

Supporting Information

Solar Urea: Towards a Sustainable Fertilizer Industry

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SUPPORTING INFORMATION

Experimental Procedures

Synthesis of Pd/LTA-3A. Pd/LTA-3A was synthesized via a microwave-assisted reaction. 20 mg of $\text{Na}_2\text{PdCl}_4 \cdot 3\text{H}_2\text{O}$ was dissolved in 10 ml of anhydrous ethanol in a Pyrex vessel, followed by adding commercial LTA-3A (Alfa Aesar) and transferring to the microwave reactor (CEM Discover, 100 W, 160 psi, $T = 120^\circ\text{C}$, 20 min). After filtration and washing, the grey Pd/LTA-3A was dried under vacuum at 120°C overnight.

Synthesis of Pd/SiO₂. The procedures are similar to that of Pd/LTA-3A only by replacing the LTA-3A sieves with SiO₂.

Synthesis of Pd nanoparticles. 20 mg of $\text{Na}_2\text{PdCl}_4 \cdot 3\text{H}_2\text{O}$ was dissolved in 10 ml of anhydrous ethanol in a Pyrex vessel, then transferred to the microwave reactor (CEM Discover, 100 W, 160 psi, $T = 120^\circ\text{C}$, 20 min). After filtration and washing, the black solid was dried under vacuum at 120°C overnight.

Characterization. The morphology of Pd/LTA-3A and LTA-3A was characterized by SEM using a FEI QUANTA FEG 250 ESEM. Powder X-ray diffraction was performed on a Bruker D2-Phaser X-ray diffractometer, using Cu K α radiation at 30 kV. EELS was done using a Hitachi CFE-TEM HF 3300. Diffuse reflectance spectra were measured using a Lambda 1050 ultraviolet/vis/NIR PerkinElmer spectrometer with an integrating sphere. TGA was performed using a Discovery TGA (TA Instruments). The test condition: ramp $5.00^\circ\text{C}/\text{min}$ to 500.00°C in the air. The *in situ* DRIFTS spectra were acquired using a Thermo Scientific iS50 FTIR spectrometer equipped with a Harrick Scientific Praying Mantis reaction chamber. Gases were flowed through the powder of Pd/LTA-3A from the top to the bottom of the chamber. Prior to measurement, the powder of Pd/LTA-3A was heated under a flow of 20 sccm He at 100°C for 2 h and the background spectra were measured. Then the gas flow rates were changed to 10 sccm He, 4 sccm NH_3 and 2 sccm CO_2 , as spectra were collected.

Urea production measurements. Catalytic performance tests were conducted in a custom-built stainless-steel batch reactor with a quartz cap, sealed with a Viton O-ring. 1.5 g Pd/LTA-3A was added into the reactor and heated under vacuum at 120°C for 30 min. Then the reactor was infiltrated with NH_3 and CO_2 at 2:1 ratio to a total pressure of 1 atm. The reactor was irradiated by a 300 W Xe lamp or heated by an Omega temperature controller for a duration of 15 min. 5 ml of ultra-pure water was then used to rinse the inner wall of reactor and collected. The production rate was calculated based on the weight of Pd. During the stability test, between each run, after rinse solution was collected for urea detection, catalyst was collected from the reactor and dried in the air for 2 days. Then the catalyst was dried under vacuum at 120°C overnight for subsequent runs.

LC-MS. The rinse solution was analyzed by Sciex API 4000, using a Sequant ZIC-HILIC column (150 mm x 2.1 mm i.d., 5.0 μm). 15 mM ammonia formate solution (phase A) and LC-MS grade acetonitrile (phase B) were used as mobile phase. The total flow rate was 500 $\mu\text{L}/\text{min}$ and the column temperature was 25°C . Isocratic step at 5% phase A lasted for 0.5 min, followed by linear gradient step at a slope of 4.59% phase A per min for 9 min. Analytes were detected with ESI-MS in the positive mode.

DFT calculation. All spin-polarized calculations were performed using the first-principles density of functional theory (DFT) theory with an exchange-correlation energy function of GGA-RPBE in the CASTEP package.^[1] The ultrasoft pseudopotentials was employed for all atoms with corresponding accuracy set as coarse (Energy: $5.0\text{e-}5$ eV/atom, maximum force: 0.1 eV/ \AA , maximum stress: 0.2 GPa, SCF: $1.0\text{e-}5$ eV/atom, cutoff energy: 220 eV, k-point: $2 \times 2 \times 1$). A (3x3) Pd (111) supercell was crafted with a slab thickness of six atoms and a vacuum thickness of 15 \AA . All energy calculations were performed after geometry optimization. The absorption sites for NH_3 such as top and interstice sites were examined by absorption energy analysis and the as-demonstrated model reached free energy minimum. The CO_2 absorption site was then chosen based on the NH_3 absorption after considering the geometry of adsorbed urea on Pd(111) surface. The adsorption energy of adsorbate was defined as

$$E_{\text{ad}} = E_{\text{M-S}} - E_{\text{S}} - E_{\text{M}}$$

where M represents molecular adsorbate and S represents the surface of Pd (111).^[2]

References

- [1] S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. Probert, K. Refson, M. C. Payne, *Z. Kristallogr.* **2005**, 220,567-570.
- [2] C. Mao, H. Li, H. Gu, J. Wang, Y. Zou, G. Qi, J. Xu, F. Deng, W. Shen, J. Li, S. Liu, J. Zhao, L. Zhang, *Chem* **2019**, 5, 2702-2717.

Supporting figures

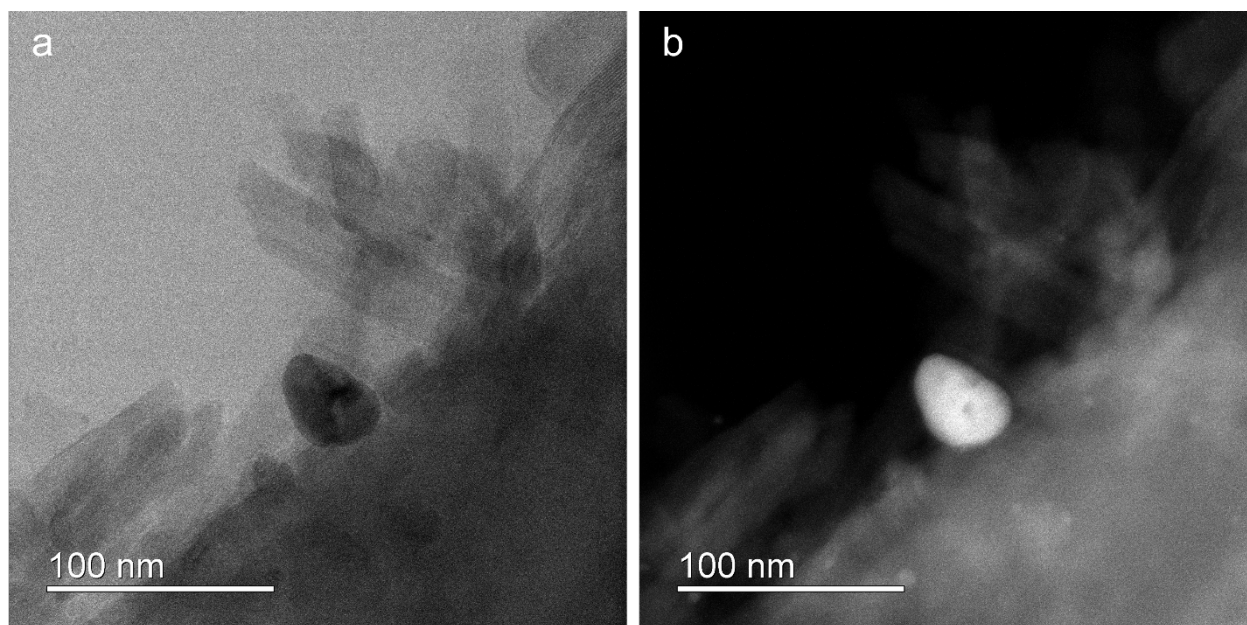


Figure S1. STEM images of Pd/LTA-3A, showing both large and ultrafine Pd nanoparticles.

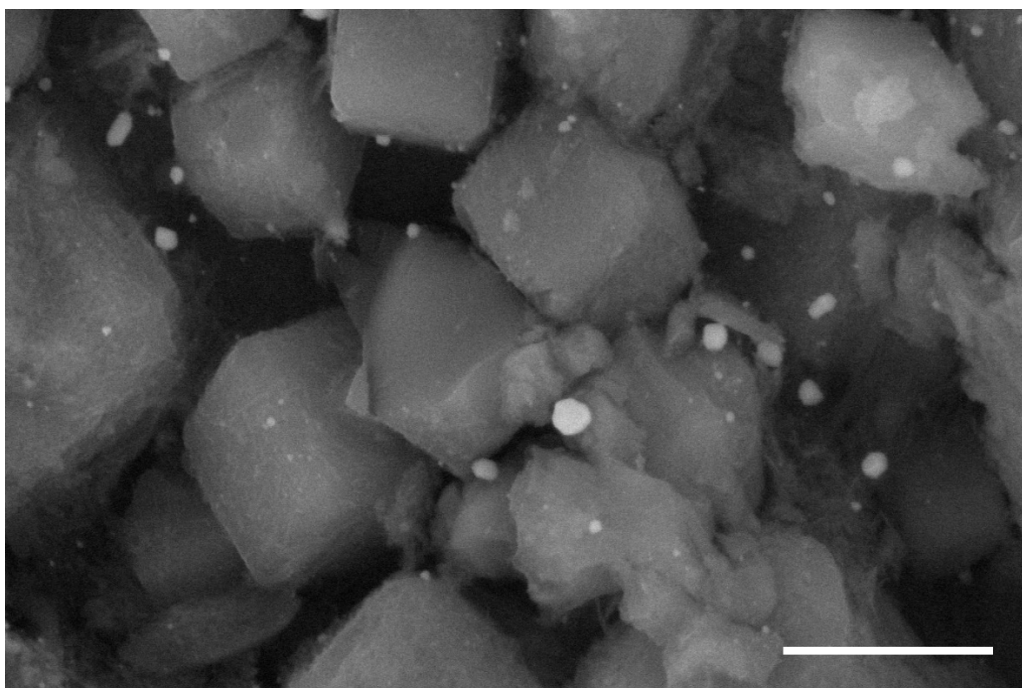


Figure S2. ESEM image of Pd/LTA-3A. Scale bar: 2 μm .

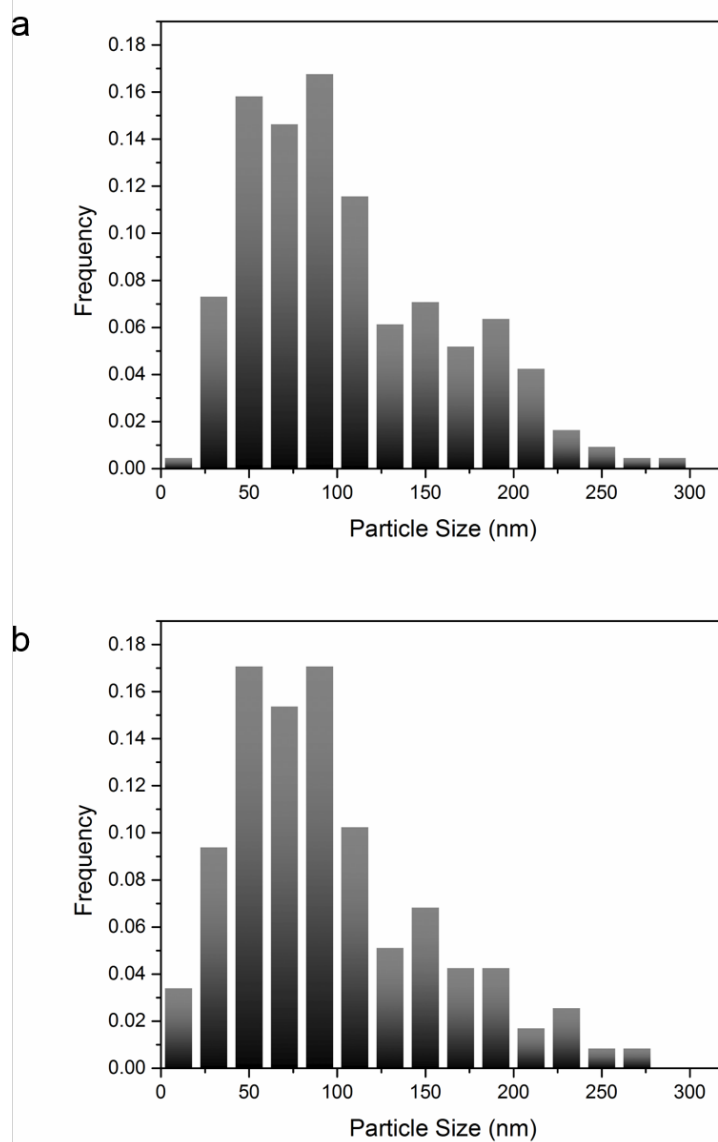


Figure S3. Size distribution of Pd nanoparticles of (a) as-synthesized Pd/LTA-3A and (b) Pd/LTA-3A after stability test, which are based on the ESEM images.

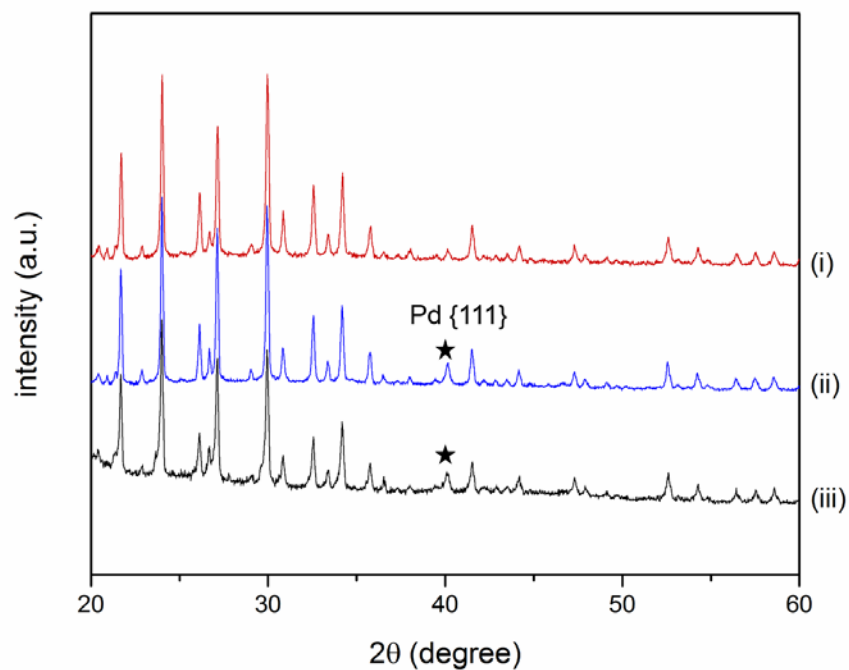


Figure S4. XRD pattern of (i), LTA-3A, (ii) as-synthesized Pd/LTA-3A and (iii) Pd/LTA-3A after stability test.

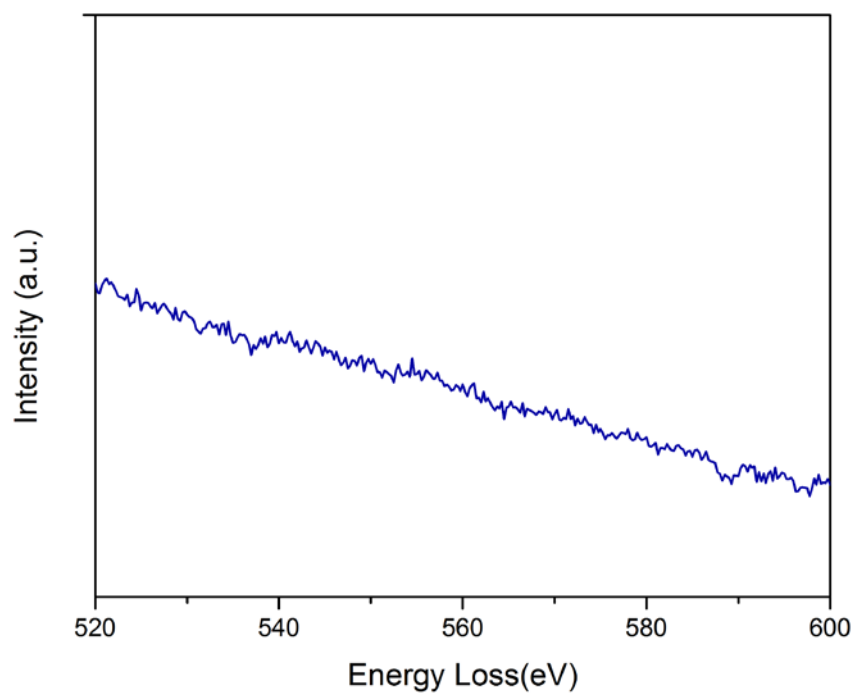


Figure S5. Oxygen K-edge EELS spectrum of Pd nanoparticles. No energy loss caused by oxygen was detected.

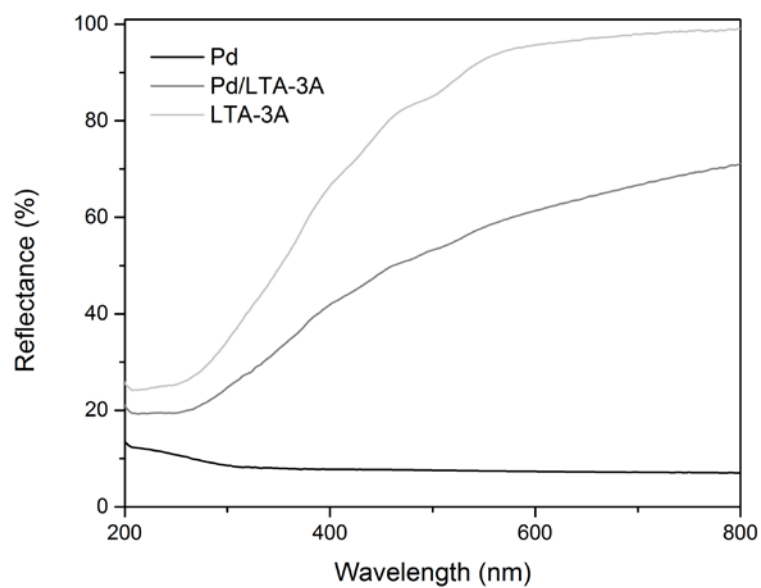


Figure S6. UV-vis spectra of Pd nanoparticles, Pd/LTA-3A and LTA-3A.

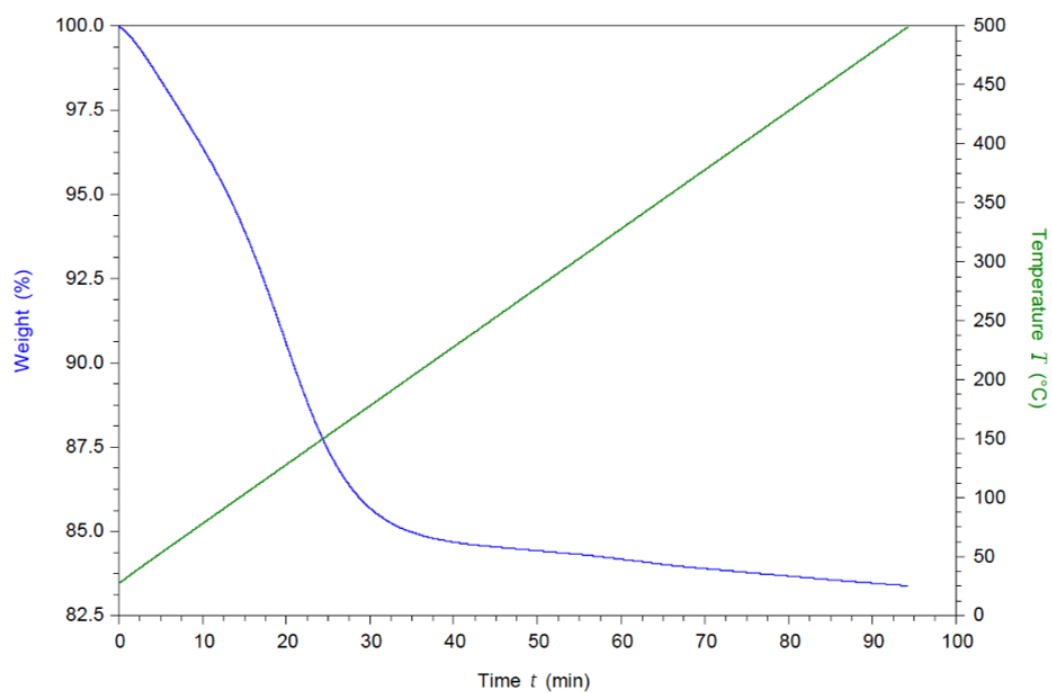


Figure S7. TGA measurements of moisture saturated Pd/LTA-3A. Condition: ramp 5.00 °C/min to 500.00 °C in the air.

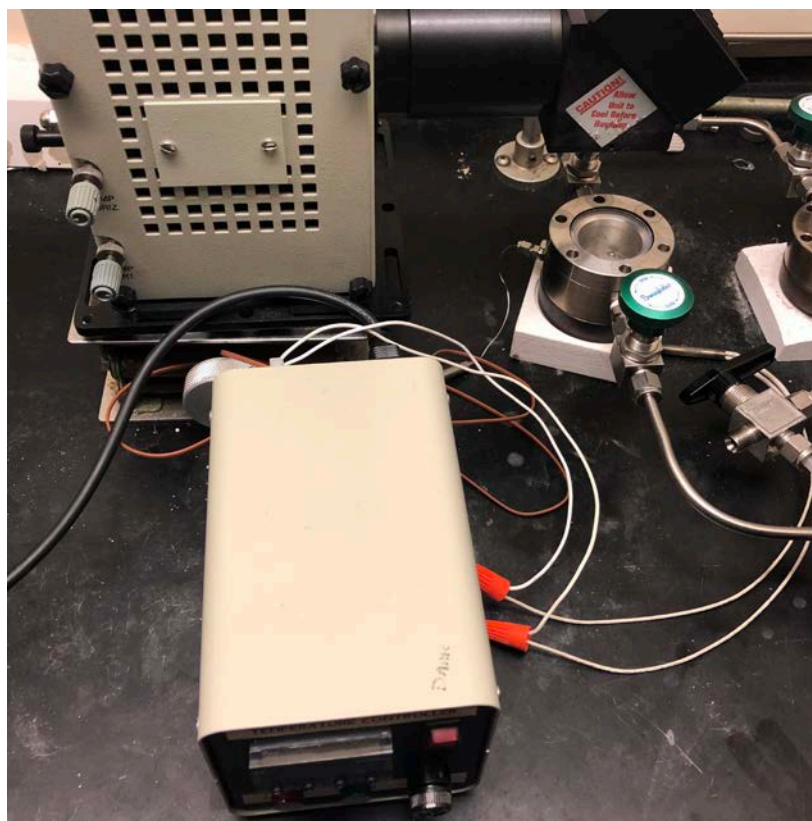


Figure S8. Stainless steel batch reactor for catalysts performance tests. The reactor is connected to a vacuum system, two gas cylinders (NH_3 and CO_2), and an on-line pressure sensor. The temperature of the catalyst was measured by catalyst-contact thermocouple.

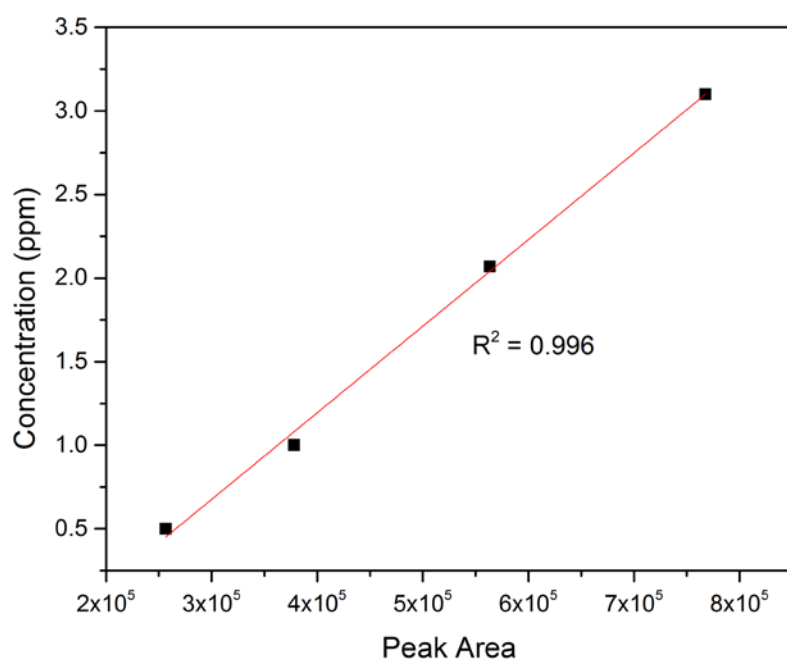


Figure S9. LC-MS calibration curve of urea standard solution concentration (ppm) and area of $m/z = 61$ (urea) peak at 3.8 min.

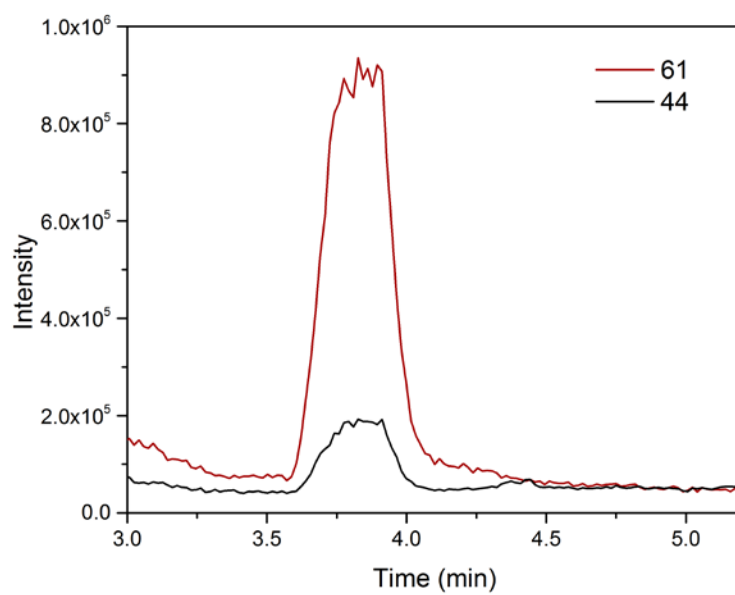


Figure S10. EIC of LC-MS spectra of urea standard solution.

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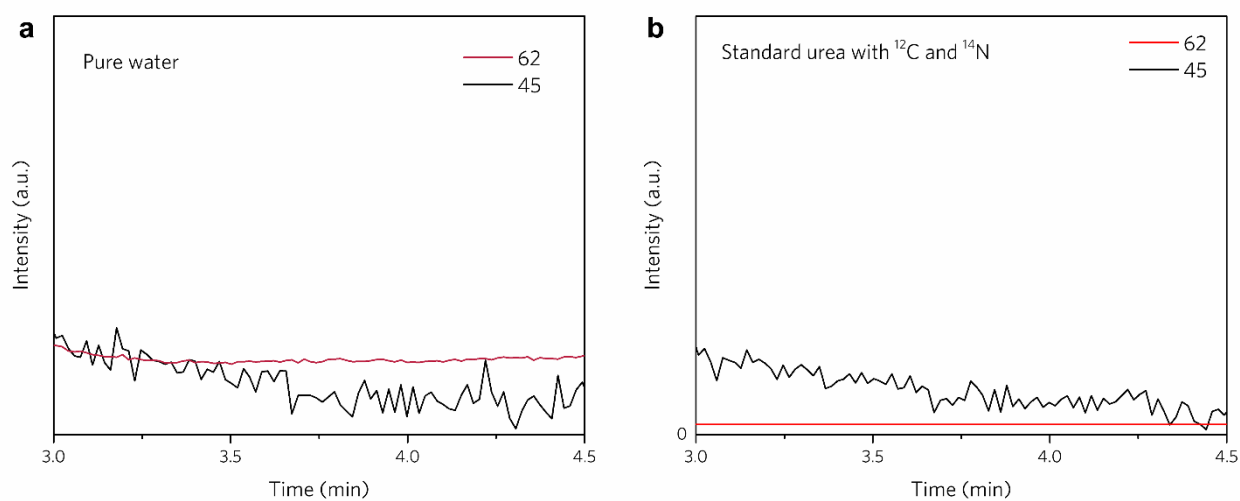


Figure S11. Superimposed EIC of LC-MS spectra of $m/z = 62, 45$ for the pure water (a) and $^{12}\text{C}, ^{14}\text{N}$ -urea (b).

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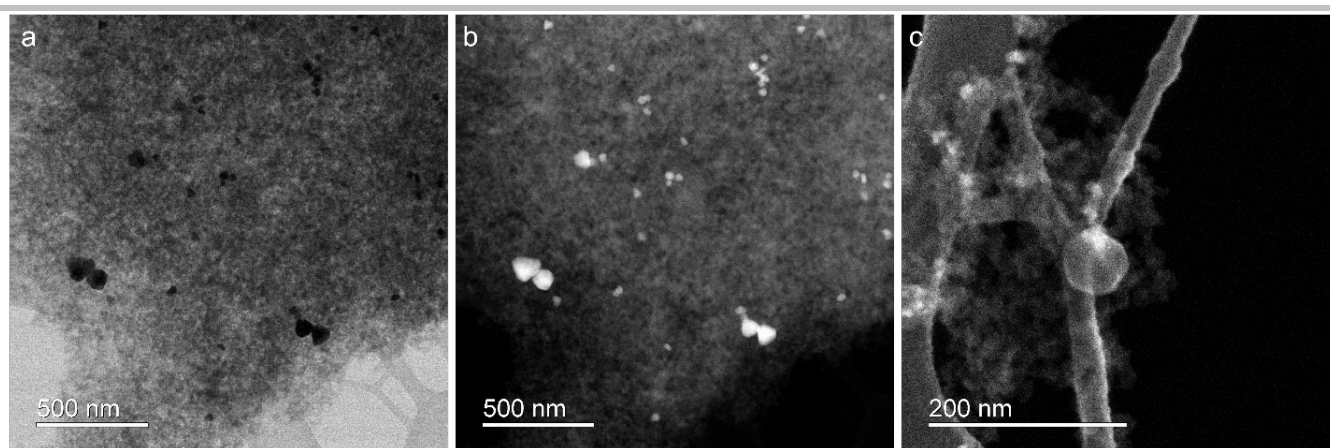


Figure S12. (a) STEM and (b, c) HAADF-STEM images of Pd/SiO₂.

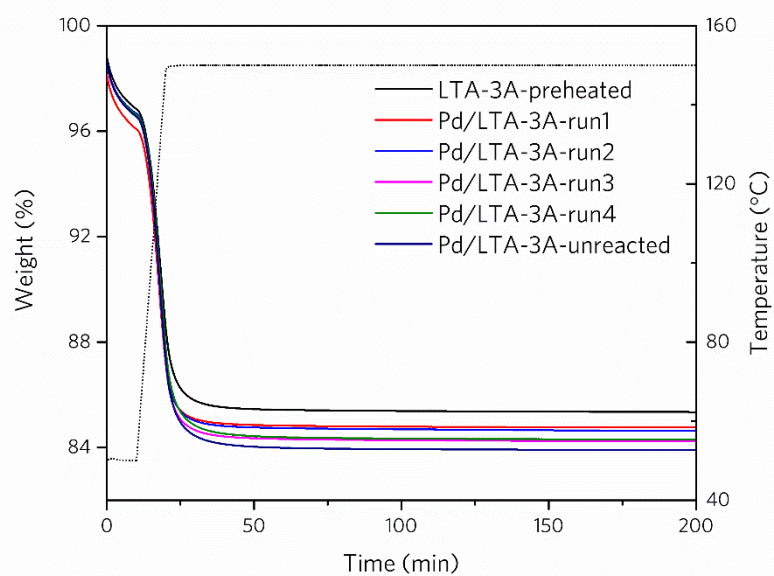


Figure S13. TGA spectra of Pd/LTA-3A measured after four separate NH_3+CO_2 runs, and control samples of LTA-3A preheated in vacuum oven and as-prepared Pd/LTA-3A stored in air before reaction.

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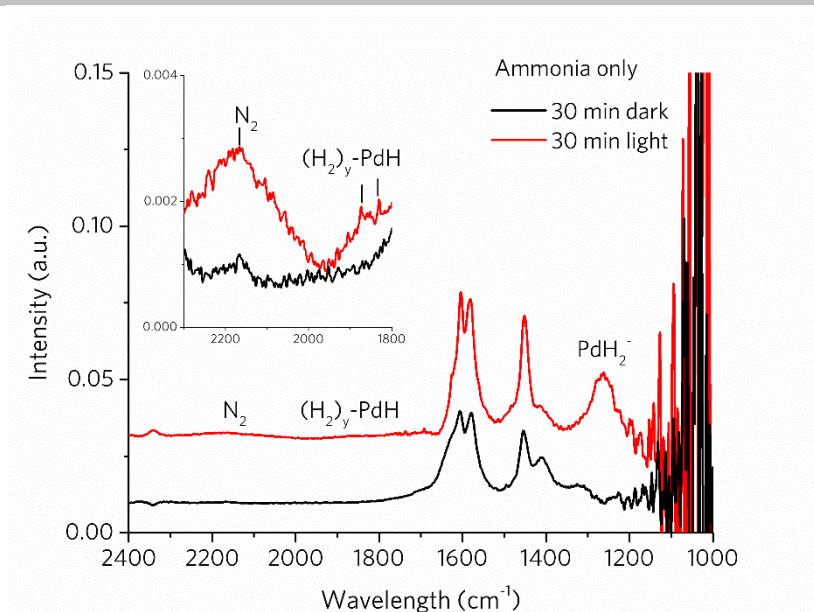


Figure S14. In situ DRIFTS measurements of Pd/LTA-3A under dark or irradiation (300 W Xe lamp). Condition: 4 sccm NH₃, and 10 sccm He, 100 °C.

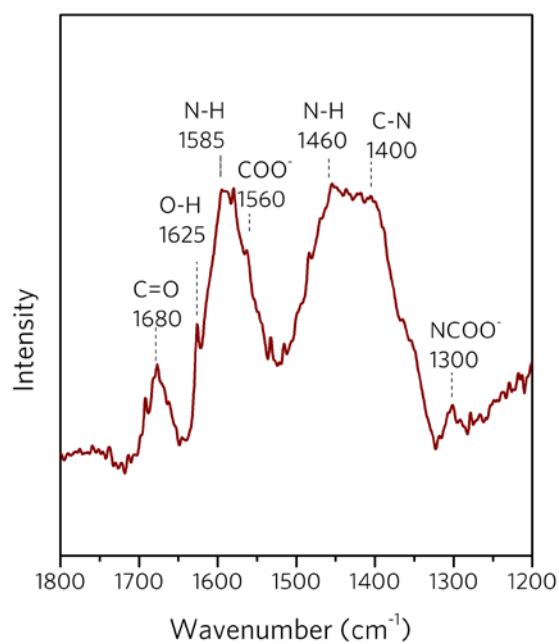


Figure S15. In situ DRIFTS measurements of Pd/LTA-3A under irradiation. Condition: 300 W Xe lamp, 4 sccm NH₃, 2 sccm CO₂ and 10 sccm He, 100 °C.

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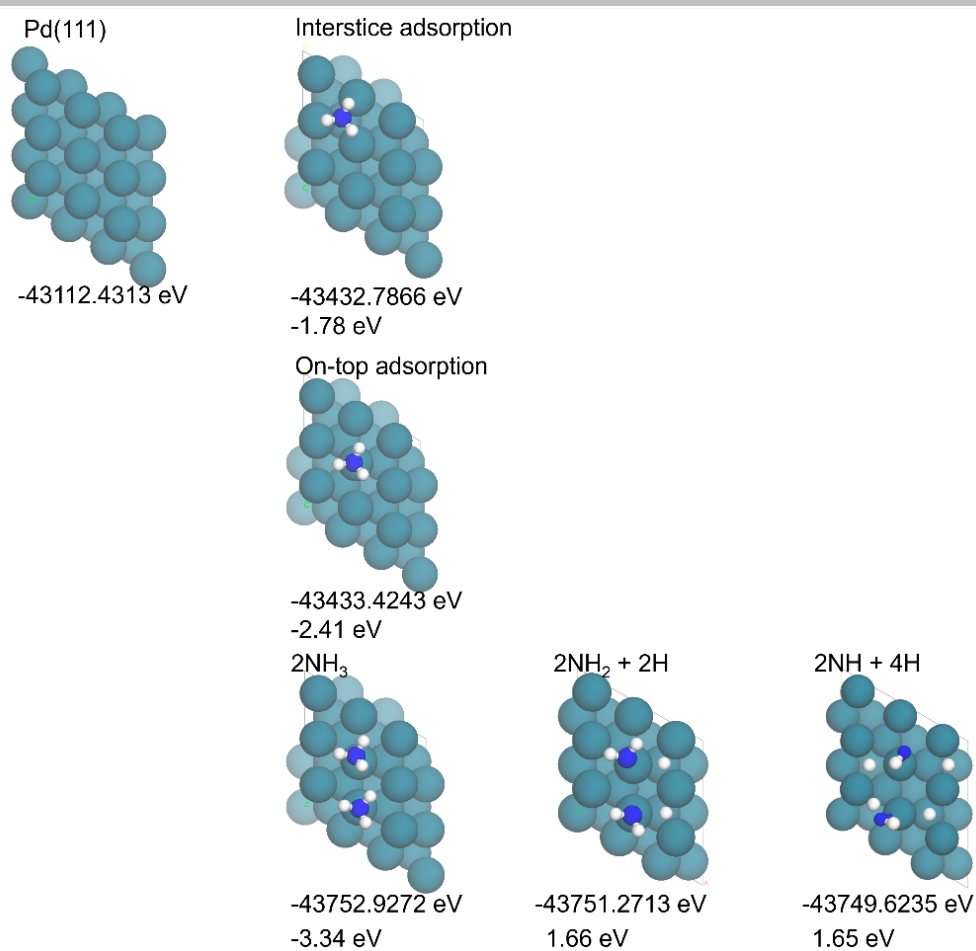


Figure S16. Fully relaxed configurations of Pd(111) and ammonia adsorption and decomposition on it, with the total and differential energies labeled.

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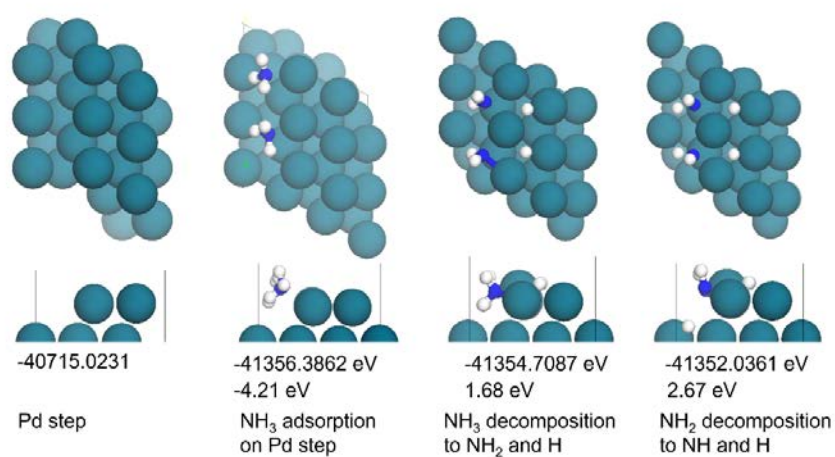


Figure S17. Fully relaxed configurations of Pd step model and ammonia adsorption and decomposition on it, with the total and differential energies labeled.