbamates obtained in the solid state into 1,3-disubstituted ureas without any catalyst, dehydrating agent or external pressure, yet with acceptable yields.

2. Experimental

2.1. General information

All reagents were reagent grade. CuCl, CuCl$_2$·2H$_2$O, ammonium bicarbonate, 1-aminobutane (n-butylamine, NBA), 1-amino-2-methylpropane (isobutylamine, IBA), 2-amino-2-methylpropane (tert-butylamine, TBA), 1-aminoheptane (n-heptylamine, NHA), 1,4-diazacyclohexane (piperazine, PIP), aminocyclohexane (cyclohexylamine, CHA), 1-aminooctane (n-octylamine, NOA), bis(2-ethoxyethyl) ether (diethylene glycol diethyl ether, DEGDEE), 2-(2-methoxyethoxy) ethanol (diethylene glycol methyl ether, DEGMME), 2-ethoxyethanol (ethylene glycol monoethyl ether, EGMEE), 3-pentanone (diethyl ketone, DEK), and ethanol (Sigma–Aldrich) were used as received. Standard NH$_3$ solution 15.2 mol dm^{-3} (Sigma–Aldrich) was used to prepare the ethanol–water–ammonia solutions. Pure CO_2 and N$_2$ used to simulate flue gas and pure NH$_3$ were obtained by Rivoira. Flow rates of air, CO_2 and NH$_3$ were measured with gas mass flow meters (Aalborg) equipped with gas controllers (Cole Parmer). The inlet and outlet CO_2 concentrations in the flue gas mixture were measured with a Varian CP-4900 gas chromatograph calibrated with 10% and 40% (v/v) CO$_2$/N$_2$ and 100% CO_2 reference gases (Rivoira).

The cyclic absorption–filtration device was quite similar to that previously described [28] and comprised the absorber and the filtration units that are connected to each other by means of a peristaltic pump (Masterflex L/S) that allows the absorbent slurry and the filtered solution to circulate continuously in a closed loop between the absorber and the filtration unit (Fig. 1). The temperature of the absorbent solution was kept constant by a thermostatted water bath (Julabo model F33-MC refrigerated bath).

The NH$_3$ absorbent solution was made by mixing 0.020 dm^3 of 15.2 mol dm^{-3} aqueous NH$_3$ with 0.270 dm^3 of ethanol. Both CO_2 (12% v/v in air) and NH$_3$ were simultaneously and continuously introduced at the bottom of the absorbent solution through two separate gas diffuser. The CO$_2$/NH$_3$ flow ratio was 1/1.5 (v/v) with a flow rate of 14 dm^3 h^{-1}. The outlet gas from the top of the absorber was dried by flowing in turn through a condenser cooled at 268 K, a concentrated H$_2$SO$_4$ solution and a gas purification tower filled with P$_2$O$_5$, before being analysed with a gas chromatograph which measured the percentage of the CO_2 absorbed at intervals of 10 min. At the end of the experiment fixed at eight hours, the solid collected by filtration was washed with CO_2 saturated ethanol and diethyl ether in turn before being dried at room temperature in a
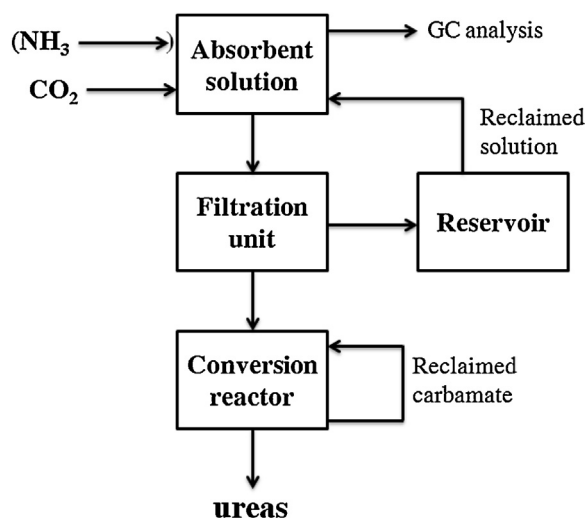

Fig. 1. Simplified flow diagram of the cyclic process configuration. Gaseous ammonia was used in conjunction with CO_2 absorption by water–ethanol NH$_3$.

stream of pure CO_2 to avoid the decomposition of both ammonium carbamate and bicarbonate.

Analogous equipment (Fig. 1) and procedure were used to capture CO_2 by non aqueous amines and to collect the corresponding solid amine carbamates. The absorber device was charged with 0.300 dm^3 of 3.0 mol dm^{-3} solutions of the different amines in bis(2-ethoxyethyl) ether (NBA, IBA, TBA), in 2-(2-methoxyethoxy) ethanol (CHA), in 2-ethoxyetanol (PIP), or in 3-pentanone (NOA). The temperature of the absorbent solution was kept constant at 293 K by a thermostatted water bath. The gas mixture containing 15% (v/v) CO_2 in air was continuously fed into the bottom of the absorber with a flow rate of 14 dm^3 h^{-1}. The outlet gas, exited from the top of the absorber, was analysed by the gas chromatograph. A complete experiment lasted 150–660 min and it was stopped when the CO_2 absorption efficiency at the end of the experiment was reduced to about 50% (average absorption efficiency in the range 91–97%). The solid was collected by filtration unit, washed with a 1/1 mixture of ethanol and diethyl ether and pure diethyl ether in turn before being dried at room temperature in a stream of N$_2$.

The batch experiments aimed at measuring the loading capacities of the different amine solutions were carried out using the same absorber and absorption procedure as above described but pure CO_2 was used and the carbonated products were not separated from the solution by filtration. The absorption was stopped when no more CO_2 was absorbed. The maximum amine loading (CO$_2$/amine molar ratio) was computed from the weight increase of the CO_2 saturated slurry contained in the absorber.

The conversion of ammonium salts into urea was carried out in a stainless steel reactor (PARR MOD. 4791) with a volume of is 0.025 dm^3 equipped with a thermocouple and pressure gauge. The reactor was heated to the appropriate temperature (438 K) by means of a silicone oil heating bath (IKA HB4). In each experiment, the reactor is charged with 12.0 g of the mixture of ammonium carbamate and bicarbonate in slightly different ratio (67–73% of carbamate, in molar ratio). For comparison purposes, blank experiments were carried with pure ammonium bicarbonate. Each conversion experiment comprised six separate heating times, 30, 45, 60, 75, 90, 105 min, aimed at measuring the urea yield as a function of heating time.

After each heating time was completed, the reactor was water cooled to room temperature and a sample of the mixture recovered from the vessel was dissolved in D$_2$O and analysed by ^{13}C NMR