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廈門大學

SYNTHESES OF VALUABLE INORGANIC MATERIALS VIA CO₂-ASSISTED
PROCEDURES AND THEIR APPLICATIONS

二氧化碳辅助下的无机材料的合成及其应用

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Major: Chemical Engineering (Industrial Catalysis)

Time of Graduation: June, 2013

A DISSERTATION SUBMITTED IN FULFILLMENT OF THE REQUIREMENTS FOR THE
AWARD OF THE DEGREE OF DOCTOR OF PHILOSOPHY IN ENGINEERING
DEPARTMENT OF CHEMICAL AND BIOCHEMICAL ENGINEERING
COLLEGE OF CHEMISTRY AND CHEMICAL ENGINEERING
XIAMEN UNIVERSITY

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SYNTHESES OF VALUABLE INORGANIC MATERIALS VIA CO₂-
ASSISTED PROCEDURES AND THEIR APPLICATIONS

- (i) CO₂-Expanded Liquid Syntheses of γ -Al₂O₃ for Application as Catalyst;
- (ii) High-Pressure CO₂ and Ionic Liquid Assisted Syntheses of Calcite Nanoparticles with Self-Catalytic Carbonation;
- (iii) Syntheses of Ca₅(PO₄)₃OH from the Synthetic Calcite and Eggshells for Applications as Catalyst and Drug Carrier.

二氧化碳辅助下的无机材料的合成及其应用

- (i) CO₂-膨胀液体合成 γ -Al₂O₃ 及其催化应用;
- (ii) 高压 CO₂ 和 离子液体辅助下方解石纳米颗粒的自催化碳化合成;
- (iii) 上述方解石以及蛋壳材料合成 Ca₅(PO₄)₃OH 及其催化和药物负载的应用.

June, 2013

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I. CERTIFICATION

I, Professor LI JUN, hereby certify that I have read this manuscript and recommend for acceptance by the Xiamen University; a dissertation entitled “SYNTHESES OF VALUABLE INORGANIC MATERIALS VIA CO₂-ASSISTED PROCEDURES AND THEIR APPLICATIONS: (i) CO₂-Expanded Liquid Syntheses of γ -Al₂O₃ for Application as Catalyst; (ii) High-Pressure CO₂ and Ionic Liquid Assisted Syntheses of Calcite Nanoparticles with Self-Catalytic Carbonation; (iii) Syntheses of Ca₅(PO₄)₃OH from the Synthetic Calcite and Eggshells for Applications as Catalyst and Drug Carrier” in fulfillment of degree of Philosopher of Engineering at Xiamen University, People’s Republic of China.

Signed.....

Supervisor

Date: June, 2013

Department of Chemical and Biochemical Engineering

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II. ORIGINAL STATEMENT

The research described in this Dissertation was conducted under the supervision of Professor LI JUN at the Department of Chemical and Biochemical Engineering, Xiamen University. I hereby declare that the work submitted is my own and that appropriate credit has been given where reference has been made to the work of others. I also confirm that it has not been previously or concurrently submitted for any other degree, diploma or any other qualifications at Xiamen University, P.R China or other institutions.

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Ibrahim Abdul - Rauf

June, 2013

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IV. DEDICATION

I dedicate this work to my dear wife, Sawdatu; a loving helpmate and a Caring mother; and to our four lovely children – Kifayatul-Llah, Tun-Taiya, Neina and Zul-Khair. It is also dedicated to all my brothers and sisters and to the memory of my parents Al-Haji Yibram Bla and Mma Marta of blessed memory.

June, 2013

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V. ACKNOWLEDGEMENTS

In all humility, I acknowledge the blessings of ALLAH for giving me a chance to study abroad thus, making my cherished dream a reality. My indebtedness goes to my supervisor, Professor LI JUN for his immense input, direction and guidance. I am really grateful and proud to be his student. I am highly grateful also, to the Government of the PEOPLES REPUBLIC OF CHINA, who through The Chinese Scholarship Council (CSC) offered me full scholarship to study in Xiamen University. Thanks also go to all the lecturers in the Chemical and Biochemical Engineering Department for being the driving force behind my training. I particularly like to thank Professor CHEN BINGHUI for his advice and motivation over the years. I cannot but be grateful to the people of CHINA through whose taxes I was offered the scholarship. Specifically, I thank all past and present members of the Supercritical Fluid Technology Laboratory; especially, Mrs. HONG YEN ZHEN for their care, understanding and unceasing support. I wish them all the best of luck and success in their future endeavours. Finally, I thank Miss Zoumara Babette for her time, support and special friendship.

May ALLAH, in His infinite Mercy shower HIS Blessings on all those who in diverse ways contributed to my success.

June, 2013

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VI. ABSTRACT

The addition of CO₂ to an organic solvent-water mixture causes expansion in volume of the liquid phase as a result of increase of mole fraction of the gas, and provides endless potential for tuning, adjusting and enhancing system properties. It also offers simple and direct synthesis of micro- and nano-sized particles with narrower size distributions. Notwithstanding, the technique appears not to have been for the synthesis of the valuable γ -Al₂O₃ in the literature. Consequently, the technique was applied for direct synthesis of γ -Al₂O₃ nanoparticles without the use of any structure directing substances or templates; the Al₂O₃ produced was further applied to the catalytic Baeyer-Villiger oxidation of cyclohexanone. Results revealed that while mesoporous amorphous flower-like γ -Al₂O₃ was synthesized at equal ethanol to water volume ratio, mesoporous honey-comb-like γ -Al₂O₃ was synthesized at higher ethanol to water volume ratios. Additionally, the γ -Al₂O₃ nanoparticles exhibited high specific surface area and pore volume with small crystallite sizes (e.g., 519.8 m²/g and 1.1 cm³/g can be achieved for the specific surface area and pore volume, respectively). Furthermore, the Al₂O₃ structures were stable from 400 °C to 800 °C. On the other hand, the Al₂O₃ could catalytically convert cyclohexanone to ϵ -caprolactone satisfactorily, and the use of the calcined catalysts (at 400 and 800 °C) produced at equal ethanol to water volume ratio avoided the usual and inevitable hydrolysis of ϵ -caprolactone to ϵ -hydroxyhexanoic acid (selectivity could be 100%). Finally, the catalyst was recyclable and stable for several reaction cycles with consistent results.

In the mean time, CaCO₃ was synthesized through high pressure carbonation route. A solid-liquid-gas carbonation system with or without an ionic liquid (IL), BmimBr, was instituted in view of enhancing the reaction of CO₂ with Ca(OH)₂. In this case, the BmimBr positively influenced the reaction at low pressures (0.1 MPa and 1.0 MPa) within 5 min, and also showed effect at medium pressure (5.0 MPa) within 2 min. Similarly, higher mixing rates (400 – 800 rpm) at medium pressure without the IL resulted in conversions greater than 95 %; in fact, an almost complete conversion (98.9 %) was achieved within 1 min at 5.0 MPa with a mixing rate of 800 rpm without the IL. Furthermore, 5.0 ml water or more was necessary for rapid conversion of 5.0 g Ca(OH)₂. Moreover, a novel solid-gas carbonation with a solid ionic liquid (SIL, tetra-n-heptyl-ammonium bromide-THepAmBr) was also implemented. The effect of reaction

temperature, reaction pressure, reaction time, amount of solid ionic liquid (THepAmBr), reuse of the SIL, and type of SIL (THepAmBr, BmimBr, BmimCl) was also investigated. Additionally, the use of additives for inducing polymorphic control was explored. For this case, calcite structure with rhombohedral lattice was produced at all CO₂ conditions investigated: supercritical (15.0 MPa, 50.0 °C), compressed (5.0 MPa, 30.0 °C), liquid (15.0 MPa, 25.0 °C), gaseous (0.1 MPa, 30.0 °C) and atmospheric (0.1 MPa, 30.0 °C). Furthermore, rapid and complete conversion was achieved under the supercritical condition with the production of nano-sized calcite particles. Meanwhile, conversion of Ca(OH)₂ increased with increasing temperature from 25.0 °C up to 50.0 °C and decreased thereafter; but increased consistently with increasing pressure. Similarly, conversion increased with increasing amount of THepAmBr leading to complete conversion at the mass ratio of 0.1:1 for THepAmBr/Ca(OH)₂. Stability tests revealed that the THepAmBr was active and stable up to several recycles. Again, inquiry into the effect of using two imidazolium based SILs (BmimBr, BmimCl) indicated that they gave conversions greater than 96 %. Furthermore, preliminary studies on the polymorphic control to aragonite particles gave interesting results; 30.2 % aragonite particles were synthesized with solid MgCl₂ and 54.7 % with solid PEG6000. Yet, time-dependent analysis of conversion showed that the reaction mechanism for the system was self-catalytic and initiated by tiny absorbed water and CO₂ dissolved in the THepAmBr. Consequently, reaction rate equation was established, which revealed that the derived conversion equation described the experimental conversion satisfactorily. These results suggest that coupling the THepAmBr with CO₂ could be an effective system for intensifying traditional gas-solid reactions.

Meanwhile, as an application of the as-produced synthetic calcite, hydroxyapatite (HAp) was produced from the calcite suspension by adding fine droplets of phosphoric acid solution with the help of the syringe pump in order to facilitate control of the pH of the reaction solution (the as-produced CO₂ also helps the reaction for HAp material). Pure and stable HAp nanoparticles (HApNPs) were synthesized without using any templates or structure directing substances at room temperature. The produced HApNPs exhibited high specific surface area (such as 209.1 m²/g) and large pore volume (such as 1.88 cm³/g), and its preliminary application in the catalytic oxidation of cyclohexanone did not produce any by-products.

For a comparison, HApNPs were also produced from burnt eggshells (CaO) at room temperature without pH control. Here, pure and rod-like HApNPs were produced at all the addition rates.

However, samples produced at an addition rate of 100 ml/h, 200 ml/h and 400 ml/h were much stable after calcination at 700 °C and 950 °C compared to those obtained at 25 ml/h and 50 ml/h. Moreover, all the samples exhibited high specific surface areas (such as 160.1 m²/g) and large pore volumes (such as 1.0 cm³/g). Even so, high-purity synthetic calcium sources are somewhat expensive coupled with the fact that resorption of HAp derived from synthetic calcium has been proven to be quite different from the bone mineral. In addition, conversion of eggshells to CaO at about 1000 °C increases the energy input of the process. Therefore, for another comparison, highly pure (99.99 %) HApNPs with smaller particle size (< 10 nm), high specific surface area (such as 284.1 m²/g) and large pore volume (such as 1.4 1.0 cm³/g) was produced from raw eggshells without the use of any surfactants or structure directing substances, and without conversion to CaO by using a two-step procedure at room temperature. Investigations showed that the surface area and pore size increased with increasing size of needle used for precursor addition to an optimum and then decreased thereafter. Vacuum drying offered the HApNPs with the highest specific surface area compared to normal and freeze drying. Finally, the as-produced HApNPs revealed high loading of ibuprofen (as much as 1.376 g/g HAp) with a supercritical CO₂ loading technique (at 40.0 °C, 18.0 MPa) and much faster dissolution rate compared to pure ibuprofen raw material.

Keywords

Alumina, carbon dioxide expanded liquid, honey-comb-like, nanoparticles, Baeyer-Villiger oxidation, cyclohexanone, ε-caprolactone, selectivity, catalyst, calcium carbonate, calcite, ionic liquid, solid-liquid-gas, self-catalytic carbonation; high-pressure, rhombohedral, solid-gas carbonation, supercritical fluid, morphology, solid ionic liquid, kinetics, hydroxyapatite, nanorods, calcium hydroxide, specific surface area, pore volume, raw eggshells, waste, syringe pump, mesoporous, ibuprofen, dissolution.

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