



Original Research Paper

Thermal decomposition of calcium carbonate polymorphs precipitated in the presence of ammonia and alkylamines

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ABSTRACT

Precipitated calcium carbonate was obtained by CO₂ bubbling in CaCl₂ solution. Ammonia and alkylamines were used to enhance CO₂ absorption and control the polymorphic phases. Vaterite and calcite mixtures were obtained, mainly vaterite in ammonia and mono-methylamine and mostly calcite in trimethylamine environment. The thermal decomposition of precipitated calcium carbonate leads to high purity CaO. During the thermal decomposition the vaterite to calcite transformation was noticed but the final spherical shape of vaterite was maintained. As the use of CaO as catalyst in biodiesel synthesis may recommend a spherical shape and high contact surface, a precipitated calcium carbonate, rich in vaterite phase, may be a good precursor for CaO catalyst preparation.

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1. Introduction

Calcium carbonate (CaCO₃) is one of the most spread inorganic salts. Both mineral and precipitated CaCO₃ (PCC) have many practical applications in industries like paper, rubber, plastics, paints, cosmetics and pharmaceuticals. Practical applications of PCC are determined by its physical and chemical properties as well as morphology: specific surface area, pore sizes, particle size distribution, polymorphic phase, purity.

Calcium carbonate has three anhydrous polymorphs with specific shapes: rhombic calcite, acicular aragonite and spherical vaterite. PCC is usually a mixture of these three polymorphs together with various hydrates or amorphous calcium carbonate. Calcite has crystallographic rhombohedral structure and is the most thermodynamically stable polymorph in ambient conditions. Aragonite (orthorhombic structure) forms at high temperatures, while vaterite (hexagonal structure) is the most unstable polymorph and can accompany calcite if the precipitation occurs at low temperature. In aqueous solutions, the thermodynamic stability of the polymorphs increases in the order vaterite → aragonite → calcite and their solubility decreases in the same order.

The control of the precipitation process, aiming to obtain a specific morphology of the PCC is extensively studied, but it is still not solved. The operating conditions such as temperature, pH and supersaturation degree can favor the nucleation and growth of a

given polymorph [1–4]. The precipitation in other solvents than water, such as mono or di-alcohols, the use of an organic template, additives or ultrasound waves may be means of controlling the size, morphology and structure of PCC [5–8]. Spherical vaterite particles are generally formed by nano-size crystallites (25–35 nm) agglomeration that gives a porous structure, with a larger surface area than the other more stable polymorphs [9].

In recent years, CaCO₃ is also used to obtain CaO for the manufacture of organic light-emitting diode in electronic industry [10] or as catalyst in biodiesel synthesis [11,12]. The interest for the synthesis of CaCO₃ as precursor for CaO catalyst is justified as the catalytic properties depend on the shape and free surface of CaO particles. The calcinations of a controlled polymorphic phase of PCC may contribute to improve the CaO characteristics. Considering that the spherical morphology and porosity of PCC are maintained after the calcinations [13,14], a spherical and porous PCC (vaterite polymorph) could be a favorable precursor for CaO catalyst.

The present study aims to investigate the influence of ammonia and alkylamines on the PCC characteristics, and finally to investigate the influence of PCC polymorphic phase and shape on the characteristics of final calcined CaO.

2. Experimental

2.1. Experimental set-up for CaCO₃ precipitation

There are two main methods for CaCO₃ synthesis: mixing a calcium salt solution with a carbonate salt solution or bubbling

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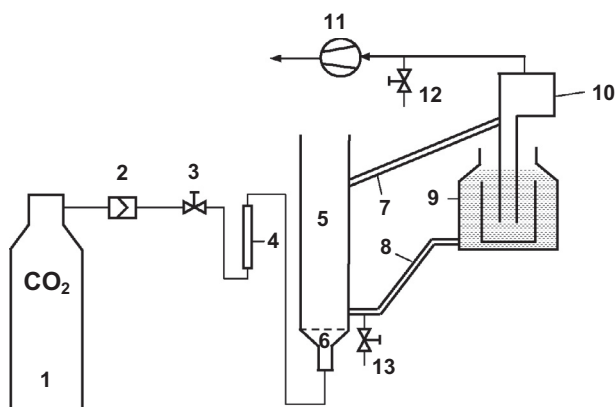


Fig. 1. Experimental setup for CaCO_3 precipitation. 1. CO_2 cylinder; 2. pressure reductor; 3. flow regulator; 4. rotameter; 5. carbonation column; 6. microporous gas distributor; 7, 8. flexible tubes; 9. recirculation vessel; 10. gas-suspension separator; 11. membrane compressor; 12. supplementary air admission; 13. suspension evacuation.

CO_2 gas in a calcium salt solution. In our experiments calcium carbonate was obtained by carbonation route starting from CaCl_2 solution and pure CO_2 gas. Ammonia and methylamines were added to the CaCl_2 solution in order to enhance CO_2 chemical absorption by anion capture (as ammonium chloride or amine hydrochlorides) and also to control the polymorphic phase, shape

Table 1

Experimental conditions in calcium carbonate precipitation.

Run	Medium	Initial pH	Final pH	Recirculation rate, L/h	CO_2 rate, L/h	Induction period, min	PCC, g
C ₁	NH_3	10.4	8.9	17.5	3.8	10	35.5
C ₂	MMA	10.6	9.1	17.5	3.8	15	31.3
C ₃	DMA	10.6	9.1	17.5	3.8	10	27.3
C ₄	TMA	10.4	8.9	17.5	3.8	5	35.8

and morphology of PCC. The precipitation took place in a glass bubble column with external circulation (Fig. 1). The bubble column with an interior diameter of 63 mm is equipped with a glass microporous gas distributor with pores diameter in the 10–16 μm range. The feed gas flowrate, measured by means of a rotameter, was maintained at the same value throughout all experiments, namely 3.8 L/h. Taking into consideration the diameter of the column, this flowrate will ensure the formation of micro-bubbles which can provide a high gas–liquid contact surface and also can constitute a template for hollow particles formation [15]. A good mixing of the liquid–solid suspension formed during the precipitation was realized by the external circulation. The external circulation loop including a liquid/suspension accumulator ensured the quantity of PCC necessary for CaO synthesis by providing a large solution inventory at the start of each run. The recirculation flowrate was maintained at a constant value by the liquid head in the

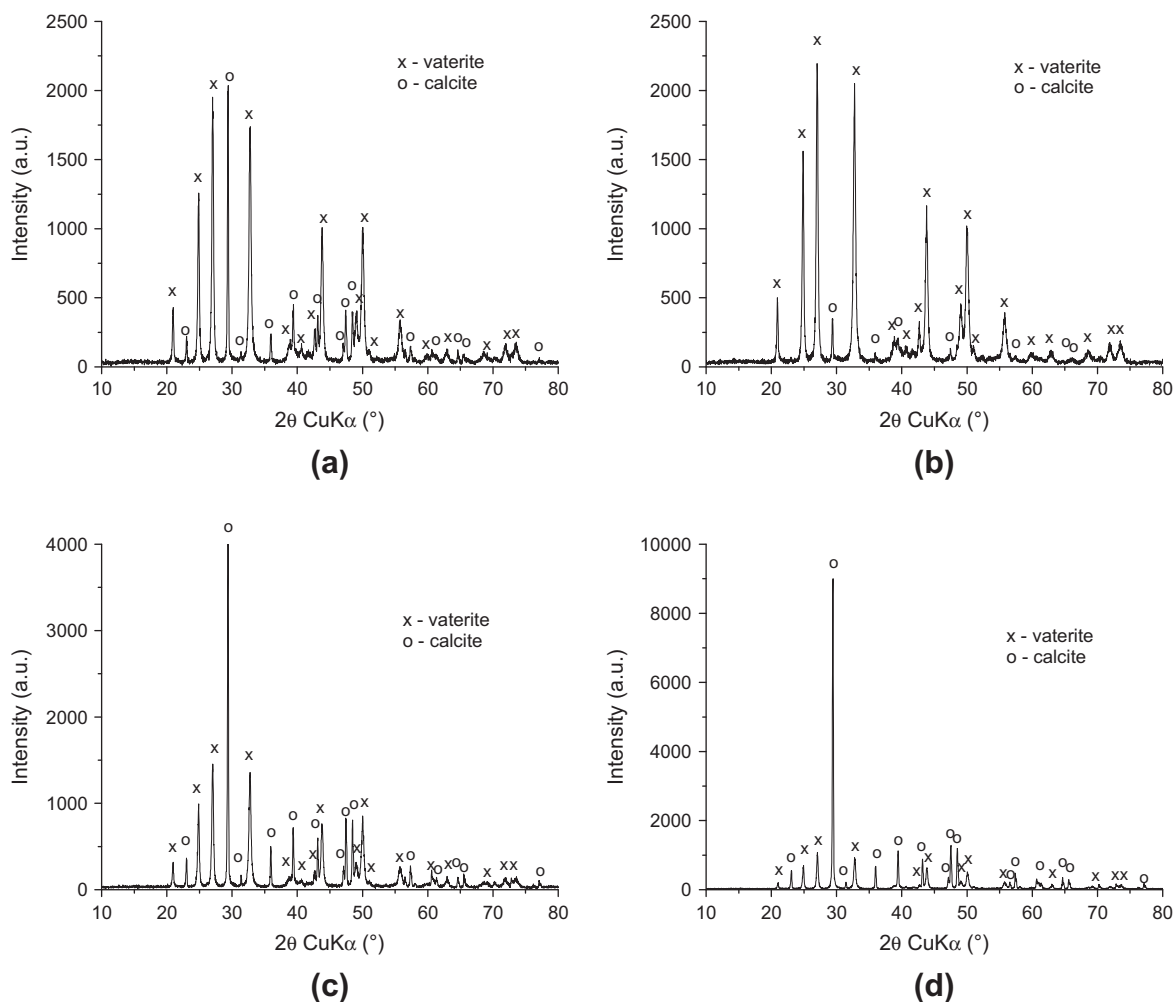


Fig. 2. X-ray diffraction analysis: (a) C₁ sample, (b) C₂ sample, (c) C₃ sample, (d) C₄ sample.

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