Electronic Supplementary Information (ESI) for:

Dopamine polymer derived isolated single-atom sites metals/N-doped porous carbon for benzene oxidation†

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Contents:

Experimental procedures

Chemical reagents

$FeCl_3 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, ethanol, methyl cyanide (MeCN), ammonium hydroxide ($NH_3 \cdot H_2O$, 25~28wt%), hydrochloric acid (HCl, 36%~38%), and hydrogen peroxide (H_2O_2, 28~30wt%) were purchased from Sinopharm Group Co., Ltd. 3-Dopamine hydrochloride, benzene, and *n*-dodecane were purchased Alfa Aesar (China) chemical Co., LTD. The water used is deionized water. All chemicals were used as received without further purification.

Preparation of ISAS M/NPC catalysts

Using the previous reported synthesis method [1] with modified to prepare the isolated single-atom sites iron/nitrogen doped porous carbon (ISAS M/NPC) catalysts. Here, the ISAS M/NPC catalysts were prepared by a top-down polymerization-pyrolysis-etching-activation (PPEA) strategy by using the dopamine as basic structural unit. Hereon, we take the synthesis of ISAS Fe/NPC catalyst as an example: (I) Preparation of FePDA precursors, 2.5 mmol of $FeCl_3 \cdot 6H_2O$ and 2.5 g of dopamine hydrochloride were dissolved in 100 mL H_2O to form solution A. Meanwhile, a mixed solution B including 200 mL ethanol, 450 mL H_2O, and 3.75 mL ammonium hydroxide (25~28wt%) was also prepared in a 1000 mL beaker. After that, the solution A was added into solution B under magnetic stirring at room temperature for 24 h. After the reaction finished, the reaction system was standing for 12 hours. Dump the top solution, the black precipitates of Fe-polydopamine (FePDA) precursors were centrifuged and washed with H_2O and ethanol for several times, and dried at 75 °C for 12 h. By the same synthesis process, when the 2.5 mmol of $CoCl_2 \cdot 6H_2O$ or $NiCl_2 \cdot 6H_2O$ instead of 2.5 mmol $FeCl_3 \cdot 6H_2O$, the Co-polydopamine (CoPDA) and Ni-polydopamine (NiPDA) precursors were also prepared. (ii) Preparation of Fe NPs/NPC, the obtained FePDA precursors were pyrolyzed under H_2/Ar (5% H_2) atmosphere at 500 °C for 3 h to get the Fe nanoparticles/nitrogen doped porous carbon (Fe NPs/NPC). By the same method, the Co NPs/NPC and Ni NPs/NPC were also obtained. (iii) Preparation of ISAS Fe/NPC, the Fe NPs/NPC were treated by 3 M HCl at 60 °C for 48 h to remove the Fe NPs, and then products were activated by H_2/Ar (5% H_2) atmosphere at 300 °C for 2 h to form the ISAS Fe/NPC. Using the same route, the ISAS Co/NPC and ISAS Ni/NPC were also synthesized. For comparison, we also obtained the nitrogen-doped porous carbon (NPC) without metals.

Characterizations

Structure information and purity of the obtained ISAS M/NPC catalysts were characterized by an X-ray powder diffractometer (XRD) with a Rigaku D/max 2500Pc XRD with monochromatized Cu Kα radiation (λ =1.5418 Å). Metal loading contents of ISAS M/NPC catalysts were tested by inductively coupled plasma optical emission spectrometry (ICP-OES). The morphologies of the samples were characterized by low resolution transmission electron microscopy (TEM, Hitachi-7700) with a working at 100 kV. High resolution TEM (HRTEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and energy dispersion spectrum (EDS) elemental mapping images were obtained on a JEOL JEM-2100F field emission electron microscope with working at 200 kV. Aberration-corrected HAADF-STEM (AC-HAADF-STEM) was obtained on a JEM-ARM200F with working at 300 kV. X-ray photoelectron spectroscopy (XPS) data were obtained on an ESCALAB MK II X-ray photoelectron spectrometer with Mg Kα as the excitation source. The N_2 adsorption-desorption isotherm curves, pore volumes, and corresponding pore sizes were measured using a Micromeritics isothermal adsorption system (ASAP 2460) at 77 K. The Fe K-edge, Co K-edge, and Ni K-edge X-ray absorption fine structure (XAFS) spectra were collected in transmission mode using a Si (111) double-crystal monochromator at the XAFS station of the 1W1B beamline in Beijing Synchrotron Radiation Facility (BSRF, P. R. China) operated at 2.5 GeV with a maximum current of 250 mA.

Catalytic benzene oxidation reaction (BOR) measurements

The BOR was carried out by previous reports by modified.[2-5] The typical catalytic process as follows: 50 mg ISAS M/NPC (M = Fe, Co, Ni) catalyst was added into 50 mL reaction tube , and then 3 mL MeCN was added. The catalyst was dispersed in the MeCN by ultrasonic assistance. And then, 0.1 mL benzene was added to the above disperse system with magnetic stirring speed was 800 rpm; subsequently, 6 mL H_2O_2 was added. A condenser tube was added to the nozzle of the reaction tube and reaction at 60 °C for 24 h. When the reaction finished, the reaction product was filtered by filtration membrane, and ethyl acetate was added to extract the catalytic product. And then, the catalytic product was analyzed by gas chromatography (GC, Thermo Fisher scientific Trace 1300 with a flame ionization detector) and GC mass spectrometry (GC-MS, Thermo Fisher scientific ISQ system) with the *n*-hexadecane as internal standard. The amount of metal Fe is kept the same to that in 50 mg of ISAS Fe/NPC for the evaluation of Fe NPs/NPC or FePDA.

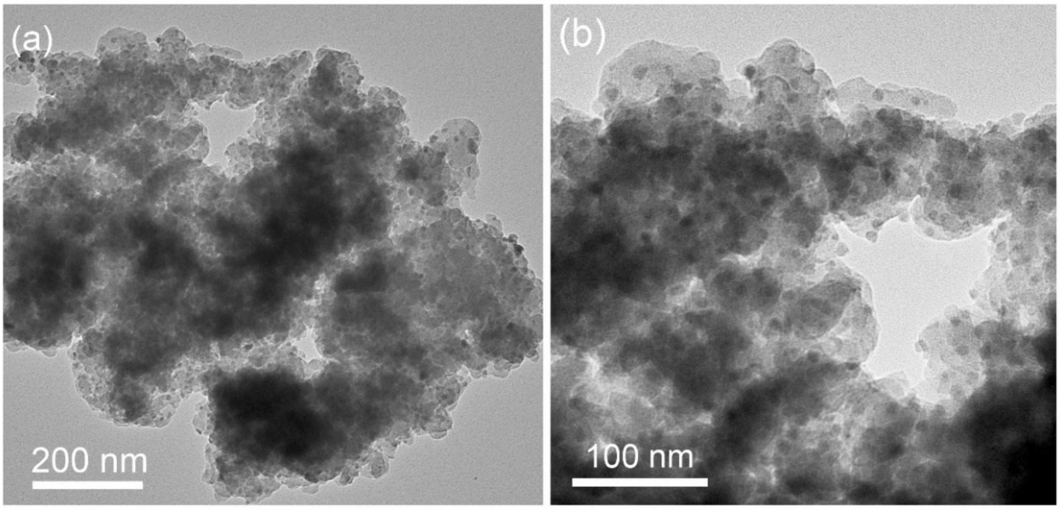

Figure S1. TEM images of Fe NPs/NPC.

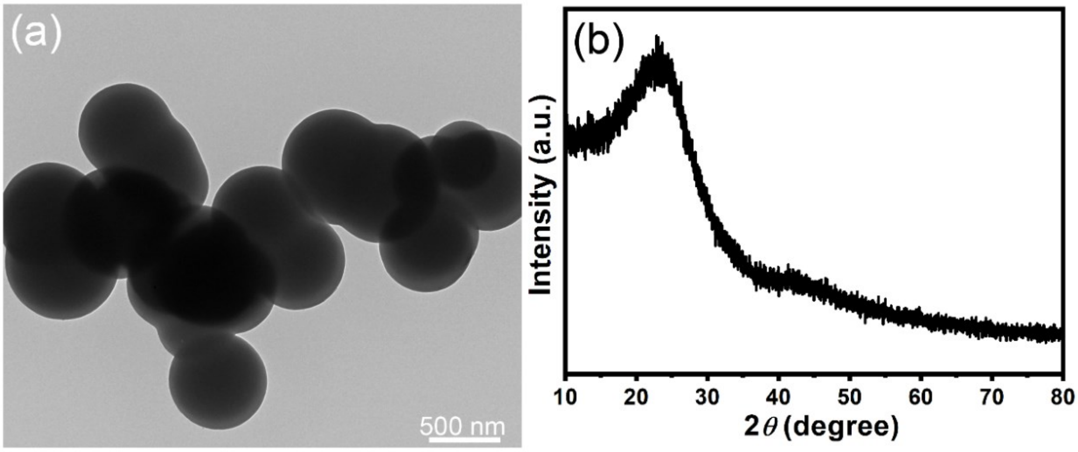

Figure S2. (a) TEM image and (b) XRD pattern of pure NPC.

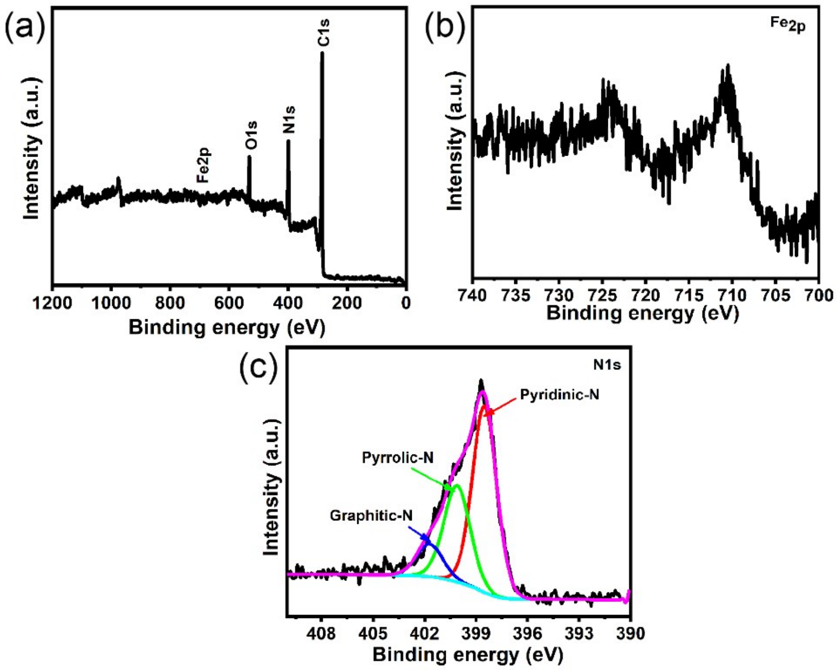

Figure S3. XPS spectra of ISAS Fe/NPC: (a) full scan, (b) Fe 2p spectrum, and (c) N 1s XPS spectrum, respectively.

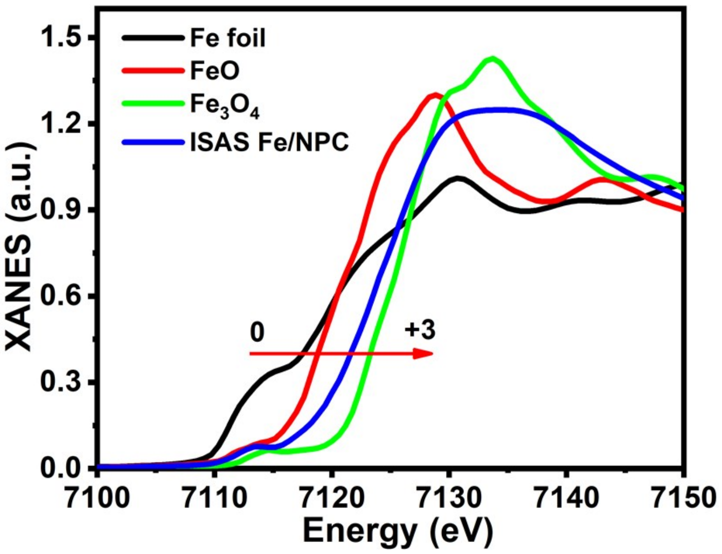

Figure S4. XANES spectra for the Fe K-edge of Fe foil, FeO, Fe_3O_4, and ISAS Fe/NPC, respectively.

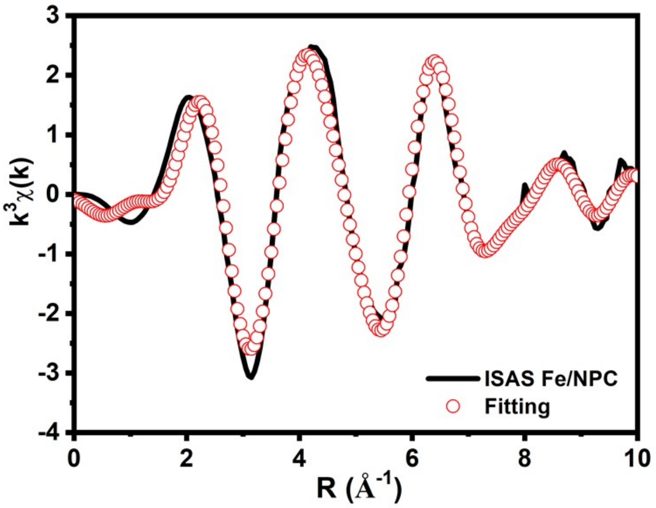

Figure S5. EXAFS fitting curve of Fe K-edge for ISAS Fe/NPC catalyst.

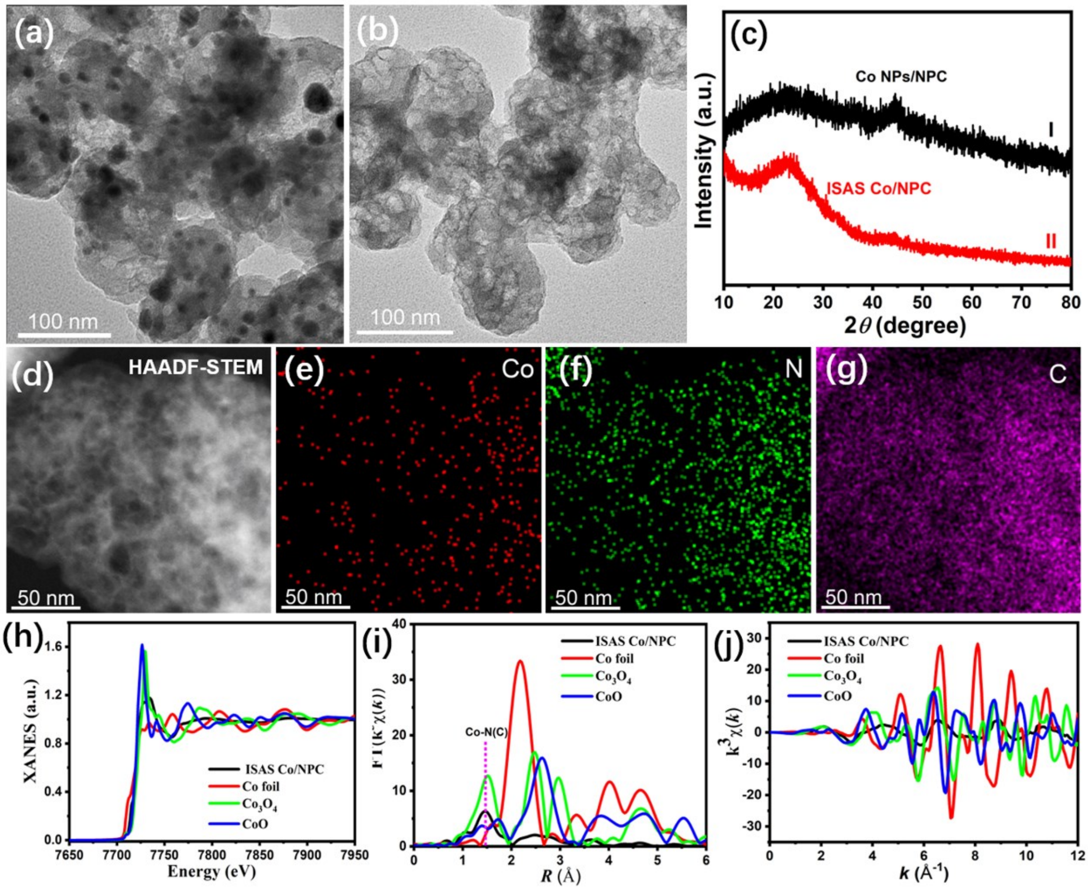

Figure S6. TEM images of (a) Co NPs@NPC and (b) ISAS Co/NPC. (c) XRD patterns of Co NPs/NPC (cI, black line) and ISAS Co/NPC (cII, red line). (d) HAADF-STEM image of ISAS Co/NPC with corresponding elemental (e) Co, (f) N, and (g) C mapping images; (h) XANES spectra, (i) FT-EXAFS spectra, and (j) the corresponding EXAFS *k* space spectra for the Co K-edge of ISAS Co/NPC (black line), Co foil (red line), CoO (blue line), and Co_3O_4 (green line), respectively.

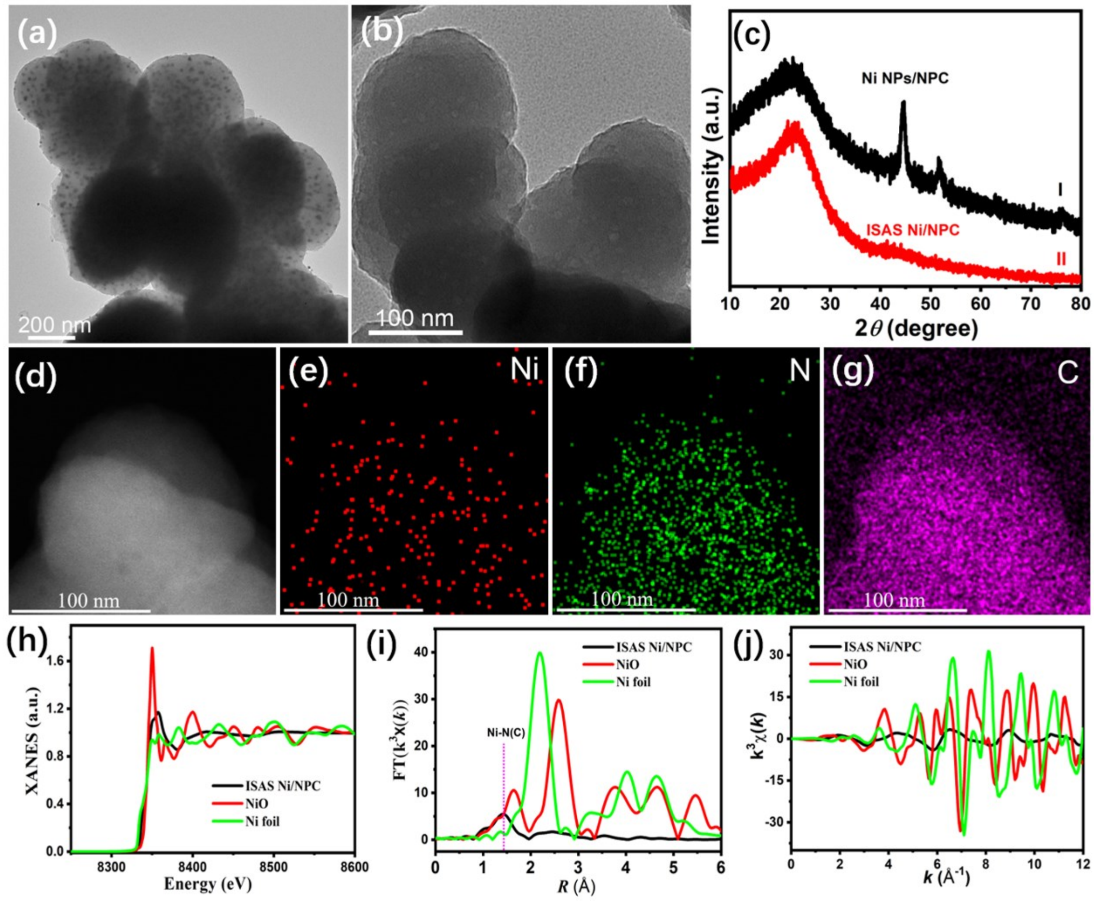

Figure S7. TEM images of (a) Ni NPs@NPC and (b) ISAS Ni/NPC; (c) XRD patterns of Ni NPs/NPC (cI, black line) and ISAS Ni/NPC (cII, red line); (d) HAADF-STEM image of ISAS Ni/NPC with corresponding elemental (e) Ni, (f) N, and (g) C mapping images; (h) XANES spectra, (i) FT-EXAFS spectra, and (j) the corresponding EXAFS *k* space spectra for the Ni K-edge of ISAS Ni/NPC (black line), Ni foil (green line), and NiO (red line), respectively.

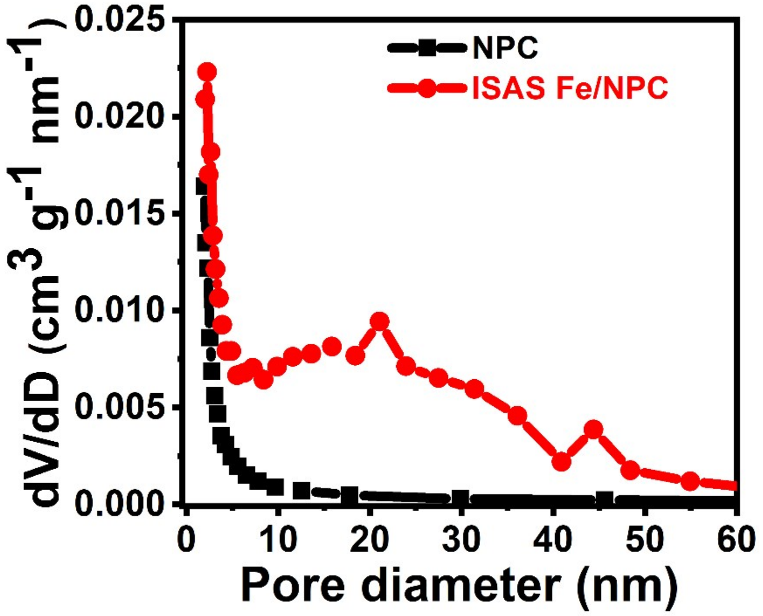

Figure S8. The corresponding pore diameter distributions for pure NPC (black line) and ISAS Fe/NPC (red line).

Table S1. The metals loading contents in ISAS M/NPC catalysts estimated by ICP measurements.

Different catalysts	**Metal loading contents (wt%)**
ISAS Fe/NPC	1.76
ISAS Co/NPC	0.74
ISAS Ni/NPC	0.31

Table S2. Structural parameters of ISAS Fe/NPC extracted from the EXAFS fitting (S_0^2=0.85).

Sample	**Scattering pair**	**CN**	**R(Å)**	**σ^2(10^{-3}Å^2)**	**ΔE_0(eV)**	**R factor**
ISAS Fe/NPC	Fe-N	4.0 ± 0.6	1.91 ± 0.02	3.1 ± 0.5	4.6 ± 0.4	0.01

Note: S_0^2 is the amplitude reduction factor; CN is the coordination number; R is interatomic distance (the bond length between central atoms and surrounding coordination atoms); σ^2 is Debye-Waller factor (a measure of thermal and static disorder in absorber-scatterer distances); ΔE_0 is edge-energy shift (the difference between the zero kinetic energy value of the sample and that of the theoretical model). R factor is used to value the goodness of the fitting.

Table S3. The C K-edge and N K-edge data for ISAS Fe/NPC and pure NPC.

Different catalysts	C K-edge (eV)			N K-edge (eV)			
	π* C=C	C-N-C	σ* C-C	Peak a_1	Peak a_2	Peak b	Peak c
ISAS Fe/NPC	283.6	286.8	290.6	396	397.2	398.2	406
Pure NPC	283.8	287	291.4	395.8	397.2	398.6	404.6

Table S4. Raman data for ISAS Fe/NPC and pure NPC.

Different catalyst	**D band (cm^{-1})**	**G band (cm^{-1})**	**2D band (cm^{-1})**	**I_D/I_G**
ISAS Fe/NPC	1352	1591	2865	0.88
Pure NPC	1348	1580	2860	0.97

Table S5. The BET specific surface areas, pore volumes, and pore sizes for ISAS Fe/NPC and pure NPC.

Different catalysts	Specific surface areas (m^2/g)	Total pore volume (cm^3/g)	Micropore (nm)	Average pore size (nm)
ISAS Fe/NPC	224	0.384	1.1	6.8
Pure NPC	370	0.183	0.5	1.97

Table S6. Comparison of the BOR activities of the ISAS M/NPC (M = Fe, Co, Ni) catalysts with previous reported various catalysts.

Different catalysts	**Oxidant**	**Reaction temperature and time**	**Metal content (wt%)**	**Benzene Conv.**	**Phenol Sel.**	***Ref.***
ISAS Fe/NPC	$\mathbf{H_2O_2}$	**60 °C, 24 h**	**1.76**	**42.6%**	**>99%**	**This work**
ISAS Co/NPC	$\mathbf{H_2O_2}$	**60 °C, 24 h**	**0.74**	**16.3%**	**>99%**	**This work**
ISAS Ni/NPC	$\mathbf{H_2O_2}$	**60 °C, 24 h**	**0.31**	**7.1%**	**>99%**	**This work**
Fe-N_4 SAs/N-C	H_2O_2	30 °C, 24 h	3.18	78.4%	100%	2
SA-Fe/CN	H_2O_2	60 °C, 24 h	0.9	45%	94%	3
FeN_4/GN	H_2O_2	RT, 24 h	2.7	23.4%	79.9%	4
Co-ISA/CNS	H_2O_2	60 °C, 24 h	0.6	68%	97%	5
Cu-SA/HCNS	H_2O_2	60 °C, 12 h	0.64	86%	96.7%	6
CNT7000	H_2O_2	60 °C, 6 h	-	6.4%	91.5%	7
Graphene	H_2O_2	60 °C, 16 h	-	18%	99%	8
VPO@GO	H_2O_2	60 °C, 8 h	-	32.8%	100%	9
4Cu/MCM-41	H_2O_2	RT, 1.67 h	-	21%	94%	10
Fe(II) Complex	H_2O_2	50 °C, 3 h	-	65%	98.5%	11
Ni(II) Complex	H_2O_2	60 °C, 5 h	-	23%	91.3	12
Titanium Silicalite	H_2O_2	100 °C, 2 h	-	8.6%	94%	13
$H_4PMo_{11}VO_{40}$	H_2O_2	RT, 1.7 h	-	26%	90.7%	14

Note: RT is room temperature.

References:

(1) K. Wu, Z. Chen, W.-C. Cheong, S. Liu, W. Zhu, X. Cao, K. Sun, Y. Lin, L. Zheng, W. Yan, Y. Pan, D. Wang, Q. Peng, C. Chen, Y. Li, *ACS Appl. Mater. Interfaces*, **2018**, *10*, 44201.

(2) Y. Pan, Y. Chen, K. Wu, Z. Chen, S. Liu, X. Cao, W.-C. Cheong, T. Meng, J. Luo, L. Zheng, C. Liu, D. Wang, Q. Peng, J. Li, C. Chen, *Nat. Commun.*, **2019**, *10*, 4290.

(3) M. Zhang, Y.-G. Wang, W. Chen, J. Dong, L. Zheng, J. Luo, J. Wan, S. Tian, W.-C. Cheong, D. Wang, Y. Li, *J. Am. Chem. Soc.*, **2017**, *139*, 10976.

(4) D. Deng, X. Chen, L. Yu, X. Wu, Q. Liu, Y. Liu, H. Yang, H. Tian, Y. Hu, P. Du, R. Si, J. Wang, X. Cui, H. Li, J. Xiao, T. Xu, J. Deng, F. Yang, P. N. Duchesne, P. Zhang, J. Zhou, L. Sun, J. Li, X. Pan, X. Bao, *Sci. Adv.*, **2015**, *1*, e1500462.

(5) Y. Zhu, W. Sun, J. Luo, W. Chen, T. Cao, L. Zheng, J. Dong, J. Zhang, M. Zhang,

Y. Han, C. Chen, Q. Peng, D. Wang, Y. Li, *Nat. Commun.*, **2018**, *9*, 3861.
(6) T. Zhang, D. Zhang, X. Han, T. Dong, X. Guo, C. Song, R. Si, W. Liu, Y. Liu, Z. Zhao, *J. Am. Chem. Soc.*, **2018**, *140*, 16936.
(7) G. Wen, S. Wu, B. Li, C. Dai, D. S. Su, *Angew. Chem. Int. Ed.*, **2015**, *54*, 4105.
(8) J.-H. Yang, G. Sun, Y. Gao, H. Zhao, P. Tang, J. Tan, A.-H. Lu, D. Ma, *Energy Environ. Sci.*, **2013**, *6*, 793.
(9) P. Borah, A. Datta, K. T. Nguyen, Y. Zhao, *Green Chem.*, **2016**, *18*, 397.
(10) K. M. Parida, D. Rath, *Appl. Catal. A-Gen.*, **2007**, *321*, 101.
(11) L. Carneiro, A. R. Silva, *Catal. Sci. Technol.*, **2016**, *6*, 8166.
(12) Y. Morimoto, S. Bunno, N. Fujieda, H. Sugimoto, S. Itoh, *J. Am. Chem. Soc.*, **2015**, *137*, 5867.
(13) L. Balducci, D. Bianchi, R. Bortolo, R. D'Aloisio, M. Ricci, R. Tassinari, R. Ungarelli, *Angew. Chem.*, **2003**, *115*, 5087.
(14) J. Zhang, Y. Tang, G. Li, C. Hu, *Appl. Catal. A-Gen.*, **2005**, *278*, 251.

Author contributions

K. W. and Z. C. designed and carried out the synthesis and characterizations of samples, tested the catalytic performance, analyzed the data and wrote the manuscript. F. Z. performed the XAFS analysis and fitted the XAFS data. R. T. and Y. C. modified the illustrations and give suggestions. W.-C. C. and Q. Z. performed the TEM and AC-STEM characterization. L. Z. and W. Y. performed the XAFS measurement. C. C. and Z. C. supervised the project. All the authors commented on the manuscript and have given approval to the final version of the manuscript.