

Thermochemical Properties of Synthesized Urea from Recovered Ammonia and Carbon Dioxide in Well-Ordered Nanospaces of Hollow Silica Spheres

Tetsuo Umegaki* and Yoshiyuki Kojima



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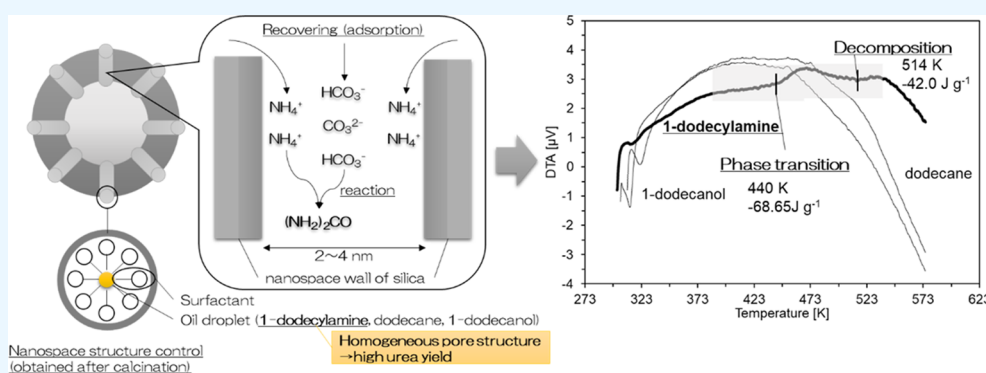


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ABSTRACT: The present work investigated the thermochemical properties of urea synthesized in well-ordered nanospaces of porous hollow silica spheres' shells from recovered ammonia and carbon dioxide in aqueous solution. Thermochemical behaviors of the urea synthesized in well-ordered nanospaces of the hollow spheres' shells prepared with 1-dodecylamine were analyzed from the results of thermogravimetric analysis (TGA) and differential thermal analysis (DTA), and endothermic peaks assigned as the phase transition and decomposition were observed at ca. 440 and 514 K, respectively, which were higher than those of pristine urea (405 and 408 K, respectively), probably because of the nanoconfinement effect. The decomposition behavior was also confirmed by the result of diffuse reflectance infrared Fourier transform (DRIFT) spectra of the samples treated at various temperatures up to 573 K, and the decomposition of urea synthesized in the well-ordered nanospaces of the hollow spheres' shells started at 468 K and completed up to 533 K.

INTRODUCTION

Enormous anthropogenic emissions of carbon dioxide by material consumption, such as fuels, foods, etc., have reportedly led to drastic climate change, probably because of its greenhouse gas effect. Various attempts to reduce its atmospheric concentration have been made through some technologies such as capture, use, and storage.^{1–3} Chemical processes for converting carbon dioxide into valuable compounds have been developed, and the processes to react carbon dioxide with reductants such as hydrogen,^{3–8} ammonia,^{9–12} etc., have been proposed as effective processes producing useful formic acid, methanol, urea, etc. Their reduction processes generally proceed under high temperature (<773 K) and pressure (<25 MPa) conditions and thus require high energy consumption for effective conversion of carbon dioxide. Our research group has first demonstrated to produce urea in the nanospaces of porous hollow silica spheres from ammonia and carbon dioxide recovered in the nanospaces from aqueous solution at much lower temperature (323 K) and

pressure (0.5 MPa argon atmosphere)¹³ in comparison to the commercial synthesis processes (>413 K, >13 MPa) from ammonia and carbon dioxide in gas and liquid phases by means of the Bazarov reaction, as shown in the following equations^{14–18}



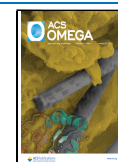
where $(\text{NH}_2)_2\text{CO}$ is urea and $\text{NH}_4\text{COONH}_2$ is ammonium carbamate. In the reaction in the liquid phase, urea was also synthesized from ions such as ammonium and carbonate ions,

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from which urea was also synthesized in the well-ordered nanospaces of hollow silica spheres reported in our previous study.^{13,15} The process effectively proceeded only in the well-ordered nanospaces with sizes of ca. 2–3 nm, probably because of its confinement effect on the reactivity of the recovered reactants (Figure 1). Such nanoconfinement effects on

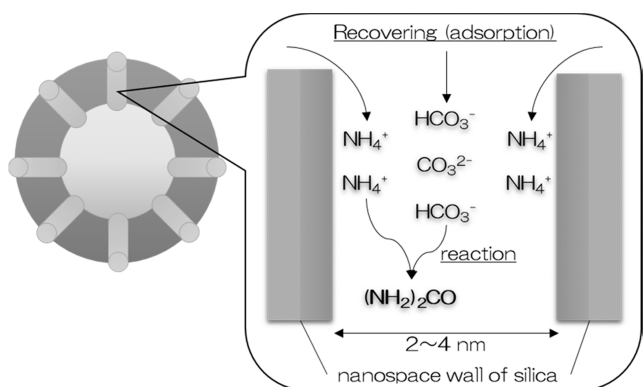


Figure 1. Scheme of urea synthesis in the nanospaces of the shell of porous hollow silica spheres.

decreasing the energy consumption of chemical reactions such as decomposition of chemical compounds have been reported.^{19–22} Also, confined compounds in nanospaces have exhibited intrinsic physical ((ex) phase transition) and chemical ((ex) decomposition) properties, for example, intrinsically low freezing points of liquid compounds such as water, in comparison to the pristine one.^{23–28} For such nanoconfinement effects, the synthesized urea in well-ordered nanospaces of the shell of the hollow spheres reported in the previous study is expected to exhibit intrinsic physical and chemical properties to apply functional materials, such as thermal storage materials, controlled-release fertilizers, etc.

Here, we first reported the thermochemical properties of urea synthesized in the nanospaces of hollow silica spheres from recovered ammonia and carbon dioxide in aqueous solution.

METHODS

Material Synthesis. Hollow silica spheres as host materials were prepared with a sol–gel-based method same as the previous work.¹³ A surfactant (cetyltrimethylammonium bromide (CTAB, 0.3 g, Kanto Chem. Co., 99.6%)), an oil droplet (dodecane (0.1371 g, Kanto Chem. Co.), 1-dodecanol (0.1761 g, Kanto Chem. Co.), or 1-dodecylamine (0.1492 g, Kanto Chem. Co.)), and sodium hydroxide (0.090 g, Kanto Chem. Co., ≥95.0%) were mixed in 150.0 mL of deionized water. After stirring the solution at 333 K for 30 min, tetraethoxysilane (TEOS, 2.25 mL, Kanto Chem. Co., >99.9%) was added dropwise into the solution, and then, the solution was stirred at 333 K for 2 h. After repeatedly centrifuging and washing in ethanol three times, the obtained powder products were calcined at 673 K for 3 h to obtain the hollow spheres. After degassing from the hollow spheres at 433 K for 7 h under vacuum conditions, the sample was immersed for 4 h in an aqueous solution including aqueous ammonia solution (12.5 mL, Kanto Chem. Co., 28–30%), copper acetate (0.2541 g, Kanto Chem. Co., 95.0%), and 12.5 mL of deionized water preliminarily bubbled with CO₂ gas (300 mL min⁻¹) for 40 min, followed by drying at 373 K for 30 min under vacuum

conditions. For comparison, commercial silica (Wakogel C-200, FUJIFILM Wako Pure Chemical Co.) was used to obtain a reference material via the same procedure described above. The solid sample was put into the closed reactor and was treated under a 0.5 MPa argon atmosphere at 323 K for 5 and 16 h.

Characterization. Thermochemical behaviors of the samples were examined on a Shimadzu DTG-60 thermogravimetric-differential thermal analyzer, with a heating rate of 2 K min⁻¹ in a nitrogen atmosphere (flow rate: 20 mL min⁻¹) up to 573 K. Diffuse reflectance infrared Fourier transform (DRIFT) spectra of the samples were recorded using a Fourier transform infrared spectrophotometer (IRsprit, Shimadzu Co. Ltd.) scanned from 5000 to 400 cm⁻¹ with a resolution of 4 cm⁻¹.

RESULTS AND DISCUSSION

Thermochemical properties of the urea synthesized in the nanospaces of hollow silica spheres prepared with 1-dodecylamine for 16 h under a 0.5 MPa argon atmosphere were estimated by the results of thermogravimetric analysis (TGA) up to 573 K, as shown in Figure 2. In Figure 2b,c, data of the

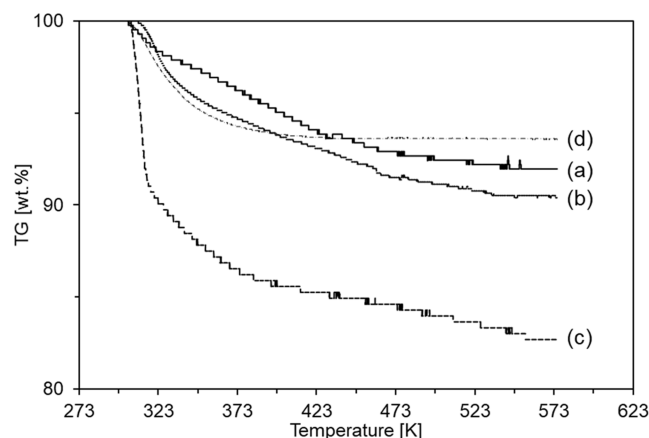


Figure 2. Thermogravimetric analyses of urea-encapsulated porous hollow silica spheres prepared with (a) 1-dodecylamine, (b) 1-dodecane, (c) 1-dodecanol, and (d) urea-encapsulated commercial silica. Synthesis conditions of encapsulated urea: (a) 16 h and (b–d) 5 h at 323 K under a 0.5 MPa argon atmosphere.

samples prepared with dodecane and 1-dodecanol for 5 h under a 0.5 MPa argon atmosphere are shown for comparison. In the TGA curve of the sample prepared with 1-dodecanol, initial drastic weight loss was observed in the temperature range up to 323 K, probably assigned as ammonium ions and carbonates on the surface of hollow silica spheres. In comparison to urea-encapsulated commercial silica in Figure 2d, which exhibited monotonical weight loss, two other gradual weight losses of the sample were observed in the temperature range of 323–373 K, probably assigned as unreacted ammonium ions and carbonates confined in the nanospaces of the hollow spheres' shell, and in the range of 373–555 K, probably assigned as the phase transition and/or decomposition of urea. Otherwise, in the TGA curve of the sample prepared with dodecane, the initial weight loss was observed in the temperature range up to ca. 343 K, probably assigned as unreacted ammonium ions and carbonates confined in the nanospaces of the hollow spheres' shells; the degree and rate of the weight loss were significantly low in comparison to the

sample prepared with 1-dodecanol. The TGA curve also included two other weight losses that were also observed in the temperature ranges of 343–460 and 460–537 K, probably assigned as the phase transition and/or decomposition of urea, respectively. In the TGA curve of the sample prepared with 1-dodecylamine in Figure 2a, relatively low weight losses in the temperature ranges of 303–323, 323–433, and 433–540 K, probably assigned as unreacted ammonium ions and carbonates confined in the nanospaces of the hollow spheres' shell, phase transition, and decomposition of urea, respectively, were observed.

These results indicate that components included in the hollow silica spheres prepared with 1-dodecylamine were stable at relatively high temperatures in comparison with those in the two other samples. Figure 3 displays differential thermal

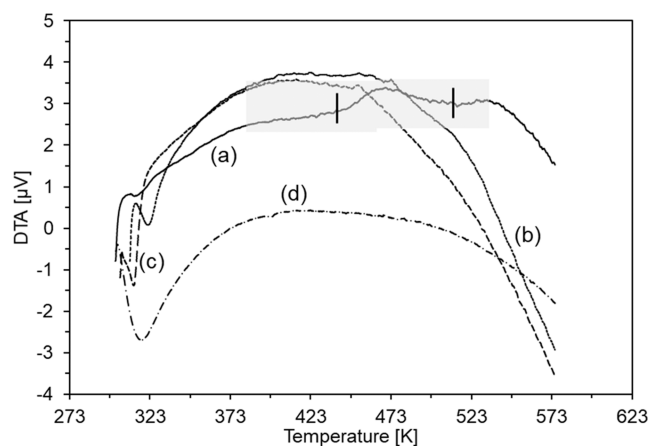


Figure 3. Differential thermal analyses of urea-encapsulated porous hollow silica spheres prepared with (a) 1-dodecylamine, (b) 1-dodecane, (c) 1-dodecanol, and (d) urea-encapsulated commercial silica. Synthesis conditions of encapsulated urea: (a) 16 h and (b–d) 5 h at 323 K under a 0.5 MPa argon atmosphere.

analysis (DTA) curves of the hollow spheres treated at 323 K under a 0.5 MPa argon atmosphere. The DTA curves of the samples prepared with dodecane and 1-dodecanol in Figure 3b,c mainly included endothermic peaks centered at ca. 313 and 322 K, respectively. The peak can be assigned as adsorbed water, ammonium ions, and/or bicarbonates remaining in the sample after the reaction to synthesize urea in the nanospaces of the hollow sphere particles. Otherwise, in the DTA curve of hollow silica spheres prepared with 1-dodecylamine (Figure 3a), the clear endothermic peak was not observed in the temperature range up to 373 K, while two peaks centered at 440 and 514 K assigned as phase transition and decomposition, respectively, of urea were observed. We previously reported that the yield of urea strongly depended on the size distributions of nanospaces of hollow silica spheres, and the amount of urea in the hollow silica spheres prepared with 1-dodecylamine (229 mg urea g-sample⁻¹) with small size and narrow distribution of nanospaces was significantly high compared with those in the hollow spheres prepared with dodecane (76 mg urea g-sample⁻¹) and 1-dodecanol (43 mg urea g-sample⁻¹).¹³ The results indicate that an appropriate amount of synthesized urea was required to identify thermochemical behaviors of the confined urea by DTA. Otherwise, the peak temperatures in Figure 3c were higher than those of pristine urea.^{29–31} From the TEM images in our previous study, the samples prepared with 1-dodecylamine, dodecane, and 1-dodecanol consisted of spherical particles with diameters of ca. 55–105 nm, ca. 75–160 nm, and ca. 75–130 nm, respectively, and the particles formed hollow voids and shells with thicknesses of ca. 5–15 nm, ca. 5 nm, and ca. 5–10 nm, respectively.¹³ Otherwise, from the result of nitrogen sorption measurements in the previous study, only a sharp peak ranging from 1.8 to 4.1 nm centered at 2.9 nm was observed in the distribution of the sample prepared with 1-dodecylamine, while the broad peaks ranging from 4 to 100 nm centered at 3.1 and 3.7 nm were also observed in the

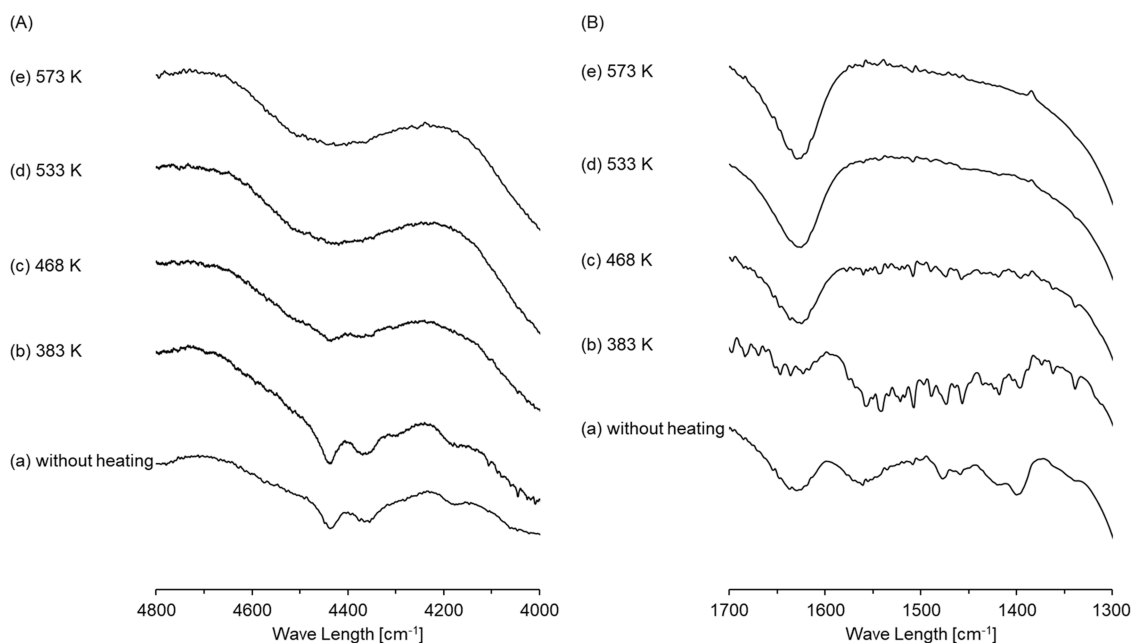


Figure 4. (A) Near- and (B) mid-DRIFT spectra of urea-encapsulated porous hollow silica spheres prepared with 1-dodecylamine treated under a 0.5 MPa argon atmosphere for 16 h (a) without heat treatment and with heat treatment at (b) 383, (c) 468, (d) 533, and (e) 573 K in a nitrogen atmosphere.

distributions of the samples prepared with dodecane and 1-dodecanol accompanied by the sharp peaks ranging from 1.9 to 5.0 nm, respectively.¹³ Consequently, from these results in the previous study and the results of DTA in the present study, it is suggested that the sample prepared with 1-dodecylamine possessed the most homogeneous nanopore structures in all of the samples, and the confined urea in the nanopores of the hollow spheres was more stable than pristine urea probably because of the nanoconfinement effect. We also estimated endothermic heat capacity resulting from thermochemical behaviors of the confined urea from the result of DTA, and heat capacities via the phase transition and decomposition were 68.7 and 42.0 J g⁻¹, respectively. In our previous study, urea was synthesized under much milder reaction conditions (at 323 K under a 0.5 MPa argon atmosphere) in the nanopores of well-ordered porous hollow silica spheres than the commercial processes (at >413 K under a >13 MPa reactant atmosphere). In addition, the synthesis reaction is exothermic; thus, the material including urea in well-ordered nanopores of porous hollow silica spheres can be applied as a functional material such as thermal storage materials (phase change materials, chemical heat pump materials, etc.).

To identify species included in the nanopores of hollow silica spheres prepared with 1-dodecylamine after the treatment of the pressurized argon atmosphere at 323 K, DRIFT spectra of the samples treated at various temperatures in the temperature range of the TGA and DTA analyses were analyzed. Figure 4 displays the spectra in near-infrared (NIR) (A) and mid-infrared (MIR) (B) regions at 293–573 K. In the spectra in the NIR region, two adsorption bands at 4500–4300 cm⁻¹ assigned as urea^{32–34} were observed up to 468 K, at around which the confined urea can start to decompose, and then disappeared above that temperature. In the MIR region, an adsorption band at ca. 1470 cm⁻¹ assigned as urea adsorbed on the surface of silica-based materials^{33,34} was also observed up to 468 K and then disappeared above that temperature. These results indicated that the confined urea in the nanopores of hollow silica spheres prepared with 1-dodecylamine started to decompose at around 468 K, and the decomposition process was completed up to ca. 533 K. In the spectra in the MIR region, adsorption bands assigned as ammonium ions adsorbed on the surface of silica-based materials^{35,36} at ca. 1400 cm⁻¹ and bicarbonate ions adsorbed on the surface of silica-based materials^{37,38} at ca. 1560 cm⁻¹ remained up to 383 K and then disappeared above 468 K, indicating that the unreacted species after treatment under the pressurized argon atmosphere completely desorbed in the temperature range from 383 to 468 K. In the MIR region, an adsorption band at ca. 1630 cm⁻¹ assigned as physisorbed water molecules,^{28,39} which adsorbed during recovered ammonia and carbon dioxide in the hollow spheres from aqueous solution was also observed. Above 533 K, the band intensity was higher than that of the samples treated under 468 K, indicating that the water byproduct via decomposition of urea was formed in the hollow spheres above 533 K.

CONCLUSIONS

Thermochemical properties of urea synthesized in well-ordered nanopores of porous hollow silica sphere shells from recovered carbon dioxide and ammonia in aqueous solution were investigated in the present study. The size distribution of the nanopores was controlled with various oil droplets (1-dodecylamine, 1-dodecane, and 1-dodecanol), which were

added for formation of the hollow voids and control of nanopores in the hollow spheres' shell. From the results of TGA and DTA of urea-confined hollow silica spheres prepared with the oil droplets, the phase transition and decomposition behaviors of the confined urea were observed only with the sample prepared with 1-dodecylamine, which possessed well-ordered nanopores in the shells and in which a high amount of urea was generated, and the temperatures of its phase transition and decomposition were higher than those of pristine urea. The decomposition behavior was also confirmed from the result of the DRIFT spectra of the samples treated at various temperatures, and decomposition of the confined urea started at 468 K and completed up to 533 K. From the results in the present study, the material including urea in well-ordered nanopores of porous hollow silica spheres can be applied as a functional material such as thermal storage materials (phase change materials, chemical heat pump materials, etc.).

AUTHOR INFORMATION

Corresponding Author

Tetsuo Umegaki – Department of Materials and Applied Chemistry, College of Science and Technology, Nihon University, Tokyo 101-8308, Japan; orcid.org/0000-0001-9837-4649; Email: umegaki.tetsuo@nihon-u.ac.jp

Author

Yoshiyuki Kojima – Department of Materials and Applied Chemistry, College of Science and Technology, Nihon University, Tokyo 101-8308, Japan

Complete contact information is available at: <https://pubs.acs.org/10.1021/acsomega.3c06534>

Author Contributions

Syntheses, characterization, and measurements of thermochemical properties were performed by T.U. Work was led by T.U. and Y.K. Data analyses and manuscript writing were done by T.U. Manuscript validation was done by all.

Notes

The authors declare no competing financial interest.

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