Supporting Information

Electron-deficient Pd Nanoparticles on Nitrogen-Doped Carbon Nanofibers for High Selectivity Alkyne Transfer Semi-hydrogenation

Huaike Li,[a] Shuai Li, [b] Guichu Yue, [c] Songwei Gao, [d] Xuefeng Zhang, [a] Keping Zhu, [a] Tingting Yang, [a] Ziyue Zhang, [a] Nü Wang, [a] Jie Bai, [c] Zhimin Cui, *[a] and Yong Zhao*[a, c]

[a.] Key Laboratory of Bioinspired Smart Interfacial Scienceand Technology of Ministry of Education, Beijing Key Laboratory of Bioinspired Energy Materials and Devices, School of Chemistry, Beihang University, Beijing, 100191, China

[b.] Advanced Materials Research Central, Northwest Institute for Nonferrous Metal Research, Xi'an, 710016, China

[c.] Chemical Engineering College, Inner Mongolia University of Technology, Hohhot, 010051, China

[d.] School of Materials Science and Engineering, Henan Polytechnic University, Jiaozuo, 454003, China

*Corresponding author: cuizhm@buaa.edu.cn; zhaoyong@buaa.edu.cn

Chemicals

Zinc nitrate hexahydrate and 2-Methylimidazole (MeIM) were obtained from Aladdin Co., Ltd. (Shanghai, China). Methanol anhydrous and N, N′- Dimethylformamide (DMF) were purchased from Jindongtianzheng Precision Chemical Reagent Co., Ltd. (Tianjin, China). Ethanol with chromatographic purity was obtained from Puredil biotechnology Co., Ltd. (Bengbu China). Sodium tetrachloropalladate were purchased from Adamas-beta Chemical Reagent Co., Ltd. (Shanghai, China). Polyacrylonitrile (PAN) (M.W. 150,000) were obtained from Sigma-Aldrich Co., Ltd., USA. Phenylacetylene (PA), 3-methylstyrene, 1-ethynyl-4-hexylbenzene, 1-chloro-3-ethenylbenzene, 1-bromo-4-ethenylbenzene, 4-methoxystyrene, 4-Vinylbiphenyl，Mesitylene and ammonia borane (AB) were purchased from Macklin Biochemical

Technology Co., Ltd. (Shanghai, China). Lindlar catalyst was purchased from Aladdin Co., Ltd. (Shanghai, China). All reagents are analytical purity without further purification except for ethanol.

Materials characterization

The morphology and microstructures of samples were characterized by ZEISS Sigma 500 scanning electron microscope (ZEISS Ltd., Germany), JEM-2100/ JEM-2100Plus transmission electron microscope (JEOL Ltd., Japan), The phase composition was investigated by X-ray powder diffraction (XRD, Bruker D8 advance diffractometer with Cu-Kα radiation (λ = 1.5418 Å)), X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher Scientific, USA) and Raman spectrometer with 532 nm wavelength (Horiba LabRAM HR Evolution, Japan). Inductive coupled plasma mass spectrometry was conducted using Agilent ICP-OES 725, USA. The specific surface area and pore size distribution were measured using Nitrogen adsorption-desorption measurements carring out on a 3H-2000PS1 analyzer at 77 K. Before starting the N_2 adsorption measurements, all the samples were activated by degassing in-situ at about 573 K for 6 h. The experiment of temperature-programmed desorption of styrene (styrene-TPD) were measured on a Micromeritics AutoChem II 2920 instrument. typically, 100 mg of samples were used for each measurement. The sample was pretreated at 300 °C in an He gas flow for 60 min. The sample was then cooled to at 50 °C and styrene pulses were injected from a calibrated on-line sampling valve. The weakly adsorbed styrene were subsequently removed by purge with He for 60 min. Subsequently, the temperature was raised to 300 °C at a rate of 10 °C/min in the flowing He and the styrene -TPD profile was recorded by the TCD detector.

Supporting Figures

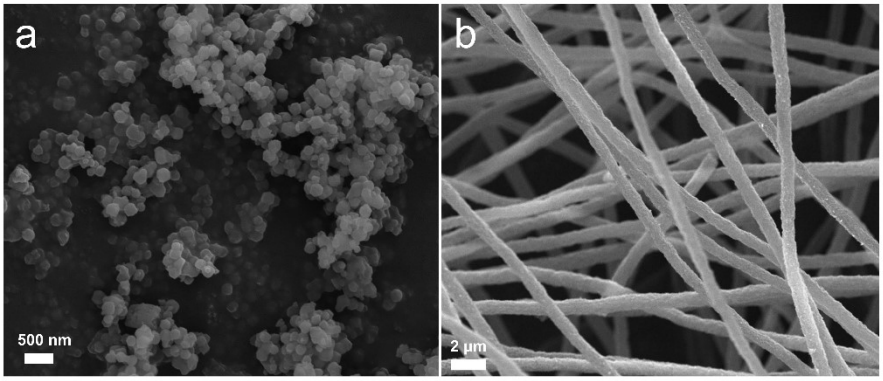

Fig. S1 SEM images of a) ZIF-8 and b) mNCNFs.

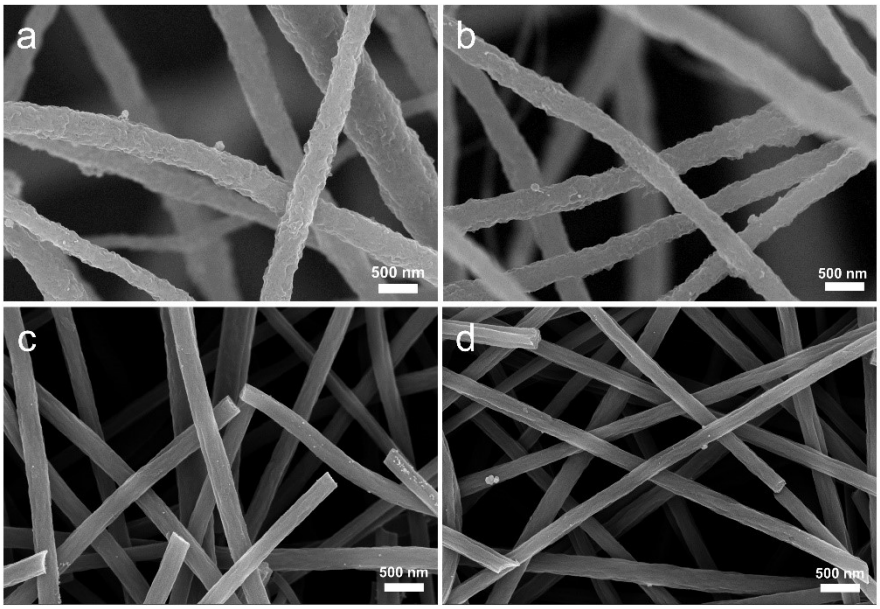

Fig. S2 SEM images of a) Pd/mNCNFs, b) Pd/mNCNFs-H, c) Pd/CNFs, and d) Pd/CNFs-H.

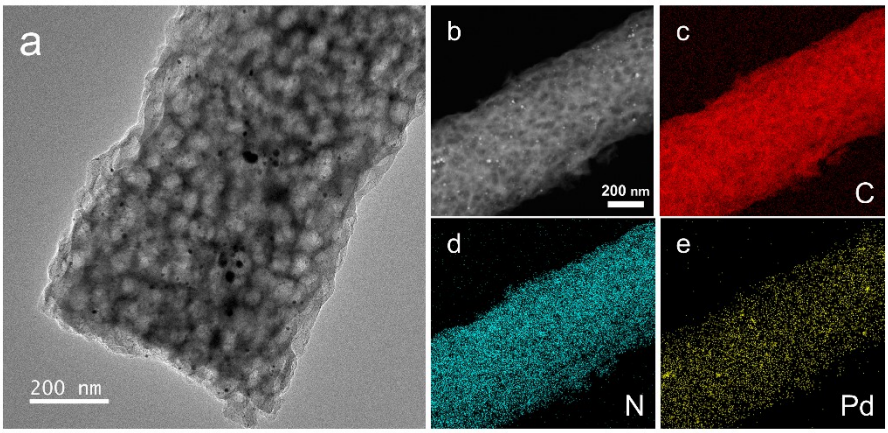

Fig. S3 a) TEM images of Pd/mNCNFs-H. b) HAADF-STEM images of Pd/mNCNFs-H. c-e) EDX elemental mapping of C, N, and Pd.

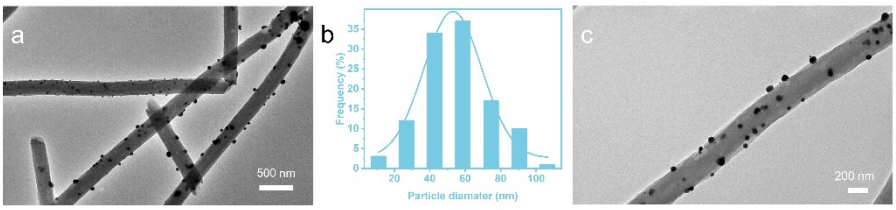

Fig. S4 a) TEM images of Pd/CNFs. b) size distributions of Pd/CNFs. c) TEM images of Pd/CNFs-H.

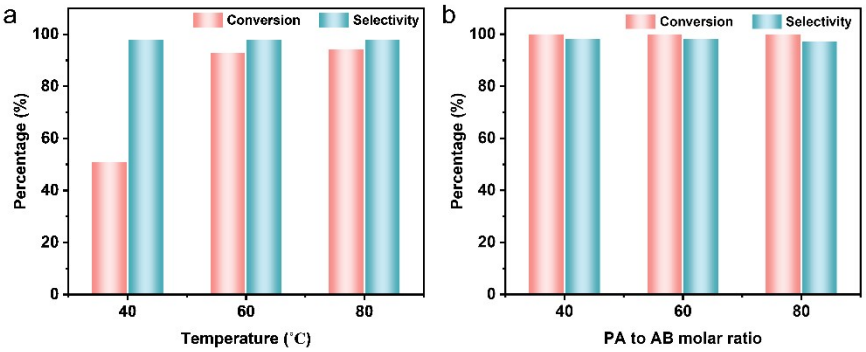

Fig. S5 Effects of (a) reaction temperatures and (b) molar ratios of PA/AB on hydrogenation of PA over Pd/mNCNFs.

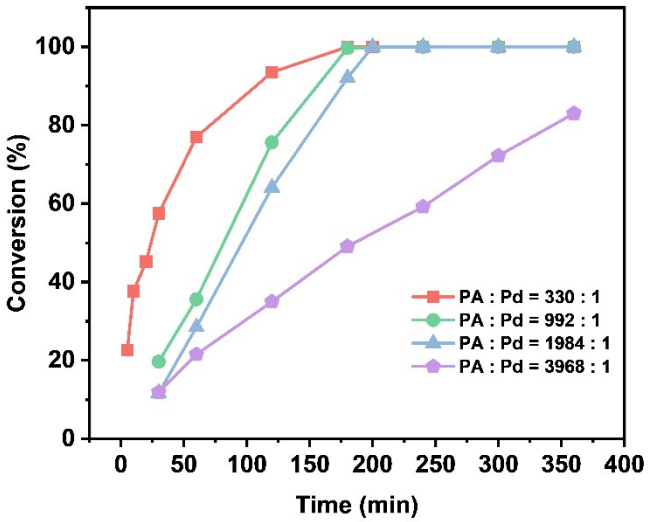

Fig. S6 Reaction profiles of the PA transfer semi-hydrogenation with AB over Pd/mNCNFs at different PA : Pd ratio.

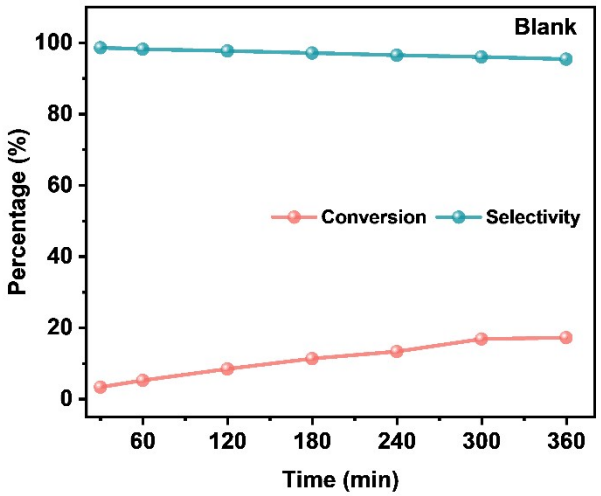

Fig. S7 Blank experiment without catalysts (only PA, ethanol, and AB).

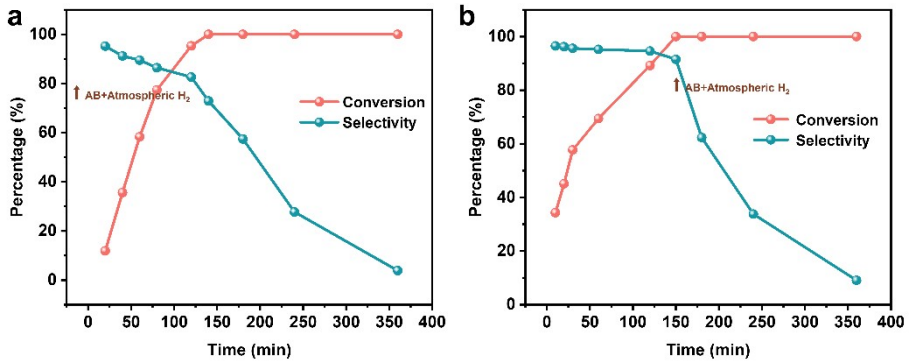

Fig. S8 Reaction profiles of transfer hydrogenation of PA with AB over Pd/CNFs with the co-presence of atmospheric H_2 a) during the whole reaction time and b) starting from the reaction time of 150 min.

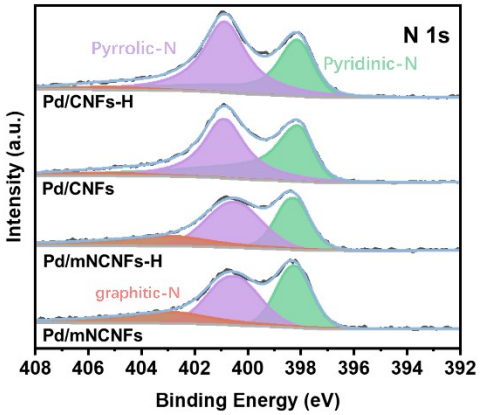

Fig. S9 N 1s XPS spectra of Pd/mNCNFs, Pd/mNCNFs-H, Pd/CNFs, and Pd/CNFs-H.

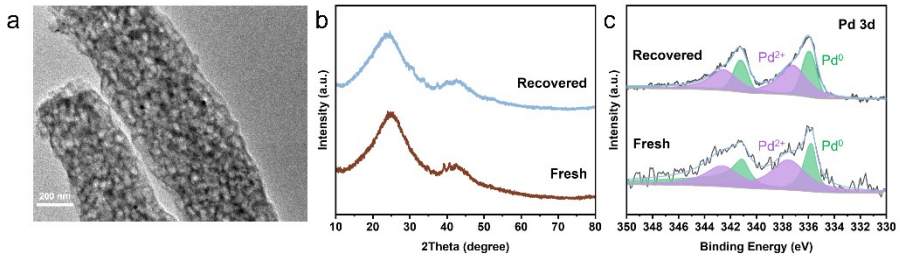

Fig. S10 a) TEM image of Pd/mNCNFs recovered after five cycle experiments. b) XRD patterns of fresh and recovered Pd/mNCNFs. c) Pd 3d XPS spectra of fresh and recovered Pd/mNCNFs.

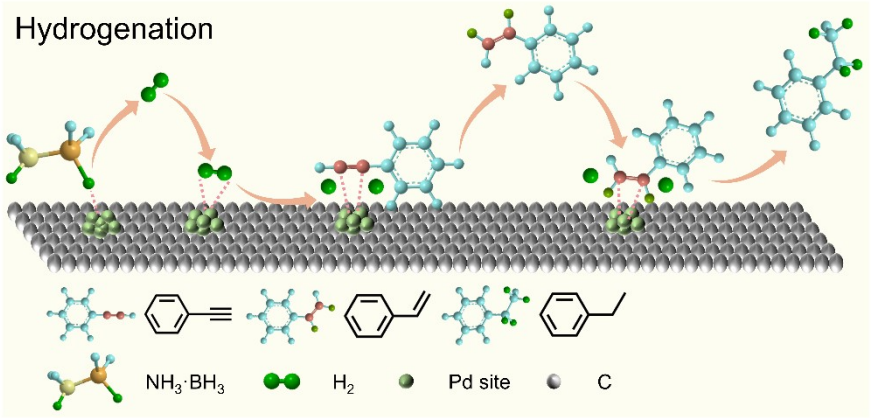

Fig. S11 Proposed reaction mechanism for hydrogenation of PA with AB upon Pd/CNFs.

Supporting Tables

Table S1 The textural properties and metal loadings of Pd/mNCNFs and Pd/CNFs.

Samples	S_{BET} (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pd loadings[a] (wt%)
Pd/mNCNFs	436.8	0.693	1.88
Pd/CNFs	8.5	0.031	1.46

[a] Determined by ICP-OES

Table S2 Catalytic performance of developed Pd/mNCNFs catalyst in comparison to the performance of Nickel or Iron-based catalysts reported in literatures.

Entry	Catalyst	Temp./°C	Con./%	Sel./%	TOF/h^{-1}	Ref.
1	Pd/mNCNFs	60	99.9	98.3	609.2	This work
2	L-lysine/Ni/Nb_2O_5	80	99.9	95.8	1.67	1
3	Ni@Y zeolite	160	81.8	95.8	3.55	2
4	nFeO_x-TiO_2	100	100	67.0	26.76	3
5	Ni_1Fe_3	40	99	91	2.50	4
6	Ni@NC-800	110	97	94	4.17	5

References

1 J. Wang, M. Wang, X. Li, X. Gu, P. Kong, R. Wang, X. Ke, G. Yu and Z. Zheng, *Appl. Catal. B-Environ.*, 2022, **313**, 121449.

2 X. Deng, R. Bai, Y. Chai, Z. Hu, N. Guan and L. Li, *CCS Chem.*, 2022, **4**, 949-962.

3 M. Tejeda-Serrano, J. R. Cabrero-Antonino, V. Mainar-Ruiz, M. López-Haro, J. C. Hernández-Garrido, J. J. Calvino, A. Leyva-Pérez and A. Corma, *ACS Catal.*, 2017, **7**, 3721-3729.

4 R. K. Rai, M. K. Awasthi, V. K. Singh, S. R. Barman, S. Behrens and S. K. Singh, *Catal. Sci. Technol.*, 2020, **10**, 4968-4980.

5 X. Wang, T. Song, G. Fu and Y. Yang, *ACS Catal.*, 2023, **13**, 11634-11643.