Volume 50 Number 34 14 September 2021 Pages 11653-12018

Dalton Transactions

An international journal of inorganic chemistry rsc.li/dalton

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Ball milling

ISSN 1477-9226



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Dalton Transactions

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Cite this: Dalton Trans., 2021, 50, 11711

Received 16th June 2021, Accepted 20th July 2021 DOI: 10.1039/d1dt02001c

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Protein powder derived nitrogen-doped carbon supported atomically dispersed iron sites for selective oxidation of ethylbenzene[†]

Yujie Cheng,^a Qingdi Sun,^a Liyun Huang,^a Qian He,^a Hao Zhang,^a Pengbo Wang,^b Ying Zhang,^c Shaolin Shi,^b Xingcong Zhang,^a Tao Gan,^a Xiaohui He*^{a,c} and Hongbing Ji ^(b) *^{a,b,c,d}

Atomically dispersed Fe species embedded in the nitrogen-containing carbon supports (Fe₁/NC) are successfully synthesized using a ball milling approach, with commercial protein powder as the nitrogen source. The catalyst exhibits outstanding performance in the oxidation of aromatic compounds containing saturated C–H bonds into corresponding ketones under ambient conditions, which is superior to those of a nanoparticle catalyst (Fe_n/NC) and a metal-free catalyst (NC).

Single atom catalysts (SACs), with their extremely high atomic utilization (~100%), unique geometric-electronic structure and easy separation operation, have emerged as a rising star in heterogeneous catalysis.^{1–4} SACs exhibit remarkable catalytic properties in a series of industrially important reactions, *e.g.*, selective oxidation, such as catalytic oxidation of alkanes,^{5,6} aromatic hydrocarbons^{7,8} and alcohols.^{9,10} Moreover, the well-defined active sites of SACs can provide a clear analysis of the structure–property relationship, and thus shed light on the reaction mechanisms at the molecular/atomic scale.¹¹

A considerable number of studies have shown that in SACs, the underlying supports not only play a significant part in the stability of the metal atoms, but also have an essential impact on the catalytic performance.^{12–14} At present, the commonly used supports in SACs mainly include metal oxides and carbon-based materials. Among them, carbon-based materials are widely applied in various industrial reactions, because of their irregular porous structures with high specific surface areas, which can enhance mass transfer effectively and facili-

tate reactions, and exhibit excellent stability under harsh reaction conditions.¹⁵ Furthermore, in order to hold metal centres stably, heteroatoms are needed in carbon-based supports, such as N, S, and P, which can provide abundant anchor sites to coordinate with metal centres to form a stable structure through electron transfer, and then effectively inhibit metal migration and sintering during the pyrolysis process.^{16,17} However, the surfaces of conventional carbon-based supports, such as activated carbon and carbon black, usually do not contain these heteroatoms. Therefore, it is highly desirable to find a cheap and readily available source of heteroatoms together with a facile introduction strategy.

From biological systems, we come to know that plenty of organic biomass possessing the merits of abundant and renewable properties contains various heteroatoms, e.g. nitrogen. Therefore, biomass materials have received extensive attention for their possible utility as the nitrogen source of carbon-based supports after simple treatments. For instance, Li et al.¹⁵ selected cocoon silk to prepare a N-doped carbonbased support by a degumming, regenerating and pyrolysis procedure and obtained Co SACs (Co-ISA/CNS). Jiang and coworkers18 synthesized Fe SACs (Fe-N-C) using animal blood as the precursor, which contained much haemoglobin. Shi's group¹⁹ used chlorella as a precursor, synthesizing carbon-supported atomically dispersed CoN₄ sites by salt melt synthesis. Due to the plentiful content of Fe in Porphyra and Auricularia, Liang's team used the two kinds of biomass adsorbed urea as precursors, preparing two SACs, Fe-ISA/NC and Fe1Pt1/NC.20,21

Commercially available protein powder, as an inexpensive and readily available biomaterial with plenty of protein, possesses rich N content (as high as 12%). It can be mixed uniformly with metal precursors and carbon-based supports through a facile ball milling process.²² During carbonization, protein powder may introduce sufficient N atoms to the support. The dense and uniform N atoms can facilitate the formation of metal–N bonds, which lead to the stability of the isolated metal sites during the pyrolysis and reaction process. Usually, commercial protein powder contains some other

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^aFine Chemical Industry Research Institute, School of Chemistry, Sun Yat-Sen University, Guangzhou 510275, Guangdong, China.

 $[\]label{eq:constraint} \ensuremath{\textit{E-mail: jihb@mail.sysu.edu.cn, hexiaohui@mail.sysu.edu.cn} \\$

^bSchool of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, China

^cHuizhou Research Institute of Sun Yat-sen University, Huizhou 516216, China ^dSchool of Chemical Engineering, Guangdong University of Petrochemical Technology, Maoming 525000, P.R.China

[†]Electronic supplementary information (ESI) available. See DOI: 10.1039/ d1dt02001c

heteroatoms such as S and P, which may also benefit the fixation of atomically dispersed metal species, but the contents are small, so the tiny influence can be ignored.

Herein, combining the merits of biomaterials and the advantages of the ball milling strategy, without any templates, solvents, and expensive equipment,²³⁻²⁵ we propose a facile and efficient method to synthesize SACs. Based on the previous work on SACs,^{3,22,26} a commercially available protein powder containing high protein is selected as the nitrogen source, and carbon black is used as the support. The two materials are mechanically ball milled with Fe(NO₃)₃·9H₂O and then pyrolvzed to obtain Fe SACs (Fe₁/NC). Conversely, if the protein powder is not added, dense Fe-based particles show up in the Fe/C catalyst under the same conditions (Fig. S1[†]), indicative of the necessity of adding the protein powder. In addition, Fe1/NC exhibits outstanding activity (95%) and selectivity of acetophenone (99%) in the oxidation of ethylbenzene at 35 °C after 48 hours, and it also shows superb stability, *i.e.* the activity and the selectivity almost do not decrease after five cycles of reactions. Furthermore, outstanding expandability is shown when Fe₁/NC is used in the oxidation reactions of other aromatic compounds saturated with C-H bonds under ambient conditions. In sum, the synthesis method avoids the cumbersome and complicated traditional preparation process of SACs and provides an efficient way to construct single metal site catalysts at the atomic scale.

Fig. 1a illustrates the synthesis process of Fe₁/NC by mechanical ball milling, and the details are described in the Experimental section of the ESI.† Typically, 145 mg of Fe $(NO_3)_3 \cdot 9H_2O$, 600 mg of commercial protein powder and 2 g of carbon black were subjected to mechanical ball milling at 400 rpm for 24 hours, and the resulting complex was pyrolysed at 600 °C under a nitrogen atmosphere for 2 hours to remove the metal precursors and carbonized protein powder, and then to anchor the metal atoms on the N sites of the support. For comparison, Fe_n/NC (the nanoparticle catalyst, adding 432 mg of Fe(NO₃)₃·9H₂O), Fe/C (without protein powder), and NC (the metal-free catalyst, without adding Fe(NO₃)₃·9H₂O), were synthesized by the same process. According to elemental analysis (EA), the raw protein powder contained up to 12.46% nitrogen and the negligible S (0.53%), and enough nitrogen (1.16%)still existed in Fe1/NC. The Brunauer-Emmett-Teller surface area (117.58 m² g⁻¹) of Fe₁/NC was detected, and the area was high enough to facilitate the dispersion of Fe. The pore volume (0.19 cm³ g⁻¹) and the pore size (2.51 nm) of Fe₁/NC revealed that the catalyst maintained the porous structure. By the inductively coupled plasma-optical emission spectrometry (ICP-OES) measurements, the contents of Fe in Fe_1/NC , Fe_n/NC and Fe/C were found to be 1.01 wt%, 2.94 wt% and 1.00 wt%, respectively (Table S1[†]). The actual iron contents of the three catalysts were similar to the theoretical values, which was one of the outstanding advantages of the ball milling method. The surface morphology and structural composition of Fe1/NC were observed using a transmission electron microscope (TEM, Fig. 1b) and a scanning transmission electron microscope (STEM, Fig. 1c), respectively; no obvious nanoparticles



Fig. 1 (a) Schematic illustration of the synthesis process of Fe₁/NC. (b) TEM image, (c) STEM image, (d) AC HAADF-STEM image, and (e) EDS elemental mapping of Fe₁/NC.

and clusters were observed on the amorphous structure of nitrogen-containing carbon materials. In addition, aberrationcorrected high-angle annular dark-field scanning transmission electron microscopy (AC HAADF-STEM, Fig. 1d) revealed that the Fe species were atomically dispersed on the surface (highlighted in yellow circles), and no nanoparticles were detected. The energy dispersion spectrum (EDS) elemental mapping images further confirmed that iron atoms were uniformly dispersed on the support (Fig. 1e). In contrast, due to the lack of anchoring atoms provided by protein powder, quantities of nanoparticles appeared on the surface of Fe/C in spite of the similar iron loading to Fe1/NC, and the average particle size was 4.59 ± 1.37 nm (Fig. S1[†]). Besides, there were obvious nanoparticles on the surface of Fen/NC with an excess Fe content, and the average particle size was 2.04 ± 1.00 nm (Fig. S2[†]). The crystalline phases of catalysts were detected by X-ray powder diffraction (XRD). As illustrated in Fig. 2a, there were two obvious characteristic peaks at 25.5° and 43.8° in Fe₁/ NC, Fe_n/NC, Fe/C, and NC, which could be attributed to the (002) and (101) crystal faces of graphitic carbon.¹⁸ No Fe-containing characteristic peaks (44.7° and 65.0°) were detected in Fe_1/NC , Fe_n/NC and Fe/C, which probably indicated that the



Fig. 2 (a) XRD images of Fe_1/NC , Fe_n/NC , Fe/C, and NC with standard PDF of C and Fe. (b) XPS spectra of Fe 2p in Fe_1/NC . (c) XANES spectra, (d) FT-EXAFS spectra for Fe_1/NC , Fe foil, Fe_2O_3 , and FePc. (e) Wavelet transform for the Fe K-edge of Fe_1/NC . (f) Corresponding R-space EXAFS fitting curves for Fe_1/NC , and the inset exhibits the atomic structure model.

iron contents were too low to show the characteristic peaks. As shown in Fig. 2b, X-ray photoelectron spectroscopy (XPS) was implemented. The peaks at about 725.6 eV and 711.3 eV in XPS images corresponded to Fe $2p_{1/2}$ and Fe $2p_{3/2}$, respectively, indicating that the electron transfer effect due to the coordination of Fe and N atoms induced charge redistribution and made Fe species in the positive valence.²⁷ The binding energy of N in Fig. S3† indicated that pyridinic N (398.4 eV), metallic N (399.5 eV), pyrrolic N (400.8 eV) and graphitic N (401.2 eV) existed in N 1s at the same time.²⁸

In order to obtain detailed messages about the chemical valence and coordination environment of Fe_1/NC , the X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements were performed. The Fe K-edge XANES spectra of Fe_1/NC , Fe foil, Fe_2O_3 , and Fe phthalocyanine (FePc) are shown in Fig. 2c, which testify that the oxidation valence of Fe in Fe_1/NC was a positive state, because the intensity of Fe_1/NC was stronger than FePc and similar to Fe_2O_3 , which was in line with the XPS results. The Fourier transform (FT) curve of Fe_1/NC showed a prime peak at nearly 1.5 Å, which can be ascribed to the Fe–N bonds (Fig. 2d). In addition, the absence of the Fe–Fe peak illustrated that no metallic Fe–Fe coordination existed in Fe_1/NC

NC, which further demonstrated that no Fe particles existed in the catalyst. The wavelet transforms (WT) of Fe₁/NC and Fe foil are exhibited in Fig. 2e. Different from the contour map of Fe foil, the maximum intensity of Fe₁/NC was only around 4.0 Å, which was obviously distinct from the maximum intensity of 7.7 Å in Fe foil. More detailed structural information was obtained by quantitative EXAFS fitting of the Fe K-edge in Fe₁/ NC (Fig. 2f). The results suggested that each Fe atom coordinated to four surrounding N atoms on average, and the bond length was about 1.98 Å (Table S2†). Herein, the possible structure is shown in Fig. 2f.

Selective oxidation is an essential method to synthesize important compounds, *e.g.* sulfoxides, ^{29,30} aldehydes, epoxides and ketones.^{31–33} In chemical production, acetophenone is one of the key intermediates with a great market demand, which can be used to produce a series of products such as alcohol, esters, perfumes and so on.¹ However, due to the inertness of the C–H bonds and the prone side reactions caused by excessive oxidation, it is still a long-term challenge to achieve ideal conversion and acetophenone selectivity under ambient conditions. As a result, we chose the selective oxidation of ethylbenzene to acetophenone with *tert*-butyl hydroperoxide (TBHP) as the oxidant to investigate the performance of Fe₁/NC (detailed in the Experimental section of the ESI[†]).

A relatively high acetophenone yield (95%) was achieved by Fe₁/NC after 48 h at 35 °C (Fig. S4[†]), and the metal free NC was inert (yield < 1%), which indicated that the Fe species played a key role in catalyzing the selective oxidation of ethylbenzene. As illustrated in Fig. 3a, when the reactions lasted 6 hours, the activity of Fe₁/NC (3.6 h^{-1}) was 12 times that of $Fe_n/NC (0.3 h^{-1})$ and three times that of Fe/C (1.2 h^{-1}). These results suggested that the isolated Fe sites showed a higher catalytic activity than agglomerated Fe particles, which was due to that the well dispersed Fe species maximized the exposed active interface of Fe1/NC, but the agglomerated Fe particles hindered the contact of most active centres of Fen/NC and Fe/C with reactants. In addition, the selectivity of Fe₁/NC and Fe_n/NC exceeds 90% after 6 hours, far more than Fe/C (54%, phenylethanol was the main by-product), which could be speculated that the selective oxidation of internal saturated C-H rather than terminal C-H was more inclined to take place on the Fe-N sites. Moreover, the effect of temperature on the reaction was also considered. As shown in Fig. 3b, the experiments were carried out at three different temperatures. When the ethylbenzene conversion was 20%, the corresponding activities of 25 °C, 35 °C and 45 °C were 1.9 h^{-1} , 3.6 h^{-1} and 5.6 h^{-1} , respectively, which indicated that the reaction was sensitive to temperature, and a higher temperature may promote the activation of TBHP to generate more active oxygen, thereby enhancing the efficiency of the reaction. In addition, the stability of Fe1/NC was also investigated. As shown in Fig. 3c, after the first 48 h of reaction, the catalyst was filtered and washed with ethanol and deionized water five times, dried at 60 °C overnight, and then reused in another cycle reaction under the same reaction conditions. After five cycles, both the conversion of ethylbenzene and the selectivity of acetophenone were not decreased. What is more, no



Fig. 3 (a) Catalytic performance for selective oxidation of ethylbenzene to acetophenone by Fe₁/NC, Fe_n/NC and Fe/C after 6 hours. Reaction conditions: catalyst dosage = 20 mg, ethylbenzene dosage = 0.25 mmol, TBHP = 1 ml, H₂O = 2 ml, *T* = 35 °C, reaction time = 6 h. (b) Activity under 25 °C, 35 °C and 45 °C respectively when the ethylbenzene conversion was 20%. (c) Recycling performance of Fe₁/NC at 35 °C. (d) AC HAADF-STEM image of Fe₁/NC after five cycles.

aggregation was observed by AC HAADF-STEM (Fig. 3d). These results showed excellent stability of structure and great reusability of Fe₁/NC, which was of great significance for industrial applications. It was noteworthy that the first reaction activity was slightly lower than that of cycle reactions; it probably was because those active sites were further activated during the suitable reaction process, which made its catalytic performance improved in the next reactions. Recently reported heterogeneous catalysts and reaction conditions for the oxidation of ethylbenzene are listed in Table S3.[†] Most of them required a high temperature to obtain the satisfactory yield of acetophenone, and 35 °C was the most ambient temperature.

The superb catalytic performance of Fe1/NC was also achieved on the selective oxidation of saturated C-H bonds in other aromatic compounds containing various functional groups under the same reaction conditions. High conversion (99%) and satisfactory selectivity (>90%) of corresponding ketones were obtained under the catalysis of Fe1/NC when the substrates had steric hindrance, such as 4-ethylanisole, N-propylbenzene and 4-ethylnitrobenzene (Table 1, entries 1–3). Besides, in the selective oxidation of compounds with the steric hindrance of bulky substituents, such as 2-ethylnaphthalene and diphenylmethane to 2'-acetonaphthone and benzophenone under the catalysis of Fe₁/NC (Table 1, entries 4 and 5), superb conversion (99%) and selectivity (>99%) were achieved. These results demonstrated that Fe1/NC had great expandability with different aromatic substrates in the selective oxidation of saturated C-H bonds.

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Reaction conditions: catalyst dosage = 20 mg, substrate dosage = 0.25 mmol, TBHP = 1 ml, H_2O = 2 ml, T = 35 °C, and reaction time = 48 h.

Conclusions

In general, we have successfully prepared SAC Fe₁/NC by a mechanical ball milling strategy, using protein powder as the nitrogen source and carbon black as the support. The iron species are anchored stably by the N elements on the support as atomically dispersed Fe–N₄ sites. Besides, Fe₁/NC exhibits superb activity, selectivity to corresponding ketones and great stability in the selective oxidation of arylalkanes under ambient conditions.

Author contributions

In this work, X.H. and Y.C. developed the concept. Y.C. designed these experiments and analysed experimental data. Y.C., Q.S. and L.H. contributed to the synthesis of catalysts and catalytic experiments. Y.C., Q.H., H.Z., P.W., and Y.Z. performed characterization studies such as XRD, TEM, XPS, and analysed the results. Y.C., S.S., X.Z. and T.G. performed the EXAFS measurements and analysed the data. Y.C. and X.H. wrote the paper. H.J. and X.H. directed the project. All authors discussed the results and contributed to the scientific interpretation.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (22078371, 21938001, and 21961160741), the Guangdong Provincial Key R&D Programme

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(2019B110206002), the Special fund for Local Science and Technology Development by the Central Government, Local Innovative and Research Teams Project of Guangdong Pearl River Talents Program (2017BT01C102), the NSF of Guangdong Province (2020A1515011141), the National Key Research and Development Program Nanotechnology Specific Project (No. 2020YFA0210900), the Science and Technology Key Project of Guangdong Province, China (2020B010188002), and the Guangdong Basic and Applied Basic Research Foundation (2020A1515110864).

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