Supporting Information

Renewable Energy Storage via Efficient Reversible Hydrogenation of Piperidine Captured CO₂

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I Experimental Section

Materials

The catalyst samples (Pd/AC, the metal loadings are 5 wt%) were purchased from Sigma-Aldrich®. Chemicals including NaHCO$_3$ (99.5%), ethanolamine (>99%), piperazine (99%), piperidine (99%), 2-amino-2-methyl-1-propanol (95%), 1-propanol (>99%) and 2-propanol (>99%) were also purchased from Sigma-Aldrich®. Ethanol, 200 proof (absolute) was purchased from Decon™ Labs.

Reduction of bicarbonate or alkyl carbonate

The experiments on the reduction of bicarbonate or alkyl carbonate were carried out in a 50 mL stirred Parr micro-reactor in the temperature range of 20 °C – 40 °C. The appropriate amount of the Pd/AC catalyst were added into 20 mL aqueous ethanol solvent with amine captured CO$_2$. The reactor was then sealed, purged with high purity N$_2$ for three times, followed by charging with H$_2$ to the set pressure. During the reaction, mixing was achieved through an internal propeller operating at 1500 RPM. Once the set temperature was attained, the reactor was held at the set temperature for certain period. After the reaction, the reactor was cooled down to approximately 20 °C, the gas pressure was recorded. Then the reactor was vented. And the liquid was collected for chemical analysis. Typical reaction conditions are: 20 mL solvent, 1 M CO$_2$-amine solution (CO$_2$ was captured and saturated with the amine solutions), 20 °C, 400 psi initial partial pressure of H$_2$, 0.1 g Pd/AC catalyst loading, 1 hour reaction time. The turnover frequency (TOF) was estimated as follows: [moles formate produced in 5 mins / (moles Pd × 23.2 %) / reaction time]. The dispersion of Pd atoms on the surface of Pd nanoparticles (NPs), which was determined by the carbon monoxide chemisorption, was 23.2%. Since the reactions were carried out in the batch
reactor, we used the kinetic rate data within the first 5 minutes of each reaction to estimate the TOF.

**Formate decomposition**

The experiments on the formate decomposition reactions were carried out in a 50 mL three-necked round bottom flask in the heating mantle. One neck of the flask was connected to a condenser which was then further connected to a NaOH solution (10 M) trap. The trap was connected to a gas burette. The condenser was used to prevent the volatilization of liquid species, and the NaOH trap absorbed CO$_2$ from the decomposition of formate. Before the reaction, the leakproofness of the reaction system was tested, and then the system was purged with N$_2$ gas for 5 minutes to ensure no O$_2$ in the reaction system. The catalytic formate decomposition for discharging hydrogen was initiated by stirring the mixture of the aqueous suspension of the Pd/AC catalyst (0.1 g) in 20 mL formate amine adduct solution (1 M) after the reaction temperature was reached. The released CO$_2$ and H$_2$ gases were introduced through the NaOH trap in which CO$_2$ was fully absorbed, and the H$_2$ gas volume was monitored using the in-line gas burette. To ensure accuracy, each reaction was repeated 3 times and the data were averaged. The turnover frequency (TOF) was estimated as follows: $\text{[moles of hydrogen produced in 5 mins / (moles of Pd \times 23.2 \%) / reaction time]}$.

**Aqueous-phase Product Analysis**

Aqueous samples collected were filtered through a 0.22 $\mu$m pore size filter for high-performance liquid chromatography (HPLC) analysis, which was performed using a Shimadzu HPLC system equipped with a dual UV-VIS Detector (Shimadzu SPD 10-AV) at 208 and 290 nm and a Refractive Index Detector (Shimadzu RID-10A). For the analysis of formic acid and the reaction
intermediates, the samples were separated in an Aminex 87-H column (Bio-Rad), using 5 mM H$_2$SO$_4$ as the mobile phase at 0.7 mL/min flow and a column temperature of 55 °C.

NMR measurements were performed on a 2-channel 400 MHz Varian VNMRS with an ATB automation probe. For quantitative $^{13}$C NMR studies, the spectra of the sample solutions were recorded at 25 °C with the following acquisition parameters: the pulse width of 90°, the delay time between two transitions (D1) = 25s, and the number of scans, (NS) = 1000. The time needed for quantitative experiments was approximately 7 hours. The internal standard was 1,4-Dioxane (the carbon chemical shift is at 67.19 ppm).

**Gas-phase Product Analysis**

After the reaction, the offgas was collected by a 0.6L Tedlar® Gas Sampling Bag and then analyzed by a Shimadzu GC-2014 gas chromatograph, equipped with a HAYESEP-N column (2.5m x 1/8in x 2.1mm. SS), a HAYESEP-D column (2.5m x 1/8in x 2.1mm. SS), a HAYESEP-S column (2m x 1/8in x 2.1mm), a HAYESEP-D column (1m x 1/8in x 2.1mm), a MOL SIEVE 5A column (3m x 1/8in x 2.1mm. SS), a Carbowax column (2m x 1/8in x 2.1mm) and a thermal conductivity detector (TCD), for quantitative analysis of gas phase products.

**In-Situ ATR-FTIR**

Attenuated total reflectance infrared (ATR-IR) was employed to obtain the information about the surface of the catalysts during the reaction. The measurements were performed using a Bruker Tensor II spectrometer and a custom-made ATR-FTIR cell. Before initiating the measurement, the catalyst sample was ground into fine powder and suspended in nanopore water (1.5 mg sample/mL water) under sonication to form ink, which was then coated onto the internal reflectance element (IRE) and dried for 1 h at 90 °C to form a thin layer. Before each measurement, the Pd/AC sample
was reduced in 10% H₂/Ar (40 mL/min) at 150 °C. After 1-hour reduction, the flow was switched to 40 mL/min N₂ and the sample was purged for 10 min before cooling down. Then 20 μL formate amine adduct was added dropwise on the inked catalysts. Then the ATR cell was sealed after purging N₂ and background spectrum of the formate amine adduct adsorbed on the catalyst was taken. During the measurement, the spectra were recorded between 4000 cm⁻¹ and 800 cm⁻¹ by averaging 128 scans at a resolution of 4 cm⁻¹ to improve the signal to noise ratio.

II Results and discussion

Figure S1. ¹³C NMR spectra of CO₂ derived ionic species intermediates after CO₂ was captured with piperidine in water, 70% Ethanol, and 100% ethanol, respectively. CO₂ capture conditions: 20 mL ethanol/water solvent, 1 M piperidine, 20 °C, 40 min. D₈ is 1,4-dioxane as an internal standard.
Figure S2. Hydrogenation of piperidine captured CO$_2$ in water (left), and ethanol (right). Reaction conditions: 0.1 g Pd/AC catalyst, 400 psi hydrogen pressure, 20 - 30 °C, 20 mL 1 M piperidine captured CO$_2$ solution in parr reactor.
Figure S3. Arrhenius plot of the dehydrogenation of formate piperidine adducts over 5 wt % Pd/AC in aqueous ethanol solutions. Reaction conditions: 0.1 g Pd/AC catalyst, 1 atm initial pressure of N₂, 1 M formate piperidine adducts, 20 ml aqueous solvent with 70% EtOH. ln k was calculated by dehydrogenation rate in 5 mins.

Figure S4. Dehydrogenation of formate piperidine adducts in water, ethanol and mixed water/ethanol solvents. Reaction conditions: 0.1 g Pd/AC catalyst, 1 atm initial N₂ pressure, 80 °C, 1 M formate piperidine adducts, 20 mL solvent.
Figure S5. Dehydrogenation of formate piperidine adducts in aqueous solvent with (upper) 70% of 1-propanol and (bottom) 70% of 2-propanol. Reaction conditions: 0.1 g Pd/AC catalyst, 1 atm initial pressure of N\textsubscript{2}, 1 M formate piperidine adducts, 20 mL solvent.
**Figure S6.** GC-TCD chromatogram of the gaseous products from the dehydrogenation of formate piperidine adduct in aqueous solvent with 70% EtOH. Reaction conditions: 0.1 g Pd/AC, 100°C, 1 atm of initial pressure of N₂. Note the peak at 4.387 min is an injection peak.

**Figure S7.** Effect of piperidine concentration on H₂ releasing rate from dehydrogenation of formate piperidine adducts. Reaction conditions: 1 M formic acid mixed with varying amounts of piperidine, 20 mL aqueous solutions with 70% EtOH, 0.1 g Pd/AC catalyst, 1 atm initial pressure of N₂, 40 °C.
Figure S8. In-Situ ATR-FTIR spectra of Pd/AC with flowing CO (pink lines). Procedure: 5% Pd/AC was coated on the window of ATR, and then 20 mL/min of 10% CO/He flew through the ATR cell. The temperature increased from 25 °C to 55 °C, stayed for 1 hour, and then introduced the N$_2$ flow at 20 mL/min.
Figure S9. In-Situ ATR-FTIR spectra of adsorbed species on Pd surface during the dehydrogenation of piperidine formate adduct. 5% Pd/AC was coated on the window of ATR, then the reactant solution (1 M piperidine formate adduct in aqueous ethanol solution with 70% EtOH) was added. FTIR spectra were recorded during the decomposition of formate at 55 °C. The negative peaks at 1589, 1375 and 1346 cm$^{-1}$ which are partially due to the intermediates still remain, this may be a joint result from consumption of formate and also certain amounts of intermediates were taken as the background at the beginning of the experiment.
Figure S10. In-situ ATR-FTIR spectra of adsorbed species on Pd surface during the dehydrogenation of formate monoethanolamine adduct. 5% Pd/AC was coated on the window of ATR, and then reactant solution (1 M monoethanolamine formate adduct in aqueous ethanol solution with 70% EtOH) was added. FTIR spectra were recorded during the decomposition of formate at 55 °C. The negative peaks at 1589, 1375 and 1346 cm$^{-1}$ which are partially due to the intermediates still remain, this may be a joint result from consumption of formate and also certain amounts of intermediates were taken as the background at the beginning of the experiment.
**Figure S11.** $^{13}$C NMR spectra of CO$_2$ derived intermediates after capturing CO$_2$ with PIPD, hydrogenation of PIPD-CO$_2$ and dehydrogenation of PIPD-Formic acid. CO$_2$ capture: 20 °C, 1 M PIPD in aqueous solvent with 70% EtOH. Hydrogenation: 20 °C, 30 mins, 0.1 g Pd/AC. Dehydrogenation: 0.1 g Pd/AC, 100 °C, 40 mins.
Scheme S1. (a) A general scheme of decarboxylation of formic acid on Pd surface. (b) A proposed mechanism for dehydrogenation of piperidine formate adduct on Pd surface. (c) A proposed mechanism for dehydrogenation of monoethanolamine formate adduct on Pd surface. In water solvent, R=H; in ethanol solvent, R=CH₃CH₂.