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## Supporting Information

### 4 **High Yield Production of Formate by Hydrogenating CO<sub>2</sub> Derived** 5 **Ammonium Carbamate / Carbonate at Room Temperature**

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## 17 I. Experimental

### 18 1. Materials

19 The catalyst samples Pd/AC, Pd/CaCO<sub>3</sub>, Pd/BaSO<sub>4</sub>, Pd/Al<sub>2</sub>O<sub>3</sub>, Ru/AC, Pt/AC, Rh/AC (all with 5 wt%  
20 metal loading) were purchased from Sigma-Aldrich®. 5 wt % Ni/AC was prepared by impregnation  
21 method (activated carbon support is VXC-72 purchased from CABOT®). Chemicals such as  
22 NH<sub>2</sub>CO<sub>2</sub>NH<sub>4</sub> (99 %), (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> (99 %), NaHCO<sub>3</sub> (99.5 %), Na<sub>2</sub>CO<sub>3</sub> (> 99.5 %), and anhydrous ethanol  
23 (200 proof, ≥99.5%) used in this paper were also purchased from Sigma-Aldrich®.

### 24 2. Reactions

#### 25 2.1 Hydrogenation reaction

26 The hydrogenation reaction experiments were carried out in the 50 mL stirred Parr micro-reactor. The  
27 appropriate amounts of substrate such as ammonium carbamate / carbonate and sodium bicarbonate /  
28 carbonate and the catalyst were added into 20 mL water. The reactor was then sealed, purged three times  
29 with high purity nitrogen, and then charged with the H<sub>2</sub> to the set pressure. During the reaction, mixing  
30 was achieved through an internal propeller operating at 620 RPM. Once the set temperature was attained,  
31 the reactor was held at the set temperature for a certain period of time and then quenched in an ice bath to  
32 quickly lower the temperature. The reactor was cooled until approximately 20 °C, and then the gas  
33 pressure was recorded and vented. The reactor was immediately broken down and the liquid was collected  
34 for analysis. The standard reaction conditions are: 20 ml solvent, 0.5 M substrate, 20 °C, 2.75 Mpa initial  
35 H<sub>2</sub> pressure, 0.1 g catalyst, and 1 hour reaction time.

36 The formate yield was calculated on the carbon basis and defined as follows:

$$37 \text{ Yield of formate} [\% - \text{C}] = \frac{\text{mol}_{\text{product}} \times \text{C atoms in product}}{\text{mol}_{\text{reactant charged}} \times \text{C atoms in reactant}} \times 100$$

38 The only product of hydrogenation of ammonium carbamate or carbonate is formate. So the yield of  
39 formate is equivalent to the conversion of ammonium carbamate or carbonate.

#### 40 2.2 Catalyst stability testing

41 The catalyst stability testing was also carried out in the same Parr micro-reactor. The catalyst after one  
42 time reaction (note as spent 1) was separated by a centrifugation and washed with water and ethanol for 5

43 times, respectively, and then the catalyst was dried at 50 °C in N<sub>2</sub> for 6 hours. The spent catalyst was  
44 reused in the repeated hydrogenation reactions. The typical reaction conditions were: 20 ml solvent (70 wt %  
45 ethanol in water), 0.5 M substrate, 20 °C, 2.75 MPa initial H<sub>2</sub> pressure, 0.1 g 5% Pd/AC catalyst, and 1  
46 hour reaction time.

### 47 **2.3 Solubility measurement**

48 The solubilities of ammonium carbonate and ammonium carbamate were measured by weight. 20 ml  
49 solvent were put into a 25 ml vial, and then ammonium carbonate or ammonium carbamate salts were  
50 added into the solvent. After a 30 min vortexing (Vortex-Genie 2) to accelerate the dissolving, the  
51 supernatants were carefully removed and the undissolved solid was freeze-dried under vacuum for 1 hour.  
52 Finally, the weight loss of the solids was used to calculate the solubility.

### 53 **3. Product analysis**

54 HPLC analysis was performed using a Shimadzu HPLC system equipped with a dual UV-VIS  
55 Detector (Shimadzu SPD 10-AV) at 208 and 290 nm and a Refractive Index Detector (Shimadzu RID-  
56 10A). For analysis of organic acids and reaction intermediates, the samples were separated in an Aminex  
57 87-H column from Bio-Rad, using 5 mM H<sub>2</sub>SO<sub>4</sub> as the mobile phase at 0.7 mL/min flow and a column  
58 temperature of 55 °C.

59 The <sup>13</sup>C NMR spectra were obtained with a 2-channel 400 MHz Varian VNMRs spectrometer with  
60 an automated triple broadband (ATB) probe. A small amount of D<sub>2</sub>O (5-10 mass % of solution) was  
61 added to get a signal lock, and 1wt% of 1,4-dioxane (67.19 ppm) was added as the internal standard. All  
62 the sample tubes were sealed and thermostated at 20 °C before being transferred to the NMR  
63 spectrometer. The <sup>13</sup>C NMR spectra were acquired at 20 °C. A relaxation delay of 25 times relaxation  
64 time (T<sub>1</sub>) and a pulse width of 90° were applied. The NMR spectra of the sample solutions before or after  
65 the reactions were recorded for 12 hours to obtain high-resolution signals.

### 66 **4. Catalyst characterization**

67 **Pulse chemisorption on catalyst samples:** The chemisorption was carried out using a Micromeritics  
68 Autochem II 2920 analyzer. The samples were pretreated under inert helium flow (50 mL/min) at 300°C  
69 for 1 h to remove adsorbed moisture, and then were reduced by 10% H<sub>2</sub> (in argon) at 250°C for 1 h,  
70 followed by purging with helium at the same temperature for another 1 h to remove the physical absorbed  
71 H<sub>2</sub> on the surface of the catalyst. The carbon monoxide pulse chemisorption experiment was carried out at  
72 40°C using helium (50 mL/min) as the carrier gas. 0.5 mL pulsed gas (10% CO in He) was fed into the

73 reactor and the CO signal was recorded every 0.2 seconds. It was repeated until the CO desorption peaks  
74 reached the saturation value. The pulsation was terminated when the peak areas of two consecutive CO  
75 peaks were the same. Between the pulses, the reactor was kept under 50 mL/min helium flow.

76 **TEM:** Transmission Electron Microscope was done on Hitachi S-4700 II Scanning Electron  
77 Microscope and operated at 200 kv.

791. **Results and discussion**

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81 **Table S1.** The catalyst effect on hydrogenation of ammonium carbamate in ethanol

Entry	Catalyst	Yield (%)
1	Pd/AC	40.5
2	Ru/AC	0.1
3	Rh/AC	0.4
4	Pt/AC	0.0
5	Ni/AC	0.0
6	Pd/Al <sub>2</sub> O <sub>3</sub>	9.6
7	Pd/CaCO <sub>3</sub>	0.6
8	Pd/BaSO <sub>4</sub>	4.3

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83 Reaction conditions: 20 mL ethanol, 0.5 M ammonium carbamate, 0.1 g catalyst, initial 2.75 MPa  
84 H<sub>2</sub>, 20 °C and 1 hour reaction.

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88 **Table S2.** Pulse chemisorption analysis results

Sample <sup>[a]</sup> (g)	Element	Metal Dispersion
Pd/AC	Pd	23.3%
Pt/AC	Pt	42.0%
Ru/AC	Ru	27.3%
Rh/AC	Rh	24.3%
Ni/AC	Ni	16.5%
Pd/Al <sub>2</sub> O <sub>3</sub>	Pd	13.6 %
Pd/CaCO <sub>3</sub>	Pd	10.3 %
Pd/BaSO <sub>4</sub>	Pd	5.8 %

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[a] The metal loading of all sample is 5 wt %.

91 **Table S3.** The formate yields of hydrogenation of different compounds with H<sub>2</sub>

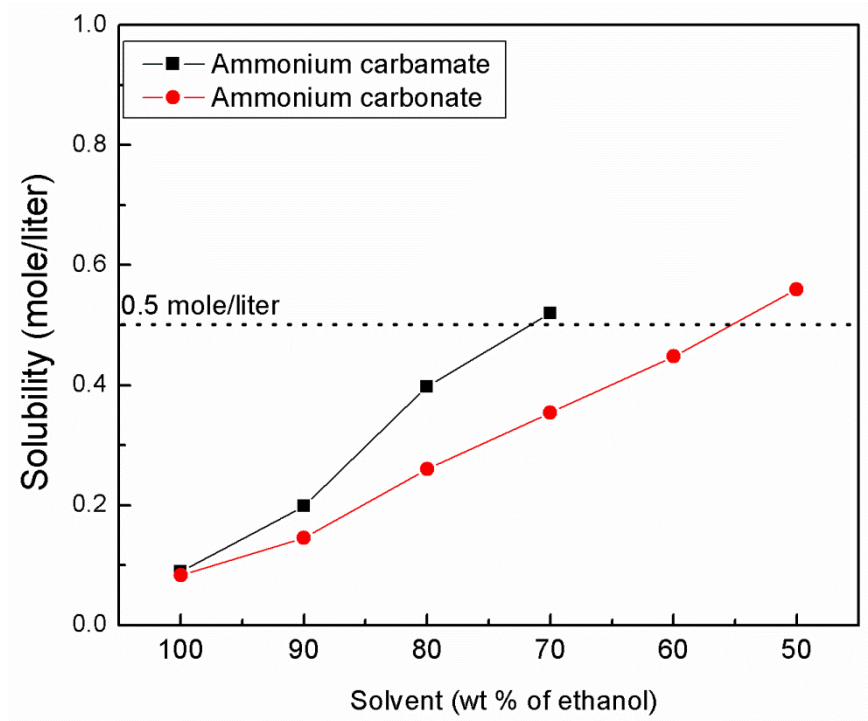
Entry	Reactants	Formate yield (%)
1	Ammonium carbamate	43.3
2	Ammonium carbonate	42.9
3	Sodium carbonate	0
4	Sodium bicarbonate	4.1
5	Methyl carbamate	0
6	Formamide	0
7	Urea	0

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93 Reaction conditions: 20 mL solvent (70 wt % ethanol in water), 0.5 mol L<sup>-1</sup> reactants, 0.1 g  
94 Pd/AC (5 wt% Pd) catalyst, initial 2.75 MPa H<sub>2</sub>, 20 °C and 1 hour reaction time.

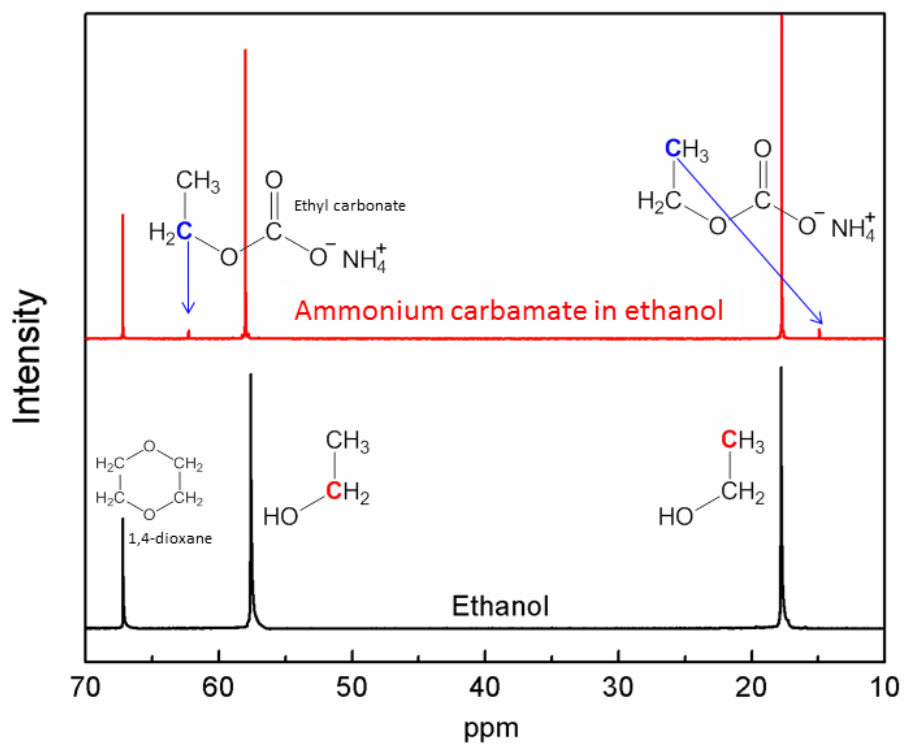
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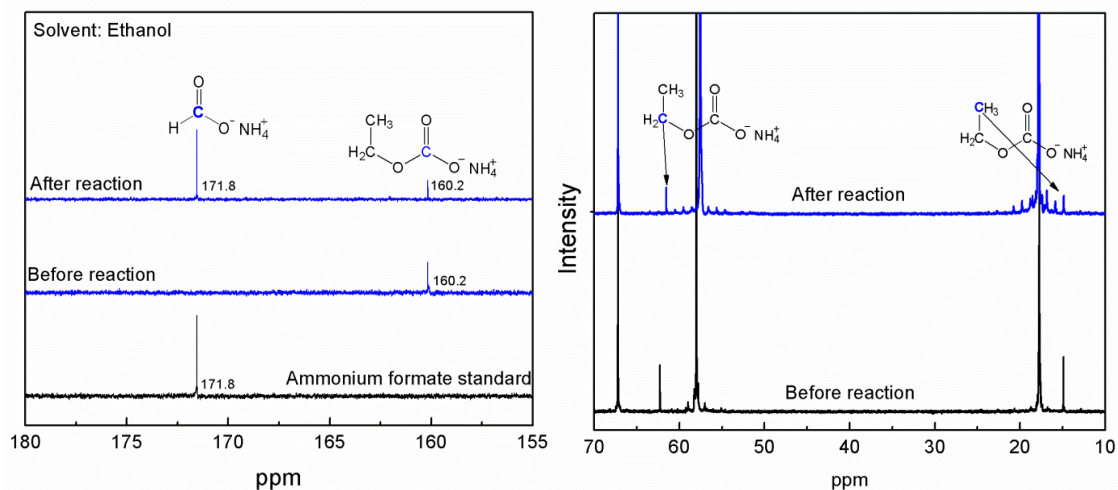
100 **Figure S1.** Solubilities of ammonium carbonate and ammonium carbamate in ethanol-water solvents.





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102 **Figure S2**  $^{13}\text{C}$  NMR spectra of ammonium carbamate dissolved in ethanol (red line) and the pure ethanol  
 103 solvent (black line). (1,4-dioxane is the internal standard)



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(a)

(b)

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108 **Figure S3** <sup>13</sup>C NMR spectra of ammonium carbamate derived compounds in the pure ethanol solutions  
 109 before and after the hydrogenation reaction (a) range from 180 to 155 ppm, (b) range from 70 to 10 ppm

110 Reaction conditions: 20 mL ethanol, 0.5 mol L<sup>-1</sup> ammonium carbamate, 0.1 g Pd/AC (5 wt% Pd)  
 111 catalyst, initial 2.75 MPa H<sub>2</sub>, 20 °C and 1 hour reaction time.

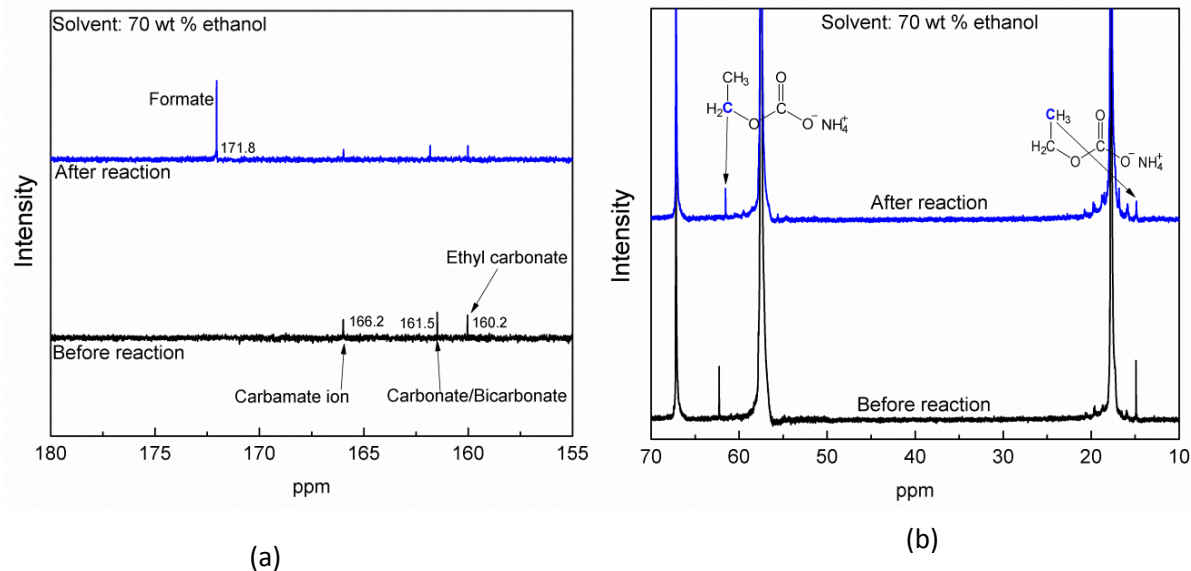
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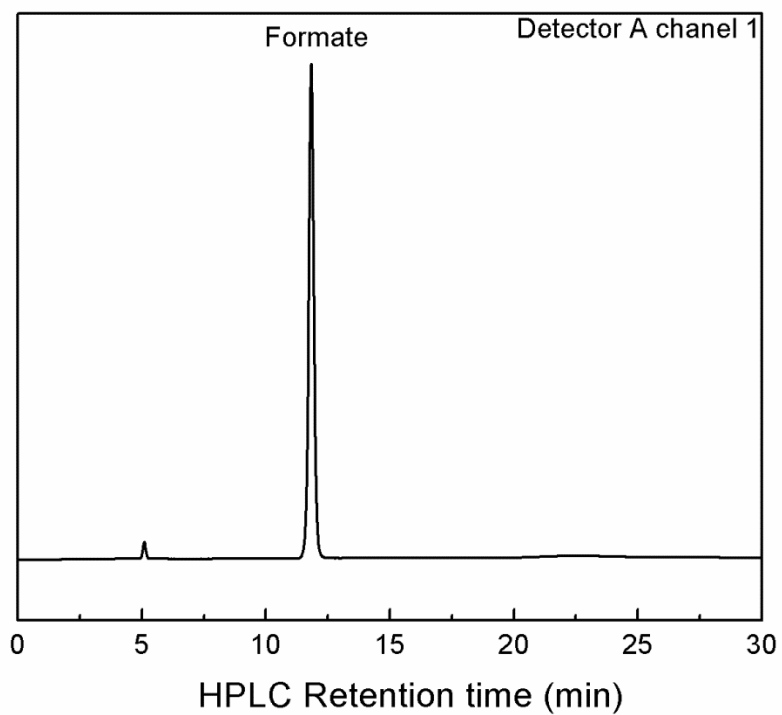
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121 **Figure S4**  $^{13}\text{C}$  NMR spectra of the ammonium carbamate derived compounds in the ethanol-water  
 122 solutions before and after the hydrogenation reaction (a) range from 180 to 155 ppm, (b) range from 70 to  
 123 10 ppm

124 Reaction conditions: 20 mL solvent (70 wt % ethanol in water), 0.5 mol L<sup>-1</sup> ammonium  
 125 carbamate, 0.1 g Pd/AC (5 wt% Pd) catalyst, initial 2.75 MPa H<sub>2</sub>, 20 °C and 1 hour reaction time.



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**Figure S5** HPLC spectra of the products of the hydrogenation of ammonium carbamate

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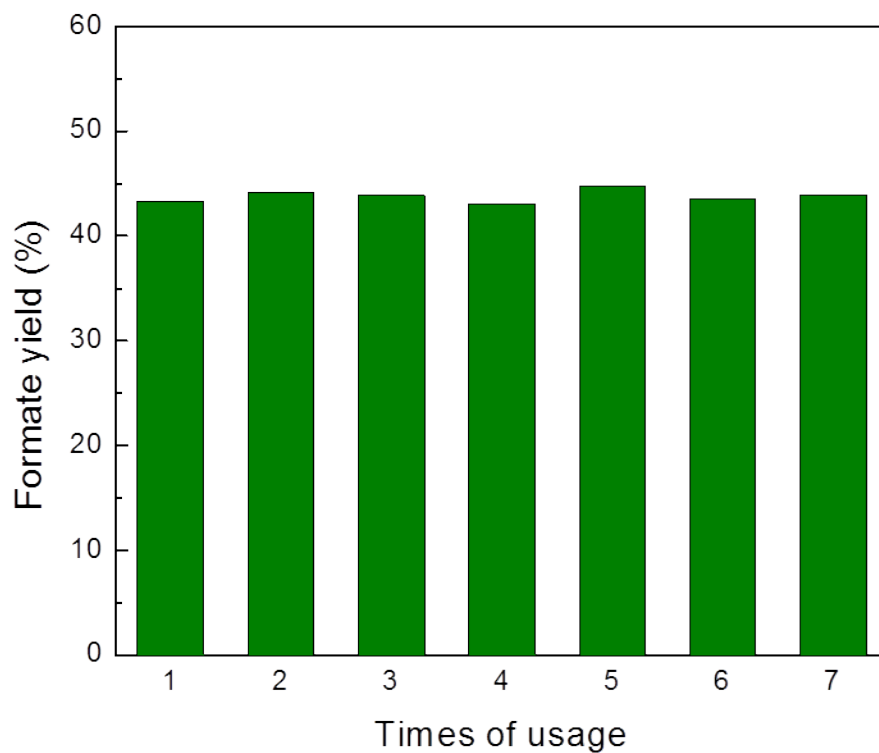
Reaction conditions: 20 mL ethanol, 0.5 mol L<sup>-1</sup> ammonium carbamate, 0.1 g Pd/AC (5 wt% Pd)

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catalyst, initial 2.75 MPa H<sub>2</sub>, 20 °C and 1 hour reaction time.

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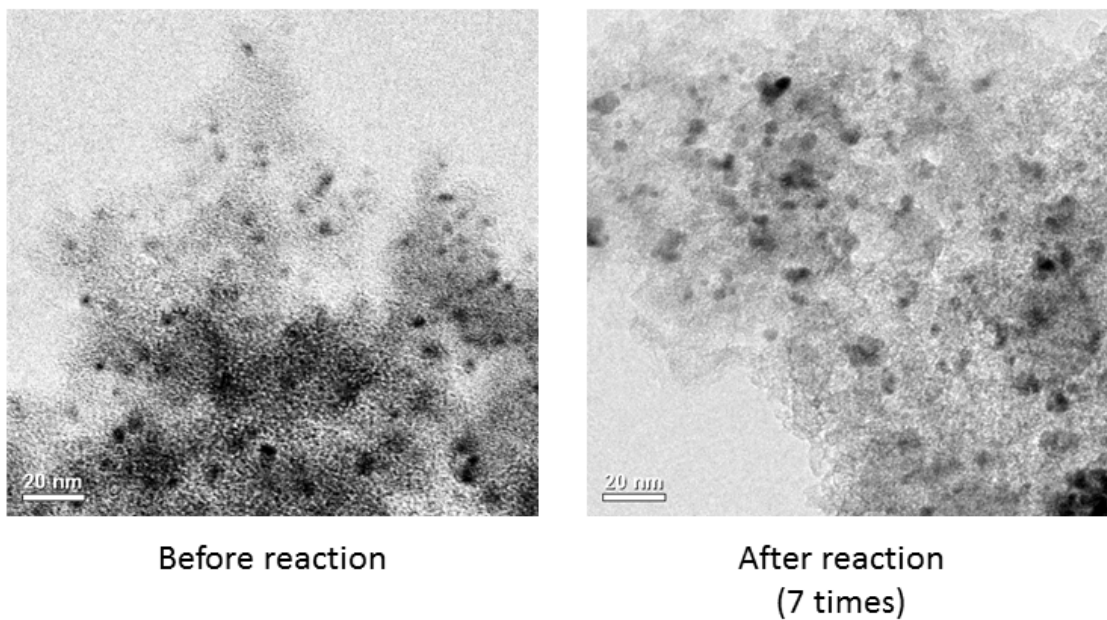
**Figure S6** Stability test of the Pd/AC catalyst

136 Reaction conditions: 20 mL solvent (70 wt % ethanol), 0.5 mol L<sup>-1</sup> ammonium carbamate, 0.1 g  
137 Pd/AC (5 wt% Pd) catalyst, initial 2.75 MPa H<sub>2</sub>, 20 °C and 1 hour reaction time.

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143 **Figure S7** TEM images of the Pd/AC catalysts before (fresh catalyst) and after (spent catalyst) 7 cycles of  
144 ammonium carbamate hydrogenation.

145 Reaction conditions: 20 mL solvent (70 wt % ethanol in water), 0.5 mol L<sup>-1</sup> ammonium  
146 carbamate, 0.1 g Pd/AC (5 wt% Pd) catalyst, initial 2.75 MPa H<sub>2</sub>, 20 °C and 1 hour reaction  
147 time.

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