

## HP-HT behavior of urea, a precursor to photocatalytic materials

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Urea,  $\text{CO}(\text{NH}_2)_2$ , is an inexpensive and easily accessible compound, known as the principal end product of nitrogenous metabolism in mammals. Although it has been studied at high pressure for more than 100 years [1], the crystal structures of its non-ambient phases have been reported only recently [2]. Still, its behavior under high pressure-high temperature (HP-HT) conditions has not been studied so far.

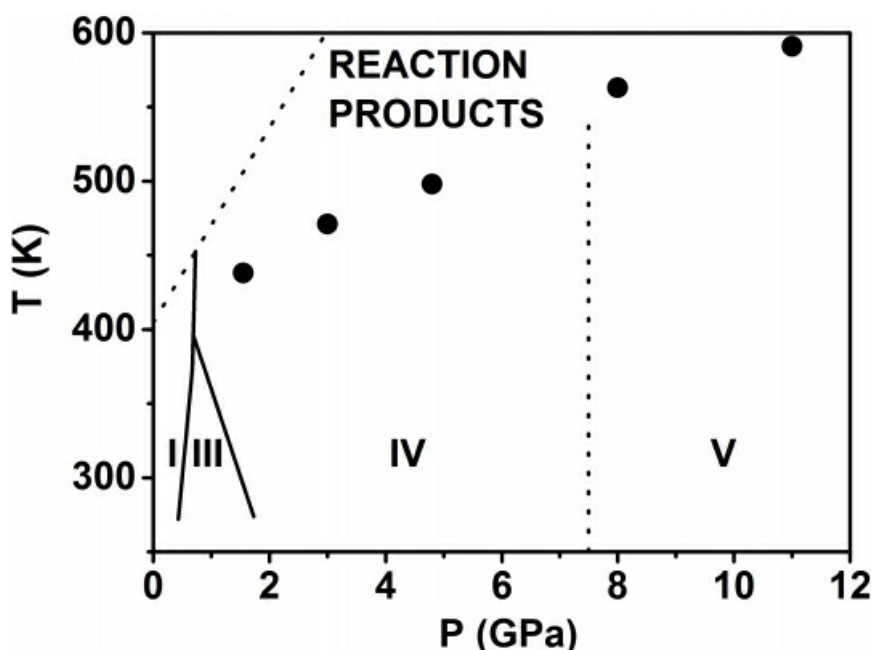
High pressure is known not only as a tool to access new crystal polymorphs, but also to synthesize novel materials starting from molecular low-Z substances. Pyrolysis of urea at the atmospheric pressure and 830 K without additive assistance is known to produce graphitic carbon nitride, an effective catalyst for water splitting. Therefore, we have undertaken a combined FT-IR absorption spectroscopy and angle dispersive XRD study to explore the phase diagram of urea up to 15 GPa and 600 K [3], and to characterize the products of its HP-HT decomposition in situ and after quenching to ambient conditions. The phase II, reported already in the volumetric study by Bridgman [1], was structurally characterized for the first time and found to be isostructural with the room-temperature HP phase IV. It was also noticed that the sluggish transitions and enhanced metastability regions for all the phases are a consequence of differences in hydrogen-bond patterns and the high energy barrier of their rearrangements. HP-HT studies in a hydrostatic pressure transmitting medium allowed to define the thermodynamic boundaries of crystal phases and draw the tentative phase diagram of urea (see the figure). The reaction boundary of urea has been also delineated. At pressure lower than 3 GPa and temperature around 420 K the 2D graphitic carbon nitride oxide of high crystallinity was formed. At higher pressure, where the reaction begins from the phase V, the selectivity is poor and the carbon nitride oxide is obtained with a lower yield, together with by-products like melamine and ammonium carbamate.

This study shows that the solid-state reactions under high pressure are directed by the structure of the molecular crystal precursor, depending on the network of hydrogen bonds. It is known that a photoactivity of graphitic carbon nitride materials is improved by introducing heteroatoms in its structure, and the HP-HT one-pot synthesis of highly crystalline oxide of graphitic carbon nitride can be an efficient method to produce this important photocatalyst. Moreover, the moderate pressure conditions indicate the possibility to scale up the process, while decreasing the synthesis temperature suggests reduced energy cost. From a fundamental point of view the negative, anomalous slope of the instability boundary, which is presumably due to the strong hydrogen bonds between molecules in the urea crystal, requires further studies.

[1] Bridgman, P. W. (1916). Proc. Am. Acad. Arts Sci. 52, 91-187.

[2] Olejniczak, A. et al. (2009). J. Phys. Chem. C 113, 15761-15767.

[3] Dziubek, K. et al. (2017). J. Phys. Chem. C 121, 2380-2387.

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