Room-Temperature Transfer Hydrogenation and Fast Separation of Unsaturated Compounds over Heterogeneous Catalysts in an Aqueous Solution of Formic Acid

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Methods:

Synthesis of CN (mpg-C3N4):5 g of cyanamide was dissolved in 7.5 g of Ludox HS40 solution (dispersion of 12nm SiO₂ particles with 40 wt% in water) and heated at 65 °C overnight to remove water. The as-formed white powder was heated at a temperature of 600 °C for 4 h (ramp: 2.3 °C min⁻¹) under the protection of N₂. The resulting brownyellow powder was treated with a 4 M HF acid for 24 h to remove the silica template. The powders were then centrifuged and washed three times with distilled water and twice with ethanol. Finally the powders were dried at 60 °C under vacuum overnight.

Synthesis of Pd/CN-8%: 1.000 g of mesoporous carbon nitride was dispersed into 250 mL of water via sonication and vigorous stir. A mixed solution of $PdCl_2$ with 1.8M HCl solution containing 88 mg of Pd component were added into the dispersion and stirred overnight. A certain amount of 1 M NaOH solution was added to tune the pH value to around 13. And then, 18.6 mL of 0.5 M NaBH₄ were added dropwise to this suspension. The obtained mixture was separated via centrifugation, washed thoroughly with distilled water and ethanol and finally dried in vacuum at 60 °C overnight.

Synthesis of Pd/CB-8%: 100 mg of carbon black (Vulcan XC 72, Cabot, graphitized at 900 °C for 2 hour in N₂ gas) was dispersed into 25 mL of water via sonication and vigorous stir. A mixed solution of PdCl₂ with 1.8 M HCl solution containing 8.8 mg of Pd component were added into the dispersion and stirred overnight. A certain amount of 1M NaOH solution was added to tune the pH value to around 13. And then, 1.9mL of 0.5 M NaBH₄ were added dropwise to this suspension. The obtained mixture was separated via centrifugation, washed thoroughly with distilled water and ethanol and finally dried in vacuum at 60 °C overnight.

Synthesis of Pd/N-LC-8%: Nitrogen-doped layered carbon with a nitrogen content of 10 at.% was obtained according to Ref. 12. In summary, a mixture of dicyandiamide (5 g) and glucose (1 g) was heated at a temperature of 800 °C for 1 hour (ramp: 2.2 °C min⁻¹ under protecting N_2 flow). 100 mg of the as-formed N-LC was dispersed into 25 mL of water via sonication and vigorous stir. A mixed solution of PdCl₂ with 1.8 M HCl solution containing 8.8 mg of Pd component were added into the dispersion and stirred overnight. A certain amount of 1 M NaOH solution was added to tune the pH value to around 13. And then, 1.9 mL of 0.5 M NaBH₄ were added dropwise to this suspension. The obtained mixture was separated via centrifugation, washed thoroughly with distilled water and ethanol and finally dried in vacuum at 60 °C overnight.

Synthesis of Pd/SBA-15-8%: 100 mg of SBA-15(obtained accirding to Ref. 13) was dispersed into 25 mL of water via sonication and vigorous stir. A mixed solution of PdCl₂ with 1.8 M HCl solution containing 8.8 mg of Pd component were added into the dispersion and stirred overnight. A certain amount of 1M NaOH solution was added to tune the pH value to around 13. And then, 1.9mL of 0.5 M NaBH₄ were added dropwise to this suspension. The obtained mixture was separated via centrifugation, washed thoroughly with distilled water and ethanol and finally dried in vacuum at 60 °C overnight.

Synthesis of $Pd^{2+}/CN-8\%$:100 mg of mesoporous carbon nitride was dispersed into 25 mL of water via sonication and vigorous stir. A mixed solution of $PdCl_2$ with 1.8M HCl solution containing 8.8 mg of Pd component were added into the dispersion and stirred overnight. A certain amount of 1 M NaOH solution was added to tune the pH value to around 13. The obtained mixture was separated via centrifugation, washed thoroughly with distilled water and ethanol and finally dried in vacuum at 60 °C overnight.

Synthesis of Pt/CN-8%: 100 mg of mesoporous carbon nitride was dispersed into 25 mL of water via sonication and vigorous stir. A solution of H_2 PtCl₄ containing 8.8 mg of Pt component were added into the dispersion and stirred overnight. A certain amount of 1 M NaOH solution was added to tune the pH value to around 13. And then, 1.9 mL of 0.5 M NaBH₄ were added dropwise to this suspension. The obtained mixture was separated via centrifugation, washed thoroughly with distilled water and ethanol and finally dried in vacuum at 60 °C overnight.

Synthesis of Au/CN-8%: 100mg of mesoporous carbon nitride was dispersed into 25 mL of water via sonication and vigorous stir. A solution of HAuCl₄ containing 8.8 mg of Au component were added into the dispersion and stirred overnight. A certain amount of 1 M NaOH solution was added to tune the pH value to around 13. And then, 1.9 mL of 0.5 M NaBH₄ were added dropwise to this suspension. The obtained mixture was separated via centrifugation, washed thoroughly with distilled water and ethanol and finally dried in vacuum at 60 °C overnight.

Synthesis of Ag/CN-8%: 100mg of mesoporous carbon nitride was dispersed into 25 mL of water via sonication and vigorous stir. A solution of AgNO₃ containing 8.8 mg of Ag component were added into the dispersion and stirred overnight. A certain amount of 1 M NaOH solution was added to tune the pH value to around 13. And then, 1.9 mL of 0.5 M NaBH₄ were added dropwise to this suspension. The obtained mixture was separated via centrifugation, washed thoroughly with distilled water and ethanol and finally dried in vacuum at 60 °C overnight.

Catalytic transfer hydrogenation of unsaturated C=C bonds. In a typical reaction, 10 mg of catalyst and 0.1 mmol of substrate were dispersed in 2.5 mL of water in a common glassround bottle, followed by addition of 98% pure FA with constant magnetic stirring (1000 rpm). The products were extracted with 2 mL of CH_2Cl_2 after reaction. The reaction products were identified by GC-MS and quantified by GC with a FID detector. The reaction temperature was kept at 298 K by using a thermostat water bath.

Reuse of Pd/CN catalyst for transfer hydrogenation of methylfuran. The used catalyst was separated bycentrifugation and then washed with 0.1 M NaOH for one time and distilled water for three times. The catalyst was then directly used for another catalytic reaction.

Regeneration of Pd/CN-used catalyst. The deactivited catalyst was redispersed in 0.1 M NaOH for more than 12 hours under stir. The obtained mixture was separated via centrifugation, and finally washed thoroughly with distilled water.

Characterization: The PXRD measurements were performed on a Rigaku D/Max 2550 X-ray diffractometer operating at the Cu K α 1radiation. The XPS measurements were performed on a KratosAXIS ULTRA DLD X-ray photoelectron spectrometer with a monochromatized X-ray source (Al KR h ν = 1486.6 eV). The TEM measurements

were performed on a JEOL JEM-2100 operated at 100 kV. The FTIR spectra were recorded using a Bruker IFS 66v/S FTIR spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector.



Figure S1. PXRD patterns of M/CN (M=Pd, Pt, Ag or Au). The weight percentages of metal components are all 8 wt% for three samples.



Figure S2. Transmission electron microscopy images (TEM) of M/CN (M=Pd, Pt, Ag or Au). The size of Ag nanoparticles is smaller than 2 nm, matching well with the broad peaks of the XRD result.

Figure S3. Plots of the yield of ethylbenzene versus the reaction time over Pd/CN with different ratio of FA. Typical conditions: 0.1 mmol of styrene, 2.5 mL of H_2O , 10 mg of catalyst, 298K.

Figure S4. The photos of different steps for transfer hydrogenation of styrene to ethylbenzene in aqueous FA solution over Pd/CN.

Figure S5. Plots of the yield of MTHF versus the reaction time over different catalysts: Pd/CN, Pd/SBA-15, Pd/C and Pd/LNC. Typical conditions: 2.5 mL of H_2O , 0.1 mmol of 2-methylfuran, 0.5 mmol of FA, 10 mg of catalyst, 285K. Yields were determined with GC by using a FID detector.

Figure S6. TEM images of Pd/L-NC, Pd/SBA-15 and Pd/C.

Table S1. Features of various catalyst supports.^[a]

Catalyst support	Surface area (m^2/g)	C (at.%)	N (at.%)	Size of Pd NPs (nm)	Pd loading (wt%)
CN	140	41	59	2-5	8
N-LC	190	91	7	2-8	8
CB	80	99	-	6-13	8

[a] Surface areas were confirmed via nitrogen sorption analysis, composition was demonstrated by the XPS analysis and the particle sizes were measured via TEM images.

Figure S7. PL spectra of CN and Pd/CN.

Figure S8. PXRD patterns (a) and TEM image (b) of the used Pd/CN after 31 runs.

Figure S9. Particle size distributions of the fresh (a) and recycled (b) Pd@CN samples.

Figure S10. FT-IR spectra of as-obtained Pd/CN, deactivated Pd/CN and regenerated Pd/CN. The chemical structure of the CN frameworks remained stable after use and regeneration.

Figure S11. (a) Plots of the yield of MTHF versus the reaction time over different catalysts: fresh Pd/CN and regenerated Pd/CN. Typical conditions: 2.5 mL of H₂O, 0.1 mmol of 2-methylfuran, 0.5 mmol of FA, 10 mg of catalyst, 285 K. Yields over regenerated Pd/CN were slightly lower due to the loss of catalyst during the recycling process. (b) Plots of the yield of MTHF versus the reaction time over Pd/CN catalyst in reusability test. Reaction conditions: 0.1 mmol of methyl furan, 5 mL of H₂O, 0.5 mmol of FA, 20 mg of catalyst, 298 K, 30 min. 30 minutes were the minimum time for full conversion of MTHF. The conversions of the MTHF at 30 min were thus selected to evaluate the resusability of the Pd/CN.

Figure 12. Reuse of Pd/SiO_2 catalyst for transfer hydrogenation of methylfuran to MTHF. The reuse of Pd/SiO_2 was conducted by following the same process for that of Pd/CN.

Figure S13. Transfer hydrogenation of 2-methylfuran at different reaction conditions. *hv*: visible light irradiation ($\lambda \ge$ 400 nm). Typical conditions: 0.1 mmol of 2-methylfuran, 2.5 mL of H₂O, 10 mg of Pd/CN catalyst, 285 K. Yields were determined with GC by using a FID detector.

Figure S14. Conversions of FA with or without 2-methylfuran (MF) over Pd/CN. Typical condition: 0.1 mmol of 2methylfuran, 0.5 mmol of FA, 2.5 mL of H₂O, 10 mg of Pd/CN (or bare CN), 1 hour. All reactions were conducted at 298 K. When 2-methylfuran was not involved, H₂ forms in our catalytic system via the decomposition of FA with a conversion of FA to be 15%. The conversion of FA was evaluated by the volume of gas on the basis of following reaction: HCOOH \rightarrow H₂ +CO₂. Such a conversion was much lower than those reactions with the presence of 2methylfuran, which convert 40% of the FA as calculated on the basis of the 2-methyltetrahydrofuran detected. It is believed that formation and activation of hydrogen gas were not essential for the reduction of unsaturated carbon bonds.

Figure S15. The GC-MAS results of the products of reduction of cinnamic acid benzyl ester. Reaction conditions: 2.5 mL of H₂O, 0.1 mmol of cinnamic acid benzyl ester, 0.3 mmol of FA, 10 mg of Pd/CN, 298 K.