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Dopamine polymer derived isolated single-atom sites metals/Ndoped porous carbon for benzene oxidation[†]

Received 00th January 20xx, Accepted 00th January 20xx Konglin Wu,^{‡a,b,c} Fei Zhan,^{‡d} Renyong Tu,^b Weng-Chon Cheong,^e Yuansheng Cheng,^a Lirong Zheng,^f Wensheng Yan,^g Qinghua Zhang,^h Zheng Chen,^{*,c} and Chen Chen^{*,b}

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Isolated single-atom sites metals/nitrogen-doped porous carbon (ISAS M/NPC, M = Fe, Co, Ni) catalyst are successfully prepared by a top-down polymerization-pyrolysis-etching-activation (PPEA) strategy, which use dopamine as precursors. Due to the isolated single atom Fe active sites and porous structure, the ISAS Fe/NPC displayed a high benzene conversion up to 42.6% and nearly 100 % phenol selectivity.

Catalysis is the soul of chemistry, the engine of chemical engineering, and the eternal theme of chemistry and chemical engineering. It is generally known that the synthetic ammonia¹ and Fischer-Tropsch synthesis² have a revolutionary impact on the human production and life. Thereby, the design and preparation of catalytic materials is the core content of catalysis. In many catalytic fields, the noble metal catalysts have been playing a leading role. The noble metals are needed to be used as catalysts in the fields of acetylene hydrochlorination, automobile exhaust gas treatment, fuel cell, electrolytic water, etc. However, due to the low reserves and high cost of precious metals, its large-scale use is limited. Therefore, the development of high-efficiency and low-cost non-noble metal catalysts to replace or partially replace precious metal catalysts has been the pursuit of researchers.

Recently, the isolated single-atom sites (ISAS) catalysts have attracted wide attention due to their numerous advantages,³ such as low cost, clear catalytic activity center, specific catalytic activity, 100% atom utilization, easy separation, etc. Many researches showed that the ISAS catalyst has become a research hotspot in the fields of water gas conversion,^{4a} gassolid catalysis,^{4b, 4c} photocatalysis,^{4d} electrocatalysis,^{4e, 4f, 4g} enzyme catalysis,^{4h, 4i} and so on. Meanwhile, the ISAS also brings new opportunities and challenges to the field of organic reaction, which act the role of bridging between the homogeneous and heterogeneous catalysis.⁵ For example, the single Pd atoms decorated on exfoliated graphitic carbon nitride (Pd-ECN) catalyst can be used in Suzuki reaction.⁶ It is found that the catalyst has similar catalytic activity with homogeneous catalyst. In the field of small molecule activation,⁷ the ISAS Pt₁/Ti_{3-x}C₂T_y MXene catalyst provides a green method to utilizing CO2 via the high-efficiency formylation of amines reaction. Furthermore, the ISAS catalysts such as RGO@AC/Pd,8 Pt₁/Ni nanocrystals,⁹ Pt₁/FeO_x,¹⁰ CoSAs/NCNS,^{11a} and Fe₁/N-C^{11b} can catalyze hydrogenation of nitro compounds with good catalytic activity. Especially, when there are two type unsaturated bonds in the substrate, i.e. C=C and N=O double bonds, the selectivity of ISAS catalysts is higher than that of commercial catalyst or micro/nanomaterials catalyst.¹² A series of ISAS catalysts have been used in the C-H activation and transformation,13-18 which show high catalytic activity and selectivity. As an important reaction, the preparation of phenol by oxidation of benzene has attracted wide attention. In previous reports, the benzene can be oxidized to phenol by homogeneous catalyst,¹⁹ but the conversion and selectivity are not high. Thereby, the ISAS catalysts due to their high catalytic activity and selectivity will bring new opportunities and challenges for benzene oxidation reaction (BOR).

Here, we report a top-down polymerization-pyrolysisetching-activation (PPEA) strategy by using the dopamine as basic structural units to construct isolated single-atom sites metals/nitrogen-doped porous carbon (ISAS M/NPC, M = Fe, Co, Ni) catalyst materials. The obtained ISAS Fe/NPC can be used as

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⁺ Electronic Supplementary Information (ESI) available: Experimental procedures, Figures S1-S8, and Tables S1-S6, See DOI: 10.1039/x0xx00000x

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low-cost heterogeneous catalyst in BOR, and displayed a high conversion to phenol. The selectivity of phenol in ISAS Fe/NPC catalyst is significantly higher than that of nanoparticles catalyst, which fully demonstrate the unique advantages of atomically dispersed metal sites. Furthermore, the top-down PPEA strategy is also applicable to the preparation of other ISAS catalysts (such as ISAS Co/NPC and ISAS Ni/NPC).



Figure 1. (a) Schematic illustration for the preparation of ISAS M/NPC catalysts, (b) XRD patterns of Fe NPs/NPC and ISAS Fe/NPC, (c) TEM image of ISAS Fe/NPC, (d) AC-STEM image of ISAS Fe/NPC, (e) HAADF-STEM image and the corresponding EDS elemental mapping images.

Figure 1a shows the preparation process of ISAS M/NPC (M = Fe, Co, Ni) catalysts by PPEA strategy, and the detailed experimental procedures are shown in Electronic Supplementary Information (ESI⁺). Here, we take the synthesis of ISAS Fe/NPC catalyst as an example for illustration the PPEA strategy: the dopamine and ferric salt were oxidization polymerization under alkaline conditions in a mixture of ethanol and water to form the Fe/polydopamine (FePDA) precursors, and then 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, Figure S1, ESI⁺). Subsequently, 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 H₂/Ar (5% H₂) atmosphere at 300 °C for 2 h to obtain the ISAS Fe/NPC. For comparison, we also obtained the nitrogen-doped porous carbon (NPC, Figure S2, ESI⁺) without metals. XRD patterns (Figure 1b) show that the Fe NPs can be removed by HCl treatment. Figure 1c displays there

are no obvious Fe-based clusters in ISAS Fe/NPC, The further spherical aberration correction-scanning Pransmission Cleetron microscope (AC-STEM) image exhibits the Fe atoms (bright white spots in Figure 1d) in the ISAS Fe/NPC are atomically dispersed on the substrate. The corresponding energy dispersion spectrum (EDS) elemental mapping results (Figure 1e) show that Fe and N were observed in the ISAS Fe/NPC. The metal content in ISAS Fe/NPC catalysts was quantitatively analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, Table S1, ESI⁺), and the metal loading content is 1.75wt% for ISAS Fe/NPC. X-ray photoelectron spectroscopy (XPS) results demonstrate that the Fe, N and C were observed (Figure S3a, ESI⁺). The weak Fe2p signal was obtained (Figure S3b, ESI⁺) because of the lower Fe loading and atomically dispersed Fe atoms on the substrate. Figure S3c (ESI⁺) shows the N1s spectrum, and three types of graphitic-N (401.7 eV), pyrrolic-N (400.1 eV), and pyridinic-N (398.5 eV) were found.



Figure 2. (a) XANES spectra and (b) FT-EXAFS spectra for the Fe K-edge of ISAS Fe/NPC, Fe foil, FeO, and Fe₃O₄; (c) the corresponding EXAFS *r* space fitting curves of ISAS Fe/NPC, (d) structure diagram of Fe-N₄ catalytic site for ISAS Fe/NPC.

In order to obtain the detailed structure information of ISAS Fe/NPC, the X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) were carried out. As shown in Figure 2a and Figure S4 (ESI+), the XANES curves for Fe K-edge in ISAS Fe/NPC, Fe foil, FeO, and Fe₃O₄ demonstrates that the oxidation state of Fe in ISAS Fe/NPC is between +2 and +3. This suggests that the Fe has a partial positive charge due to the coordination of N around the atomically dispersed Fe site.¹³ Fourier-transformed (FT) EXAFS (FT-EXAFS) spectrum (k³-weighted) for ISAS Fe/NPC (Figure 2b) shows a main peak at 1.5 Å, which can be attributed to the Fe-N scattering path. No peak derived from Fe-Fe coordination is found. The detailed structural parameters were obtained by quantitative EXAFS fitting of the Fe K-edge in ISAS Fe/NPC, and the corresponding fitting results are shown in Figure 2c, Figure S5 (ESI⁺), and Table S2 (ESI⁺). The fitting data reveal that one Fe atom is combined with four N atoms at the first coordination shell in ISAS Fe/NPC, meanwhile the Fe-N bond length is about 1.91 Å. These results further indicate that the atomically dispersed Fe sites in the ISAS Fe/NPC catalyst are existed in the

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form of Fe-N₄ moieties. Thereby, the possible structure model for ISAS Fe/NPC catalyst is shown in Figure 2d. Moreover, the ISAS Co/NPC (Figure S6, ESI⁺) and ISAS Ni/NPC (Figure S7, ESI⁺) catalysts were also prepared by the same PPEA strategy. The metal loading contents are 0.74wt% for ISAS Co/NPC and 0.31wt% for ISAS Ni/NPC (Table S1, ESI⁺).



Figure 3. (a) C K-edge and (b) N K-edge for pure NPC and ISAS Fe/NPC, (c) Raman spectra for pure NPC and ISAS Fe/NPC; (f) N_2 absorption and desorption curves for pure NPC and ISAS Fe/NPC.

Near edge X-ray absorption fine structure (NEXAFS) was used to test the structure information of ISAS Fe/NPC and pure NPC. As shown in Figure 3a and Table S3 (ESI⁺), three distinct peaks were observed in C K-edge spectra for ISAS Fe/NPC (red line) and NPC (black line). The peaks at 283.6 eV and 290.6 eV are attributed to the dipole transition sp²-hybridized carbon of $\pi^*C=C$ and σ^*C-C ,²⁰ while the sharp peak at 286.8 eV was sp³hybridized carbon of π^*C-N-C/Fe was observed.^{20a, 20b} Due to the strong interaction between C, N, and Fe, the peak of sp³hybridized carbon in ISAS Fe/NPC is more sharp than that of pure NPC, and the peak is also shifted to lower energy. Meanwhile, the N K-edge spectra (Figure 3b) for ISAS Fe/NPC (red line) and NPC (black line) show that the resonances of peaks a_1 and peaks a_2 , and peaks b are π^* -transitions for pyridinic-N and pyrrolic-N, and the peaks c are σ^* -transitions for graphitic-N are observed.^{20b, 20c} The peak a₁ and peak a₂ in ISAS Fe/NPC are sharper than that of NPC, but the peak b in ISAS Fe/NPC is weaker than that of NPC. Here, the NEXAFS result is consistent with that of XPS.

Raman spectroscopy was applied to characterize the ISAS Fe/NPC and NPC. The D and G bands are observed in the Raman spectra (Figure 3c). As shown in Figure 3c and Table S4 (ESI⁺), the D and G bands are 1348 cm⁻¹ and 1580 cm⁻¹ for NPC (black line), and the D and G bands are 1353 cm⁻¹ and 1591 cm⁻¹ for ISAS Fe/NPC (red line), respectively. Compared with pure NPC, the D band of ISAS Fe/NPC is shifted to the higher wavenumber, indicating that there are abundant defects in ISAS Fe/NPC.^{13d, 21} Furthermore, the strong G band is assigned to the sp²-hybridized carbon structure and the obvious broad 2D band demonstrates the presence of layered structures in ISAS Fe/NPC.²¹ Moreover, the specific surface areas and porosity of

the ISAS Fe/NPC and NPC were studied by N_{2V/2}dsQLption_{TE} desorption isotherm curves (Figure 3d and Figure 38, PESFP). Based on the Brunauer–Emmett–Teller (BET) evaluating method, the BET specific surface areas and pore sizes were obtained (Table S5, ESI⁺). Obviously, the ISAS Fe/NPC shows a type IV feature (Figure 3d, red line) and the NPC displays a type I feature (Figure 3d, black line). The BET specific surface area, micropore size, and average pore size are 224 m²/g, 1.1 nm, and 6.8 nm for ISAS Fe/NPC, and are 370 m²/g, 0.5 nm, and 1.97 nm for pure NPC.

Table 1. Catalytic BOR by different catalysts.



•	conversion (%) ^a	Phenol (%)	<i>p</i> -benzoquinone (%)
ISAS Fe/NPC ^a	42.6	>99	<1
ISAS Co/NPC ^a	16.3	>99	<1
ISAS Ni/NPC ^a	7.1	>99	<1
Fe NPs/NPC ^b	6.5	78	22
NPC ^a	1.6	90	10
FePDA ^a	0.4	92	8
Blank ^c	-	-	-

^a Conditions: catalyst, 50 mg; methyl cyanide (MeCN), 3 mL; benzene, 0.1 mL; H₂O₂, 6 mL; reaction temperature, 60 °C; reaction time, 24 h. ^b Conditions: catalyst, amount of Fe is kept the same to that in 50 mg of ISAS Fe/NPC; MeCN, 3 mL; benzene, 0.1 mL; H₂O₂, 6 mL; reaction temperature, 60 °C; reaction time, 24 h. ^c Conditions: without catalyst; MeCN, 3 mL; benzene, 0.1 mL; H₂O₂, 6 mL; reaction temperature, 60 °C; reaction time, 24 h. ^d Conversion and selectivity were determined by GC-MS and GC analysis.

The catalytic activities of the obtained ISAS M/NPC (M = Fe, Co, Ni) catalysts in BOR were investigated.¹³ As shown in Table 1, the catalytic BOR results show that the benzene conversion for ISAS Fe/NPC is 42.6%, ISAS Co/NPC is 16.3%, and ISAS Ni/NPC is 7.1%, which is higher than that of pure NPC (1.6%) without ISAS metals and FePDA precursors (0.6%). Interestingly, the selectivity of phenol was higher than 99% in all ISAS M/NPC (M = Fe, Co, Ni) catalysts. When the Fe NPs/NPC catalyst was used with equivalent Fe content, the benzene conversion and phenol selectivity are significantly lower, only 6.5% and 78%, respectively. This further proves that ISAS catalysts can achieve high selectivity accompanied by high activity. Here, the rich pore structures of the ISAS Fe/NPC catalyst are conducive to mass transfer and provides favorable organic molecular channels for the catalytic reaction. Compared with the previously reported catalysts for BOR (Table S6, ESI+), the obtained ISAS M/NPC (M = Fe, Co, Ni) catalysts exhibited competitive catalytic activities. The above results indicate that the ISAS catalysts are beneficial to improve the selectivity of organic reactions.

In summary, the high-efficient benzene oxidation catalysts of isolated single-atom sites metals/nitrogen-doped porous carbon (ISAS M/NPC-HA, M = Fe, Co, Ni) were successfully synthesized by a polymerization-pyrolysis-etching-activation (PPEA) strategy. Among them, ISAS Fe/NPC could realize 42.6%

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conversion, and the selectivity to phenol for all ISAS catalysts is higher than 99%. These results show that ISAS catalysts have high catalytic activity and selectivity in organic reactions, and which have great potential industrial application value in the future.

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Conflicts of interest

There are no conflicts to declare.

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